SYNTHESIS AND CHARACTERIZATION OF ALIPHATIC-AROMATIC POLYESTERS

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To Shankar

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(T. E. Sandhya)

ABSTRACT

This thesis presents the synthesis, characterization and crystallization behavior of copolyesters of dimethyl terephthalate and 1,4-butanediol with various cycloaliphatic diols and diesters. Aliphatic polyesters containing cycloaliphatic diols and diesters were also synthesized and characterized.

A series of poly(butylene terephthalate-co-1,4-cyclohexylene dimethylene terephthalate) (P(BT-co-CT)) and poly(butylene terephthalate-co-1,4- cyclohexane dicarboxylate) (P(BT-co-BCD)) copolymers with various CT and BCD contents were synthesized by melt condensation. The NMR spectroscopic analysis indicates that the copolymers are statistically random, irrespective of the composition. The thermal analysis and XRD studies show that these copolymers could crystallize in all compositions. The poly(BT-co-CT) copolymers exhibited typical eutectic behavior in melting and crystallization and the eutectic composition is $PBT_{75}CT_{25}$ indicating iso-dimorphic cocrystallization behavior. On the other hand, poly(BT-co-BCD) copolyesters showed isomorphic crystallization but did not show eutectic behavior in melting and crystallization. The glass transition temperature showed linear dependency on composition in these copolymers.

The crystallization behavior and crystallization kinetics of the commercial PCCD was studied by DSC and compared with PBT and PCT. PCT is a rapidly crystallizing polymer like PBT and has short crystallization half time (less than 0.5 minute over wide range of temperature from 110 to 275°C). PCCD, on the other hand, crystallizes slowly and shows unique minimum crystallization half time at two different temperatures.

Cyclopentane ring containing monomers, 1,3-bis(hydroxymethyl) cyclopentane and dimethyl-1,3-cyclopentane dicarboxylate were synthesized. Copolyesters of dimethyl terephthalate and 1,4-butanediol containing 1,3-bis(hydroxymethyl) cyclopentane (CPDM) and dimethyl-1,3-cyclopentane dicarboxylate (CPDE), namely, poly (butylene terephthalate-co-1,3-cyclopentylene dimethylene terephthalate) [P(BT-co-CPDT)] and poly (butylene terephthalate-co-butylene cyclopentane dicarboxylate) [P(BT-co-BCP)] were synthesized by melt condensation. The thermal analysis and XRD studies show that poly(BT-co-CPDT) copolymers could crystallize in all compositions. The poly(BT-co-CPDT) copolymers exhibit typical eutectic behavior in melting and crystallization and iso-dimorphic cocrystallization. The homopolyester of 1,3-bis (hydroxy methyl) cyclopentane and DMT (PCPDT) was found to be a semicrystalline polyester. PCPDT has lower crystallization rate compared to PBT and shows well defined banded spherulitic morphology. The homopolyester of dimethyl-1,3-cyclopentane dicarboxylate with DMT (PBCP) was found to be an amorphous polyester. The poly(BT-co-BCP) copolyesters containing upto 50 % BCP component was found to be semicrystalline. In the composition range where the copolyesters crystallized, the samples show isomorphic crystallization but do not show eutectic behaviour in melting and crystallization. The glass transition temperature exhibits linear dependency on composition in these copolymers.

Aliphatic polyesters, poly(cyclohexanedimethylene cyclohexanedicarboxylate) (PCCD) and poly (cyclopentane dimethylene cyclopentane dicarboyxlate) (PCPCPD) were synthesized and characterized. The PCCD synthesized contains 67 % axial,equatorial-cyclohexane dicarboxylate and is an amorphous polymer. PCPCPD was found to be an amorphous rubbery polymer at room temperature with a T_g well below room temperautre.

A series of poly(butylene terephthalate-co-2,3-norbornane dimethylene terephthalate) (P(BT-co-NBDT)) and poly (butylene terephthalate-co-2,3-norbornane dicarboyxlate) (P(BT-co-BNB)) copolymers with various NBT and BNB contents were synthesized by melt condensation. The NMR spectroscopic analysis indicates that the coploymers are random. The thermal analysis and XRD studies shows that the PNBDT is an amorphous polyester with a T_g of 113°C. The poly(BT-co-NBDT) copolyesters could crystallize in compositions upto 20 % NBDT content, while the composition having 50 % NBDT is amorphous.

On the other hand, PBNB was found to be an amorphous polyester with a T_g of 15°C. The poly(BT-co-BNB) copolyesters show isomorphic crystallization but did not show eutectic behaviour in melting and crystallization.

Copolyesters of TMCBD/BD containing, dimethyl terephthalate, 1,4-cyclohexane dicarboxylate, 1,3-cyclopentane dicarboxylate and 2,3-norbornane dicarboxylate are synthesized and found to be amorphous. The incorporation of the rigid cyclobutane diol boosts the T_g by about ~ 45^{o}C compared to the corresponding homopolymers.

GLOSSARY

BD	1,4-butanediol
BHCT	Bis(hydroxymethyl cyclohexane) terephthalte
BT	Butylene terephthalate unit
BHBT	Bishydroxybutyl terephthalte
B	Degree of randomness
BCD	Butylene cyclohexane dicarboxylate unit
BPA	Bisphenol-A
CHDM	1,4-cyclohexane dimethanol
CHDA	1,4-cyclohexane dicarboxylic acid
CT	Cyclohexylene dimethylene terephthalate unit
CPDE	1,3-cyclopentane dicarboxylate, dimethyl ester
CPDM	1,3-cyclopentane dimethanol (1,3-bishydroxymethyl)cyclopentane)
CPDT	Cyclopentylene dimethylene terephthalate unit
DMT	Dimethyl terephthalate
DMCD	Dimethyl-1,4-cyclohexane dicarboxylate
DSC	Differential scanning calorimetry
DMNBDE	2-exo, 3-exo-dimethyl bicyclo[2.2.1]heptane-2-endo,3-endo-dicarboxylic acid dimethyl ester
DEG	Diethylene glycol
DMI	Dimethyl isophthalate
DMN	2,6-dimethyl naphthalate
DMS	Dynamic mechanical spectroscopy
EG	Ethylene glycol
GC	Gas chromatography
ΔH_m	Enthalpy of melting
ΔH_c	Enthalpy of crystallization
ΔH_f	Enthalpy of
ΔH_{cc}	Enthalpy of cold crystallization
HDT	Heat distorsion temperature
HBPA	Hydrogenated bisphenol-A
IDT	Intial decomposition temperature
IR	Infrared
IPA	Isophthalic acid
k	Overall rate constant
LAH	Lithium aluminum hydride
L_{nB}	Average sequence length of butylene unit
L_{nC}	Average sequence length of cyclohexylene dimethylene unit
L_{nCD}	Average sequence length of cyclohexane dicarboyxlate unit
L_{nT}	Average sequence length of terephthalate unit
LCP	Liquid crystalline polymer
M_n	Number average molecular weight
M_w	Weight average molecular weight
NBDE	dimethyl bicyclo[2.2.1]heptane 2-exo,3-endo dicarboxylate (dimethyl 2-exo,3-endo norbornane dicarboxylate)

NBDM	2-endo, 3-endo bis(hydroxymethyl) bicyclo [2.2.1]heptane (2-endo, 3-endo norbornane dimethanol)
NMR	Nuclear magnetic resonance
N_2	Nitrogen gas
N	Avrami exponent
NPG	Neopentyl glycol
NDA	Nadic anhydride
PBT	Poly(butylene terephthalate)
PCT	Poly(cyclohexylene dimethylene terephthalate)
PET	Poly(ethylene terephthalate)
PCCD	Poly(cyclohexylene dimethylene cyclohexane dicarboxylate)
PBCD	Poly(butylene-1,4-cyclohexane dicarboxylate)
PCPDT	poly (1,3-cyclopentane dimethylene terephthalate)
PNBDT	poly(2,3-norbornane dimethylene terephthalate)
PBNB	poly (butylene-2,3-norbornane dicarboxylate)
P(BT-co-BNB)	poly (butylene terephthalate-co-butylene-2,3-norbornane dicarboxylate)
P(BT-co-NBDT)	of poly (butylene terephthalate-co-norbornane dimethylene terepthalate) copolyesters
PEN	Poly(ethylene naphthalate)
P(BT-co-CT)	Poly(butylenes terephthalate-co-cyclohexylene dimethylene terephthalate)
P(BT-co-BCD)	Poly(butylene terephthalate-co-butylene cyclohexane dicarboxylate)
P(BT-co-CPDT	Poly (butylene terephthalate-co-1,3-cyclopentylene dimethylene terephthalate)
P(BT-co-BCP)	Poly (butylene terephthalate-co-butylene cyclopentane dicarboxylate)
PTT	Poly(trimethylene terephthalate)
PD	1,3 propane diol
PAN	Poly(alkylene naphthalate)
PBN	Poly(butylene naphthalate)
PTN	Poly(trimethylene naphthalate)
PC	Polycarbonate
PCTI	Poly(cyclohexanedimethylene terephthalate-co-isophthalate)
SSP	Solid state polymerization
TPA	Terephthalic acid
TCE	1,1’,2,2’-Tetrachloroethane
$t_{1/2}$	Crystallization half time
TGA	Thermogravimetric analysis
T_C	Temperature at which polymer was crystallized
T_{mc}	Crystallization temperature upon cooling
T_g	Glass transition temperature
T_m	Melting temperature
$T_m°$	Equilibrium melting temperature
T_{cc}	Crystallization temperature upon heating
T_γ	γ - relaxation temperature
T_g	Glass transition temperature

TMP	Trimethylol propane
UV	Ultraviolet
WAXD	Wide angle X-ray diffraction
WAXS	Wide angle X-ray scattering
XRD	X-ray dirraction
η_{inh}	Inherent viscosity
ΔH_m	Enthalpy of melting
ΔH_c	Enthalpy of crystallization

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Chapter 1: Structure property relationship in aliphatic-aromatic polyesters

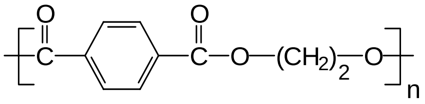
1.1 Introduction

Aliphatic-aromatic polyesters belong to the class of thermoplastic polyesters. They constitute a significant item of commerce, entering into almost every imaginable end use: fibers, textiles, industrial yarns, tire cords, ropes, molded items, consumer goods, medical accessories, automotive and electronic items, packaging materials, bottles, containers etc[1]. The broad spectrum of their applications illustrates the diverse utility of such materials. The principal polyesters of this class are poly (ethylene terephthalate)s (PET), poly(butylenes terephthalate)s (PBT), poly(cyclohexanedimethylene terephthalate)s (PCT) and poly(ethylene naphthalane-2,6-dicarboxylate)s (PEN). The crystalline aliphatic-aromatic polyesters, PET and PBT possess excellent physical, mechanical, electrical, and thermal properties. Additional properties that characterize these polymers as engineering plastics are excellent surface properties, toughness, low water absorption and dimensional stability suited for continuous use at desired temperatures[2]. This chapter discusses the information available on the effect of linear and cyclic aliphatic monomers on the various properties of aliphatic aromatic polyesters.

1.2 Poly(alkylene terephthalate)s

1.2.1 Poly(ethylene terephthalate)s

PET is the most visible member of the polyester group and is a condensation homopolyester made from dimethyl terephthalate (DMT) and ethylene glycol (EG) and has a repeating structure



(1)

PET was discovered and its potential as a fiber-forming polymer recognized in England by Whinfield and Dickson in 1941[3]. Despite the excellent properties of this polymer for fiber production it could not be commercialized immediately. However, in the early 1950s, ICI, Ltd. (UK) and E. I. duPont de Nemours & Co., Inc. (USA) started its manufacture. PET was made by the reaction of DMT with excess EG in the presence of catalysts to promote ester interchange and polymerization.

PET with a weight-average molecular weight M_w of approximately 35,000-40,000 is used for textile fibers, oriented films, and reinforcement with glass fibers. However, this range of molecular weights is inappropriate for injection molding because the resulting molded parts are brittle and higher M_w values of about 80,000 are required. High molecular weight PET can be obtained by solid state polymerization[4, 5, 6]. During the PET synthesis, starting from either DMT or TPA, an intermolecular ether forming reaction takes place between the β-hydroxyethyl ester end groups, generating diethylene glycol (DEG), which is incorporated in the polymer. Such resins are characterized by a reduced melting point and crystallinity, lower mechanical strength, decreased thermo-oxidative resistance and poorer UV stability[7,8].

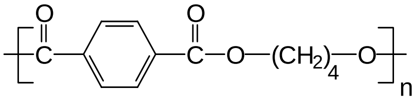
Engineering PET is used in many industries, including electrical and electronic, automotive, lighting, power tools, materials handling, sporting goods, plumbing goods and tableware. It replaces thermoset resins where good electrical properties are required together with better impact strength and easy processing in shorter cycles with scrap reutilization.

PET products are chemically inert, clear, visually attractive, and their lightweight creates significant savings in distribution costs. No new plastic is introduced currently without consideration of its recycling potential and in this regard PET is quite relevant. Chemical recycling of PET has also been considered but required additional costs in terms of energy and production. Physical recycling of PET bottles is particularly important due to the huge volume of scrap. The application for recycled PET include polyester carpets, fleece jackets, paintbrush bristles, bottles and containers for nonfood use, or multi material containers in which the recycled PET layer is sandwiched between layers of virgin PET.

Notwithstanding its very good physical properties and chemical stability, PET itself was not outstandingly successful as an injection molding resin due to its low rate of crystallization in a cold mold. The mold has to be heated to 130-140°C, well above the T_g, to obtain adequate crystallization rates. Nevertheless, satisfactory moldings were still not obtained due to the uncontrolled crystal morphology. During the mid-1960s and in later years, fast-crystallizing grades of PET were developed which gave uniform and controlled morphology because of the presence of specific additives acting as nucleating agents[9].

1.2.2 Poly(butylene terephthalate)s

The thermoplastic polyester poly(butylene terephthalate) (PBT) **(2)** is prepared by polycondensation of 1,4-butanediol with dimethyl terephthalate. The development of PBT started more than 50 years ago with the work of Slack[10].



(2)

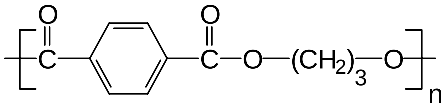
Because of the low rate of crystallization of PET, a nucleant and a crystallization promoter were necessary to obtain sufficiently crystallized material within an acceptable cycle time. Since proper injection molding of PET compounds was somewhat difficult for most molders at that time, a number of companies started to develop injection-moldable PBT compounds. This resulted in the introduction of fiber-reinforced PBT compounds by Celanese in 1970. Because of its very easy processing and rapid crystallization, injection-moldable PBT compounds quickly became more popular than PET compounds. PBT (as well as PET) resins are high-performance materials that can be converted to various functional components and structural parts that used to be made of metal or thermosets. Property combinations such as high mechanical strength, high heat distortion temperature (up to 215°C for glass fiber-reinforced PBT), continuous use temperature of 140°C, dimensional and chemical stability and short cycle times in injection molding are primarily responsible for the success of this engineering plastic. The properties of PBT are strongly dependent on the crystalline portion and the resulting morphology after processing. PBT is a prominent member of the engineering thermoplastics and is characterized by (i) high stiffness and strength, (ii) high toughness at low temperatures, (iii) high heat-deflection temperature, (iv) high stress-cracking resistance, (v) high resistance to fuels, oils, fats and many solvents, (vi) low coefficient of linear expansion, (viii) low water absorption. (viii) good friction and wear characteristics, and (ix) good processability. PBT is highly suitable for electrical applications, automotive, telecommunication, machine components, food and medical applications.

PBT is polymerized in a two-stage process[11]. In the first stage (the transesterification stage) bishydroxybutyl terephthalate (BHBT) is formed through the transesterification of dimethyl terephthalate (DMT) with 1,4-butanediol. In the second stage, the polycondesation, the BHBT is polycondensed into PBT with elimination of 1,4-butanediol. Solid-state polycondensation is used when a high molecular weight PBT is required.

The properties of PBT can be modified in many ways to meet the requirements of specific fields of application, as is the case with most engineering plastics[11]. Copolymeriztion, blending with other polymers (e.g., rubber, PC, ASA) and the addition of reinforcements, flame retardants, stabilizers, etc., during compounding are different ways to modify the properties of PBT. PBT is blended with amorphous polymers to reduce shrinkage and to increase dimensional stability.

1.2.3 Poly(trimethylene terephthalate)

Poly(trimethylene terepthalate) (PTT) **(3)** is a newly commercialized aliphatic-aromatic polyester. Although first synthesized by Whinfield and Dickson in 1941, it remained an obscure polymer because one of its raw material, 1,3-propanediol (PDO), was not readily available. The recent chemical breakthrough from Shell Chemical has allowed PDO to be made relatively inexpensively.

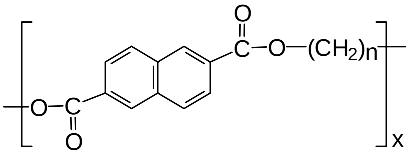


(3)

It has been commercially introduced for fiber, film and engineering thermoplastics applications[12] in 1998. PTT finds use in carpet, textile and nonwoven fibers, and for special use as racket guts and musical bowstrings, papermaking machine fabrics, umbrella fabric, cheese packaging, artificial leather and hook-and-loop fasteners have been developed. PTT can also be processed into film for packaging and by molding for use as magnetic recording disks, bottles and electric connectors. Recently PTT has been widely studied because of its better elastic recovery than PET and PBT[13-18]. Because of its excellent resilience, the properties of PTT are in ways more similar to those of polyamides, such as nylon 66, than to those of other polyesters like PET and PBT. Mechanical performances of PTT are roughly between those of PET and PBT, and it can be melt processed using a variety of processing methods to produce fiber, films and molded parts[19]. Mechanical properties of PTT are substantially enhanced when the material is reinforced by glass or other high modulus short fibers[19].

1.2.4 Poly(alkylene naphthalate)s

In the past, the study of high performance engineering plastics was centered on the benzene ring structure. The newly developed high performance polyalkylene naphthalates (PAN) with their superior physical, mechanical properties and processability have caught the world's attention. The most important feature of PAN polymers is increased stiffness of the polymer chains, because of the presence of the naphthalene ring. Of the polyalkylene naphthalates studied, polyethylene-2,6-nathphalate (PEN) and polybutylene-2,6-naphthalate (PBN) exhibit superior thermal, mechanical, barrier and chemical resistance properties compared to PET and PBT[20,21].



(4)

PEN is the condensation product of 2,6-naphthalene dicarboxylic acid and ethylene glycol, with a chemical formula as shown in **(4)**, where n = 2. Compared to its analog, PET, only a limited number of papers have been published on PEN. It was only in 1973 that PEN became commercially available from Teijin Ltd., Japan. The increasing interest in PEN commercialization was triggered by reports that the dicarboxylic acid monomer might become available in commercial-scale quantities.

PEN contains condensed aromatic rings (the naphthalene group) instead of the single ring present in PET. The naphthalene moiety in PEN imparts stiffness to the linear polymer backbone, leading to improved thermal and chemical resistance and excellent mechanical properties, such as tensile strength and dimensional stability. PEN has a glass transition temperature and melting temperature of 125° and, 268°C respectively[22]. PEN is a slow crystallizing polymer because of the presence of a rigid naphthalene ring. PEN has oxygen barrier properties that are 4 to 5 times higher than those of PET, making this polymer attractive for packaging applications. The superior properties of PEN are closer to the high standards set by modern mechanical, thermal and electrical engineering.

Being a kind of high-performance polymer, PEN can be widely used for electric appliances, such as base films for long-play videotape of high quality.

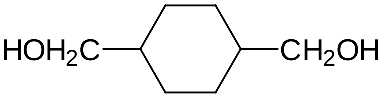
Poly(butylene naphthalene-2,6-dicarboxylate) (PBN) (n= 4) is a new polyester, with excellent chemical resistance, as also mechanical, thermal and insulating properties. Especially, PBN fibers can be used in many applications. It has a T_m of 247°C and a T_g of 48°C[23]. PBN, like PBT shows fast crystallization rates compared with other polyesters. The enhanced PBN chain mobility due to the flexibility of the long butylenes groups, as well as the interchain interactions due to the naphthalene rings, can give rise to fast nucleation and spherulitic growth from the melt. PBN cannot be obtained in amorphous glassy state by cooling from the melt in contrast to PEN[24]. The other homologue, poly(trimethylene 2,6-naphthalenedicarboxylate) (PTN), however, has received little attention[25-27]. The melting point and glass-transition temperature are 204 and 83°C, respectively.

1.3 Polyesters containing cyclic diols

The discovery of PET and the attribution of its properties to the effect of the phenyl ring[28] spurred the study of numerous other ring containing polyesters. Their characteristics depend on the structure, symmetry and conformational features of the cyclic units and on the relative proportions of cyclic and acyclic components in the repeating units. Generally, when the cyclic components predominate and the polyester is crystalline, it has melting temperature [T_m] higher than acyclic polyesters. The cyclic components may be aromatic, alicyclic or heterocyclic. The glass-transition temperatures [T_g] are also higher with larger cyclic component, irrespective of crystalline or amorphous nature of the polyesters. This effect is due to the restriction of chain motion in the ring as compared to the acyclic unit of similar length.

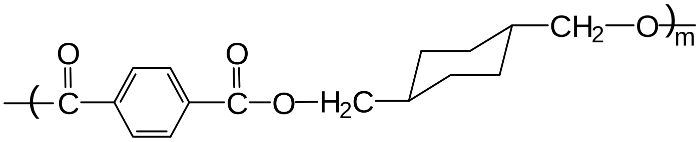
1.3.1 1,4-Cyclohexanedimethanol (CHDM)

The alicyclic diol 1,4-cyclohexane diemethanol (CHDM) **(5)** is a thermally stable, rigid diol and has been used for synthesis of polyesters[29,30]. It is synthesized by the hydrogenation of DMT to dimethyl cyclohexane-1,4-dicarboxylate and further reduction under high pressure to the bis primary alcohol, which usually yields a 68/32 mixture of *trans* and *cis* forms. Commercially available CHDM has about 70-72% *trans* content, slightly below the thermodynamic equilibrium (~76% *trans* isomer).



(5)

Poly (cyclohexylenedimethylene terephthalate) (PCT), **(6)** was first produced by Eastman Kodak in the 1950s as a polyester fiber[31]. PCT was introduced as a molding resin in 1987 as glass filled and flame-retarded grades with specific end use[32] such as connectors for both the electronic and automotive markets. PCT has a high heat deflection temperature (HDT ~260°C) and is significantly less expensive than liquid crystalline polymers (LCP). One specific advantage of PCT is that it has similar flow characteristics (although at higher temperature) during molding as that of PET and PBT, which means that extensive mold redesign is not necessary.



(6)

PCT has low moisture uptake and is not affected by changes in humidity. PCT has both a high melting point (285-290°C) and a high melt viscosity leading to high processing temperatures of 300°C, which leads to thermal and thermo-oxidative degradation and severe drop in viscosity during molding, giving brittle parts[33]. The presence of two tertiary hydrogen atoms both in the β-position to the ester group is a source of structural weakness. PCT does not crystallize as rapidly as PBT or nylon; its crystallization behavior is similar to that of PET and nucleants, and plasticizers are often added to improve molding performance.

Condensation of 1,4-cyclohexanedimethanol with mixtures of dimethyl iso- and terephthalates gives poly (1,4-cyclohexylenedimethylene terephthalate-co-iso-phthalate) (PCTI), which is a tough amorphous polymer[34]. In addition to its high T_m, PCT has improved stability compared to PET. It has better heat-distortion temperature characteristics compared to PET. Thus, a specimen of PET had a heat-distortion temperature of 160ºC, whereas the polyester derived by condensing CHDM (75% trans isomer) with a mixture of DMT and DMI has a heat-distortion of 210ºC[35].

Poly(1,4-cyclohexylenedimethylene terephthalate) (PCT) is in effect a copolymer of terephthalic acid with two diols, the *cis* and *trans* forms of cyclohexanedimethanol. These two isomers do not form copolymer with a minimum melting point, but instead the melting point rises monotonically between the two T_m values of the pure isomeric homopolymers[36] (**Table 1.1**). The pure *cis* polymer melts at ~250°C and the pure *trans* polymer at ~310°C. The T_g likewise rises from about 60°C (cis) to about 90°C (trans). But there is little difference in the degrees of crystallinity or crystallization rates over the composition range. Apparently, the polyester molecules containing the *cis* diol can fit readily into the crystalline lattice of the polyester containing the *trans* diol (and vice versa). Boye[37] has reported a continuous transformation of the X-ray diffraction pattern from that characteristic of the polyester containing the *cis* isomer to that characteristic of the polyester containing the *trans* isomer. Such a facile substitution of one isomeric polyester into the crystalline lattice of the other is unusual in view of the measured difference in repeat unit of the two isomeric polyesters[37]. The usual commercial form of PCT has an isomer ratio of approximately 70/30 trans/cis, this being governed by the isomer ratio of the diol (CHDM) produced at the hydrogenation stage.

Kibler et al[29] prepared a series of polyesters of *trans*-1,4-cyclohexane dimethanol and *cis*-1,4-cyclohexane dimethanol with various aliphatic (**Table 1.10, series 10**) and aromatic diacids (**Table 1.1**) and compared with analogous series of polyesters prepared from p-xylylene glycol. The polyesters of *trans*-1,4-cyclohexanedimethanol and the aliphatic dibasic acids with an even number of carbon atoms melt at a slightly higher temperature than the analogous polyesters from p-xylylene glycol (**Table 1.1**). In the case of polyesters from aliphatic dibasic acids with an odd number of carbon atoms, the situation is reversed and the polyesters of *trans*-1,4-cyclohexanedimethanol melt at a slightly lower temperature. In so far as polyesters from aliphatic dibasic acids are concerned, it must be concluded that the *trans*-1,4-cyclohexylene and the p-phenylene rings are about equal in their ability to confer high melting points upon polyester molecules containing them[32].

Polyesters prepared from aromatic dibasic acids and *trans*-1,4-cyclohexane dimethanol or p-xylylene glycol[31] contain a combination of rigidity and/or symmetry in the acid component with rigidity and symmetry in the diol component. In such cases *trans*-1,4-cyclohexanedimethanol appears to be superior to p-xylylene glycol insofar as the T_m is concerned. With *trans*-1,4-cyclohexanedimethanol, polyesters of exceptionally high melting points are formed while the polyesters prepared with *cis* isomer of 1,4-cyclohexanedimethanol (**Table 1.1**) had lower T_m than the *trans* derivative that arises due to reduced symmetry of the repeat unit.

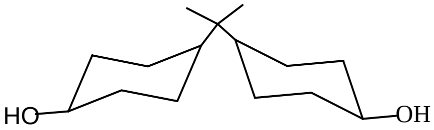
Table 1.1 Polyesters of *p*-xylylene Glycol, *cis* and *trans*-1,4-Cyclohexanedimethanol[31]

Acid	*p*-xylylene glycol		*trans*-1,4cyclohexane dimethanol		*cis*-1,4-cyclohexane dimethanol	
	T_m (°C)	$\{\eta\}^a$ dL/g	T_m (°C)	$\{\eta\}^a$ dL/g	T_m (°C)	$\{\eta\}^a$ dL/g
Trans-1,4-cyclohexane dicarboxylic	85-106	0.25	244-246	0.86	203-205	0.82
Isopththalic	94-100	-	190-197	0.26	-	-
Terephthalic	263-272	0.59	312-318	0.58	251-256	0.85
2,6-Naphthalene dicarboxylic	275-280	0.56	335-341	0.55	281-287	0.86

^{a}Measured in phenol/tetrachloroethane (60/40 w/w) at 25°C

1.3.2 2,2-Bis(4-hydroxycyclohexyl)propane (HBPA)

HBPA **(7)** is a potentially useful diol for the preparation of polyesters[37.] Catalytic hydrogenation of bisphenol-A (BPA) provides HBPA[38] as mixture of three isomers: cis, cis (a,a); cis, trans (a, e) and trans, trans (e,e).



(7)

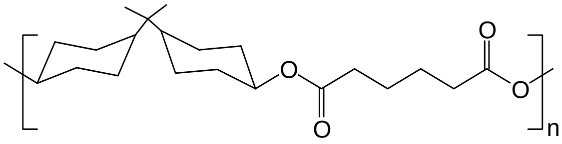
The thermal and mechanical properties of the polyesters derived are known to depend on the isomeric composition of starting HBPA. It has been used as a comonomer in polycondensation reactions for the synthesis of polyesters. Conversely, these polymers were low molecular weight, copolymerized with a triol, and/or end-capped with an epoxide or olefin[40-47]. Gaughan et al[38] have reported synthesis of high molecular weight polyesters of HBPA with various aliphatic and aromatic acids using tin catalyst (**Table 1.2**). Dialkyl acid esters reacted poorly compared to the corresponding free acids. Long chain acids (e.g., sebacic acid) afforded polymers with low T_m. The completely aliphatic polyester made from HBPA and adipic acid possessed a higher T_m than polymers from succinic and sebacic acids. Isophthalic and terephthalic acids form low molecular weight polyesters with sublimation of acids.

Table 1.2 Thermal properties of 2,2-bis(4-hydroxycyclohexyl)propane polyesters[38]

Diacid	T_g (°C)	T_m (°C)
Succinic	113	180
Adipic	75	200
Sebacic	25	Noncrystalline
Isophthalic	127	267
Terephthalic acid	135	350[a]

[a] The polymer decomposed on melting

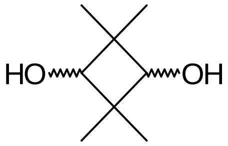
Poly[2,2-bis(4-oxycyclohexyl)propane adipate] **(8)** had better physical properties when compared to engineering plastics like PBT, PC and Nylon 66[38]. The polymer displayed excellent notched impact strength and elongation. This is attributed to the structure, which can dissipate energy through molecular motion by the chair-boat-chair flipping motion.



(8)

1.3.3 2,2,4,4-tetramethyl-1,3-cyclobutanediol (TMCBD)

2,2,4,4-tetraalkyl-1,3-cyclobutylenes are a class of rigid thermally stable, symmetrical alicyclic diols suitable for the preparation of polyesters. This molecular unit can be incorporated into polymers using, for example, cis/trans-2,2,4,4-tetramethyl-1,3-cyclobutanediol (TMCBD) **(9)**[48-79]



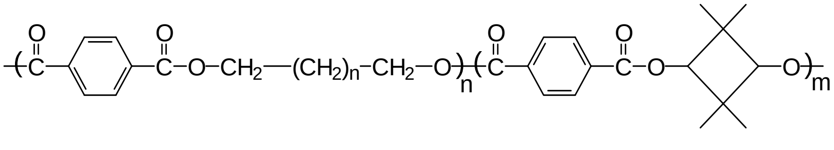
(9)

TMCBD is prepared in high yield by pyrolysis of isobutyric acid[48] or isobutyric anhydride[49-54] to form dimethylketene, which spontaneously dimerizes to cyclic diketone, a molecule known since 1906[55-58]. Hydrogenation of the diketone using ruthenium[59,60] nickel[59-62], or rhodium[62] catalysts produces up to 98 % yield of 2,2,4,4-tetramethyl-1,3-cyclobutanediol as a mixture of *cis/trans* (48/52) isomers. Isolation of the pure isomers is tedious and expensive[63], so the monomer is used as a *cis/trans* mixture in polymerization.

The TMCBD hydroxyl groups are secondary and sterically hindered by adjacent methyl groups; hence polymerizations using TMCBD are more difficult than that of primary diols. Tin[72] and lead[73] catalysts are used successfully with TMCBD, although the latter tends to produce gray polymer. Transesterification catalysts, such as titanium tetrabutoxide, show surprisingly poor activity with TMCBD[76]. Dibutyltin oxide is more effective for transesterification of TMCBD with dimethyl terephthalate than other frequently used catalysts.

Aromatic polyesters of TMCBD reported to date have been primarily high melting, semicrystalline materials[72-75]. Melting points for the polyesters from dimethyl terephthalate and TMCBD, i.e., the homopolymers, are 316-319°C (38/62 cis/trans)[72] 296-308°C (cis)[74] and >350°C (trans)[74]. Many of the reported terephthalate copolyesters of TMCBD with other diols also are semicrystalline. Examples include copolymers with 1,6-hexanediol (T_m = 180-190°C) and 1,4-cyclohexanedimethanol (T_m = 192-204[72] and 200-238°C[74]).

Kelsey et al[80] synthesized random aromatic copolyesters **(10)** using conformationally rigid *cis/trans*-2,2,4,4-tetramethyl-1,3-cyclobutanediol and flexible C_2-C_4 aliphatic glycols over a range of compositions. These terephthalate based copolyesters were found to exhibit high impact resistance combined with good thermal properties, ultraviolet stability, optical clarity and low color. The copolymers were amorphous when the TMCBD content was about 40-90 mol % of total diol[78,80].

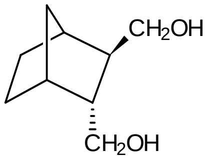


(10)

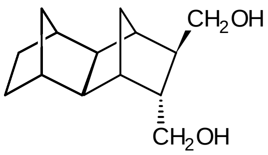
The copolymers were amorphous when the TMCBD (~50/50 *cis/trans*) content was about 40 to 90 mol% of total diol. The glass transition temperatures were 80-168ºC, depending on the proportion of rigid TMCBD units. The crystalline behavior of the TMCBD/diol terephthalate copolyesters is governed by the proportion of TMCBD and also to some extent by the *cis/trans* isomer ratio. The TMCBD terephthalate "homopolymer" is semicrystalline, with a T_m onset above 300ºC[72-75]. The copolyesters were amorphous, transparent materials and soluble in CH_2Cl_2 when the proportion of TMCBD was about 40-90 mol % of total diol and the TMCBD *cis/trans* ratio was near 50/50. Below about 40- mol% TMCBD the TMCBD/PD copolyester became semicrystalline. At 25% TMCBD, the copolyester exhibited cold crystallization and a distinct T_m. Studies show that higher *trans/cis* TMCBD isomer ratios may promote crystallinity. The copolyesters can be used in applications in which high clarity, low shrinkage during molding, weatherability and toughness are desired. Examples are molded articles such as lenses, glazing, packaging and compact disks.

1.3.4 Bicyclo[2.2.1]heptane (norbornane) rings

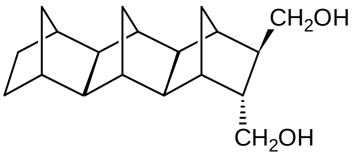
Norbornane and norbornane condensed structures are readily available source whose potential for incorporation in polymers has not been fully evaluated. Jackson and Caldwell[81] disclosed the use of the bisphenols of such structures for the preparation of polycarbonates having glass transition temperatures (T_g) that increase as the size of the polycyclic side group become greater. They attribute this increase in T_g to stiffness and bulk factors. Norbornane and norbornane condensed diesters and dimethanols have been synthesized by Wilson and Hamb[82] for the synthesis of polyesters.



(11a)



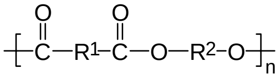
(11b)



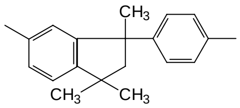
(11c)

Polyesters synthesized from norbornane-2,3-*trans*-dimethanol (**11a**), perhydro-1,4:5,8-dimethanonaphthalnene-2,3-*trans*-dimethanol (**11b**) and perhydro-1,4:5,8:9,10-trimethano- anthracene-2,3-*trans*-dimethanol (**11c**) with dimethyl terephthalate and 1,1,3-trimethyl-3-(4-carboxyphenyl)-5-carboxyindan (**Table 1.3)** were low molecular weight polyesters and they had very high T_g >100°C. Increasing the number of norbornane residues in polymer side chains results in increase in T_g from 117 to 197°C in the case of terephthalate polyesters and from 172 to 227°C for polyesters prepared from carboxyindan. This is due to the increase in the size of norbornane moiety relative to the polymer repeat unit. The chain stiffness and bulkiness of the polymer chain is also increased. In addition to the increase of stiffness three-dimensional norbornane ring results in reduced segmental mobility. This latter effect becomes increasingly important with added norbornane residues.

Table 1.3 T_g and inherent viscosity values of polymers prepared from **(11a)**, **(11b)** and **(11c)** and dimethyl terephthalate or 1,1,3-trimethyl-3-(4-carboxyphenyl)-5-carboxyindan[82]



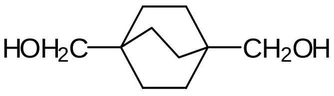
$$\left[\overset{O}{\overset{\|}{C}} - R^1 - \overset{O}{\overset{\|}{C}} - O - R^2 - O \right]_n$$

R^1	$-CH_2-CH_2-$		**(11a)**		**(11b)**		**(11c)**	
R^2	$\eta_{inh}{}^d$ dL/g	T_g (°C)	$\eta_{inh}{}^d$ dL/g	T_g (°C)	$\eta_{inh}{}^d$ dl/g	T_g (°C)	$\eta_{inh}{}^d$ dL/g	T_g (°C)
Terephthalic acid	-	22[a]	0.38	117	0.19	154	0.27	197[b]
	0.33[b]	92[c]	0.38	172	0.28	195[b]	0.20	227[b]

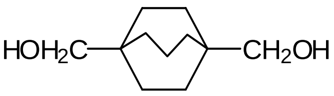
[a]Data of Smith et al[83], [b]Measured in chloroform, [c]2.5°C/min [d]Measured in1:1 (w/w) phenol-chlorobenzene solution at 25°C.

1.3.5 Bicylco[2.2.2]octane and bicyclo[3.2.2] nonane rings.

Taimr and Smith[84] have studied polyesters containing bicylco[2.2.2]octane and bicyclo[3.2.2] nonane rings. The diol, 1,4-bis(hydroxymethyl)bicyclo [2.2.2] octane[84,85] has a rigid symmetrical structure (steric size) similar to that of *cis*-1,4-cyclohexanedimethanol in the boat conformation.



(12a)



(12b)

Polyesters synthesized from 1,4-bis(hydroxymethyl)bicyclo [2.2.2] octane **(12a)** and aliphatic dicarboxylic acids were semicrystalline, while the polyesters synthesized from

1,5-bis(hydroxymethyl)bicyclo[3.2.2] nonane **(12b)** were non crystalline gums (**Table 1.4**). The terephthalate polyester of **(12a)** had a very high T_m >300°C while the polyesters synthesized from **(12b)** were low melting and low molecular weight.

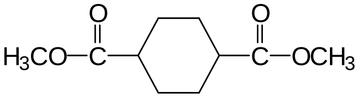
Tabe 1.4. Thermal properties of polyesters of p-xylylene glycol, 1,4-cyclohexane dimethanol, bicyclo[2.2.2] and [3.2.2] diols with various diacids[84]

	T_m of polyester, (°C)			
Diacid	p-xylylene glycol	1,4-cyclohexane dimethanol	1,4-bis(hydroxy methyl)bicyclo [2.2.2]octane	1,5-bis(hydroxy methyl)bicyclo [3.2.2]nonane
Adipic acid	78-81	122-124	99-101	80-82
Suberic acid	79-82	94-96	74-77	amorphous
Azelaic acid	63-66	45-50	34-37	amorphous
Sebacic acid	88-93	72-78	63-65	amorphous
Terephthalic acid	263-272	312-318	304-307	150-170

1.4 Polyesters containing cyclic diacid/diesters

1.4.1 1,4-cyclohexanedicarboxylate

1,4-Cyclohexane dicarboxylic acid or the ester of 1,4-CHDA (DMCD) **(13)** can be used for the synthesis of polyesters. DMCD is available with >95% trans content. The thermodynamic equilibrium for DMCD is at ~66% trans content. It is preferable to have trans-enriched DMCD as starting component above the thermodynamic equilibrium. Jackson et al[75]have synthesized aliphatic polyesters of CHDA with various diols (**Table1.5**). Polyesters synthesized from straight chain diols have low T_g, while the polyesters synthesized from cyclic diols have high T_g.



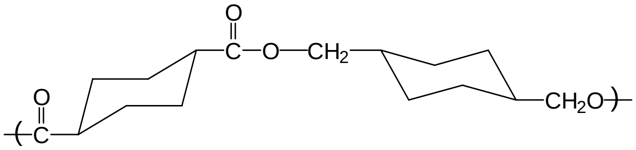
(13)

Table 1.5 Polyesters of trans-1,4-cyclohexanedicarboxylic acid with various diols[75]

Diol constituent	$[\eta]^a$	T_g, (ºC)	Relative cryst., %
Ethylene glycol	0.84	18	0
1,3-propanediol	0.91	-6	0
1,4-butanediol	1.13	-10	19.5
2,2-dimethyl-1,3-propanediol	1.06	30	5
1,4-cyclohexanedimethanol	0.52	52	0
2,2,4,4-tetramethyl-1,3-cyclobutanediol	0.77	169	0
Bisphenol-A	1.09	150	0

[a]Measured in 60/40 (w/w) phenol-tetrachloroethane at 25°C

Crystallizable polyesters of cycloaliphatic diacids or derivatives thereof with aliphatic and/or cycloaliphatic diols have relatively high melting points and are UV resistant as they do not appreciably absorb in the UV region [75,87]. Poly(1,4-cyclohexanedimethyl-1,4-cyclohexanedicarboxylate), PCCD **(14)**, is an aliphatic polyester having desirable properties for weatherable applications[88-91]. It is characterized by desirable properties such as high crystallinity and resistance to weathering upon exposure to ultraviolet radiation. These properties have increased interest in commercialization in the recent years. The T_m of PCCD is in the range of 220-235ºC and has a T_c in the range of 152-171ºC.



(14)

In the preparation of polyesters such as PBT or PET from glycols and dimethyl terephthalate, it is customary to employ a stoichiometric excess of the volatile glycol (e.g., ethylene glycol or 1,4-butanediol) of the order of 20-50% excess and remove the excess by distillation after the first oligomerization or “pre-condensation” step, subsequently followed by an ester interchange reaction for building molecular weight. This is, however, not possible in the case of PCCD preparation since the diol employed, namely, 1,4-cyclohexanedimethanol (CHDM) is relatively non-volatile (boiling point ~ 286ºC). Hence it is necessary to do the reaction of CHDM with 1,4-

cyclohexzanedicarboxylic acid dimethyl ester (DMCD) in one step and exercise tight control of stoichiometry to produce a high molecular weight product, typically a M_w of 70,000 or greater. For example, DMCD is typically employed in about 0.5 mole percent excess.

Various factors were found to affect the crystallinity of PCCD. They are the isomeric state of CHDM and DMCD, the tendency of crosslinking and/or branching reactions, which occur during polymerization. The proportion of the *trans* isomer in DMCD as supplied is of the order of 99%. During the PCCD-forming reaction, isomerization of DMCD can take place with an increase in the level of the *cis* isomer, resulting in the decrease of crystallinity. CHDM does not undergo isomerization during polymerization.

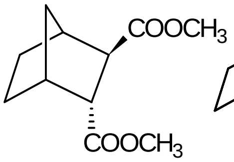
The T_m of the polymer is dependent on the *trans:cis* ratio in the polyester. US patent 6,455,664 B1[91] describes the rate of isomerization vs. polymerization as an important parameter that is desirably controlled during the process for the formation of PCCD. The variability in T_m is attributed to the trans isomer content of the CHDM and DMCD moieties in the polymer, due to *trans* to *cis* isomerization of the DMCD portions of the polymer backbone, especially at extended reaction times. Higher trans content results in a higher T_m, higher degree of crystallinity and faster crystallization rates.

Also, it has been observed that some degree of gel formation occurs during polymerization, decreasing the T_c and, thus, the crystallinity. This is apparently the result of crosslinking-branching reactions. USP 6,084, 055[90] describes a method for synthesize of PCCD with a high M_w in the range of 70,000 to 93,000 and with a high degree of crystallinity and capability of rapid crystallization. The T_m was found to be in the range of 212-234ºC and a T_c above 175ºC.

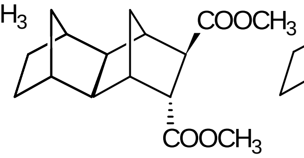
USP 5,986,040[89] to Patel and Smith describes molding compositions based upon blends of thermoplastic resin incorporating 1,4-cyclohexanedicarboxylic acid units in the polymer chain having good impact resistance, good processability and transparency.

1.4.2. Bicylco[2.2.1] heptane ring

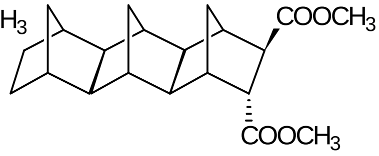
Norbornane and norbornane condensed diesters were synthesized by Wilson and Hamb[82] for the synthesis of polyesters. The polyesters prepared from the various isomers of diethyl norbornanedicarboxylate and ethylene glycol exhibited the T_g values shown in **Table 1.6**.



(15a)

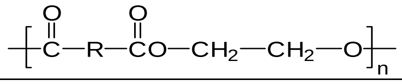


(15b)

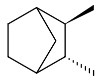
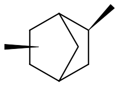
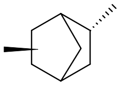
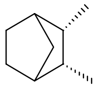


(15c)

Table 1.6 T_g values and inherent viscosities of polymers prepared from isomers of diethyl norbornanedicarboxylate and ethylene glycol[82]

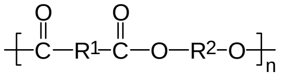


$$\left[-\overset{O}{\overset{\|}{C}}-R-\overset{O}{\overset{\|}{C}}O-CH_2-CH_2-O- \right]_n$$

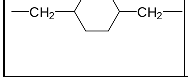
R	η_{inh}[a] dL/g	T_g (°C)
	0.98	41
	Partially crosslinked	40
	0.79	23
	0.63	36[a]

[a]Measured in tetrahydrofuran

Table 1.7 T_g and inherent viscosity values for polymers prepared from diethyl norbornane-2,3-*trans*-dicarboxylate **(15a)**, diethyl perhydro-1,4:5,8-dimethano naphthalene-2,3-*trans*-dicarboxylate **(15b)** and diethyl perhydro-1,4:5,8:9,10-trimethano-2,3-*trans*-dicarboxylate **(15c)** and ethylene glycol or 1,4-cyclohexanedimethanol[82]



$$\left[-\overset{O}{\overset{\|}{C}}-R^1-\overset{O}{\overset{\|}{C}}-O-R^2-O- \right]_n$$

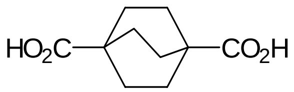
R^1=	$-CH_2CH_2-$		**(15a)**		**(15b)**		**(15c)**	
R^2	η_{inh}[b] dl/g	T_g, (°C)	η_{inh}[b] dl/g	T_g, (°C)	η_{inh}[b] dl/g	T_g, (°C)	η_{inh}[b] dl/g	T_g, (°C)
$-CH_2-CH_2-$	0.56	-5[a]	0.98	41	0.56	95	0.27	156
	0.29	-4[a]	0.34	67	0.38	111	0.27	146[a]

[a] 2.5 °C/min [b]Measured in1:1 (w/w) phenol-chlorobenzene solution at 25°C.

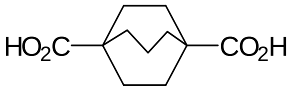
The effect of increasing the concentration of the norbornane moiety on T_g by introducing it as a polymer side chain for the polyesters of dimethyl succinate, **(15a)**, **(15b)** and **(15c)** with ethylene glycol and 1,4-cyclohexanediemthanol is shown in **Table 1.7**. Increasing the number of norbornane residues emanating from the polymer chain is seen to cause increases in the T_g of these polymers.

1.4.3 Bicylco[2.2.2]octane-1,4-dicarboxylate and bicyclo[3.2.2] nonane-1,5-dicarboxylate

Polyesters of bicyclo[2.2.2] and [3.2.2] dicarboxylic acids and various aliphatic diols were synthesized by Taimr and Smith[84] **(Table 1.8).** When the aliphatic diol contains an even number of carbon atoms, there is again little difference between an aromatic ring and a bicyclo[2.2.2]octane dicarboxylate insofar as the melting point is concerned. However, polyesters prepared from diols with an odd number of carbon atoms and terephthalic acid melt at a higher temperature than the analogous polyesters with a bicyclo[2.2.2]octane ring. The polyesters synthesized from bicyclo[3.2.2] nonane dicarboxylate **(16a)** have lower melting points than bicyclo[2.2.2] octane dicarboxylates **(16b)**.



(16a)



(16b)

Table 1. 8 T_m of polyester: comparison of the diacid ring system, HO_2C-R-CO_2H[84]

	T_m of polyester, (°C)		
Diol unit	TPA	**(16a)**	**(16b)**
Ethane diol	258-262	[a]	[a]
1,3-Propane diol	225	140-143	[d]
1,4-Butane diol	225	233-238	127-130
1,5-Pentanediol	136-140	54-56	[d]
1,6-hexanediol	157	144-147	50-55
1,4-cyclohexamedimethanol	312-318	310-315	188-192

[a]Amorphous [d] Noncrystallizable gum

Table 1.9 T_m of bridged polyesters having bicyclo diol and diacid units[84]

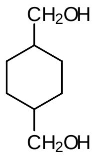
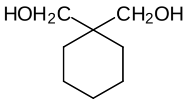
	Diacid unit					
	(16a)			**(16b)**		
Diol unit	T_m, (°C)	η_{inh}^{a}	T_{10}^{b}	T_m, (°C)	η_{inh}^{a}	T_{10}^{b}
(12a)	380-390	0.25	452	225-227	0.24	455
(12b)	244-246	0.21	455	172-177	0.27	457

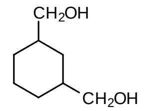
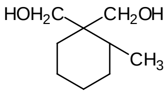
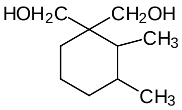
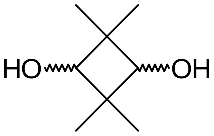
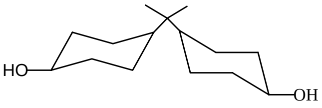
[a]Measured in 60/40 (w/w) phenol-tetrachloroethane [b] decomposition temperature at 10% loss

A few polymers derived from triptycene have been reported[92]. Among this group, the terephthalate-bis(hydroxymethyl)triptycene polymer melts at 350-380°C compared with 304-307°C for the terephthalate-bis(hydroxymethyl)bicyclo[2.2.2]octane polymer. The structural difference between these two polymers is essentially the three benzene rings fused to the bicyclo[2.2.2]octane ring. The additional rigidity conferred upon the repeat unit by this structure, must account for the higher melting point of the triptycene polymer[92].

The patent literature on the various cycloaliphatic diols and diesters/diacids used for the synthesis of the polyesters are summarized in **Table 1.10** and **1.11**.

Table 1.10 Patent literature on polyesters of various cycloaliphatic diols

S. No.	Cycloaliphatic diol	Comonomers	Reference
1		TPA, 1,4-CHDA	35
2		C_2-C_{12} diacid, TPA, IPA, 1,4-trans-CHDA, 2,6-NDA	29
3		DMT, 1,4-BD	93
4		DMT, EG	320
5		DMT, 1,2-propanediol	94
6		TMCBD, DMT,EG	95
7		DMT, EG	96
8		DMT, DMI, DMN, EG	97

9		Phthalic anhydride	98
10		Terephthaloyl chloride	99
11		Terephthaloyl chloride	99
12	TMCBD 	DMT, trans-1,4-cyclohexane dicarboxylic acid, CHDM	73
13		DMT	72
14		Azelaic acid	100
15		DMT, CHDM	101
16		1,4-CHDA, TPA	75
17		CHDA, CHDM	102
18		1,2-CHDA, 1,3-CHDA, 1,4-CHDA, adipic acid	103
19		DMT, EG, PD, BD	78
20		DMT, CHDM	104
21		Diphenyl ester of 1,4-CHDA, TPA, CHDM	74
22		1,3-PD, 1,4-BD	77
23		DMT, EG	79
24	HBPA 	IPA, Adipic acid, trimethylol propane, neopentyl glycol	105
25		TPA, IPA, TMP, NPG	106
26		TPA, EG, glycerol	107
27		DMT, DMI, EG, NPG, Fumaric acid	108
28		DMT, EG, NPG	109

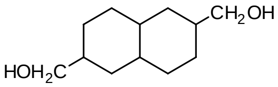
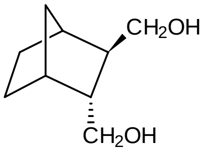
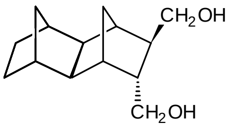
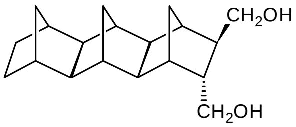
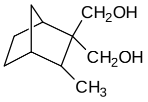
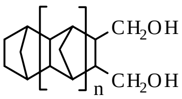
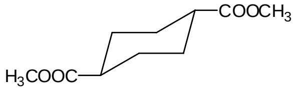
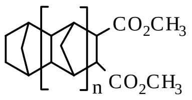
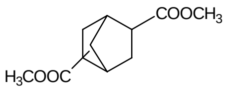
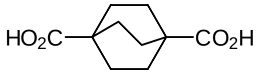
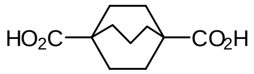
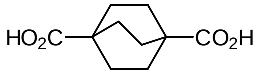
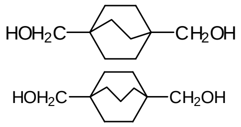
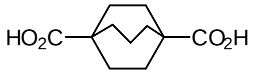
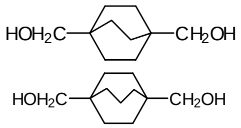
29		DMT, Nadic anhydride, NPG, EG	110
30		1,4-CHDA, NPG, TMP	111
31		1,4-CHDA, NPG, TMP	112
32		TPA, IPA, 1,4-CHDA, 1,3-CHDA, NPG, EG, CHDM	113
33		TPA, IPA, succinic acid, adipic acid, sebacic acid	38
34		1,2-CHDA, 1,3-CHDA, 1,4-CHDA, TMP	114
35		DMT	82, 115
36		DMT	82
37		DMT	82
38		TPC	99
39		TPA, EG	116
40		TPA, EG	117

Table 1.11 Patent literature on polyesters of various cycloaliphatic diacids

S. No.	Diacid/Diester	Comonomer	Reference
1.		CHDM	35, 88-91
2		EG, PD, BD, CHDM, TMCBD	75
3		CHDM, long chain dimer acid	118
4		HBPA, TMP, NPG, TPA, IPA	113
5		CHDM, BD, DMT,	119
6	 n = 0-2	EG, CHDM	82
7		EG	82
8		EG, PD, BD, PD, HD, CHDM	84
9		EG, PD, BD, PD, HD, CHDM	84
10			84
11			84

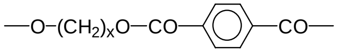
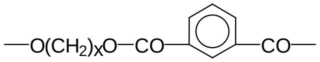
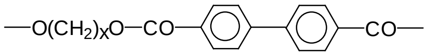
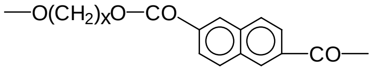
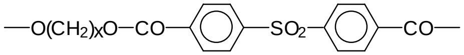
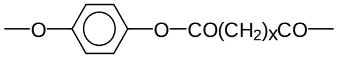
1.5 Relationship of monomer structure to polymer properties

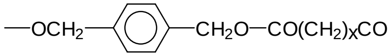
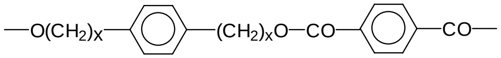
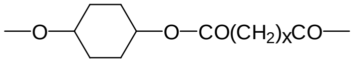
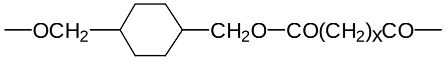
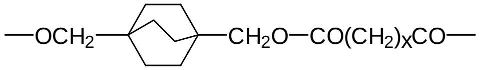
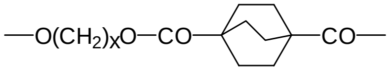
The terephthalate polyesters **(Series 1, Table 1.12)** are tough, colorless crystalline solids with melting temperatures alternating between successive even- and odd-numbered methylene units and passing through a minimum at $(CH_2)_7$ before approaching the limiting polymethylene value[1]. The T_g and T_γ values (both properties of the amorphous phase) fall steadily with increasing methylene-group content. There are considerable differences in the propensity for and rates of crystallization, which varies with the number of methylene groups. When x = 3, 4, 6 or higher even numbers, crystallization is rapid from the melt. When for x = 5 and 7, crystallization is slow. PET is readily quenched from the melt to an amorphous state. The amorphous phase is indefinitely stable unless crystallization is induced by heating or by the action of solvents. The density of the poly(alkylene terephthalate)s varies with crystallinity and ranges between 1.2-1.4 g/cc. At ambient temperatures, the lower members (x= 2,3,4; when crystalline) dissolve in phenols, phenol-chlorohydrocarbon mixtures, and trihalogenoacetic acids. There is a wider range of solvents at higher temperatures. Poly(hexamethylene terephthalate) (PHT), by contrast, is freely soluble in chloroform.

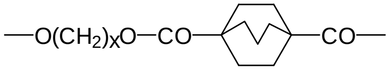
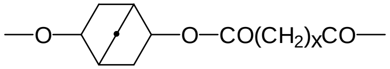
Replacement of the hydrogen atoms by other atoms or groups, eg, halogen, alkyl, or alkoxy exhibit T_g, T_m similar to those already mentioned for poly(alkylene terephthalates). The unsymmetrically substituted isomeric pair poly(1,2-propylene terephthalate) and poly(ethylene methylterephthalate), are amorphous resins. The symmetrically disubstituted poly(ethylene 2,5-dimethylterephthalate) is crystalline but lower melting (T_m = 175-180°C) than PET[1]. However, in the unsymmetrically substituted members, crystallinity can be reestablished by altering the balance between the sizes of the monomer units. Consequently, poly(ethylene fluoroterephthalate), poly(tetramethylene methylterephthalate), and poly(hexamethylene bromo terephthalate) are all crystalline[120]. Terephthalate polyesters with longer alkyl groups or with multiple alkyl substituents on the diol moiety are known[121,122]; of the poly(2,3-dialkyltetramehtylene terephthalate)s, only those with two methyl or with two hexadecyl substituents are crystalline with T_m of 123 and 14°C, and T_g of 43 and -26°C, respectively.

The poly(alkylene isophthalate)s **(Series 2, Table 1.12)** illustrate the importance of symmetry in the repeat unit. These polymers with meta-substituted rings crystallize only with difficulty and require external influence such as solvent or heat for crystallization etc. The 'as-measured' heat of fusion of poly(tetramehtylene isophthalate) is only half that of poly (tetramethylene terephthalate), though when the values are adjusted to 100% crystallinity, the isophthalate has the higher value.[123,123] Polyesters of phthalic acid (ortho substitution), even with symmetrical diols, lack true structural regularity because of the

Table 1.12 Transition temperatures of Ring-containing polyesters[1]

Series	Structural type	Repeating-unit formula	Tm, °C, for repeating unit with x =										
			0	1	2	3	4	5	6	7	8	9	10
1	Poly(alkylene terephthalate)			269	265	233	232	134	154	85	132	95	125
	T_g^a				115	95	80	45	45		45	35	25
	T_g^b			101	69	35	22	10	-9	3		-3	-5
	T_γ^a				-30	-30	-60	-95	-107		-100	-115	-125
					-45		-83	-102	-110				
2	Poly(alkylene isophthalate)				240	132	152	amorph	140				
3	Poly(alkylene 4,4'-bibenzoate)				>350	280	328	217	240	150	193	128	164
4	Poly(alkylene 2,6-naphthalene dicarboxylate)			340	266	199	241	135	211	130	185	124	144
5	Poly(alkylene sulfonyl-4,4'-dibenzoate)				340	320		288	279		215		230
6	Poly(p-phenylene alkylene dicarboxylate)		>350	267	310	194	230	165	186	135	165		

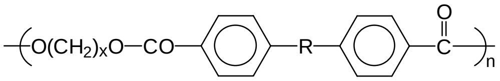
7	Poly(p-xylylene alkylene dicarboxylate)		214		115	58	81	67	82	74	93	94
8	Poly(p-phenylene dialkylene terephthalate)		>350	265	320	155	220	125				
9	Poly(trans-1,4-cyclohexanediyl aldylene dicarboxylate)				268	212	225	163		127	144	
10	Poly((1,4-cyclohexanedimethylene alkylene dicarboxylate)											
	Cis-				62		55	Liq	50	41	50	46
	Trans-		215		147	50	124	42	96	50	78	85
11	Poly([2.2.2]bicyclooctane-1,4-dimethylenealkylene dicarboxylate)						101		77	37	65	
12	Poly(alkylene[2.2.2]-bicyclooctane-1,4-dicarboxylate)					143	238	56	147			

13	Poly(alkylene[3.2.2]-bicyclononane-1,4-dicarboxylate			amorph	130	amorph	55
14	Poly(norcamphane-2,5-diyl alkylene dicarboxylate)		250		150		

steric volumes of the -COO- groups which do not allow the groups to be coplanar with each other and with the benzene ring; the resulting randomly disposed out-of-plane twists, therefore, presents a non-periodic pattern along the chains and the materials do not crystallize.

Series 3 (Table 1.12) shows the effect of extending the length of the rigid component of structure in the dicarboxylic acid moiety, such as by the use of biphenylene moiety. The melting temperatures are raised substantially as compared with the members of **Series 1** having the same numbers of methylene groups in the repeat unit.

A similar, though a less marked effect is seen for most members of **Series 4 (Table 1.12)** where the span of the 2,6-naphthalenediyl unit is smaller than for the 4,4'-biphenylene group[1]. Numerous polyesters of the general formula are known.



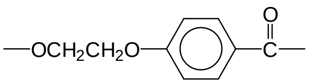
(17)

When x=2 and ‘R’ is a group of low polarity, such as -O-, -S-, $-CH_2-$, $-CH_2CH_2-$, or -O(CH2Y)$_y$O-, the melting temperatures lie within the range 150-250°C. However, when ‘R’ is a strongly polar $-SO_2-$ group **(Series 5, Table 1.12)**, together with the benzene rings, extended rigid structures results leading to polymers with enhance T_m.

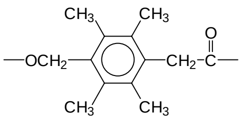
In the polymers of **Series 6 (Table 1.12)** which are isomeric with those of **Series 1** (by inversion of the ester groups around the C_6H_4-O axis) because of the steric volumes of the ortho-hydrogen atoms, the T_m tend to be higher.

In **Series 7**, the impedance is relieved by the intervening benzylic methylene groups (which additionally has no preferred conformations around the C_6H_40-CH_2 bonds) and low T_ms are observed, but higher melting temperatures are restored in **Series 8** where the acid unit is benzenoid.

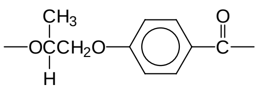
The foregoing effects of structural variation are met equally in AB-type polyesters.



(18)



(19)



(20)

Thus, polymer **(18)** where R = H, melts at 225°C, for R=OCH_3, Cl, CH_3, respectively[125,126] steric impedance leads to T_m values of 272, 285 and 292°C respectively, and the highly hindered substance **(19)** has T_m = 327°C[127]. On the other hand, in **(20)**, which is isomeric with **(18)**, where R = CH_3, the restriction to rotation around the C_6H_4-O axis is alleviated by the distancing of the methyl group from the polymer resulting in T_m = 149°C (in isotactic and optically active form), considerably lower than for **(16)**, where R = H and in accordance with the normal substitution effect[128].

The remaining groups in **Table 1.12 (Series 9-14)** [29,84,85] exemplify the effects of incorporating alicyclic rings into the repeating units. As with the aromatic series, the properties are influenced by (i) the ring:chain ratio, (ii) the directionality of the ester groups (iii) stereochemistry (*cis* or *trans* forms) of the rings and (iv) by symmetry variations where the rings are bridged. However, it is to be noted that polymers with high T_m can be obtained even in the absence of aromatic components, which was once thought to be a necessity.

The polyesters of trans-1,4-cyclohexanedimethanol and the aliphatic dibasic acids with an even number of carbon atoms melt at a slightly higher temperature than the analogous polyesters from p-xylylene glycol. In the case of polyesters from aliphatic dibasic acids with an odd number of carbon atoms, the situation is reversed and the polyesters of trans-1,4-cyclohexanedimethanol melt at a slightly lower temperature **(Table 1.1)**. Insofar as polyesters from aliphatic dibasic acids are concerned, it must be concluded that the trans-1,4-cyclohexylene and the p-phenylene rings are about equal in their ability to confer high melting points to the polyester molecules containing these moities[18]. Furthermore, this ability must be due to the rigidity and symmetry of the rings, properties that are not uniquely characteristic of the aromatic rings.

Polyesters prepared from aromatic dibasic acids and trans-1,4-cyclohexane dimethanol or p-xylylene glycol contain a combination of rigidity and/or symmetry in the acid component with rigidity and symmetry in the diol component. In such cases trans-1,4-cyclohexanedimethanol appears to be superior to p-xylylene glycol insofar as the T_m is concerned. With trans-1,4-cyclohexanedimethanol, polyesters of exceptionally high melting points are formed.

In the case of the polyesters synthesized from norbornane and norbornane condensed diesters and dimethanols[82], (**Table 1.3**), have T_g >100°C. Increasing the number of norbornane residue in polymer side chains results in linear increase in T_g. The increase is an apparent function of the size of norbornane moiety relative to the polymer repeat unit. Varying the points of substitution in the norbornane moiety has been found to have little effect on the T_g of polyesters prepared from these compounds

Table 1.4 compares the T_m of polymers which differ only in the nature of the ring present in the diol portion of the repeat unit, i.e., 1,4-phenylene**,** *trans*-1,4-cyclohexylene, 1,4-bicyclo[2.2.2]octane and 1,5-bicyclo[3.2.2]nonane[84]. The T_m of the polyesters synthesized from aromatic glycol and cycloaliphatic glycols are comparable. While the polyesters synthesized from bicyclo[3.2.2] nonane are low melting. This is due to the reduced symmertry of the bicyclo ring. The terephthalate polyesters of cyclohexane dimethanol and 1,4-bis(hydroxymethyl)bicyclo [2.2.2] octane are higher melting than p-xylene glycol.

Turning to polyesters prepared from the bicyclo dicarboxylic acids[84] **(Table 1.8)** a somewhat different behavior is be observed. If the aliphatic diol contains an even number of carbon atoms, there is again little difference between an aromatic ring and a bicyclo[2.2.2]octane ring insofar as the melting point is concerned. However, polyesters prepared from diols with an odd number of carbon atoms and terephthalic acid melt at a higher temperature than the analogous polyesters with a bicyclo[2.2.2]octane ring. The polyesters prepared from bicyclo[3.2.2]nonane dicarboxylates have low T_m than the terephthalate and bicyclo[2.2.2] octane dicarboyxlate.

The effect of combining two rigid bridged ring systems in a polymer repeat unit is shown in **Table 1.9**. A combination of two bicyclo[2.2.2]octane rings produces a polymer of remarkably high T_m considering that it is completely free of any aromatic component. Replacement of one of these rings by a less symmetrical bicyclo[3.2.2]nonane ring produces a sharp drop in T_m. A combination of two bicyclo[3.2.2] nonane rings again produces a sharp drop in melting point, a further reflection of the importance of symmetry[84].

The polyesters containing the bicyclo[2.2.2]octane and bicyclo[3.2.2]nonane ring containing diols and diacids have decomposition temperature around 400 and 420-430°C for T_{10} (10 % weight loss) and T_{50} (50 % weight loss). When two rings are present in the repeat unit, of which one maybe a bridged ring, shows a higher thermal stability. The T_{10} and T_{50} values of 420-430 and 440-450°C are observed. Polymers based on 1,4-cyclohexane dimethanol appear somewhat less stable than their bridged analogs. When two bridged rings are present in the same repeat unit (Table 1.9) the polyesters show thermal stability >450°C. The higher thermal stability of these polymers are attributed to the fact that the β-hydrogen elimination is not possible in these bicyclic ring containing monomers[84].

Semicrystalline polyterephthalates such as PET, PTT and PBT exhibit T_g's around 40-70ºC. But for quenched, amorphous samples, the T_g is lower, e.g., about 40ºC for amorphous PTT[129]. The T_g for the homopolymer of TMCBD **(7)** (52% trans) and terephthalic acid is 174ºC (184ºC, 60% trans[75]). Therefore, the rigid TMCBD unit boosts the T_g by about 130-140ºC compared to the case of the corresponding polyterephthalate linear diol analogues. The effect of the rigid TMCBD unit on T_g is similar in magnitude to common rigid aromatic backbone groups.

1.6 Properties

1.6.1 Crystallization and morphology

Cyrstallinity and crystallization are important properties of aliphtaic-aromatic polyesters, and have been studied by various methods for PET and PBT[130-141]. In fact, properties of crystallizable polyesters are strongly dependent on the morphological structure (size, shape, perfection, volume fraction, and orientation of crystallites), which is formed by crystallization from the molten state. Thus, for crystallizable polymers, crystallization behavior is an interesting research subject to control morphological structure and to understand the resultant properties[142].

In the absence of nucleating agents and plasticizers, PET crystallizes slowly and, therefore, is best used in application where crystallinity and strength can be enhanced through mechanical orientation, for example, oriented fibers, biaxially oriented films, and soft-drink bottles produced by stretch-blow-molding techniques, which introduce a high degree of orientation in the finished part[143,144]. The PET crystallization rate is dependent on the molecular weight of the polymer[145], as shown in **Table 1.13**, which compares with the crystallization halftime for various molecular weights.

Table 1.13 Effect of molecular weight[145] on crystallization halftime[a] of PET[b]

Molecular weight[c], number average	Halftime of crystallization, min
11,200	3.5
13,600	9.00
14,000	15.00
15,200	17.5
15,800	18.5

[c]Obtained from VPO.

As the molecular weight is lowered, chain mobility and the crystallization rate increases. Engineering PET grades are highly crystalline; film and bottle grades are more amorphous. For injection molding grades, fast crystallization rates are necessary at lower mold temperatures to give parts with a high degree of crystallinity. In addition, the crystals and spherulites must be small to maintain high impact strength. In order to realize acceptable crystallization rates of PET at mold temperatures below 100°C, modifications are necessary to induce crystallization at a rapid rate. By selecting the proper molecular weight for modification, crystallization halftimes can be reduced significantly. A measure of crystallinity can be obtained by determining the ratio of the heat of cold crystallization ΔH_{cc} of amorphous polymers to the heat of fusion ΔH_f of fully crystalline polymer.

In contrast with PET, PBT is one of the fastest crystallizing polymers and does not require nucleating agents[146,147]. It is particularly well suited for extrusion and injection-molding application, where the high rates of crystallization ensure short processing cycles and excellent thermodynamically and dimensionally stable parts. The crystallization kinetics of PBT has only been partially investigated[144]. An interesting property, which has led to useful blends of PET and PBT, is that these polymers are miscible in all proportions in the melt, but crystallize as separate phases on cooling[121].

1.6.2 Crystallization kinetics

A very important characteristic of semicrystalline polymers that strongly influences the utility of the material for a given application is the crystallization rate. For example, PET, used extensively in fiber and packaging applications, possesses a relatively minor share of the injection molding market because of its relatively slow rate of crystallization. In contrast, PBT is used extensively for injection-molding applications because of its relatively fast crystallization rate[2]. Fast crystallization allows for high production rates of molded articles, since the time needed for the material to solidify in the mold is a function of crystallization rate.

The study of bulk crystallization kinetics of polymers is an important step in understanding, predicting and designing structural formation under various processing conditions. In general, the well-known Avrami equation and secondary nucleation theory could describe well the crystallization kinetics of polymers. The crystallization kinetics of polymers is analyzed using a classical Avrami equation[148-150] as given in the following equation:

$$1-X_t = \exp(-kt^n)$$

where, X_t is the developnment of crystallinity X_c at time t. The k value is the Avrami rate constant and the n value is the Avrami exponent. Both k and n depend on the nucleation and growth mechanisms of spherulites. The value of n is usually an integer between 1 and 4 for different crystallization mechanisms. It has also been observed that n is a fraction due to the secondary crystallization or the crystal imperfection. Indeed, for spherulitic growth and athermal nucleation n is expected to be 3. In the case of thermal nucleation, it is expected to be 4. On the other hand, the n value close to 2 may hint an athermal nucleation process followed by a two-dimensional crystal growth[151].

Generally, the complete relationship between crystallization temperature and crystallization rate is difficult to obtain when the crystallization rate is too fast. The extensive literature on the crystallization of PET was the subject of a recent review[152]. For PET, the Avrami exponent n ranging from 2 ~ 4 has been reported, depending on the molecular weight, chemical purity, melt condition, and crystallization temperature[151,153-155]. For example, the overall crystallization kinetics change from slow crystallization with an Avrami exponent n = 2 at 90-160ºC to n = 3 in the faster crystallization, and finally approaches n = 4 above 230ºC where the crystallization rate is slow again. As for PBT, the Avrami exponent n = 2.6-2.8 has been reported, and the melt crystallizes faster than the PET under same supercooling condition[151,156]. Huang and Chang[157] have studied the crystallization behavior for PTT from melt state and compared the crystallization parameters with those for PET and PBT. The average value of the n determined in each crystallization temperature is about 2.8, indicating that both the nucleation and the growth mechanism are the same in the crystallization temperature range (202-210ºC) investigated. The isothermal melt and cold crystallization behaviors for PTT was studied by Hong et al[158]. For the isothermal melt crystallization, the values of n varied between 2 and 3 with changing crystallization temperature, indicating the mixed growth and nucleation mechanisms. Meanwhile, the cold crystallization with an n of 5 indicated a character of three-dimensional solid sheaf growth with athermal nucleation.

The crystallization rate of the three commercially important polyalkylene terephthalates, PET, PBT and PTT was studied by Chisholm and Zimmer[159]. A comparison of $t_{1/2}$ (measure of overall crystallization) values at equivalent super cooling clearly showed that the rate of crystallization for the three polymer followed the trend: PBT>PTT>PET. Analysis of the crystallization kinetics data using the Avrami equation suggested that crystallization of all three virgin polyesters was similar and consistent with a crystallization process occurring by heterogeneous nucleation and three dimensional spherulitic growths. The average Avrami exponent for virgin PBT, PPT, and PET was 2.48, 2.54, and 2.30, respectively.

PEN is a slowly crystallizing polymer because of the presence of a rigid naphthalene ring and a short flexible ethylene group in the repeating unit and the crystallization has been studied in detail[160,161]. PEN like PET crystallizes from the melt or from the quenched amorphous glass if it is heated above the T_g (cold crystallization). In both cases, time dependence for the isothermal development of crystallinity is described by the Avrami equation. Although reported values of the exponent n range from 2 to 4, n = 2.5 is a good representative value for both PET and PEN. The dominant morphology is spherulitic in nature. However, hedritelike structure sometimes grows at higher temperature. Hu et al[162] have reported that the crystallization rate is about the same for cold and melt crystallization and passes through a broad maximum (minimum in $_{t1/2}$) at about 200-220ºC[160,161,163]. The higher rate of melt crystallization compared to cold crystallization at 180ºC is attributed to formation of additional nuclei during cooling of the melt from 290ºC to the crystallization temperature. The Avrami exponent n was close to 3, corresponding to spherulitic growth with other nucleation, that is, all the crystals started to grow at the same time.

PBN shows fast crystallization rates compared with other polyesters[164]. The enhanced PBN chain mobility due to the flexibility of the long butylene groups, as well as the inter-chain interactions due to the naphthalene rings, can give rise to fast nucleation and crystal growth from the melt. So that PBN cannot be obtained in the amorphous glassy state by cooling from the melt in contrast to PEN. Papageorgiou and Karayannidis[165] studied PBN crystallization rates and morphology, by both isothermal and non-isothermal crystallization. The values were found to be between 2.16 and 2.38 for isothermal and for non-isothermal between 3.2- 4.4.

1.6.3 Crystallization behaviour of copolyesters

In the crystallization behavior of a binary A/B-type random copolymer, which consists of both crystalline components, there is the possibility of finding some degree of isomorphism due to co-crystallization between A and B units with similar repeating units[166]. The co-crystallization behavior is found in copolyesters[29,167-172]. Co-crystallization requires a similar main-chain conformation between two comonomer segments in the crystal lattice. The co-crystallization behaviour can be divided into three types depending on the chemical structure of the A and B comonomeric units.

A. Crystallization of A or B units takes place either in an A-polymer or a B-polymer crystal with complete rejection of the comonomer units from the crystals, exhibiting the crystal lattice transition from the A-crystal to the B-crystal at some intermediate copolymer composition.

B. A units can crystallize with complete rejection of the B units from the crystals, whereas B units can co-crystallize with incorporation of A units to some extent, depending on the copolymer composition. In both (i) and (ii) the T_m is dependent on the copolymer composition and exhibits a minimum (eutectic point) at some intermediate composition at which the crystal lattice transition is usually observed.

C. A and B units can co-crystallize into a single crystal structure (copolymer isomorphism) over the full range of copolymer composition, exhibiting a continuous change in the lattice parameters from the A-crystal to the B-crystal and in the melting temperatures without reaching a minimum point.

The crystallization behaviour in random copolymers is controlled by local crystallization due to fractionation of the crystallizable sequences. The short parts of the crystallizable sequences cannot be involved in crystallization but the longer parts are capable of undergoing crystallization. The crystallizability of each comonomer unit may be a function of the crystallizable sequence distribution, the cohesive energy of molecules, the molecular mobility and the surface free energy of the crystal such as the end and lateral crystal surface energies. All of these parameters should be dependent on the copolymer composition. The crystallization behavior of a random copolymer system is strongly influenced by copolymer sequence distribution. A small variation in the chemical structure brings about considerable changes in the crystallization behaviour.

Okui et al[172] have studied the crystallization behavior of poly(ethylene terephthalate-co-1,4-cyclohexylenedimethylene terephthalate) P(ET/CT) random copolyesters. The copolyesters rich in ET units form crystals with complete rejection of the CT units, whereas CT units can co-crystallize with ET units to some extent in the composition region rich in CT units. The T_m of these copolymers are depressed with an increase in CT in the compositions and show a minimum at the intermediate composition of about 30-40 mol% CT at which the crystal lattice transition occurred.

Baozhong Li et al[173,174] have studied the crystallization behavior of poly(ethylene terephthalate-co-isophthalate) PET/PEI random copolyesters with different molar ratios. With increasing PEI, the copolyesters become less crystallizable and even amorphous when the composition of PEI is above 20%. The WAXD profiles of the crystallizable copolyesters shows that the crystals come from PET homopolymers. The crystallinities of the crystallizable copolyester become lower and crystals grow imperfectly when the composition of PEI increases.

The crystallization behavior in a random copolymer is largely influenced by the copolymer sequence. Zhu and Wegner[175] asserted that only the sequences of the average length crystallize, with shorter and longer sequences being excluded from crystal. Im et al[176] studied the crystallization behavior of poly(ethylene 2,6-naphthalene-co-hexamethylene 2,6-naphthalene) (PEN/PHN) random copolymers. They observed that the molar fraction exhibiting a minimum in the T_m was about 60 mol % HD content. From the results of the crystal lattice spacing they concluded that, when only sequences of ethylene units in the PEN/PHN random copolymer are crystallized, sequences of hexamethylene units are exactly excluded from the crystal formation.

1.6.4 Mechanical properties

Aliphatic aromatic polyesters find end use applications as engineering thermoplastics and hence mechanical properties like tensile yield strength, flexural modulus and impact strength play a key role. The impact strength of a polymer depends significantly on the position of the T_g and the kinetics and degree of crystallization[177]. One of the contemporary research topics on the physical properties of plastic materials is to determine the location of the “tough – brittle” transitions for commercial polymers. Amorphous polymers exhibit brittle fracture well below their T_g, but they become tougher as the T_g is approached. As the temperature increases well above the $T_{g,}$ a rubbery state is developed and the term impact strength ceases to have significance. In crystalline polymers, the toughness depends on the degree of crystallinity and on the size of the spherulitic structures. Large degrees of crystallinity will lead to inflexible masses, which, in turn will result in moderate impact strength. Similarly large spherulitic structures will also result in low impact strength.

The toughness of a polymer also relates to the ability of parts of the polymer chain to conserve certain mobility even at low temperatures. The low temperature relaxation maximum in the dynamic loss modulus is the hallmark for the temperature region in which these molecular motions begin. Therefore the temperature and amplitude of this relaxation is closely related to the toughness of a polymer. Good toughness is usually observed even at low temperature if the γ relaxation occurs at a low temperature and has comparatively high amplitude.

Low temperature relaxations have an effect on the impact strength of polymers. In the past three decades, many studies have focused on the secondary relaxation of polymers[178-181]. Part of the impetus has been to establish a relationship between these secondary relaxations and mechanical properties. The correlation have been established on the basis of the observations that ductile materials have a pronounced low-temperature secondary loss peaks in their dynamic mechanic spectra. The ductile-brittle transition temperature, the temperature or strain rate at which the mode of failure changes from ductile to brittle, was often correlated to secondary relaxation peak temperatures. The broadest review of this correlation was given by Boyer[182] and he compared the temperature dependence of impact strength of several thermoplastics to their respective secondary relaxation peaks and found transitions occurring near loss peak temperatures. However Hejboer[72] noted that the temperatures of secondary loss peaks and the transitions in impact strength could differ considerably. These differences were due to the difficulty in accessing the impact frequencies, which lie in the kilohertz range by dynamic mechanical measurements. Polymers show three transitions, namely, α, β, and γ transitions corresponding to T_m, T_g and T_γ[183]. The dynamic mechanicl analysis of polymers gives insight into the sub-T_g relaxations (low temperature relaxations) occurring in the polymer chain, γ and δ relaxations. Consideration of dymanic mechanical analysis results of polymers suggest that the γ transition is connected with motions in the aliphatic part of the chain and that T_g (β relaxation) is connected to the phenylene carbonyl bond. A series of poly (methylene terephthalate) polymers has been investigated[183] by measurement of dynamic mechanical properties, NMR, IR spectra and X-ray diffraction. Three transitions α, β, γ corresponding to T_m, T_g and to the motions in the aliphatic part of the chain respectively were observed. This study revealed that increasing the number of methylene units resulted in a decrease in the secondary loss peak temperature.

The secondary relaxation of PET has been studied by many researchers[184-187]. PET shows γ relaxation at -70°C. PCT [poly (cyclohexylenedimethylene terephthalate)] shows γ relaxation at -73°C for the cis polymer and -100°C for the trans polymer[188]. Chen and Yee[189] studied a series of PET/PCT copolyesters to ascertain the molecular structure effects on the secondary relaxation and impact strength of the copolyester by DMS. The similarity in shape and temperature between PCT (with a trans/cis ratio of 68/32) and PET loss peaks indicate that a common mechanism for secondary relaxation exists. Hiltner[188] and Baer suggest an analogy between the cis and trans components of the relaxation of PCT to trans and gauche conformations of methylene bonds comprising the loss peak for PET. It was found that the cyclohexylene rings undergo conformational transition from chair to the twist boat to the chair conformation, when moving cooperatively with rings in the adjacent repeat units, inducing translational motions of the terephthalate groups. The concerted motion gives rise to longer-ranged translational excursions along the chain which increase molecular volume fluctuations and facilitate macroscopic shear yielding. A comparison between the secondary loss peak of the copolymers and poly(cylohexyl methacrylate) peak lead to the conclusion that the secondary relaxation of the copolyesters is likely to involve conformational transitions of the cyclohexylene ring. In addition, poly(1,4-cyclohexylene 2,5-dimethylene terephthalate) exhibits two secondary loss peaks, a lower temperature peak very similar in position to the poly(cyclohexyl methacrylate) peak and a higher temperature peak due to the substituted terephthalate linkage. They concluded that these polyesters have aliphatic and terephthalate motions which are separable.

Chen and Yee[190] established a correlation between the yield behavior of copolymers based on poly(ethylene terephthalate) and poly(1,4-cyclohexylenedimethylene terephthalate) (PCT) and their secondary relaxation motions. The yield stress was found to decrease as the cyclohexylene content increases for different temperatures and strain rates. The conformational changes of the cyclohexylene rings reduce the barriers between chain segments sufficiently to facilitate chain slippage. The ductile/brittle transition is viewed as a competition between yielding and crazing with changes in the transition temperature dependent on activation of molecular motions of the cyclohexylene groups.

There currently exists in the vast field of performance plastics a need for a low cost polyester material, which can be easily molded or otherwise formed into various articles requiring a superior combination of high impact strength, high hardness, and high heat resistance. These properties would be especially desirable in melt processable polyesters used for injection molded plastics, fibers, and film and sheeting. The performance plastics utilized in industry generally have (1) high impact strength with a notched Izod strength of at least 53.4 J/m, according to ASTM D256; (2) high hardness, such as a material having a Rockwell L hardness of at least 70, according to ASTM D785; and (3) high heat resistance, heat deflection temperature of at least 70°C at 264 psi loading, according to ASTM D648. There are no polyesters available today having a balance of these three properties.

Polyterephthalates of C_2-C_4 linear diols (PET, PTT and PBT) have poor impact resistance with typical notched Izod values <80 J/m[191-193]. Backbone groups that increase the rigidity of polymer chains by increasing steric interactions or by decreasing conformational flexibility often result in polymers with low impact resistance.

Commercial engineering thermoplastics with T_g's above 100ºC usually have Izod impacts < 250 J/m, often below 100 J/m. Poly(hexamethylene terephthalamide) and bisphenol A polycarbonate are two exceptions(same as before ref), the latter exhibiting a notched Izod of 650-850 J/m and T_g ~ 150ºC[192,194].

Commonly used melt processable polyesters in the performance plastics industry are copolymers made from terephthalic acid, 1,4-cyclohexanedimethanol and ethylene glycol (PET/CT copolyesters)[195]. These copolymers have been the best available melt processable polyesters for most uses due to the fact that they provide for good machinability during processing, provide high impact strength and have relatively low cost. However, these currently used copolyesters are often deficient in that they suffer from low heat resistance and only moderate hardness.

Many articles that are currently formed from PET/CT copolyesters, have increased hardness and/or heat resistance. Examples of articles formed from PET/CT copolyesters having hardness and heat resistance include molded polyester exterior panels used in automobiles and farming equipment, small molded polyester appliance parts, and exterior and interior glazing sheets used to replace windows and glass. The PET/CT copolyesters must contain a substantial amount of CHDM to provide high impact strength.

The glycol component of PET/ CT copolyesters is modified with ethylene glycol in order to strike a balance between the stiffness of PET and the toughness of CHDM polyesters. Increasing the mole percentage of ethylene glycol present in PET/CT copolyesters increases the hardness and decreases impact strength. However, high hardness could not be achieved in the case of PET/CT copolyesters.

Currently copolyesters having high hardness levels and high heat resistance are usually prepared from all-aromatic components. The rigidity and relatively high Tg of the aromatic constituents provide for more hardness and heat resistance. However, the very same properties also tend to make the copolyesters more brittle, providing insufficient impact strength.

The copolyesters from terephthalic acid, 2,2,4,4-tetramethyl-1,3-cyclobutanediol and ethylene glycol[195] have a surprising combination of high impact strength, high hardness and high heat resistance. This superior combination of performance properties is due to the specific composition (**Table 1.14**) of terephthalic acid, 2,2,4,4-tetramethyl-1,3-cyclobutanediol and EG which constituted the copolyester. The diols EG and TMCBD are highly rigid and have high T_g and impact strength.

Table 1.14 Properties of copolyesters of terephthalic acid, TMCBD and ethylene glycol[195]

TMCBD mol %	Ethylene glycol mol %	Izod impact strength[a] (Joules/m)	Rockwell L Hardness[b]	Heat deflection temerature[c] (°C)
0	100	35.2	76	61
13	87	41.1	76	66
34	66	83.8	84	80
50	50	129.8	90	90
56	64	396.2	92	79
44	36	662.2	94	102
69	31	611.4	95	108
84	16	137.8	103	118
100	0	*	*	*

*The polyester molded with extreme difficulty and degraded severly during processing, [a]The notched Izod impact strength of these copolymers was determined according to the procedures of ASTM D256 using an average of five breaks; [b]The Rockwell L hardness was determined following the procedure of ASTM D785; [c]Heat deflection temperature at 264 psi loading was determined according to the procedure of ASTM D648

Table 1.15 Properties of copolyesters of terephthalic acid, 1,4-cyclohexanedimethanol and ethylene glycol[195]

TMCBD mol %	Ethylene glycol mol %	Izod impact strength[a] (Joules/m)	Rockwell L Hardness[b]	Heat deflection temerature[c] (°C)
0	100	44.9	81	62
16	84	55.0	70	60
31	69	48.6	63	64
44	56	90.8	63	61
50	50	921.7	62	66
59	41	1531.5	59	64
77	23	1580.0	56	67
83	17	1170.0	56	65
100	0	1000.7	57	67

[a]The notched Izod impact strength of these copolymers was determined according to the procedures of ASTM D256 using an average of five breaks; [b]The Rockwell L hardness was determined following the procedure of ASTM D785; [c]Heat deflection temperature at 264 psi loading was determined according to the procedure of ASTM D648

Increasing the amount of ethylene glycol in P(ET/CT) copolyesters generally decreases impact strength and increases hardness (**Table 1.15)**. In the case of TMCBD/EG copolyesters, increasing the mole percent of EG significantly lowers the hardness and heat resistance of the copolyester while generally decreasing impact strength. This is surprising since TMCBD is a compound which is more rigid and has a higher T_g than CHDM, and would be expected to combine with a rigid monomer like EG to provide copolyesters having high rigidity, hardness and brittleness than PETCT copolyesters. The copolyester produced from a defined composition of terephthalic acid, TMCBD and EG has a superior combination of impact strength, hardness, and heat resistance than has never been possible with P(ET/CT) copolyesters or other polyesters. Copolyesters having TMCBD from 30 to 85 mol % were synthesized. Copolyesters containing less than about 25 mol % TMCBD tend to have only low to moderate hardness and heat resistance and unacceptable impact strength. However, copolyesters containing more than 85 mol% TMCBD have excessively high inherent viscosities which make the copolyesters difficult to mold or process without excessive thermal degradation.

Terephthalic acid/TMCBD copolyesters having less than about 15 mol% EG do not have adequate hardness or heat resistance. Copolyesters having more that 75 mol % EG do not have an impact strength adequate for use in engineering plastic applications. Because the TMCBD group effectively contributes to the T_g, one might expect that the TMCBD copolyesters would be brittle materials due to the incorporation of this rigid structure. However, the amorphous TMCBD/diol terephthalate copolymers proved to be exceptionally tough materials with notched Izod impacts as high as 1070 J/m. The Izod impact was inversely related to the TMCBD content of the copolymers. Because T_g is proportional to the TMCBD content, there is a tradeoff between toughness and thermal resistance. Nevertheless, compositions in the range of about 50-80 mol % TMCBD were found to have excellent toughness combined with T_g's>100ºC. The balance between T_g and toughness can be tailored to specific requirements by adjusting the proportion of TMCBD in the composition.

The TMCBD/diol terephthalate copolymers can match the Izod impact of polycarbonate when the proportion of TMCBD is about 50-60 mol %, although the T_g's of these compositions are somewhat lower than that of polycarbonate (notched Izod of 650-850 J/m and T_g ~ 150ºC). Conversely, the TMCBD copolymer T_g can approach that of polycarbonate using about 70-80 mol % TMCBD and still retain a Izod impact >250 J/m, which is adequate for many applications. TMCBD /EG terephthalte copolyesters have improved impact behavior, with a maximum of 660 J/m notched Izod impact at TMCBD /EG diol ratio of 64/36 compared to maximum of 1070 J/m for 40/60 TMCBD /PD.

The high impact resistance of bisphenol-A polycarbonate has been attributed to cooperative chain motions that are related to sub-T_g (low energy) relaxations extending over several structural units[196]. Another example, albeit with T_g's below 100ºC, are the terephthalate copolyesters of ethylene glycol and 1,4-cyclohexanedimethanol (CHDM) which exhibit high Izod impact at room temperature (e.g., >1000 J/m), especially for compositions with high proportions of CHDM. The high impact of CHDM copolymer has been attributed to the conformation flexibility of the cyclohexylene rings and the influence of this flexibility on chain mobility[198,199].

The TMCBD terephthalate copolymers also undergo shear yielding under impact. The very high impact resistance of these compositions seems remarkable because, unlike CHDM, the tetramethylcyclobutylene unit is conformationally rigid. The inverse relationship between impact and TMCBD content, unlike the behavior of CHDM copolymers, is also intriguing. The molecular structure of TMCBD is significantly different from the structure of either BPA or CHDM, so the molecular basis for the high impact resistance of the TMCBD /diol copolyterephthalates cannot be explained. Further study of these copolyesters and other polymer of TMCBD should provide valuable insights into the molecular parameters that influence impact resistance.

1.6.5 Weathering

Aliphatic-aromatic polyester resins have limited weather resistance, which can be made acceptable by adding stabilizers[1b]. Pigmented products, primarily black, are recommended for improved outdoor stability. Polymer degradation from UV exposure, particularly in presence of heat, moisture, oxygen or atmospheric pollutants, can result in embrittlement, chalking, surface crazing, discoloration, and loss of physical properties such as strength and impact. Adding UV-screening agents, absorbers and quenchers, can achieve stabilization of these materials against weathering damage.

Weather resistant aliphatic-aromatic polyester powder coating resins use either neopentyl glycol or ethylene glycol as the major glycol component in combination with TPA to provide certain desirable properties to the coating formulation. Small amounts of other glycols or polyols and diacids or polyacids are incorporated to influence performance and physical properties. Such combination is effective in producing powder coating resins having Tg's in the 50-80°C range.

In order to form a smooth finish, the powder coating must melt within a particular temperature range to permit timely and ample flow of the polymeric material prior to crosslinking. It is also essential that the formulated coating powders remain in a free flowing, finely divided state for a reasonable period of time after they are manufactured and packaged. Most polyester resins that are used as binders for powder coating are amorphous solids. The use of multiple components to produce resins having specialized properties generally reduces their potential for crystallinity. The resulting Tg of these resins must exceed the storage temperature to which the formulated powder will be exposed. When storage temperature reaches or exceeds the Tg , the amorphous resin begins to cold flow resulting in agglomeration of the finely divided particles, thereby rendering the powder unsuitable for application. Therefore T_g and melt viscosity are important considerations for powder coating resins.

Considerable amount of work done on weather resistant powder coating materials has been captured in patents mentioned in the **Table 1.10**. Johnson and Sade[128] have studied new monomers for polyester powder coating resins. All aliphatic powder coatings for improved UV resistance could be prepared using 1,4-cyclohexanedicarboxylic acid (1,4-CHDA). The use of 1,4-CHDA in polyester resins provides improved flexibility and resistance to yellowing (as a result of exposure to UV) compared to diacids like TPA and IPA. Unfortunately, when all the TPA is replaced by 1,4-CHDA in the polyester powder coating resins, the T_g decreases. In order to overcome the detrimental effect on T_g, one or more additional monomers must be added in order to compensate for the T_g deficiency. When hydrogenated HBPA is used in the coating preparation, it enhances the T_g. Molecular modes revealed that the three isomers are sterically hindered from rotational and conformational changes, factors that would be predicted to enhance T_g.

Polymers used in the manufacture of powder coatings are classified broadly as either thermosetting or thermoplastic. In the application of thermoplastic powder coatings, heat is applied to the coating on the substrate to melt the particles of the powder coating and thereby permit the particles to flow together and form a smooth coating. Thermosetting coatings, when compared to coatings derived from thermoplastic compositions, generally are tougher, more resistant to solvents and detergents, have better adhesion to metal substrates and do not soften when exposed to elevated temperatures. Polyester resins that exhibit good weatherability and meet the basic T_g requirements for powder coatings are becoming increasingly important, particularly for outdoor applications.

Aliphatic polyesters containing cyclohexanedicarboyxlic acid (CHDA) and 2,2,4,4-tetramethyl-1,3-cyclobutanediol are useful as film and molding plastics[200] and as adhesives[200] and have improved weatherability[117]. These polyesters are high molecular weight polyesters useful in molding plastics. All-aliphatic polyester resins based on CHDA and hydrogenated bisphenol A and/or cycloaliphatic diols are useful as weatherable powder coating resins[127].

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2.1 Introduction

Aliphatic aromatic polyesters are a class of thermoplastic polyesters with useful properties like high heat distortion temperature, high rigidity, good mechanical properties, toughness, excellent surface appearance, good chemical resistance and stable electrical-insulation properties[1]. The commercially successful polymers of this class are the poly (ethylene terephthalate), poly (butylene terephthalate) and poly (ethylene naphthalate)s[2]. Among these polymers, PBT is a fast crystallizing polymer and, hence, well suited for extrusion and injection molding applications. Properties of PBT are influenced by the degree and nature of crystallization and on the morphology of the material i.e., the way in which the polymer chains are arranged in the amorphous and crystalline domains in the material[3]. However, at T_g (~ 40°C) the mobility of the polymer chains in the amorphous regions increases considerably, resulting in decrease in stiffness. Hence PBT is not suitable for applications involving high heat[4].

The properties of PBT can be modified in many ways to meet the requirements of specific fields of application. Copolymerization, blending with other polymers and addition of additives are different ways to modify the properties of PBT. It is well known that aromatic groups impart molecular rigidity, which contributes to improved properties of semicrystalline polymers. Cycloaliphatic diols also impart molecular rigidity to the polyester chain. The main focus of this thesis is to systematically examine a series of PBT based aliphatic-aromatic copolyesters with a view to understand the relationship between monomer structure and polyester properties. To that end, three monomers having different structures are chosen and are based on cyclohexane, cyclopentane and norbornane ring structures. The objectives of the present study is to synthesize various cycloaliphatic diols and diesters based on the above monomers having different molecular rigidity and the synthesis of copolyesters there from with dimethyl terephthalate and 1,4-butanediol.

2.2 Objectives of the present work

2.2.1 Synthesis and chracterization of poly (alkylene terephthalate)s containing cyclohexane ring.

Polyesters derived from 1,4-cyclohexane dimethanol (CHDM), poly (cyclohexane dimethylene terepthalate) (PCT) has a high T_m ranging from 250-305°C depending on the cis/trans ratio[5,6]. The T_g, similarly, increases from 60° (*cis*) to 90°C (*trans*). Cycloaliphatic diols such as CHDM have been used for the purpose of improving the performance of polyesters[7,8]. The improved impact property of copolyesters of PET/PCT has been attributed to the conformational flexibility of the cyclohexane rings and its influence on chain mobility[9-11]. Copolyesters of dimethyl terephthalate and 1,4-butanediol containing 1,4-cyclohexane dicarboyxlate moiety are found to be crystallizable and exhibits improved ductility and mold flow[12].

One of the objective of the present work is to synthesize copolyesters of dimethyl terephthalate and 1,4-butanediol containing 1,4-bis(hydroxymethyl) cyclohexane and 1,4-cyclohexane dicarboxylate. The copolyester sequence will be determined by means of ^{1}H *and* ^{13}C *NMR spectroscopy. The effect of incorporation of comonomer on the thermal properties will be studied by DSC and TGA. The crystallization behavior of the copolyesters will be studied by DSC and WAXD.*

2.2.2 Synthesis and characterization of polyesters and copolyesters containing cyclopentane ring.

Polyesters synthesized from cylcopentane ring containing diols and diesters have not been reported. *Hence, one of the objective of the study is to synthesize cyclopentane ring containing monomers, namely, 1,3-bis(hydroxy methyl) cyclopentane and dimethyl-1,3-cyclopentane dicarboxylate. Homopolyester of 1,3-bis(hydroxy methyl) cyclopentane and dimethyl-1,3-cyclopentane dicarboxylate with DMT will be synthesized and characterized by NMR spectrocopy. Copolyesters of dimethyl terephthalate and 1,4-butanediol containing 1,3-bis(hydroxy methyl) cyclopentane and dimethyl-1,3-cyclopentane dicarboxylate will be synthesized. The sequence of the copolyesters will be determined by means of* ^{1}H *and* ^{13}C *NMR spectroscopy. The effect of incorporation of the cyloalphatic comonomers on the thermal properties will be studied by DSC and TGA. The crystallization behavior of the copolyesters will be studied by DSC and WAXS. The* *spherulitic morphology of the homopolyester and the copolyesters will be studied by polarized optical microscopy.*

PCCD is aliphatic polyester having desirable properties such as high crystallinity and superior weathering characteristics upon exposure to ultraviolet radiation[16]. The *cis* to *trans* ratio of cycloaliphatic moiety in the polymer chain influences the thermal and crystallization behavior. The commercially available PCCD has about 90% trans content and is a crystallizable polymer. *Hence one of the objectives is to synthesize PCCD with high cis content and compare the thermal properties with a commercially available sample. Another objective of the present study is to synthesize polyester from 1,3-bis(hydroxy methyl) cyclopentane and dimethyl-1,3-cyclopentane dicarboxylate and compare the properties with that of PCCD*

The crystallization kinetics of PBT has been studied in detail[13-15], however, the crystallization kinetics of PCT and PCCD has not been reported in open literature. *Thus another objective of the present work is to study the detailed crystallization kinetics of PCT and PCCD and compare with that of PBT.*

2.2.3 Synthesis and characterization of polyesters and copolyesters containing norbornane ring.

Polyesters synthesized from norbornane diesters and dimethanols[17] have high glass transition temperature (T_g >100°C) and exhibit little tendency to crystallize. Polyesters prepared from substituted 1,1-norbornane dimethanol[18,19] has a T_g of 118°C. These polyesters can be used to prepare transparent materials that neither crystallize nor are brittle. The polyesters containing norbornane moiety have not only high T_g but also possess excellent dimensional stability. *The objective of the work is to (i) synthesize monomers containing norbornane ring, namely, 2,3-bis(hydroxymethyl)bicyclo[2,2,1] heptane, dimethyl bicyclo([2,2,1] heptane 2,3-dicarboxylate, and dimethyl-2,3-dimethyl bicyclo[2,2,1]heptane-2,3-dicarboxylate. (ii) Synthesize homopolyester of 2,3-bis (hydroxy- methyl)bicyclo[2,2,1] heptane and dimethyl bicyclo[2,2,1] heptane 2,3-dicarboxylate and dimtheyl-2,3-dimethyl bicyclo[2,2,1]heptane-2,3-dicarboxylate with dimethyl terephthalate. (iii) Synthesize copolyesters of dimethyl terephthalate and 1,4-butanediol containing 2,3-bis (hydroxy- methyl)bicyclo[2,2,1] heptane, dimethyl bicyclo[2,2,1] heptane 2,3-dicarboxylate and dimethyl-2,3-dimethyl* *bicyclo[2,2,1]heptane-2,3-dicarboxylate . The comonomer sequence in copolyesters will be determined by means of ^{1}H and ^{13}C NMR spectroscopy. The effect of incorporation of these cyloalphatic comonomers in PBT on the thermal properties will be studied by DSC and TGA. The crystallization behavior of the copolyesters will be studied by DSC and WAXS.*

Polyesters of 2,2,4,4-tetramethyl-1,3-cyclobutanediol (TMCBD) reported[20,21,22] are primarily high melting, semicrystalline materials. The incorporation of the rigid cyclobutane diol moiety in the polyesters leads to improved properties like high impact resistance combined with good thermal properties, ultraviolet stability, optical clarity. properties. Aliphatic polyesters synthesized from TMCBD and 1,4-cyclohexanedicarboyxlic acid have T_g>100°C and improved weatherability and UV resistance[23,24]. *Thus, yet another objective of this study is to synthesize aliphatic copolyesters of 2,2,4,4-tetramethyl-1,3-cyclobutanediol with various cycloaliphatic diesters and compare the properties with the copolyester of dimethyl terephtalate, 1,4-butanediol and 2,2,4,4-tetramethyl-1,3-cyclobutanediol.*

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Chapter 3: I. Synthesis and characterization of poly (alkylene terephthalate)s containing cyclohexane ring in the chain

3.1 Introduction

Poly(butylene terephthalate) (PBT) is an important thermoplastic polyester widely used in a range of engineering applications[1]. However, PBT has poor impact properties. It has a low glass transition temperature (T_g ~30°C) and, hence, not suitable for applications involving high heat. On the other hand, poly(1,4-cyclohexylene dimethylene terephthalate) (PCT) is a semicrystalline polyester[2,3] having high melting temperature (T_m) 278-318°C and T_g 60-90°C depending on the *e,e* diol content of 50-100%. It requires temperatures above 300°C for injection molding which is close to its decompostion temperature[4]. However, 1,4-cyclohexanedimethanol (CHDM) has been used as a comonomer for synthesis of copolyesters for the purpose of improving the performance of the polymer, for example impact strength, heat resistance, water resistance, weatherability and transparency. Copolyesters of PET containing CHDM (10-60 mole %) have improved properties like high transparency, excellent heat stability, improved impact strength, moldability and recyclability and are used for various applications[5,6]. Jackson et al[7] reported the synthesis of copolyesters of terepthalic aicd, 1,2-propanediol and CHDM which are tough, flexible and are useful in manufacture of plastics, films, blown bottles and other shaped articles. The injection-molded copolyesters have high toughness and low coefficient of thermal expansion. Copolyesters of dimethyl terephthalate and 1,4-butandiol containing 5-20% of CHDM units are reported to possess good impact strength[8]. Copolymerization modifies both the crystallization behavior as well as crystallinity which are strongly influenced by composition, kind and arrangement of structural units in the chain. Barring a solitary papent[8] no information is available on the synthesis and properties of copolyesters of 1,4-butanediol, CHDM and DMT.

Copolyesters of dimethyl terephthalate and 1,4-butanediol containing 1,4-cyclohexane dicarboxylate moiety were found to be crystallizable and exhibit improved ductility and mold flow[9]. The molar ratio of cycloaliphatic acid to aromatic diacid determines the impact strength of the resulting copolyesters[9]. Injection molding compositions based upon blends of thermoplastic resin incorporating 1,4-cyclohexanedicarboyxlic acid groups in the polymer chain have been described in the literature[10,11]. The polyesters have good impact resistance, good processability and transparency.

The *a,e* to *e,e* ratio of cycloaliphatic moiety in the polymer chain is an important factor and can greatly effect thermal and crystallization behavior. Polyesters with high *e,e* content are usually semi-crystalline and those with a high *a,e* content are amorphous, or have much lower T_m and T_g. Poly(butylene-1,4-cyclohexane dicarboxylate) synthesized from the all e,e isomer has a T_m of 124°C, while the *a,e* derivative has a T_m of 55°C[12]. Another important aspect of the copolyesters is the crystallization behavior when the components are of fast crystallizing nature. Only a few systems have been reported, e.g., poly(butylene terephthalate-co-butylene 2,6-naphthalate)[13] poly(butylene naphthalate-co-1,4-cyclohexylenedimethylene 2,6-naphthalate)[14] and poly(3-hydroxybutyrate-co-hydroxyvalerate)[15-18], where melting temperature and some crystallinity are observed over the entire range of compositions[13-22].

In this chapter poly(butylene terephthalate-co-1,4-cyclohexane dimethylene terephthalate) (P(BT-co-CT)) and poly(butylene terephthalate-co-1,4-cyclohexane dicarboxylate) (P(BT-co-BCD)) random copolyesters were synthesized by melt polymerization. Thermal and crystallization behaviour of these copolymers have been studied and compared with poly(butylene terephthalate) (PBT), poly (1,4-cyclohexylene dimethylene terephthalate) (PCT) and poly(butylene cyclohexane dicarboxylate) (PBCD).

3.2 Experimental

3.2.1 Materials

Dimethyl terephthalate (DMT), (99+%) 1,4-butanediol (BD), 1,4-cyclohexanedimethanol (*e,e/a,e* 70/30) (CHDM), 1,4-cyclohexane dicarboxylic acid (CHDA) (99% mixture of *e,e/a,e*) and titanium(IV) isopropoxide were obtained from Sigma-Aldrich, Inc., USA. Phenol and 1,1,2,2-tetrachloro ethane were obtained from sd. Fine chemicals, Mumbai, India.

3.2.2 Reagents and Purification

DMT was recrystallized from methanol. BD was distilled and stored over molecular seives. CHDM was dried in vacuum oven prior to use. Titanium(IV) isopropoxide was distilled under vacuum and used as a solution in dry toluene. Phenol and 1,1,2,2-tetrachloro ethane were freshly distilled before use. 1,4-cyclohexane dicarboxylic acid (mixture of *e,e/a,e*) was used as such. 1,4-cyclohexane dicarboxylic acid was esterified to dimethyl-1,4-cyclohexane dicarboxylate (DMCD) by standard esterification procedure. DMCD was purified by vacuum distillation.

3.2.3 Synthesis of polyesters and copolyesters containing dimethyl terepthalate, butanediol and cyclohexane dimethanol

3.2.3.1 Synthesis of poly(butylene terephthalate) (PBT)

DMT (5 g, 0.026 mol), 1,4-butanediol (3.6 g, 0.038 mol) and titanium isopropoxide (0.1 wt %) were taken in a two neck round bottom flask equipped with N_2 inlet, air condensor and spiral trap to collect the distillate. A 1:1.5 molar ratio of DMT to diol was used. The reaction mixture was heated at 180-210°C for 3 h and then at 230°C for 3 h under a constant flow of N_2. The temperature was then raised to 250°C and the pressure was gradually decreased to 0.02 mbar when the excess butanediol distilled out and the polycondensation reaction was further continued at 250°C for 8 h. The flask was cooled under vacuum and polymer was recovered and the yield was 5.75 g (99 %).

η_{inh} (phenol/TCE 60/40 w/w) - 0.9 dL/g

^{1}H NMR ($CDCl_3/CF_3COOD$) δ: 2.02 (4H, s, CH_2), 4.50 (4H, s, $C\underline{H_2}O$) 8.12 (4H, s,aromatic protons)

^{13}C NMR ($CDCl_3/CF_3COOD$) δ: 25.1 ($\underline{C}H_2$), 65.9 ($O\underline{C}H_2$), 129.8 (aromatic carbons), 133.7 (quaternary aromatic carbon), 167.6 (carbonyl).

3.2.3.2 Synthesis of poly(1,4-cyclohexane dimethylene terephthalate) (PCT)

3.2.3.2.1 Melt condensation of DMT and 1,4-CHDM[23]

DMT (5.08 g, 0.026 mol), CHDM (6.45 g, 0.045 mol) was taken in a tube reactor fitted with N_2 inlet, short distillation condensor and a spiral trap. The flask was heated to 190°C and held for 1 h. The temperature was then raised to 270°C and the pressure was gradually reduced to 0.02 mbar. Once the pressure was reduced to 0.02 mbar the temperature was raised to 310°C and heated for 4 h. The system was cooled under vacuum. Charring of the polymer was observed.

3.2.3.2.2 Polycondensation of bis(hydroxymethyl cyclohexane)terephthalate (BHCT)

(a) Synthesis of BHCT BHCT was prepared according to the procedure by Wang et al[24]. DMT (13.02g, 0.067 mol), 1,4-CHDM (26.2g, 0.182 mol) and titanium isopropoxide (0.1 wt %) were placed in a 250 mL glass reactor fitted with overhead stirrer, N_2 inlet and an air condenser. The reaction mixture was heated at 200°C when methanol distilled out.

The hot reaction mixture was poured into excess water when the BHCT precipitated out. The precipitate was filtered, washed several times with water, dried and recrystallized from toluene. The yield was 32.05 g (99 %)and the melting point 160-165°C.

Elemental analysis - Found (Calc.) C: 68.85 (68.89) H: 7.85 (8.1) O: 23.3 (22.98)

^{1}H NMR ($CDCl_3$) δ: 8.11 (4H, s, terephthalate) 4.30, 4.16 (4H, dd, OCH_2) 3.56, 3.47 (4H, dd, OCH_2) 0.9-2 (20H, m, ring protons)

(b) Polycondensation of BHCT

BHCT (3.06 g) was taken in a glass reactor with N_2 inlet and stirring arrangement. Titanium isopropoxide solution was added under N_2 and the mixture heated to 260°C and held for 1 h in a oil bath. The temperature was raised to 300°C and heated for 2 h. The pressure was gradually reduced to 0.08 mbar and isothermally held at 300°C for 1 h. The reactor was cooled under N_2. The polymer obtained did not dissolve in phenol/TCE to enable determination of viscosity.

3.2.3.2.3 Solid state polymerization

DMT (5.01g, 0.026 mol), CHDM (7.06g, 0.049 mol) and titanium isopropoxide (0.01 wt %) were taken in a tube reactor fitted with N_2 inlet, air condensor and spiral trap to collect the methanol. The transesterification reaction was done at 190-210°C for 1 h till methanol distillation ceased. Polycondensation was done at 270°C for 30 min and at 290°C under reduced pressure (0.02 mbar) for 15 min. The hot polymer was poured into cold water, filtered and washed several times with hot water. The oligomer was dried in vacuum oven. The oligomer powder was taken in dry toluene, titanium isopropoxide (0.01 wt %) in toluene was added and stirred for 1 h and the toluene was removed under vacuum, dried and subjected to solid state polymerization at 220°C for 5 h and at 250°C for 5 h under reduced pressure (0.02 mbar).

η_{inh} (phenol/TCE 60/40 w/w) - 0.66 dL/g

^{1}H NMR ($CDCl_3/CF_3COOD$) δ: 1.2-1.99 (10H, s, ring protons), 4.37, 4.27 (4H, dd,CH_2O), 8.15 (4H, s, terephthalate protons)

^{13}C NMR ($CDCl_3/CF_3COOD$) δ: 25.12 (CH_2), 28.66 (CH_2), 34.39 ($\underline{C}H$), 36.94 ($\underline{C}H$), 69.24 ($\underline{C}H_2O$), 71.38 ($\underline{C}H_2O$), 129.89 (terephthalate carbons), 133.88 (terephthalate quaternary carbon), 167.9 (carbonyl)

3.2.3.3 Synthesis of poly(butylene-co-1,4-cyclohexane dimethylene terephthalate) copolyesters (P(BT-co-CT))

DMT, BD, CHDM and titanium isopropoxide (0.1 wt %) were taken in a two neck tube reactor equipped with N_2 gas inlet, short path vacuum distillation adaptor and a spiral trap to collect the distillate. A 1:1.13 ratio of DMT to diol was used in all polymerizations. The transesterification was carried out at 180-210°C for 1 h, followed by another of 4 h at 230-250 °C. Polycondensation reactions were performed at 250-310°C and the pressure was slowly reduced to 0.02 mbar over 30 min and isothermally held for 6 h. The reactor was cooled under vacuum and polymer was recovered.

3.2.4 Synthesis of polyester and copolyesters containing 1,4-cyclohexane dicarboxylate

3.2.4.1 Synthesis of poly(butylene-1,4-cyclohexane dicarboxylate) (PBCD)

Dimethyl-1,4-cyclohexane dicarboxylate (3.99 g, 0.02 mol), 1,4-butanediol (2.7 g, 0.03 mol) and titanium isopropoxide (0.1 wt%) were charged into a two neck round bottom flask equipped with a magnetic stirring bar, N_2 inlet, air condenser and spiral trap to collect the distillate, methanol. The reaction mixture was heated at 200-230°C for 8 h and the pressure was reduced to 0.02 mbar and heated at 250°C for 10 h. The flask was cooled under vacuum and the polymer was recovered. Yield = 4.5 g (99 %).

η_{inh} (phenol/TCE 60/40 w/w) - 0.6 dL/g

GPC ($CHCl_3$) - M_n = 16,500 M_w = 37, 300 (M_w/M_n - 2.2)

^1H NMR ($CDCl_3$) δ: 1.3-2.1 (12H, m, ring protons), 2.46, 2.28 (2H, s, CH), 4.1 (4H, s, OCH_2)

^{13}C NMR ($CDCl_3$) δ: 25.3 (CH_2), 25.91 (ring CH_2), 27.92 (ring CH_2), 40.59, 42.42 (CH), 63.63 (CH_2O), 174.72, 175.18 (carbonyl)

3.2.4.2. Synthesis of poly(butylene terephthalate-co-1,4-cyclohexane dicarboxylate) (P(BT-co-BCD))

DMT, dimethyl-1,4-cyclohexane dicarboxylate (DMCD), 1,4-butanediol and titanium isopropoxide (0.01 wt %) were charged into a two neck round bottom flask equipped with a magnetic stirring bar, N_2 inlet, air condenser and spiral trap to collect the distillate, methanol. A 1:1.5 ratio of diester to diol was used in all polymerization reactions and the DMT/DMCD ratio was varied (90/10, 70/30 and 50/50). The flask was heated to 200-

230°C for 8.5 h and the pressure was reduced to 0.02 mbar and heated at 250°C for 11 h. The flask was cooled under vacuum and the polymer was recovered.

3.3 Analysis

Inherent viscosities were measured at 30°C in an automated Schott Gerate AVS 24 viscometer, using an Ubbelohde suspended level viscometer in phenol/1,1',2,2'-tetrachloroethane (TCE) (60:40 w/w) at a polymer concentration of 0.5 wt%. The PCT prepared by SSP was melted at 330°C and cooled under vaccum before dissolution in solvent for viscosity measurement. The as formed polymer did not dissolve in the solvent. Molecular weight and molecular weight distribution (MWD) of the samples were determined using a Thermoquest Gel Permeation Chromatograph unit (TQGPC). The TQGPC consists of (a) pump P-100 capable of delivering the exact flow rate within a precisio of ±0.001 ml/min, (b) an auto sampler AS-300 and (c) adetectors UV-100 and RI-150. The column set used for the analysis were PSS GPC/SEC columns of 50 A°, 100A°, 500 A°, 10^3 A°, 10^4 A° and 10^5 A°, which were calibrated using standard polystyrene samples. The mobile phase used was chloroform (Qualigens, HPLC grade).

3.3.1 Wide-Angle X-Ray diffraction

The X-ray diffraction experiments were performed using a Rigaku Dmax 2500 diffractometer. The system consists of a rotating anode generator and wide-angle powder goniometer. The generator was operated at 40 kV and 150 mA. The samples were ground into fine powder and used for the measurements. The samples were scanned between $2\theta = 5$ to 35^o at a speed of 1 deg/min. Very small amount of silicon powder was mixed with samples for calibration purpose.

3.3.2 Thermal analysis

The calorimetric measurements were done using Perkin-Elmer DSC-7. The samples were heated/cooled at a rate of 10ºC/min under nitrogen environment. The melting temperature and heat of fusion were obtained from the heating thermogram and crystallization temperature upon cooling (T_c) from the cooling thermogram.

To determine the equilibrium melting temperatures ($T_m°$) of the polyesters and copolyesters, isothermal crystallization was carried out on DSC at temperatures close to melting temperature. The sample was heated to a temperature 30°C higher than its melting temperature, held for 4 min in order to remove past history, and rapidly cooled to the predetermined crystallization temperature (T_c) at a rate of 200°C/min. The sample was isothermally crystallized for about 6 to 10 hours. After the crystallization the sample was heated at 10°C/min. The melting temperature (T_m) of isothermally crystallized sample was determined from the heating thermogram. The equlibrium melting temperature ($T_m°$) for all the samples were determined from the Hoffman-Weeks plot.

3.3.3 Solution NMR measurements

^1H and ^{13}C NMR spectra were obtained on a Brucker DRX 500 spectrometer at 25 ± 1ºC, operating at 500 and 125 MHz respectively. About 12 and 100 mg of sample dissolved in 0.5 ml of solvent($CDCl_3$)/trifluoroacteic acid (TFA-d_1) for ^1H and ^{13}C NMR spectra, respectively. The spectra were internally referenced to tetramethyl silane. For quantitataive ^{13}C NMR analysis of the microstructure, the relaxation delay and spectral width was 2 µs and 250 ppm, respectively. 1000 FID's were acquired with 3K data points and Fourier transformed.

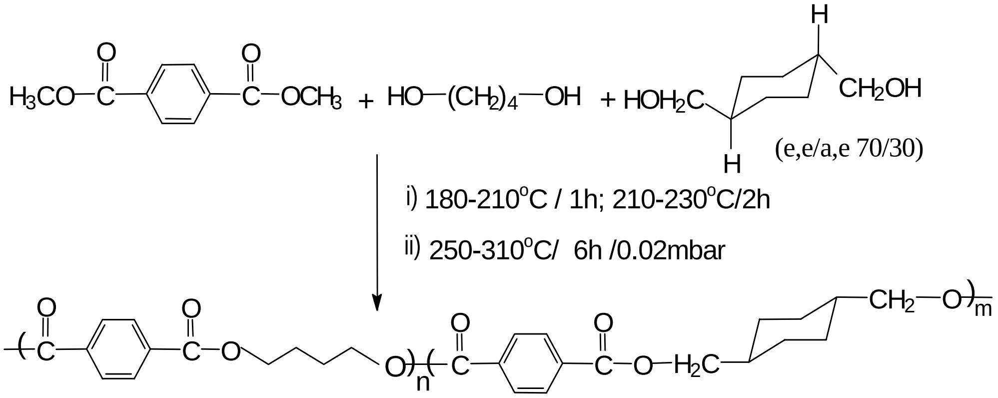
3.4 Results and Discussion

3.4.1 Synthesis and properties of poly(butylene-co-1,4-cyclohexane dimethylene terephthalate) copolyesters

3.4.1.1 Synthesis and characterization of poly(BT-co-CT) copolyesters

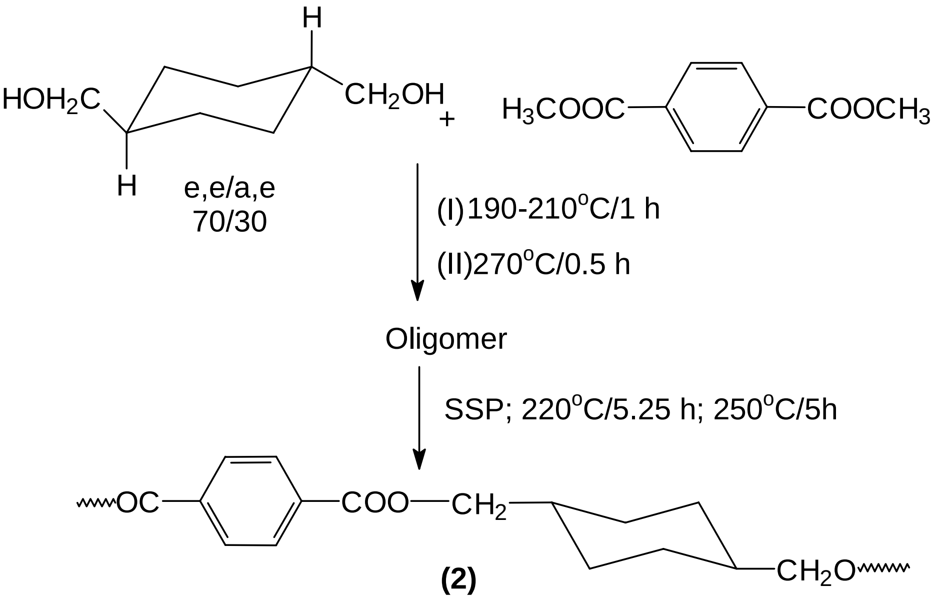
PBT and poly(BT-co-CT) copolymers **(1)** were synthesized by standard melt condensation procedure from DMT, 1,4-BD and 1,4-CHDM (*e,e/a,e* 70/30) using titanium isopropoxide catalyst. The reaction scheme is depicted in **Scheme 3.1**. A series of copolyesters were synthesized by changing the ratio of BD/CHDM from 92/08 to 22/78.

All the copolyesters have viscosities in the range of 0.5-0.9 dL/g and there was no change in the *e,e/a,e* ratio of CHDM after the polymerization. However, PCT **(2)** could not be synthesized by melt method as it underwent degradation. Hence it was synthesised by solid state polymerization[25] (**Scheme 3.2)**. Oligomer with an inherent viscosity (η_{inh}) of 0.1 dL/g was synthesized by melt condensation and subsequently subjected to SSP to obtain high molecular weight PCT of viscosity 0.66 dL/g. **Table 3.1** gives the SSP conditions and melting and crystallization temperatures.



(1)

Scheme 3.1 Synthesis of poly(butylene terephthalate-co-cyclohexylene dimethylene terephthalate)



(2)

Scheme 3.2 Synthesis of poly(cyclohexylene dimethylene terephthalate) (PCT) by SSP

Table 3.1 Thermal and viscosity data of PCT **(2)** samples during SSP

Sample/conditions	η_{inh} ^{a} (dL/g)	T_m (°C)	T_c (°C)
Oligomer	0.10	267	258
220°C/5.25 h	0.45	297	249
250°C/5 h	0.66	299	246

[a] Inherent viscosities were determined in 60/40 w/w phenol/TCE mixture after melting the samples under vacuum

3.4.1.2 Sequence analysis

The chemical structure of poly(BT-co-CT) **(1)** copolyester with notations used for NMR assignments are shown in **Figure 3.1**. The composition of the copolyesters are determined by the ^{1}H NMR and the spectra is shown in **Figure 3.2**.

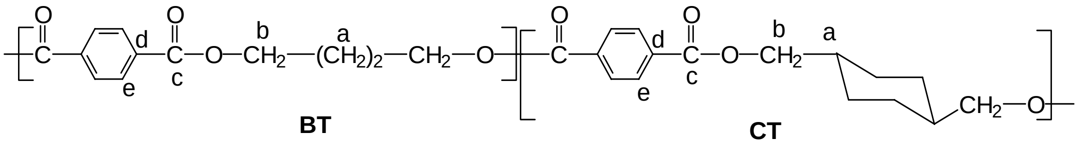


Figure 3.1 Chemical structure of poly(BT-co-CT) copolyesters with notations used for NMR assignments

The cyclohexylene dimethylene groups of CT unit have two isomers *cis* (equatorial, axial, *e*,*a*) and *trans* (equatorial, equatorial, *e*,*e* or axial, axial, *a*,*a*), the latter (*e*,*e* CT) is more stable than former (*a*,*e* CT). The oxymethylene protons are divided into three groups, viz, BT, *a*,*e* CT and *e*,*e* CT. The copolymer composition of BT, *a*,*e* CT, *e*,*e* CT was estimated from relative peak intensities of oxymethylene proton resonance of butylene and cyclohexylene dimethylene peaks. The ^{1}H and ^{13}C NMR peak assignments of PBT, PCT and P(BT-co-CT) copolyester is shown in **Table 3.2**. The *e*,*e*/*a*,*e* ratio determined for all the copolymers are found to be the same as the feed ratio.

Table 3.2 ^{1}H and ^{13}C NMR Chemical Shifts (δ in ppm) of PBT, PCT and poly(BT-co-CT) copolyesters

	^{1}H Chemical shifts					
	^BH_a	^BH_b	^BH_e	^CH_a	^CH_b	^CH_e
PBT	2.02	4.5	8.12			
PCT				1.2-1.99	4.37(d), 4.27(d)	8.15
$PBT_{45}CT_{55}$	2.04	4.52	8.14	1.2-2.00	4.38(d), 4.27(d)	8.15

	^{13}C Chemical Shifts							
	^BC_b	^BC_c	^BC_d	^BC_e	^CC_b	^CC_c	^CC_d	^CC_e
PBT	65.9	167.6	133.7	129.8				
PCT					71.3, 69.2	167.9	133.9	129.8
$PBT_{45}CT_{55}$	65.9	167.6	133.7	129.8	71.3, 69.2	167.7	133.9	129.8

The sequence of the BT and CT units in the copolymer could be determined from the ^{13}C NMR spectra. The quaternary aromatic carbon peak is more sensitive to sequence effects than any other aromatic carbons due to interactions through space and bond between neighboring units and was used for sequence quantification[26-28].

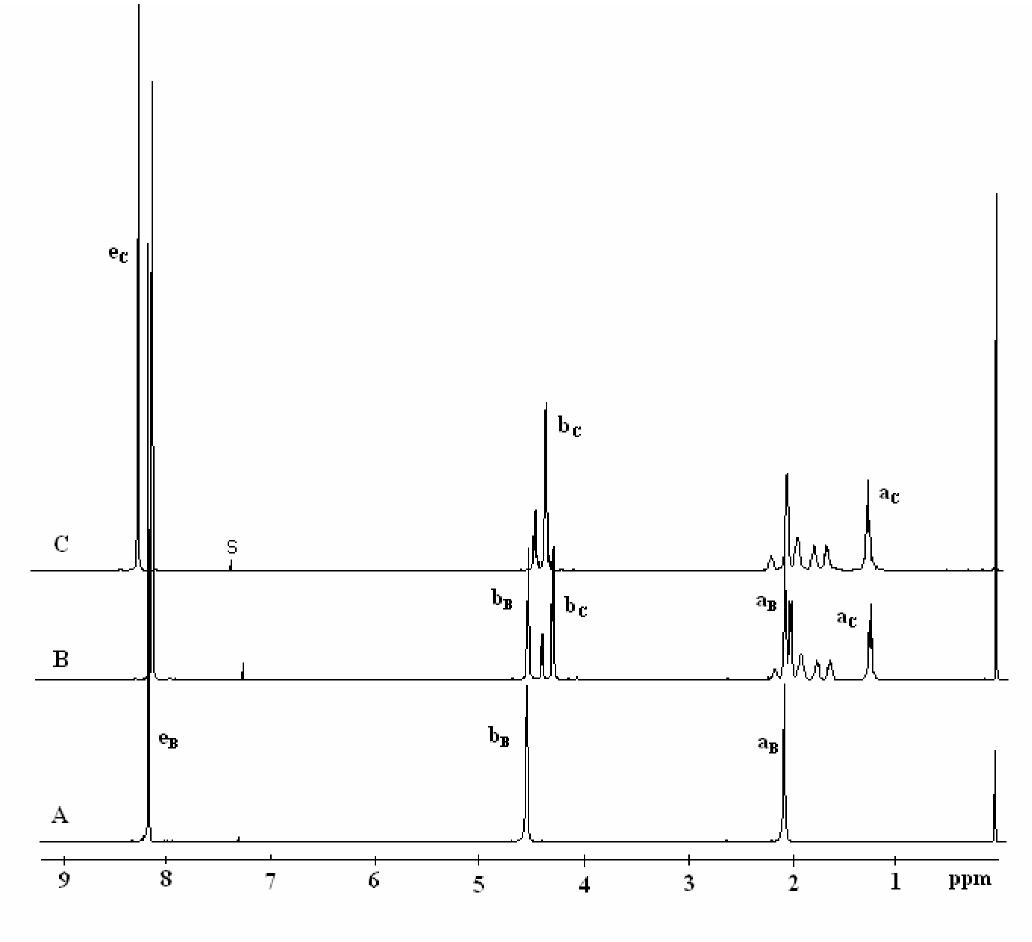


Figure 3.2 ^1H NMR spectra of (A) PBT, (B) $PBT_{45}CT_{55}$ and (C) PCT

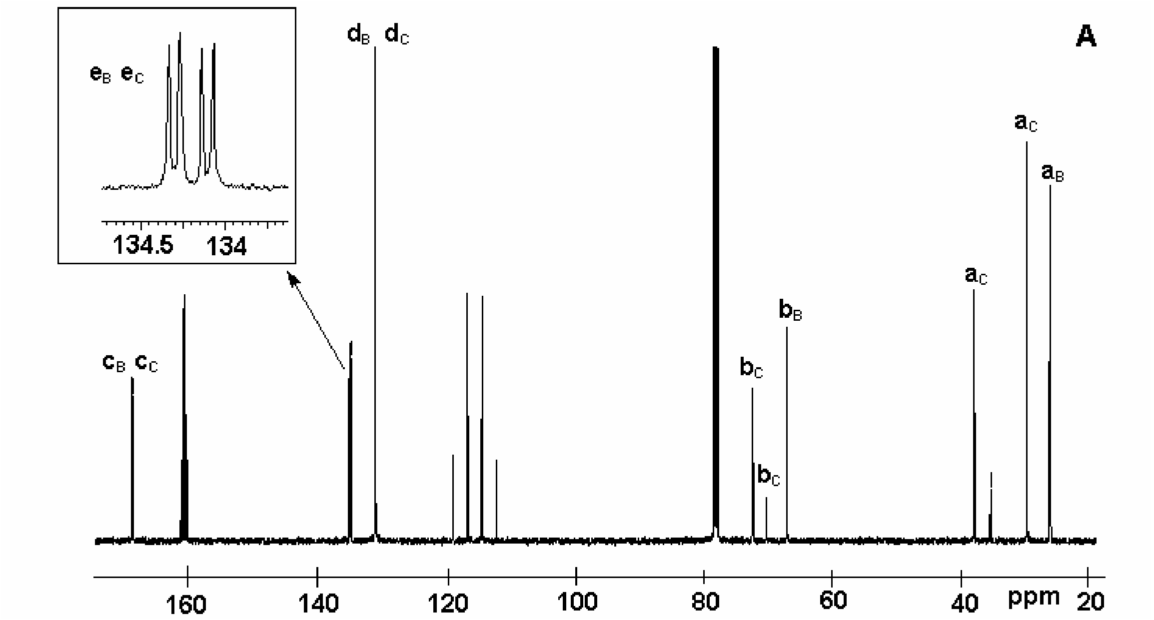


Figure 3.3 ^{13}C NMR spectrum of PBT$_{45}$CT$_{55}$

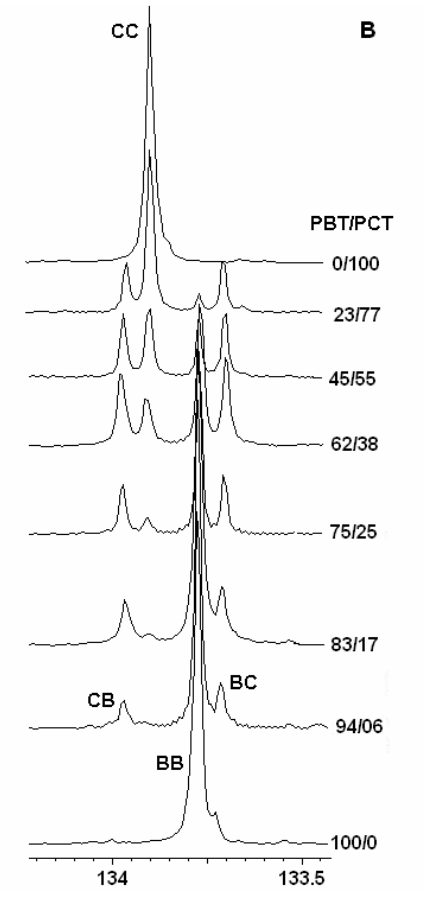


Figure 3.4 ^{13}C NMR spectra of quaternary carbon resonance of PBT, PCT and poly(BT-co-CT) copolyesters

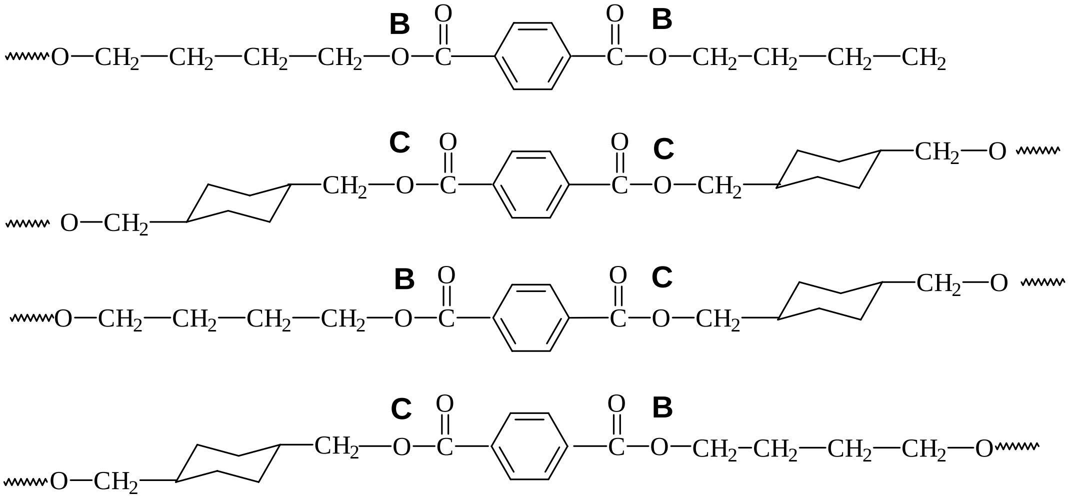


Figure 3.5 Possible diad sequences of the quaternary carbon in the poly(BT-co-CT) copolyesters

The ^{13}C NMR spectrum is shown in **Figure 3.3** and the peak assignments are given in the **Table 3.2**. The quaternary carbon of the terepthalate (labelled as d) is split into four different signals corresponding to the four diads, BB(133.8), CC(133.88), BC(133.68), CB(133.95) as shown in **Figure 3.4** and the four different diads possible are depicted in **Figure 3.5**. According to Yamadera and Murano[29], if four kinds of signals due to homolinks and heterolinks are observed in the NMR spectrum of the copolymer, then the average sequence length and the degree of randomness of the copolymer can be determined. The molar fractions of the butylene terephthalate (B) unit and cyclohexylene dimethylene terephthalate (C) units were obtained from integration of the peaks.

$$P_B = \frac{f_{BC} + f_{CB}}{2} + f_{BB} \qquad P_C = \frac{f_{BC} + f_{CB}}{2} + f_{CC} \qquad \textbf{(3.1)}$$

Where P_B is the molar fraction of the butylene terephthalate unit, P_C the molar fraction of the cyclohexane dimethylene terephthalate unit and f_{BB}, f_{CC}, f_{BC} and f_{CB} correspond to the proportion of the integrated intensities of BB, CC, BC and CB.

If one could inspect the units along the copolymer chain from one end to the other, the probability of finding a butylene unit placed next to a cyclohexylene unit (or cyclohexylene unit placed next to a butylene unit) would be given by P_{BC} and P_{CB} as given in equation **(3.2)**

$$P_{BC} = \frac{f_{BC} + f_{CB}}{2P_B} \qquad P_{CB} = \frac{f_{BC} + f_{CB}}{2P_C} \qquad \textbf{(3.2)}$$

The number-average sequence length of butylene terephthalate (BT) and cyclohexylene dimethylene terephthalate (CT) units L_{nB} and L_{nC} repectively and the degree of randomness (B) were calculated using following equations **(3.3)** and **(3.4)**

$$L_{nB} = \frac{2P_B}{f_{BC} + f_{CB}} \qquad L_{nC} = \frac{2P_C}{f_{BC} + f_{CB}} \qquad \textbf{(3.3)}$$

$$B = P_{BC} + P_{CB} \qquad \textbf{(3.4)}$$

For random copolyesters B is unity. A value of B equal to zero indicates a mixture of homopolymers, whilst a value of 2 indicates an alternating distribution[29]. **Table 3.3** shows the average sequence length and the degree of randomness for the copolyesters. The diad distribution was also calculated based on Bernoullian statistical model[30] and are plotted in **Figure 3.6** along with the experimentally determined values.

Table 3.3 Sequence distribution and randomness of poly(BT-co-CT) copolyesters determined by ^{13}C NMR

	Feed composition		Copolymer composition[b]		CHDM isomer compostion[a]		Average sequence length		Degree of randomness
Copolyester[a]	X_B	X_C	X_B	X_C	*a,e*	*e,e*	L_{nB}	L_{nC}	B
PBT	100	0	100	0	-	-	-	-	-
$PBT_{93}CT_{07}$	92	08	94	06	30	70	7.7	1.2	0.95
$PBT_{84}CT_{16}$	90	10	83	17	28	72	5.3	1.3	0.98
$PBT_{74}CT_{26}$	80	20	75	25	25	75	3.7	1.4	0.99
$PBT_{61}CT_{39}$	66	34	62	38	25	75	2.4	1.7	1.01
$PBT_{45}CT_{55}$	50	50	45	55	25	75	1.8	2.3	0.98
$PBT_{22}CT_{78}$	30	70	23	77	23	77	1.4	5.0	0.93
PCT	0	100	0	100	26	74	-	-	-

[a] Experimental values were obtained from integration of oxymethylene proton resonance of butanediol and cylohexanedimethanol from ^{1}H NMR spectra

[b] calculated from ^{13}C NMR

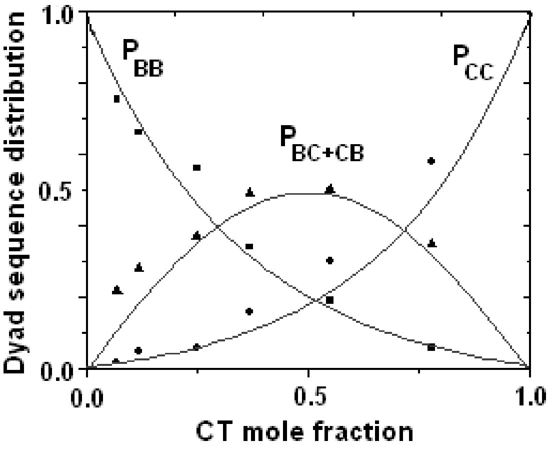


Figure 3.6 Diad sequence distribution as a function of copolymer composition. The solid lines represent the distribution calculated by Bernoullian statistics.

In all cases it is observed that the experimentally determined average sequence lengths were in accordance with that predicted on the basis of ideal copolycondensation statistics with randomness close to unity[29-32].

3.4.1.3 Thermal properties

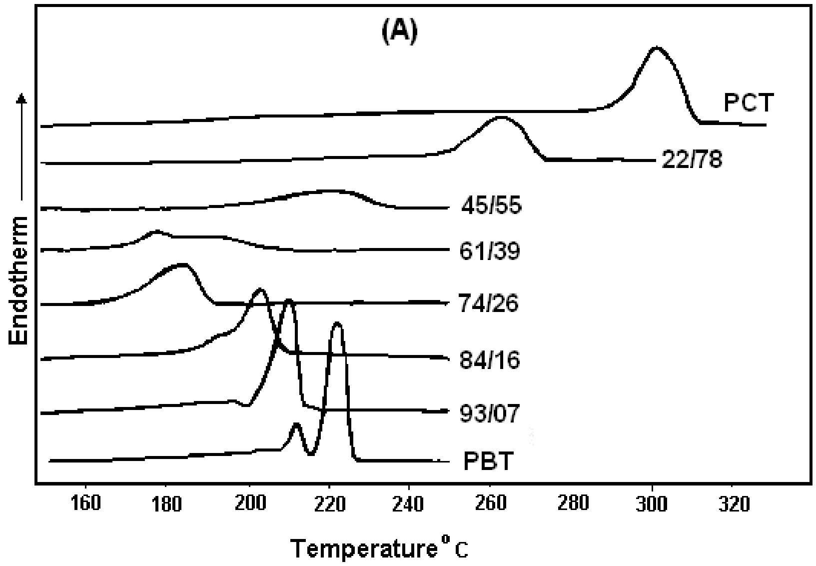
The thermal behavior of the copolyesters was studied by differential scanning calorimetry and is summarized in **Table 3.4**. The copolyesters, in all composition range showed melting endotherm on heating and crystallization exotherm on cooling. The presence of clear melting and crystallization peak indicates cocrystallization behavior of the copolyesters over the entire range of composition. Only few systems show such a behavior[13-22] **Figure 3.7** shows the crystallization exotherms on cooling and the melting endotherms of the copolyesters during the second heating. It may be noted that the polymer samples have varying thermal history and hence the thermal properties obtained during the first heating cannot be compared. The various parameters extracted from the thermograms are shown in **Table 3.4**.

The crystallization, melting and glass transition temperatures of the copolyesters are shown in **Figure 3.8**. All the copolyesters have single T_g and show a linear increase with increase in CHDM content. The melting and crystallization temperatures of the copolyesters show eutectic behavior and the eutectic composition is $PBT_{74}CT_{26}$. The typical eutectic behavior indicates that the cocrystallizaion is iso-dimorphic in nature and monomer units of one type are included in the crystal lattice of the other type.

Table 3.4 Thermal properties of poly(butylene-co-1,4-cyclohexylene dimethylene terephthalate) (P(BT-co-CT)) copolyesters

Polyester	η_{inh}[a] dL/g	T_g[b] (°C)	T_m (°C)	ΔH_m (J/g)	T_{mc} (°C)	ΔH_c (J/g)	IDT[c]
PBT	0.90	40	226	41	193	49	374
$PBT_{93}CT_{07}$	0.50	48	212	36	175	45	393
$PBT_{84}CT_{16}$	0.57	51	205	34	163	41	374
$PBT_{74}CT_{26}$	0.66	59	187	27	149	30	377
$PBT_{61}CT_{39}$	0.60	61	192	25	139	26	384
$PBT_{45}CT_{55}$	0.75	67	218	19	159	24	388
$PBT_{22}CT_{78}$	0.51	77	262	30	237	31	392
PCT	0.66	90	296	43	246	58	397

[a]Measured in phenol/TCE 60/40 (w/w); [b]Measured by DSC with a heating rate of 10°C/min after quenching from the melt; [c] Measured by TGA



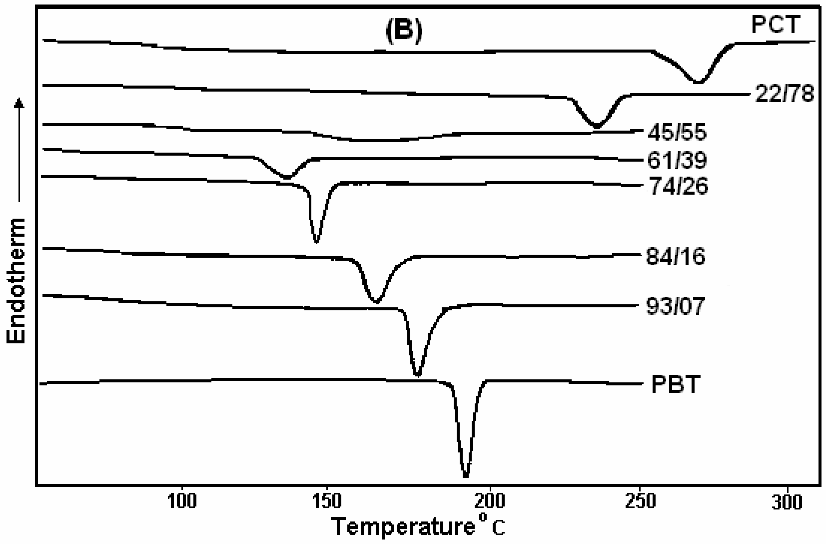


Figure 3.7 DSC heating (A) and cooling (B) thermograms of PBT, PCT and poly(BT-co-CT) copolyesters.

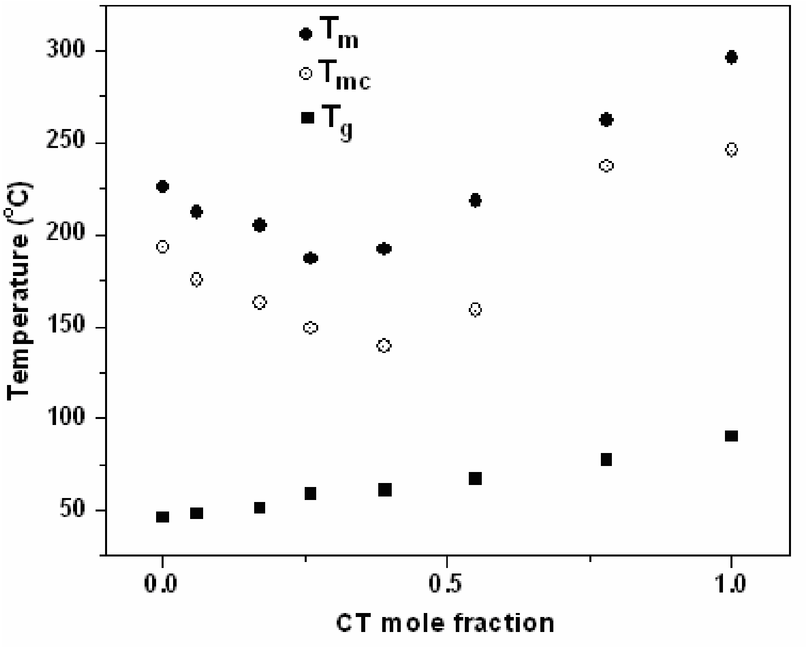


Figure 3.8 Melting temperature (T_m), melt-crystallization temperature (T_{mc}) and glass transition temperature (T_g) as a function of copolymer composition

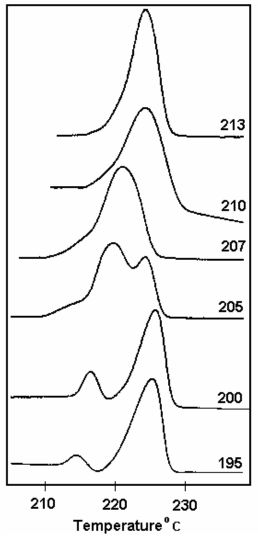
3.4.1.4 Equilibrium melting temperatures of copolyesters

The equilibrium melting temperature of semicrystalline polymer is an important physical parameter. In general, semicrystalline polymers are processed above the equilibrium melting temperature. The equilibrium melting temperatures of the copolyesters were determined from the melting temperatures of isothermally crystallized samples close to melting temperature. **Figure 3.9** shows the melting endotherms of various samples crystallized at different temperatures. In general, most samples show double melting peaks and the melting temperatures shift to higher temperatures with increasing crystallization temperatures. The PBT and PCT homopolymers show similar behaviour. The low temperature peak becomes more dominant with increasing crystallization temperature, while the high temperature peak decreases. This behaviour indicates that, in the case of homo polymers, the low temperature peak represent melting of the material crystallized at the crystallization temperature. The high temperature peak relates to the material that undergoes reorganisation during heating to melting and this fraction decreases with increasing crystallization temperature[33,34].

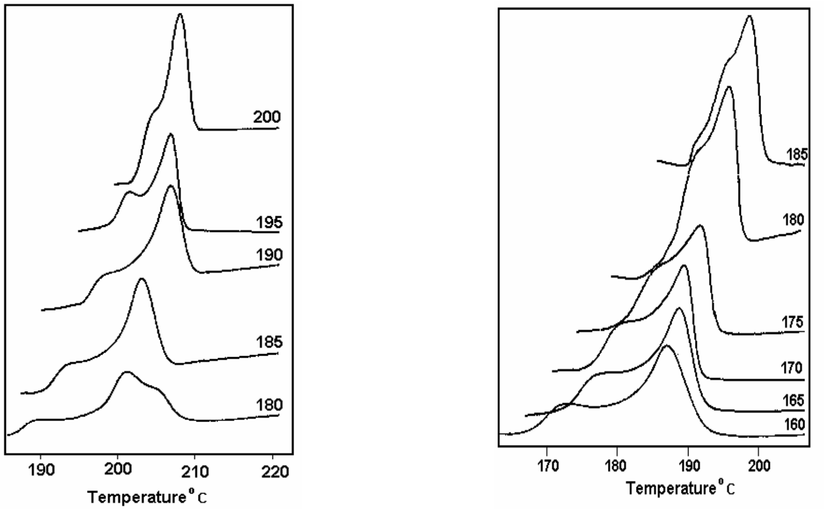
The behaviour of melting endotherms change with composition for copolymers. The copolymer poly(BT-co-CT) **(1)** 84/16, 74/26 and 22/78 show similar behaviour and they exhibit a small low temperature endotherm, about 10°C higher than the T_c followed by the main melting peak. The small low temperature peak shifts to high temperature on increasing the crystallization temperature but the fraction remains unchanged. The dominant high temperature peak shifts to higher temperature with increase in crystallization temperature. This behaviour indicates that both the peaks arise due to the polymer crystallized at the crystallization temperature and the low temperature peak is due to the melting of the less stable material having lower lamellar thickness[33-37]. The copolymer compositions 61/39 and 45/55 show double peak nature and peak positions change but the shape of the thermogram does not change with increasing crystallization temperature. **Figure 3.10** shows the plot of observed melting temperature and crystallization temperature according to Hoffman-Week plots[38].

$$T^{\circ}_m - T_m = M(T^{\circ}_m - T_c) \quad \textbf{(3.5)}$$

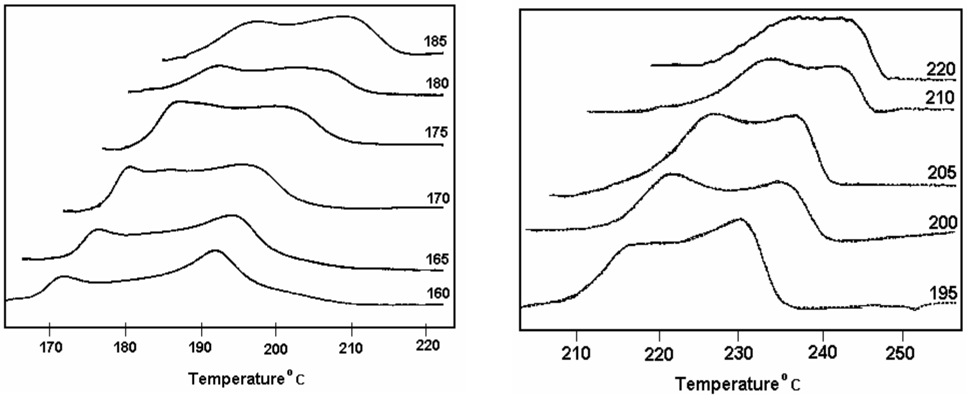
where T_m represents the melting temperature of the sample after isothermal crystallization. The data are fitted by straight line: the intersections of these straight lines with the line T_m=T_c give the equilibrium melting temperature (T°_m) of the copolyesters. In **Figure 3.11** the $T_m°$ of copolymers and the homopolymer are plotted and the corresponding T_m are also shown. The $T_m°$ also shows behavior similar to T_m and the copolymer 74/26 is the eutectic composition. The $T_m°$ of PBT obtained in the present case is 236°C and is with in the reported range of 236-247[39-43]. However, in the case of PCT the $T_m°$ obtained is 333°C which is 28°C higher than the reported valueof 305°C[20].



PBT

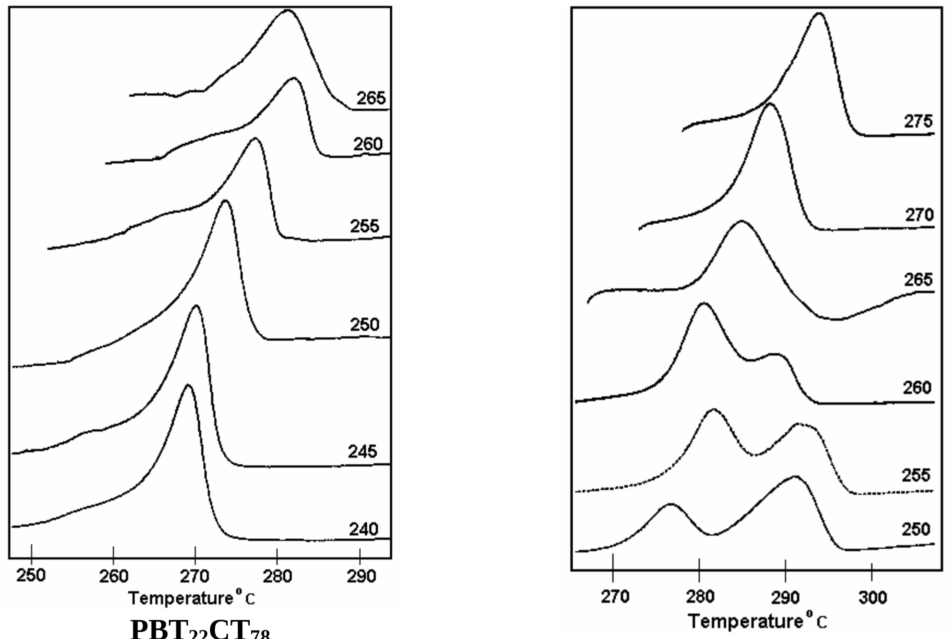


PBT$_{84}$CT$_{16}$ **PBT$_{74}$CT$_{26}$**



PBT$_{61}$CT$_{39}$ **PBT$_{45}$CT$_{55}$**

Figure 3.9 DSC heating thermograms for samples crystallized at various temperatures (heating rate 10°C/min) contd.........



PBT$_{22}$CT$_{78}$

PCT

Figure 3.9 DSC heating thermograms for samples crystallized at various temperatures (heating rate 10°C/min)

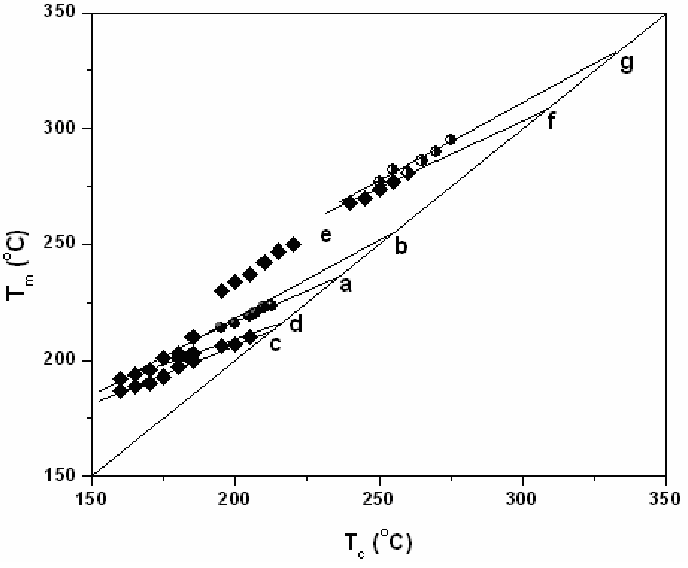


Figure 3.10 Hoffman-Weeks plots of first melting peak temperature (T_m) as a function of T_C for (a) PBT, (b) PBT$_{84}$CT$_{16}$ (c) PBT$_{74}$CT$_{26}$, (d) PBT$_{61}$CT$_{39}$, (e) PBT$_{45}$CT$_{55}$, (f) PBT$_{22}$CT$_{78}$, (g) PCT.

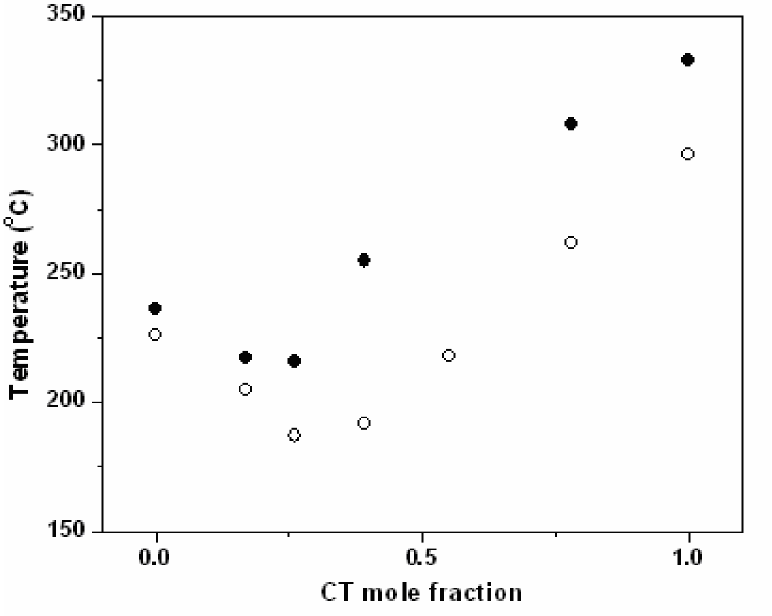


Figure 3.11 Equlibrium melting temperature, $T_m°$ (,) and T_m (–) as a function of copolymer composition

3.4.1.5 X-ray diffraction studies

The room temperature structure of the samples was analyzed by WAXS. As obtained samples showed diffraction pattern typical of semicrystalline polymers. The diffraction patterns of the samples having compositions close to the eutectic composition are not well resolved. Hence, all the samples were annealed close to their melting temperature for 2 h. After annealing the diffraction peaks were well developed. From the peak position the d-spacings were calculated using the Bragg equation. **Figure 3.12** shows the WAXS pattern of the annealed PBT, PCT and P(BT-co-CT) copolymers. The crystal structure of PBT[43-46] and PCT[47] are reported to be triclinic. PBT shows strong peaks at diffraction angles 16.02, 17.25, 23.28 and 25.16. These peaks are indexed as $0\bar{1}0$, 010, 100 and $\bar{1}11$ planes of triclinic. PCT shows peaks at 15.63, 16.63, 23.41 and 25.6 and are assinged to 011, 010, 100 and $\bar{1}11$ planes. The variation of d-spacing with composition shows a break in the region around 30% PCT (**Figure 3.13**).

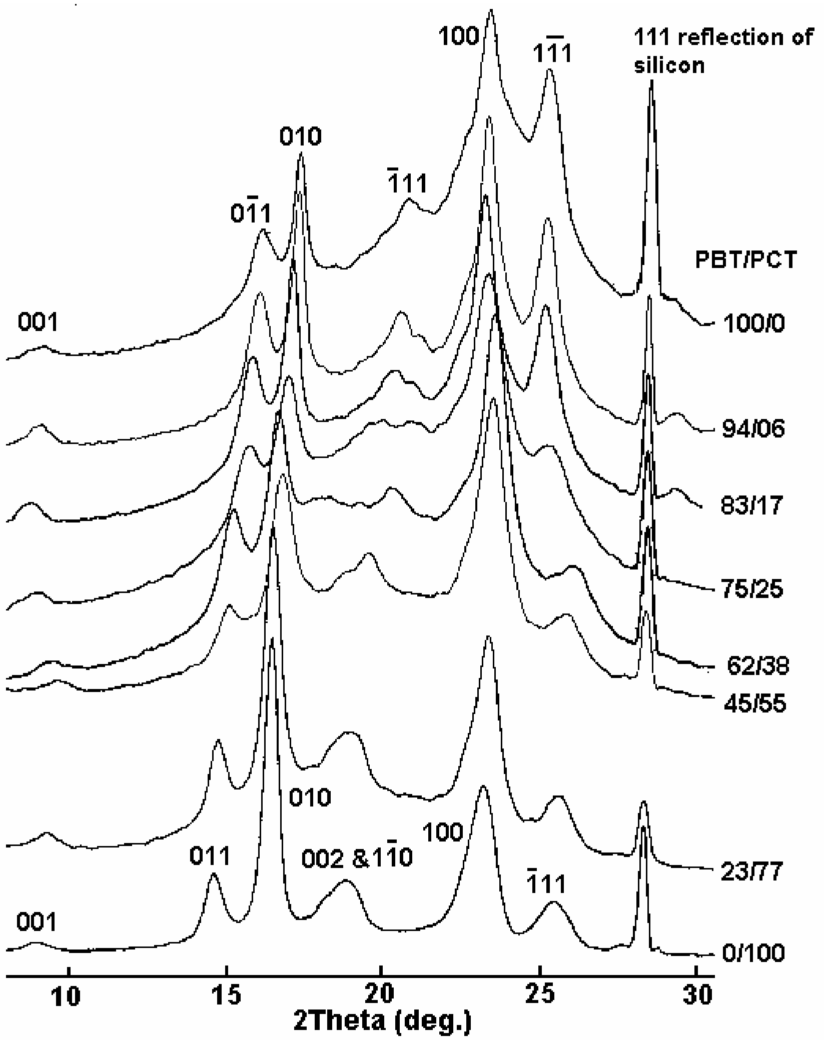


Figure 3.12 X-ray diffraction patterns of annealed poly(BT-co-CT) copolyesters

The diffraction patterns of copolyesters rich in PBT (74-100% BT) component only show patterns similar to PBT indicating that the copolyesters crystallized in the PBT lattice. When the mole fraction of PCT increases (39-100% CT), the copolyesters crystallized in the PCT lattice. The change in the lattice also occurs close to the eutectic composition. This shows the ability of PCT to control the crystallization even when it is present in minor proportion. This could arise due to the higher rigidity of PCT, compared to PBT.

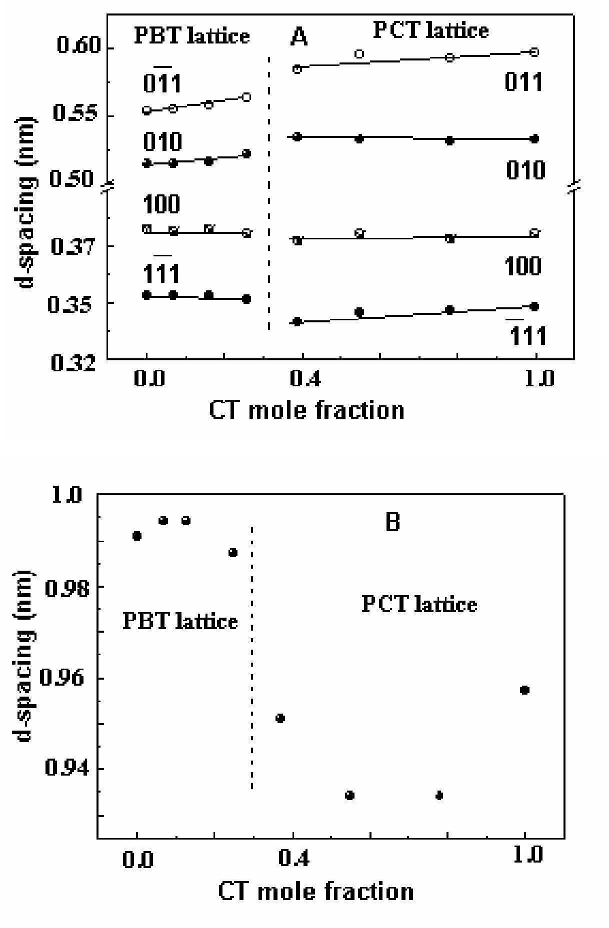


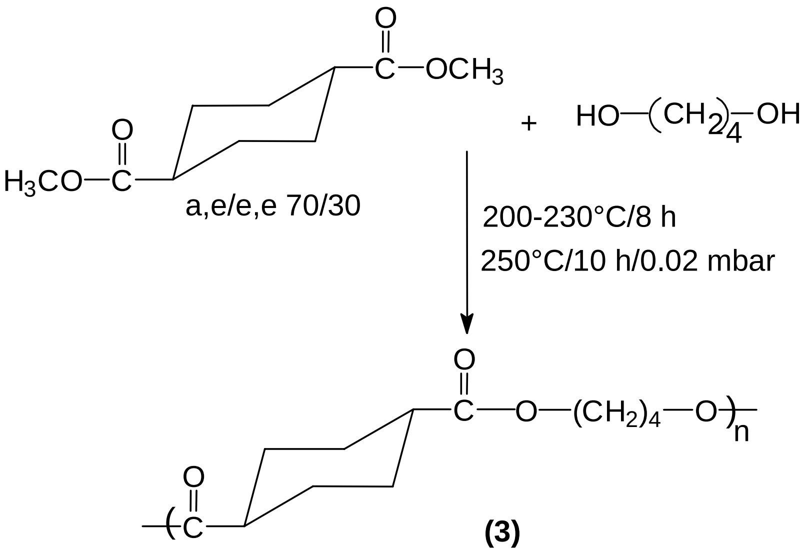
Figure 3.13 (A) d-spacings of $0\bar{1}1$, 010 , 100 and $\bar{1}11$ reflections and (B) 001 spacing(along chain direction) as a function of copolymer composition

According to Jun et al[48], an average sequence length higher than 3 is required to form crystallites. However, in the present case, copolyesters could crystallize even when the sequence length is less than 3. This indicates similarity in the repeat unit of PBT and PCT. The length of BT and CT units a calculated using conjugate gradient and Newton-Raphson method using Cerius 2 software were found to be similar (1.23 nm for PBT and 1.33 nm for PCT). It appears that similar repeat unit lengths makes the copolyesters to cocrystallize in the same lattice even when the individual sequence length is less than 3.

3.4.2 Synthesis and properties of poly(BT-co-BCD) copolyesters

3.4.2.1 Synthesis and structure of poly(butylene-1,4- cyclohexane dicarboxylate) (PBCD)

Poly (butylene-1,4- cyclohexane dicarboxylate) (PBCD) **(3)** was synthesized by melt condensation in the presence of titanium isopropoxide catalyst as illustrated in **Scheme 3.3.**



Scheme 3.3 Synthesis of poly(butylene-1,4-cyclohexane dicarboxylate) (PBCD)

PBCD **(3)** was characterized by ^{1}H, ^{13}C NMR and GPC. **Figure 3.14** shows the ^{1}H NMR spectrum of PBCD. The O-CH_2- proton, H_a, appears at 4.1 ppm. The *a,e* and *e,e* protons, $H_{b,}$ appear at 2.46 and 2.28 ppm respectively. ^{13}C NMR (**Figure 3.15**) shows carbonyl carbon, $C_{e,}$ at 174.72 and 175.18 for the *a,e* and *e,e* isomers of cyclohexane dicarboxylate, respectively. The *e,e/a,e* ratio of cyclohexane dicarboxylate in the polymer is 70/30.

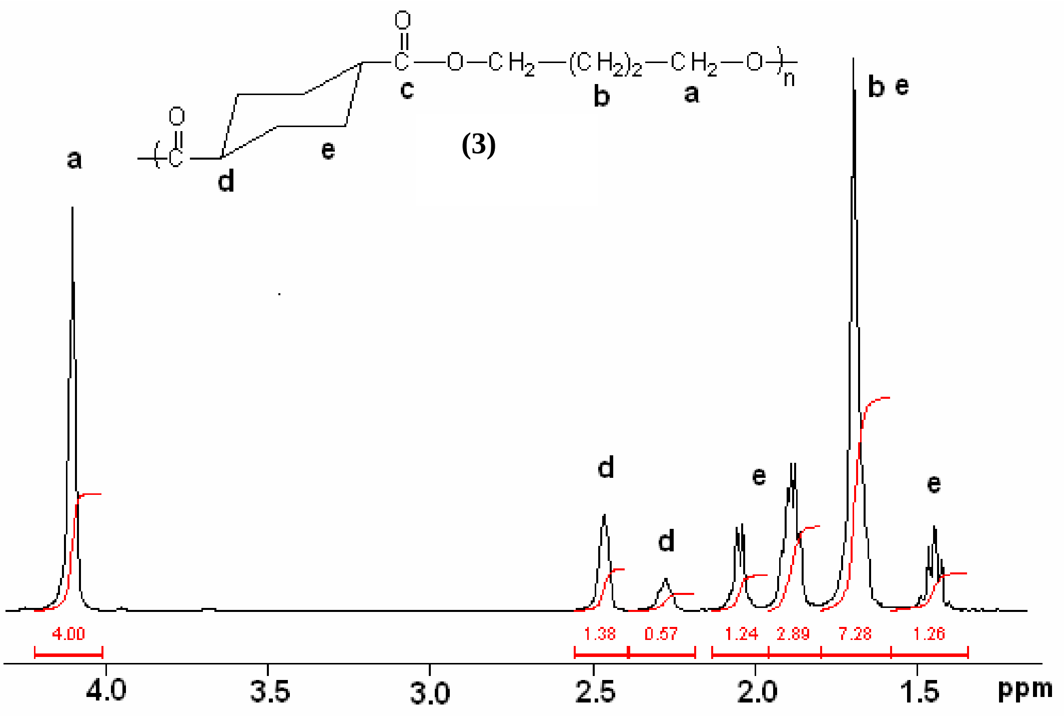


Figure 3.14 ^{1}H-NMR spectrum of poly (butylene-1,4- cyclohexane dicarboxylate) (PBCD)

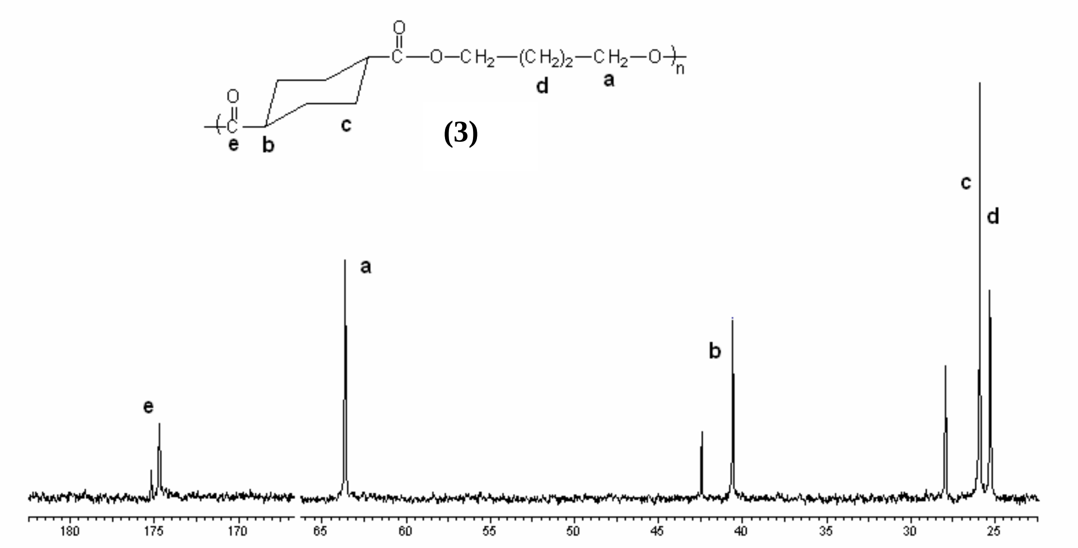
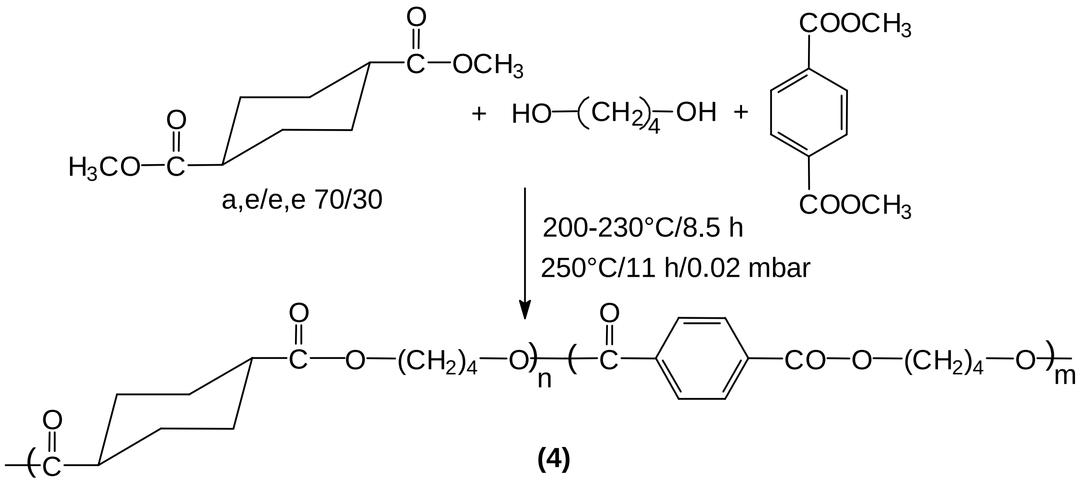


Figure 3.15 ^{13}C NMR spectrum of poly (butylene-1,4- cyclohexane dicarboxylate) (PBCD)

3.4.2.2 Synthesis and structure of poly(butylene terephthalate-co-butylene cyclohexane dicarboxylate) (poly(BT-co-BCD))

A series of poly(BT-co-BCD) **(4)** copolyesters with various copolymer compositions were synthesized from DMT, DMCD and 1,4-butanediol by melt condensation. The scheme for the synthesis is shown in **Scheme 3.4**. The ratio of DMT/DMCD in the polymer was calculated from the oxybutylene proton, H_a. The copolyesters had viscosity in the range of 0.96-1.24 dL/g (**Table 3.7**). The copolyester $PBT_{50}BCD_{50}$ was found to be soluble in chloroform, while the other copolyester compositions were insoluble in chloroform. The number average and weight average molecular weights of $PBT_{50}BCD_{50}$ were found to be 56,300 and 1,10,500 respectively with a dispersity of 2.2.



Scheme 3.4 Synthesis of poly(butylene terephthalate-co-butylene cyclohexane dicarboxylate) (poly(BT-co-BCD))

3.4.2.3 Sequence analysis

The chemical structure of the copolyester poly(BT-co-BCD) **(4)** is given in **Figure 3.16,** where BCD is butylene cylcohexane dicarboxylate unit and BT is the butylene terephthalate unit.

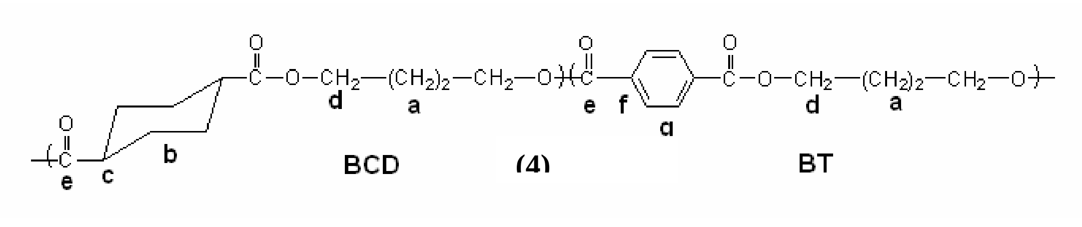


Figure 3.16 Chemical structure of poly(BT-co-BCD) copolyester with notations used for NMR assignments

The ^{1}H NMR spectrum of $PBT_{50}BCD_{50}$ copolyester with assignment of each peak is shown in **Figure 3.17.** In the ^{1}H NMR specturm, the peak for PBT appears at 4.5 and for PBCD appears at 4.1 ppm.

Table 3.5 ^{1}H and ^{13}C NMR Chemical Shifts (δ in ppm) of PBT, PBCD and P(BT-co-BCD) copolyesters

^{1}H Chemical shifts							
	^TH_a	^TH_d	^TH_g	$^{CD}H_a$	$^{CD}H_b$	$^{CD}H_c$	$^{CD}H_d$
PBT	2.02	4.5	8.12				
PBCD				1.7	1.3-2.1	2.46, 2.28	4.1
P(BT-co-BCD)	1.97	4.44, 4.38	8.1	1.7	1.3-2.5	2.28, 2.47	4.15, 4.10
^{13}C Chemical Shifts							
	^TC_d	^TC_e	^TC_f	^TC_g	$^{CD}C_d$	$^{CD}C_e$	$^{CD}C_c$
PBT	65.9	167.6	133.7	129.8			
PBCD					63.6	174.7, 175.1	40.6, 42.4
P(BT-co-BCD)	64.8	166.9	133.82	129.7	63.7	174.8, 175.3	40.7, 42.5

The copolyester sequence was determined using the region of ^{1}H NMR corresponding to the oxybutylene moiety. An expanded ^{1}H NMR spectrum in the range of 4-5 ppm is also shown in **Figure 3.18,** the oxybutylene protons, H_a, is split into four peaks corresponding to the different possible environment : TT, TCD, CDT, CDCD, where T corresponds to terephthalate and CD corresponds to cyclohexane dicarboxylate unit, as shown in **Figure 3.19.** Molar fractions of terephthalate and cyclohexane dicarboxylate were obtained from the relative intensities of the four kinds of signals in the NMR spectrum; f_{TT}, f_{CDCD}, f_{TCD} and f_{CDT} correspond to the proportion of the integrated intensities of TT, CDCD, TCD and CDT respectively. The number average sequence length of a terephthalate unit (L_{nT}) and cyclohexane dicarboxylate unit (L_{nCD}) and the degree of randomness B are summarized in **Table 3.6.**

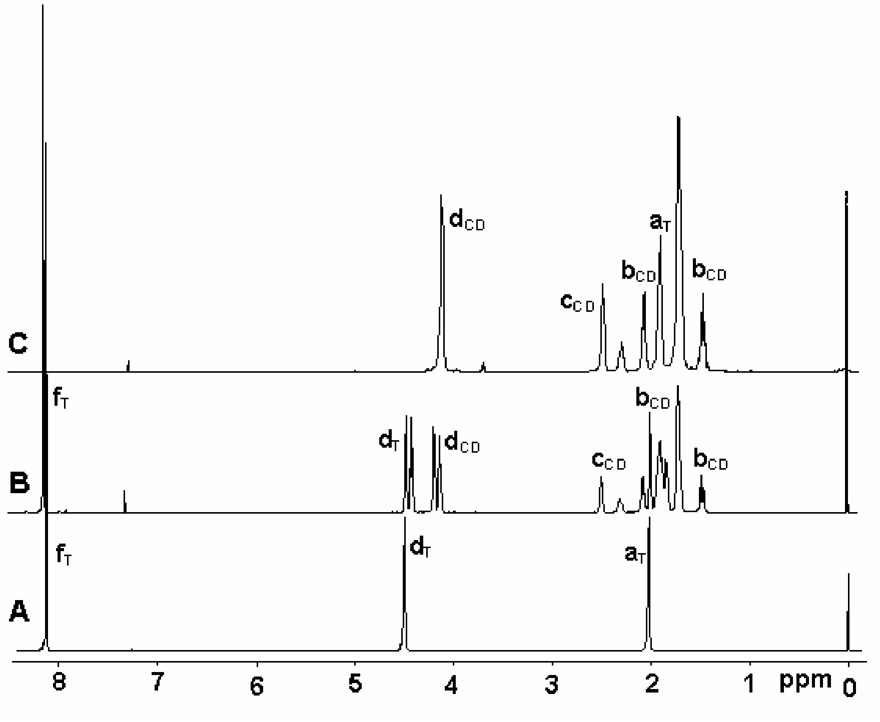


Figure 3.17 ^{1}H NMR spectra of (A) PBT, (B) PBT$_{50}$BCD$_{50}$ and (C) PBCD

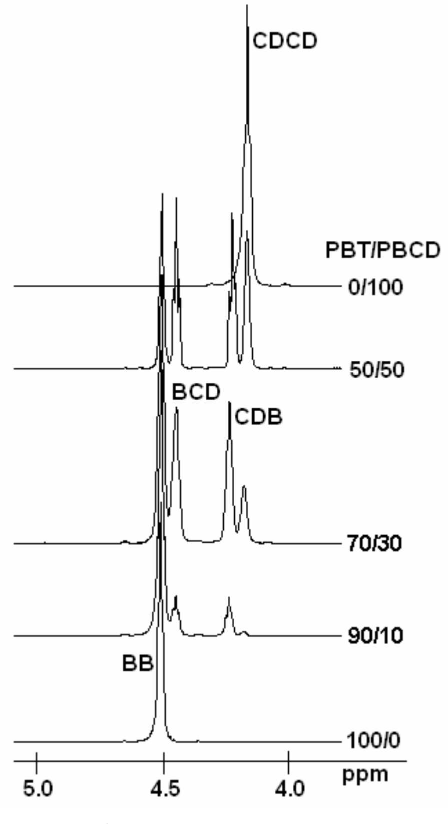


Figure 3.18 Expanded 500 MHz ^{1}H NMR spectra (the alcoholic CH$_2$ proton region) of PBT, PBCD **(3)** and poly(BT-co-BCD)

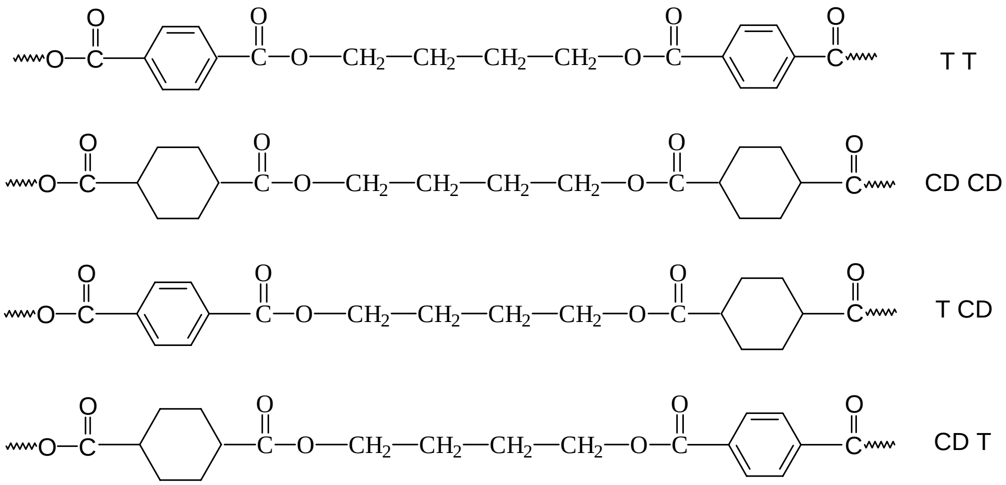


Figure 3.19 Different environments of butylenic protons

Table 3.6 Composition, sequence length and randomness of poly(BT-co-BCD) copolyesters determined by ^{1}H NMR

Copolyester	Feed composition (mol %)		Copolymer composition[a] (mol %)		η_{inh} dL/g)	Average sequence length		B
	BT	BCD	BT	BCD		L_{nT}	L_{nCD}	
PBT	100	0	100	0	0.90	-	-	-
$PBT_{90}BCD_{10}$	90	10	90	10	1.24	8.51	1.16	1.01
$PBT_{70}BCD_{30}$	70	30	70	30	0.87	3.26	1.43	1.00
$PBT_{50}BCD_{50}$	50	50	50	50	0.96	1.78	1.98	1.06
PBCD	0	100	0	100	0.60	-	-	-

The ^{13}C NMR assignments of poly(BT-co-BCD) **(4)** copolyester is given in **Table 3.5** and the spectrum is shown in **Figure 3.20**. The carbonyl carbon, C_e, of cyclohexane dicarboxylate appears at 174.8 and that of terepthalate occurs at 165.63. The butylenic carbon, C_d, appears at 63.69 and 64.79 for cyclohexane dicarboxylate and terephthalate respectively.

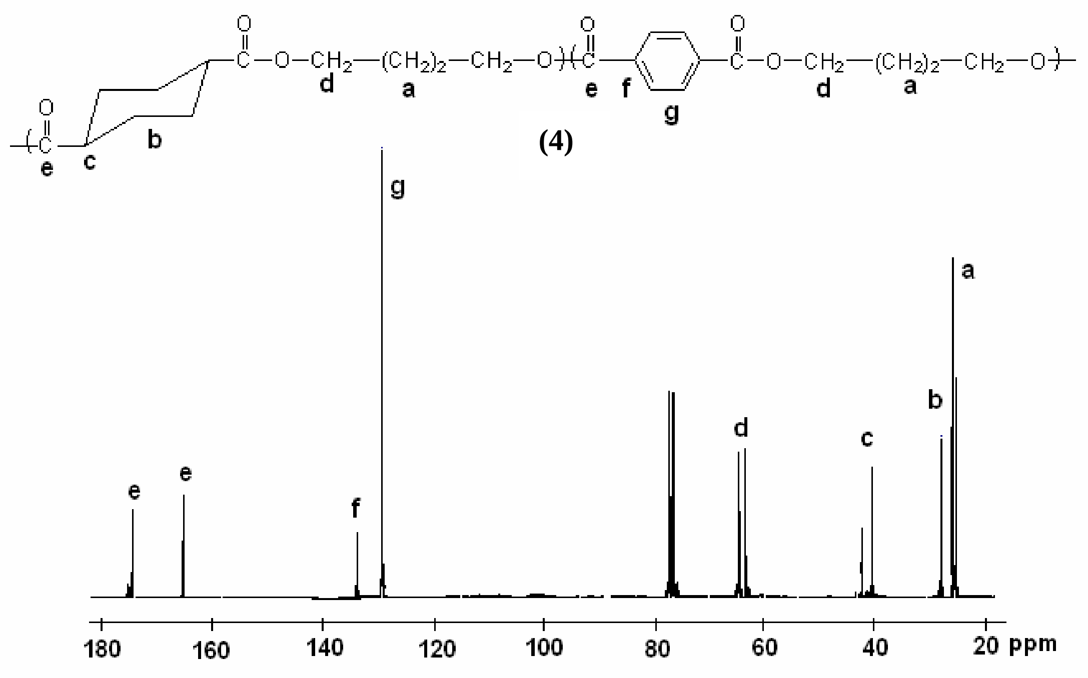


Figure 3.20 A typical ^{13}C NMR spectrum of of poly(butylene terephthalate-co-cyclohexane dicarboxylate) (poly(BT-co-BCD))

3.4.2.4 Thermal properties

The thermal behavior of the copolyesters was studied by differential scanning calorimetry. The melting endotherms and the crystallization exotherms are shown in **Figure 3.21** and the data is summarized in **Table 3.7**. PBCD **(3)** containing 70 % *a,e*-1,4-cyclohexane dicarboxylate is a semicrystalline polyester with a T_m of 55°C and a T_g of -10°C. It is reported[9,49] that the PBCD **(3)** containing e,e-*1,4*-cyclohexane dicarboxylate is a semicrystalline polyester with a T_m of 163°C, T_c of 112°C and a T_g of 31°C.

The copolyesters could be crystallized over the entire composition range and showed melting endotherm on heating. The presence of clear melting indicates cocrystallization behavior of the copolyesters over the entire range of composition. The melting and glass transition temperatures show linear relationship with composition (**Figure 3.22**) and do not show eutectic behavior. The absence of eutectic composition indicates that the cocrystallizaion is isomorphic in nature and monomer units of one type are included in the crystal lattice of the other type. A similar isomorphic crystallization behavior has been reported by Jeong et al in the case of poly (hexamethylene 2,6-naphthlate-co-1,4-cyclohexylene dimethylene 2,6-naphthalate)[14].

Table 3.7 Thermal properties of PBT, PBCD and poly(BT-co-BCD) copolyesters

Polyester	η_{inh}[a] dL/g	T_g (°C)	T_m (°C)	ΔH_m (J/g)	T_{mc} (°C)	ΔH_c (J/g)	IDT[b]
PBT	0.90	40	226	41	193	49	374
$PBT_{90}BCD_{10}$	1.24	36	203	29	156	34	390
$PBT_{70}BCD_{30}$	0.87	20	172	25	105	20	387
$PBT_{50}BCD_{50}$	0.96	9	130	19	[c]	[c]	382
PBCD	0.6	-10	56	32	[c]	[c]	400

[a]Measured in phenol/TCE 60/40 (w/w); [b] Measured by TGA; [c]copolyester does not crystallize on cooling

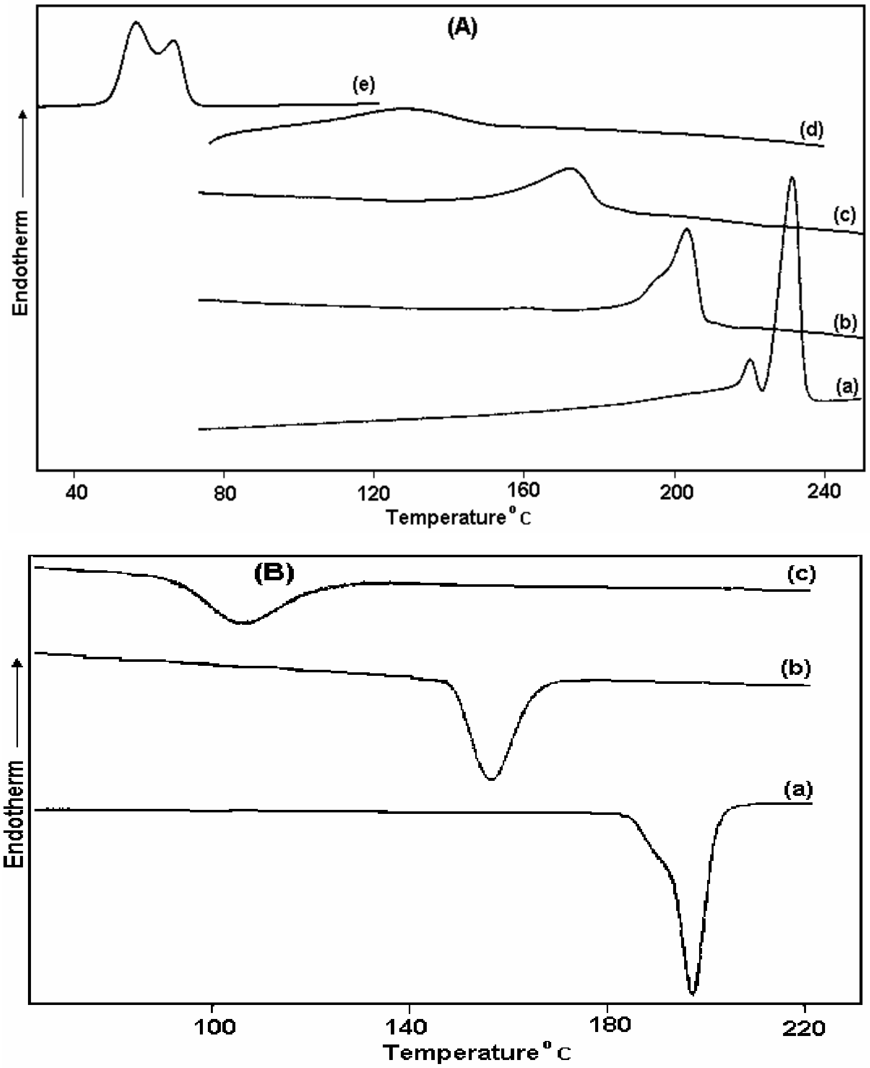


Figure 3.21 DSC heating (A) and cooling (B) thermograms of (a) PBT; (b) $PBT_{90}BCD_{10}$; (c) $PBT_{70}BCD_{30}$; (d) $PBT_{50}BCD_{50}$

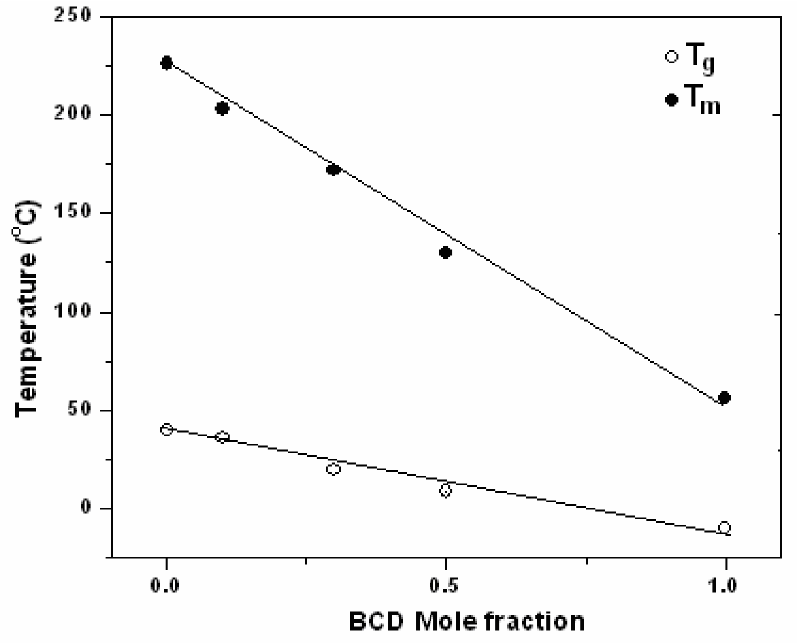


Figure 3.22 Melting and glass transition temperature as a function of BCD mole fraction

3.4.2.5 X-ray diffraction studies

Figure 3.23 shows the x-ray diffraction patterns of poly(BT-co-BCD) **(4)** along with patterns of PBT and PBCD **(3)**. In the case of PBCD, appropriate samples could not be prepared for X-ray diffraction experiments. Hence thin film sample has been cast from the solution and the film sample was scanned in the X-ray diffractometer to obtain the x-ray diffraction pattern of the PBCD. The diffraction pattern of PBCD indicates that the packing of chains in the lattice is different from that of PBT. The d-spacings of the reflections are plotted in **Figure 3.24** and the d-spacing change linearly with increase in comonomer content. The smooth change over of PBT lattice into PBCD shows that the cocrystallization is isomorphic in nature. Similar kind of changeover in lattice and isomorphic cocrystallization behaviour has also been observed for poly(hexamethylene naphthalate-co-cyclohexylene dimethylene naphthalate) system[14].

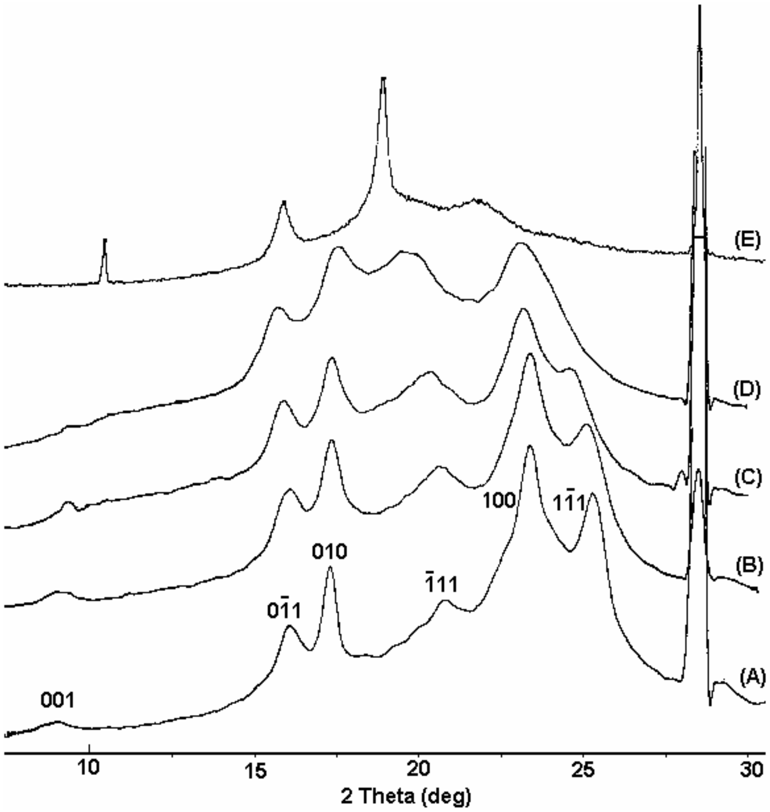


Figure 3.23 WAXD patterns of annealed samples: (A) PBT (B) $PBT_{90}BCD_{10}$ (C) $PBT_{70}BCD_{30}$, (D) $PBT_{50}BCD_{50}$ (E) PBCD

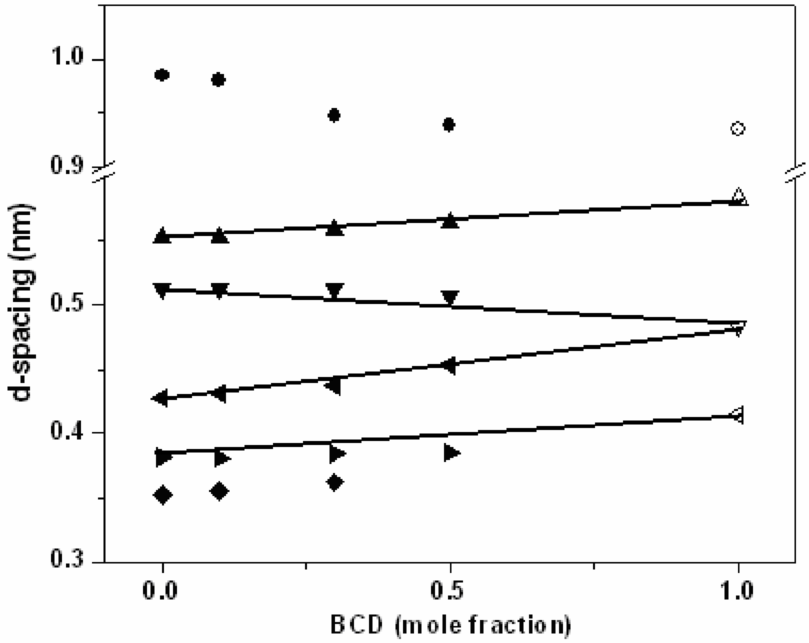


Figure 3.24 Changes of d-spacigs for poly(BT-co-BCD) copolymers with copolymer composition (,) 001(along chain direction), (7) 0$\bar{1}$1, (B)010, (Ω)$\bar{1}$11 (β)100 and (Λ)1$\bar{1}$1 reflections (based on PBT structure) as a function of copolymer composition

3.5 Conclusion

A series of poly(butylene terephthalate-co-1,4-cyclohexylene dimethylene terephthalate) (P(BT-co-CT)) **(2)** and poly (butylenes terephthalate-co-1,4- cyclohexane dicarboxylate) (P(BT-co-BCD)) **(4)** copolymers with various CT and BCD contents were synthesized by melt condensation. The NMR spectroscopy confirmed that the copolyesters are statistically random, irrespective of the composition. The thermal analysis and XRD studies showed that the copolymers crystallize in all ranges of composition studied. The poly(BT-co-CT) copolymers exhibit typical eutectic behaviour in melting and crystallization and the eutectic composition is $PBT_{75}CT_{25}$ indicating iso-dimorphic cocrystallization behavior. On the other hand, poly(BT-co-BCD)s **(4)** showed isomorphic crystallization and did not show eutectic behaviour in melting and crystallization. The glass transition temperature showed linear dependency on composition in these copolymers.

The copolyesters butylene terephthalate exhibit a wide range of melting temperature and glass transition temperature. Incorporation of comonomer changes the melting temperature of the copolyesters from 130 to 262°C and the glass transition temperature varies from 9 to 77°C. Essentially these changes brought in by the change in the polymer structure by the incorporation of comonomer. Incorporation of cyclohexane dimethanol, as a comonomer results in copolymers in which the T_c and T_m follow a eutectic behaviour. These copolyesters have T_g’s higher than PBT. While incorporation of 1,4-cyclohexane dicarboxylate comonomer, which is the ester component, results in copolyesters which have T_g lower than PBT, the T_m does not show eutectic behaviour.

II. Crystallization kinetics of poly(butylene terephthalate), poly(cyclohexylene dimethylene terephthalate) and poly(cyclohexylenedimethylene cyclohexane dicarboxylate)

3.6 Introduction

A detailed understanding of the crystallization kinetics is very important for the processing of semicrystalline polymers. The crystallization kinetics of PBT has been studied in detail[50-52]; however, the crystallization kinetics of PCT and PCCD has not been reported in the open literature. Hence, it is of interest to study the detailed crystallization kinetics of PCT and PCCD and compare with that of PBT. The PCCD synthesized in the laboratory has high *a,e* ratio and consequently the polymer does not crystallize and remains amorphous. On the other hand, commercially available PCCD, which has a high *e,e* content of 91%, has been used to study the crystallization kinetics. It may also be noted that the crystallization depends on many factors such as molecular weight, nature of end groups and the catalyst used for polycondensation. Therefore, detailed crystallization kinetics of laboratory synthesized PBT has also been made instead of making use of such information available in the literature and compared with that of PCT and PCCD.

The crystallization behavior and crystallization kinetics of the commercial PCCD was studied by DSC and compared with PBT and PCT.

3.7 Materials

Poly(1,4-cyclohexane dimethylene cyclohexane dicarboxylate) (PCCD) was obtained from GE, India, with an η_{inh} of 0.8 dL/g (in Phenol/TCE 60/40 w/w) and M_w ~70,000. PBT and PCT were synthesized in the laboratory.

3.8 Analysis

Differential Scanning Calorimetry

The calorimetric measurements were done using Perkin-Elmer DSC-7. The samples were heated/cooled at a rate of 10ºC/min under nitrogen environment. The melting temperature and heat of fusion were obtained from the heating thermogram and crystallization temperature upon cooling (T_{mc}) from the cooling thermogram.

Crystallization kinetics studies were performed using Perkin Elmer DSC-7. Two procedures were used depending on the crystallization temperature. For isothermal crystallization in the high temperature region, the samples were heated to a temperature 20 °C above the melting temperature and held for 5 min. Then the sample was cooled rapidly at a rate of 200°C/min to the crystallization temperature and held at that temperature till the crystallization was completed. Isothermal crystallization in the low temperature region was performed by placing the quenched samples in the DSC cell at the selected temperature. The melting temperature (T_m) of the crystallized sample was determined from the heating thermogram. Avarami analysis for crystallization was done on the crystallization exotherm data.

3.9 Results and Discussion

Crystallization kinetics

The experimental protocol used in the isothermal crystallization studies is outlined below: The sample was initially heated to about 30°C above the melting temperature and held for about 2 minutes to remove the past thermal history. After the holding period, the sample was cooled rapidly (200^{o}C/min.) to the crystallization temperature. After the completion of the crystallization the sample was heated to melting. In the case of PCT **(2)**, the fast crystallization rate made it impossible to study the low temperature range because the sample crystallized before reaching the indended crystallization temperature. Hence, an amorphous sample was prepared by quickly quenching the PCT melt in the ice water and then heating the amorphous sample to the indended crystallization temperature. The crystallization isotherms were analyzed using the Avrami equation[53-57].

$$\ln[-\ln (1-\theta t)] = n \ln t + \ln k$$

Where “k” is the overall kinetic rate constant, which depends on the rate of nucleation and growth and ‘n’ the Avrami exponent, which is the parameter that depends on the nature of the primary nucleation and the geometry of growing crystals. The values of ‘k’ and ‘n’ can be determined from the intercept and the slope of a straight line in the plot of $\ln[-\ln(1-\theta_t)]$ against ln t. It is often found that ‘n’ is not an integer. The value of 'k' is also very sensitive to temperature and the nature of samples (catalyst system and molecular weight).

Table 3.8 Avrami exponents for various types of nucleation and growth[58]

n	Mechanism
4	Spherulitic growth from sporadic nuclei
3	Spherulitic growth from instantaneous nuclei
3	Disc like growth from sporadic nuclei
2	Disc like growth from instantaneous nuclei
2	Rod like growth from sporadic nuclei
1	Rod like growth from instantaneous nuclei

The commercial PCCD **(**Chapter 4**, (12))** sample obtained is amorphous and on heating exhibits a thermogram typical of a semicrystalline polymer. The sample exhibits T_g at about 71°C and then cold crystallization at 116^{o}C. On further heating the sample melts at 223^{o}C, and exhibits double melting peaks typical of semicrystalline polymers (**Figure 3.25**). The PCCD in general does not exhibit crystallization on cooling from the melt at normal cooling rates used in the DSC experiments. However it shows a crystallization peak at 141^{o}C when the cooling rate is 2^{o}C/min. Hence isothermal crystallization studies could be performed at all temperatures between T_g and T_m by rapid cooling from the melt to the crystallization temperature. The crystallization exotherms obtained at various crystallization temperatures are shown in **Figure 3.26.**

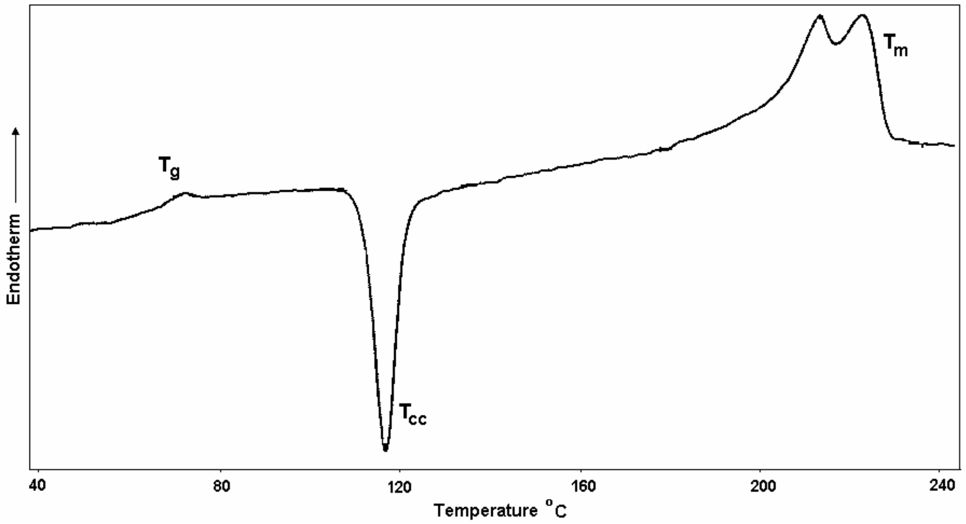


Figure 3.25 DSC thermogram of commercial PCCD

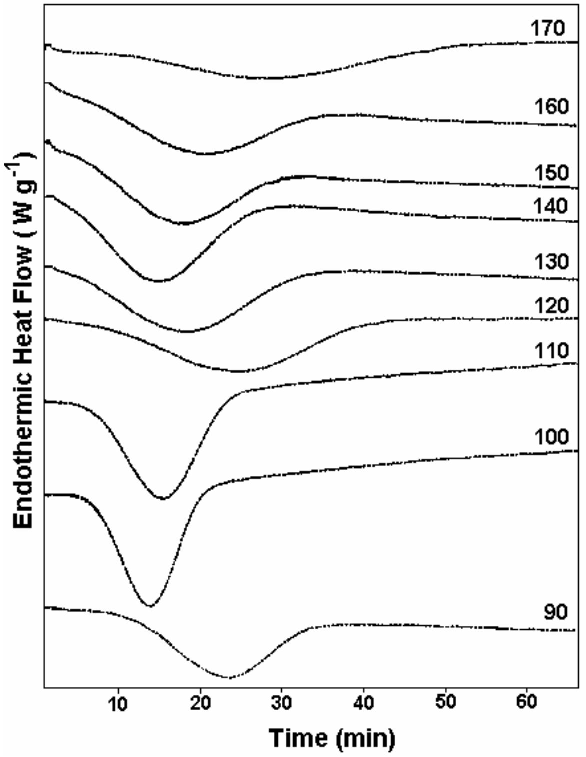


Figure 3.26 Isothermal DSC curves for crystallization of PCCD at various crystallization temperatures

Table 3.9 Half time of crystallization and Avrami constants for PCCD

Crystallization temperature (°C)	Half time of Crystallization $t_{1/2}$ (min)	n	K (min^{-n})
90	22.8	-	
100	13.7	-	1.2×10^{-3}
110	15.1	4.2	18.8×10^{-6}
120	23.4	3.2	3.0×10^{-5}
130	17.3	2.6	1.0×10^{-3}
140	15.2	2.8	4.0×10^{-3}
150	15.9	2.7	2.4×10^{-3}
160	18.0	3.1	2.5×10^{-3}
165	25.1	3.6	1.7×10^{-3}
170	37.0	3.4	2.8×10^{-6}
180	73.0	3.2	6.5×10^{-7}

In the case PCT **(2)** isothermal crystallization could be performed only at low temperature and high temperature regions where the crystallization rate is low enough to obtain meaningful exotherms. Amorphous samples were used in the low temperature region. Nevertheless, at few temperatures the rate is too fast to record the starting of the crystallization isotherms. However, crystallization peak temperatures could be seen in the crystallization isotherms. The isotherms are shown in **Figure 3.27**.

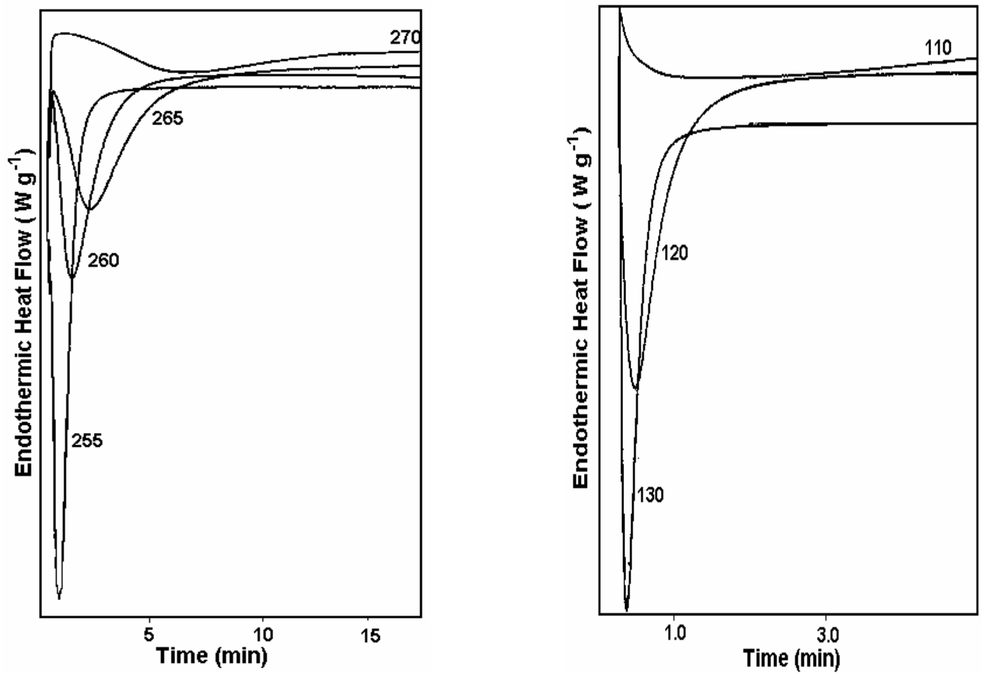


Figure 3.27 Isothermal DSC curves for crystallization of PCT at various crystallization temperatures

Table 3.10 Half time of crystallization and Avrami constants for PCT

Crystallization temperature (°C)	Half time of Crystallization $t_{1/2}$ (min)	n	K (min^{-n})
110	3.0	1.7	$1.0\text{x}10^{-1}$
120	0.6	2.8	$2.2\ \text{x}10^{1}$
130	0.4	-	-
245	0.6	-	-
250	0.6	-	-
255	1.0	-	-
260	1.7	2.9	$1.3\text{x}10^{-1}$
265	2.7	2.5	$6.8\text{x}10^{-2}$
270	7.8	2.7	$2.7\text{x}10^{-3}$
275	11.1	3.1	$4.1\text{x}10^{-4}$

For PBT, on the other hand, only the high temperature region could be studied, as the crystallization rate is too fast to allow samples to be quenched into an amorphous state. The crystallization isotherms obtained at high temperatures are shown in **Figure 3.28**.

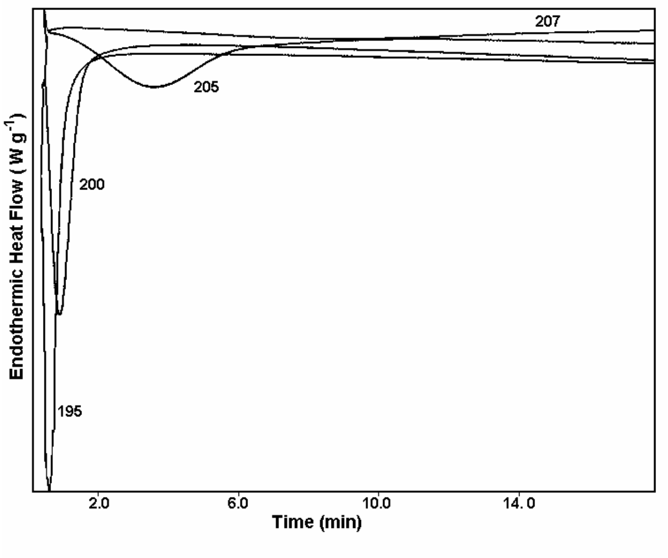


Figure 3.28 Isothermal DSC curves for crystallization of PBT at various crystallization temperatures

Table 3.11 Half time of crystallization and Avrami constants for PBT

Crystallization temperature (°C)	Half time of Crystallization $t_{1/2}$ (min)	n	K (min^{-n})
190	0.4	-	-
200	0.9	-	-
205	3.8	3.0	1.0x10^{-2}
207	9.3	2.9	1.0x10^{-3}
210	14.2	3.9	2.4x10^{-5}

The crystallization half times obtained for various crystallization temperatures from the crystallization isotherms for PCCD, PCT and PBT are shown in **Figure 3.29.** The PCT shows a typical 'U' shaped curve with a wide temperature range and from 130 to 250^{o}C the crystallization rate is very rapid. In the case of PBT only the high temperature range is shown and the crystallization rate becomes very rapid below 200^{o}C. The PCCD on the other hand shows 'W' shaped curve, which is rather unusual. The increase in the crystallization half time occurs in the small temperature range around 120^{o}C. The Avrami exponent, n, calculated for various temperatures are shown in **Tables 3.9, 3.10** and **3.11** for PCCD, PCT and PBT respectively. The values in general fall between 2 and 4 indicating normal crystallization kinetics for these samples.

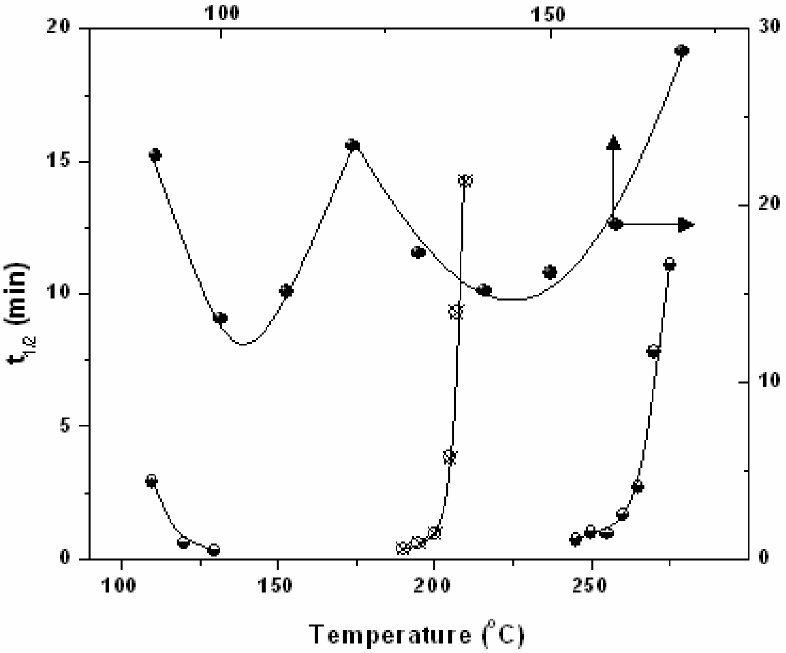


Figure 3.29 Crystallization temperature vs. half time of crystallization of PBT (0), PCT (5) and PCCD (□)

3.10 Conclusion

A detailed crystallization kinetics study has been done on PCT **(2)** and PCCD (Chapter 4 **(12)**) for the first time and compared with PBT. PCT is a rapidly crystallizing polymer like PBT and has short crystallization half time. The crystallization half time is less than 0.5 minute over wide range of temperature from 110 to 275°C. PCCD, on the other hand, slowly crystallizes and shows unique minimum crystallization half time at two different temperatures. It is interesting to note that though PCT and PCCD has similar chemical structures, the PCT exhibits a higher crystallization rate. The difference in the crystallization behavior of PCT and PCCD may be attributed to their structures, i.e PCT has a planar benzene ring structure while the cyclohexane ring is non-planar. The non-planar nature of the cyclohexane structure inhibits the quick packing of the chains in the lattice and consequently reduces the crystallization rates.

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Chapter 4: I. Synthesis and characterization of polyesters and copolyesters containing cyclopentane ring in the chain

4.1 Introduction

This chapter describes the results obtained on the synthesis and properties of copolyesters of dimethyl terephthalate and 1,4-butanediol containing cyclopentane ring in the chain. Synthesis of polyesters from cyclopentane systems has not been reported in literature. Cyclopentane ring containing diol and diester, namely, 1,3-bis(hydroxymethyl) cyclopentane (or 1,3-cyclopentane dimethanol) and dimethyl-1,3-cyclopentane dicarboxylate were synthesized starting from norbornene. Copolyesters of dimethyl terephthalate and 1,4-butanediol containing 1,3-bis(hydroxymethyl) cyclopentane (CPDM) and dimethyl-1,3-cyclopentane dicarboxylate (CPDE), namely, poly (butylene terephthalate-co-1,3-cyclopentylene dimethylene terephthalate) [P(BT-co-CPDT)] and poly (butylene terephthalate-co-butylene cyclopentane dicarboxylate) [P(BT-co-BCP)] were synthesized by melt condensation. The sequence analysis of the copolyesters was done by ^{1}H and ^{13}CNMR spectroscopy. The thermal properties were studied by DSC and TGA. The crystallization behavior and kinetics were studied by WAXS and DSC. The morphology of the copolyesters was studied using polarized optical microscopy.

4.2 Experimental

4.2.1 Materials

Norbornene, tetrabutyl ammonium bromide, lithium aluminum hydride (LAH), dimethyl terephthalate (DMT), 1,4-butanediol (BD) and titanium (IV) isopropoxide were obtained from Sigma-Aldrich, Inc., USA. Potassium permanganate, hydrochloric acid, sulphuric acid, sodium hydroxide, ethylene chloride, benzene, methanol, diethyl ether, hexane, chloroform, phenol, 1,1,2,2-tetrachloroethane were obtained from s.d fine-Chem. Ltd., Mumbai. Sodium metabisulfite, tetrahydrofuran, toluene were obtained from Merck, Mumbai.

4.2.2 Reagents and purification

THF was refluxed over sodium and distilled prior to use. Toluene was stored over calcium chloride, distilled, and further dried over sodium and freshly distilled prior to use. DMT was recrystallized from methanol. BD was distilled and stored over molecular sieves. Titanium (IV) isopropoxide was distilled under vacuum and used as a solution in dry toluene. Phenol and 1,1,2,2-tetrachloroethane were freshly distilled before use.

4.2.3 Synthesis of monomers

4.2.3.1 Synthesis of *Cis*-1,3-cyclopentane dicarboxylic acid (CPDA) (2)

Potassium permanganate (23.8 g, 0.15 mol) was dissolved in 250 ml water in a 1L two neck round bottom flask equipped with addition funnel and magnetic stirring bar. After the complete dissolution of $KMnO_4$, the flask was cooled to ~3-5°C. Tetra butyl ammonium bromide (2.46 g) and 100 mL benzene were added under vigorous stirring. Bicyclo [2.2.1] heptene **(1)** (4.8 g, 0.05 mol) in 150 mL of benzene was added with vigorous stirring over 1 h. The reaction mixture was allowed to warm up to room temperature and was stirred for 3 h. The MnO_2 was filtered off and the filtrate washed with water several times. The filtrate was decolorized with sodium metabisulfite and acidified to pH 4. The benzene and water layer were separated; the water layer was saturated by the addition of excess sodium chloride and concentrated at rotary evaporator. The residue was extracted with diethyl ether. The ether extract was dried on anhydrous sodium sulphate and evaporated to give 7.13 g (88 %) of *cis*-1,3-cyclopentane dicarboxylic acid (CPDA) **(2)**. The acid was recrystallized from ether/hexane (50/50). m. p. 120°C (lit.[1] 119-120°C)

Elemental (found) - C - 52.9 (53.0), H - 6.2 (6.3)

Mass (m/z) – 158 (M^+), 125, 112, 97, 86, 73, 67(100), 55

IR (neat) – 3350 (O-H), 1699 (C=O), 1471 (C-H), 1293 (C-O)

^{1}H NMR (200 MHz, DMSO-d_6) δ: 1.5-2.25 (6H, m, ring protons), 2.6-2.8 (2H, m, CH) 12.1 (2H, OH)

^{13}C NMR (300 MHz, DMSO-d_6) δ: 29.44 (CH_2), 33.3 (CH_2), 43.74 (CH), 176.99 (carbonyl)

4.2.3.2 Isomerization of *Cis*-1,3-cyclopentane dicarboxylic acid (3)

A solution of *cis*-1,3-cyclopentane dicarboxylic acid **(2)** (6.1 g, 0.038 mol) in 122 ml of 20.2% hydrochloric acid was refluxed for 120 h at 110°C. The water was removed using rotary evaporator at room temperature and the residue was dissolved in ether and filtered. The ether extract was dried over anhydrous sodium sulphate. Evaporation of the ether extract gave 6 g of mixture of cis/trans 1,3-cyclopentane dicarboxylic acid **(2+3)**. The GC analysis and ^{13}C NMR spectra show the cis/trans ratio to be 1:1.

^{13}C NMR (300 MHz, DMSO-d_6) δ: 29.41(cis CH_2), 29.78 (trans CH_2), 32.9(cis CH_2), 33.27 (trans CH_2), 43.34 (*cis* CH), 43.71 (*trans* CH),176.92 (*cis* carbonyl), 177.14 (*trans* carbonyl)

4.2.3.3 Synthesis of dimethyl-1,3-cyclopentane dicarboxylate (CPDE) (4,5)

1,3-cyclopentane dicarboxylic acid (8.0 g, 0.05 mol), 40 mL of ethylene chloride, 25 mL of methanol and 1.5 mL of H_2SO_4 were taken in a round bottom flask and refluxed for 12 h. The mixture was cooled, washed successively with water, saturated sodium bicarbonate and water. The organic layer was dried over anhydrous sodium sulphate and evaporated to give 8.5 g (91%) of the cis **(4)** or cis/trans dimethyl-1,3-cyclopentane dicarboxylate **(4+5)**. The diester was purified by distillation. b. p. 55-60°C/0.02 mbar (lit.[4] b.p. cis 140°C/25mm, trans 130°C/25 mm).

GC - retention time – 4.92 min (cis) 4.84, 4.94 min (*cis/trans* 50/50)

IR (neat) - 1744 (C=O), 1459 (C-H), 1302 (C-O), 918(C-H)

^{1}H NMR ($CDCl_3$) δ: 1.8-2.2 (6H, m, ring protons), 2.15 (2H, m, CH), 3.65 (6H, s, OCH_3)

^{13}C NMR ($CDCl_3$) δ: 28.63 (CH_2), 32.84 (CH2), 43.25 (CH), 51.03 (OCH_3), 174.94 (*cis* carbonyl); 28.85, 29.51 (CH_2), 32.67, 33.07 (CH_2), 42.96, 43.48 (CH), 51.34 (OCH_3), 175.25 (*cis* carbonyl), 175. 84 *(trans* carbonyl)

4.2.3.4 Synthesis of *Cis*-1,3-bishydroxy methyl cyclopentane (CPDM) (6)

A three-neck 500 mL round bottom flask equipped with magnetic stirring bar, addition funnel, reflux condenser and a three-way vacuum adapter was flame dried, charged with lithium aluminum hydride (6.4 g) and dry THF (180 mL). Cyclopentane dicarboxylic acid (10.6 g, 0.067 mol) was dissolved in dry THF (180 mL) and added over a period of 1 h. The reaction mixture was refluxed for 24 h, cooled to room temperature and treated successively with 6.4 mL H_2O, 6.4 mL of 15% NaOH and 19.2 mL of H_2O. The precipitate was filtered and the solvent was evaporated. The crude yield of 1,3-cyclopentane dimethanol **(6)** obtained was 7.8 g (90%), which was further purified by vacuum distillation. b. p. 92°C/0.02 mbar(b.p[2]. 118°C/0.5 mm).

GC - retention time - 7.8 min

Mass (m/z) - 94, 81, 79, 67 (100) 57

IR (neat)- 3331(OH), 2945, 2866(CH_2)

^{1}H NMR (DMSO-d_6) δ: 0.5-2.35 (8H, m, ring protons), 3.26 (4H, t, CH_2O), 4.39 (2H, t, OH)

^{13}C NMR (DMSO-d_6) δ: 28.41 (CH_2), 33.02 (CH_2), 42.39 (CH), 65.76 ($\underline{C}H_2OH$)

4.2.4 Synthesis of polyester and copolyesters containing *cis*-1,3-bis(hydroxymethyl) cyclopentane (CPDM) (6)

4.2.4.1 Synthesis of poly (1,3-cyclopentane dimethylene terephthalate) (PCPDT) (7)

DMT (2.5 g, 0.013 mol), 1,3-bishydroxy methyl cyclopentane (CPDM) **(6)** (1.84 g, 0.014 mol) and titanium isopropoxide (0.1 wt % w.r.t DMT) were taken in a two neck round bottom flask equipped with a magnetic stirring bar, N_2 inlet, air condenser and spiral trap to collect distillate. The flask was heated to 160°C under a stream of N_2 when methanol distilled out. Reaction was continued at 160-200°C for 3 h and further at 210°C for 4 h and the pressure was gradually reduced over 30 min to 0.02 mbar and isothermally held for 11 h at 230°C. The reaction flask was cooled under vacuum. Yield = 3.2 g (95 %).

η_{inh} (60/40 phenol/TCE w/w) = 0.8 dL/g

GPC ($CHCl_3$) - M_n = 43,500, M_w = 69,100 (M_w/M_n = 1.6).

^{1}H NMR ($CDCl_3/CF_3COOD$) δ:1-1.8 (3H, m, ring protons), 1.9 (2H, m, ring protons), 2.14 (1H, m, ring proton), 2.46 (2H, m, CH), 4.26, 4.3 (4H, d, CH_2O), 8.07 (4H, s, aromatic protons).

^{13}C NMR ($CDCl_3/CF_3COOD$) δ: 28.4 (CH_2), 33.38 (CH_2), 38.76 (CH), 68.86 (OCH_2), 129.41 (aromatic), 133.98 (quaternary aromatic), 165.66 (carbonyl)

4.2.4.2 Synthesis of poly (butylene terephthalate-co-cyclopentane dimethylene terephthalate) (P(BT-co-CPDT)) (8)

DMT, 1,4-BD, 1,3-bishydroxymethyl cyclopentane and titanium isopropoxide (0.1 wt% w.r.t DMT) were taken in a two neck round bottom flask equipped with magnetic stirring bar, N_2 inlet, short path vacuum distillation adaptor, spiral trap and a vacuum control assembly. A 1:1.15 ratio of DMT to diol was used in all polymerizations and BD/CPDM ratio was varied (90/10, 80/20, 50/50 and 20/80). The reaction was carried out at 160-220°C for 6-8 h. The pressure was gradually reduced to 0.02 mbar over 20 min and reaction continued at 230-250°C for 10-12 h. The flask was cooled under vacuum.

4.2.5 Synthesis of polyesters and copolyesters containing dimethyl-1,3-cyclopentane dicarboxylate (CPDE)

4.2.5.1 Synthesis of poly (butylene-1,3-cyclopentane dicarboxylate) (PBCP) (9,10)

4.2.5.1.1 From *cis*-CPDE (4)

Cis-dimethyl-1,3-cyclopentane dicarboxylate **(4)**(2.63 g, 0.014 mol), BD (1.91 g. 0.02 mol) and titanium isopropoxide (0.1 wt % w.r.t DMT) were taken in a two neck round bottom flask fitted with N_2 gas inlet, air condenser and spiral trap. The reaction mixture was heated at 160-180°C for 2 h when methanol distilled out. The reaction was continued at 210-230°C for 8 h. The pressure was gradually reduced to 0.02 mbar and reaction continued at 230°C for 10 h. The flask was cooled under vacuum. A rubbery polymer was obtained. Yield = 1.91 g (97 %).

η_{inh} = 0.66 dL/g ($CHCl_3$)

GPC ($CHCl_3$) - M_n = 57,100 M_w = 1,51,000 (M_w/M_n - 2.6)

^{1}H NMR ($CDCl_3$) δ: 1.68 (4H, s, CH_2), 1.93 (4H, m, ring CH_2) 2-2.3 (2H, m, ring CH_2) 2.79 (2H, m, *cis* CH) 4.08 (4H, s, OCH_2),

^{13}C NMR ($CDCl_3$) δ: 25.24 (CH_2), 28.99 (CH_2), 33.2 (CH_2), 43.79 (CH), 63.85 (OCH_2), 174.97 (carbonyl)

4.2.5.1.2 From *cis/trans*-CPDE (4,5)

Dimethyl-1,3-cyclopentane dicarboxylate (cis/trans 50/50) **(4,5)** (2.01g, 0.011 mol), BD (1.46 g, 0.016 mol) and titanium isopropoxide (0.1 wt % w.r.t. CPDE) were taken in a two neck round bottom flask fitted with N_2 gas inlet, air condenser and spiral trap. The reaction mixture was heated at 180-210°C for 10 h and subsequently at 230-250°C for 10 h. The flask was cooled under vacuum. A rubbery polymer was obtained. Yield = 2.15 g (96 %).

η_{inh} ($CHCl_3$) = 0.8 dL/g.

GPC ($CHCl_3$) - M_n = 36,200 M_w = 1,70,600 (M_w/M_n - 4.7)

^{1}H NMR ($CDCl_3$) δ: 1.72 (4H, s, CH_2) 1.72-2.35 (6H, m, CH_2) 2.86, 2.97 (2H, m, CH) 4.14 (4H, s, OCH_2)

^{13}C NMR ($CDCl_3$) δ: 25.06, 29.1, 29.84, 32.71, 33.11 (CH_2), 43.59 (*cis* CH), 44.03 (*trans* CH), 64.91 (OCH_2), 177.2 (*cis* carbonyl), 177.57 (*trans* carbonyl)

4.2.5.2 Synthesis of poly(butylene terephthalate-co-1,3-cyclopentane dicarboyxlate) (P(BT-co-PBCP)) (11)

DMT, CPDE, BD and titanium isopropoxide (0.1 wt% w.r.t diester) were taken in a two neck round bottom flask equipped with N_2 inlet, short path vacuum distillation adaptor and a spiral trap. A 1:1.5 ratio of diester to diol was used in all polymerization reactions and the DMT/CPDE ratio was varied (90/10, 80/20, 70/30 and 50/50). The reaction mixture was heated at 160-220°C for 6-8 h under a stream of N_2 gas. The pressure was gradually reduced over 1h to 0.02 mbar, as the excess butanediol distilled out and reaction continued at 230-250°C for 10-12 h. The flask was cooled under vacuum. The viscosity and thermal properties of the copolyesters are given in the results and discussion section.

4.3 Analysis

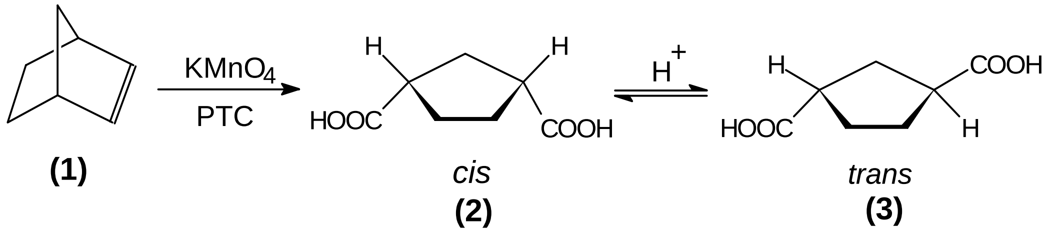
4.3.1 Monomer Characterization

^{1}H and ^{13}C NMR were recorded in $CDCl_3$ or DMSO-d_6 on a Bruker AC-200 NMR spectrometer. The IR spectrums were recorded as neat or in chloroform on FTIR 16 PC Perkin Elmer spectrophotometer. Elemental analysis was done on CHNS-O, EA1108-Elemental Anlyser, Carlo-Erba Instruments, Italy. Gas chromatography was done using a BP1 Column. The temperature program used for CPDE was: Oven - 150°C (5 min) to 200°C at 10°C/min, injector - 260°C and detector 270°C and temperature program for CPDM: Oven 80°C (1 min) to 200°C at 10°C/min injector- 250°C detector- 260°C.
Polymer characterization is discussed in Chapter 3.

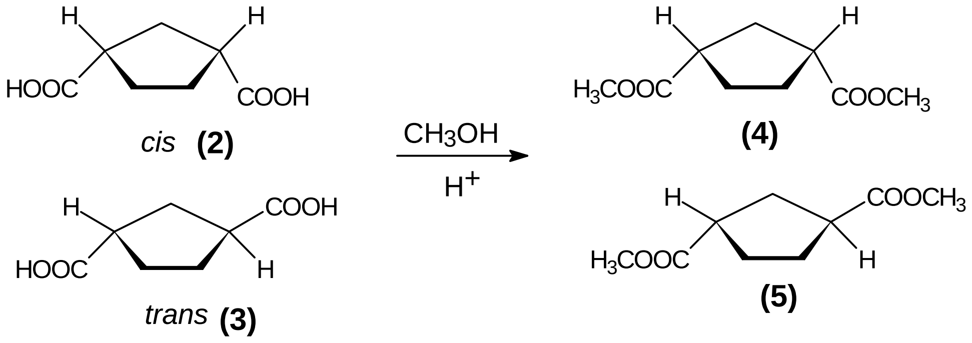
4.4 Results and Discussion

4.4.1 Synthesis of monomers

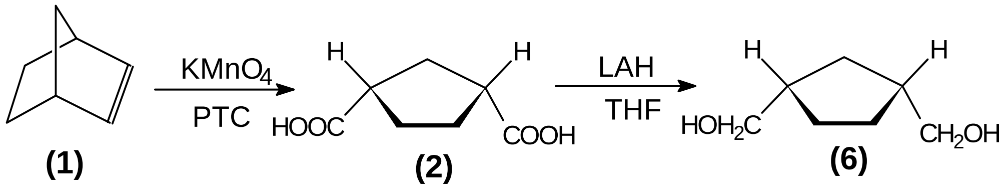
Cis-1,3-cyclopentane dicarboxylic acid (CPDA) **(2)** was synthesized from bicyclo [2.2.1]heptene **(1)** by use of aqueous potassium permanganate, which leads to the pure *cis* epimer[2]. The ^{1}H and ^{13}C NMR spectrum *cis*-CPDA is shown in **Figures 4.1 and 4.5.** The *Cis*-CPDA **(2)** was isomerized to (±) *trans*-CPDA **(2+3)** by refluxing in HCl (*cis*-CPDA is known to isomerize to the *trans* acid under acidic conditions[3]) and the reaction scheme is illustrated in **Scheme 4.1.** The diasteriomeric CPDA was equilibrated in boiling 20% aqueous HCl to a 1:1 *cis*-*trans* mixture. However, pure *trans* acid could be obtained by separation of the resultant mixture of acids by treatment with acetyl chloride, followed by extraction with ether and resolution of trans-form with the aid of brucine. The *cis* acid formed the anhydride and could be separated from *trans*-acid[4,5]. The 13C NMR of *cis* and *cis/trans*-CPDA is shown in **Figure 4.5**.



Scheme 4.1 Synthesis and isomerization of 1,3-cyclopentane dicarboxylic acid



Scheme 4.2 Synthesis of dimethyl-1,3-cyclopentane dicarboxylate



Scheme 4.3 Synthesis of *cis*-1,3-bis(hydroxymethyl) cyclopentane

The dimethyl ester of the *cis*-CPDA **(2)** or *cis/trans*-CPDA **(2+3)** was obtained by esterification in methanol[6] **(Scheme 4.2)**. The 1H and 13C NMR spectrum of cis-CPDE is shown in **Figures 4.2** and **4.5** The diol, 1,3-bis(hydroxy methyl) cyclopentane (CPDM) **(6)** was synthesized by LAH reduction[7] of the *cis*-CPDA **(2)** (**Scheme 4.3**) and a 90% yield was obtained. The ^{1}H and ^{13}C NMR spectrum of CPDM is shown in **Figures 4.3** and **4.4**.

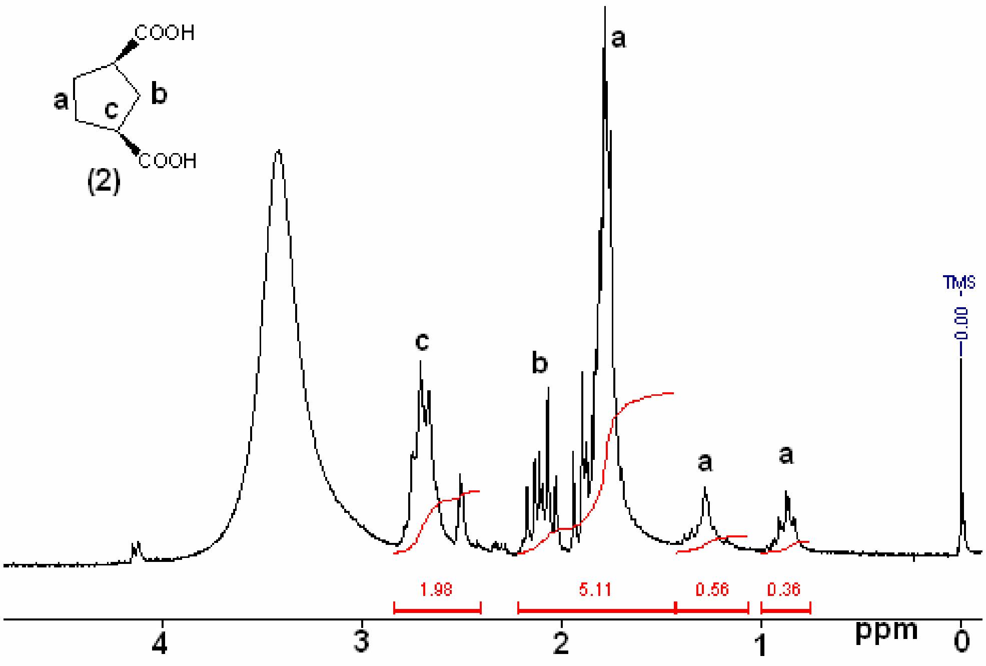


Figure 4.1 ^{1}H NMR of 1,3-cyclopentane dicarboxylic acid

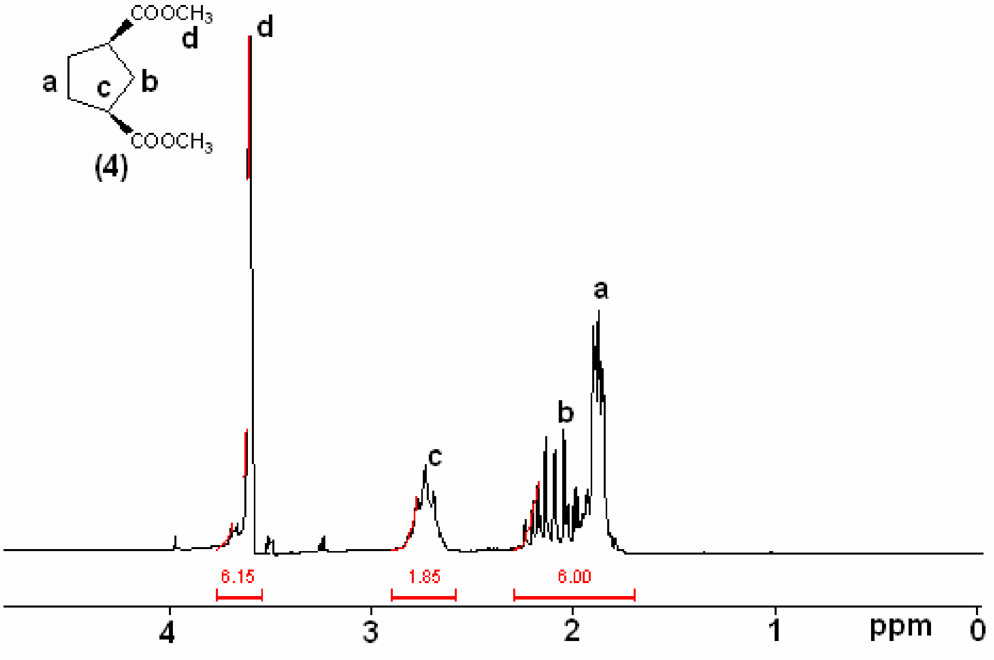


Figure 4.2 ^{1}H NMR of dimethyl-1,3-cyclopentane dicarboxylate

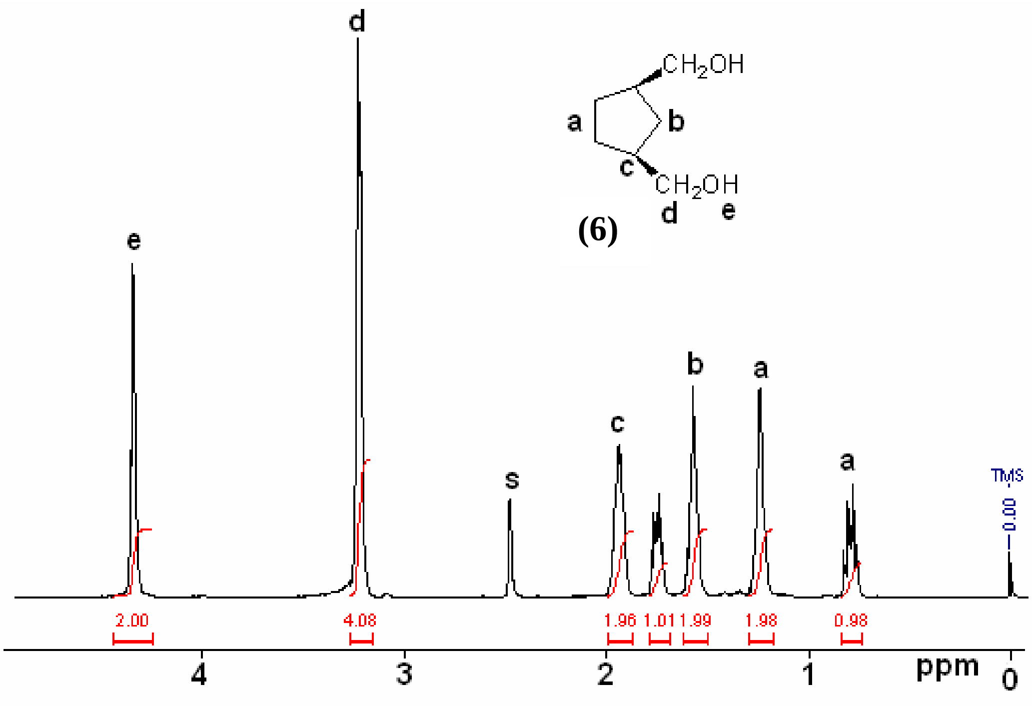


Figure 4.3 ^{1}H NMR of 1,3-bis(hydroxymethyl) cyclopentane

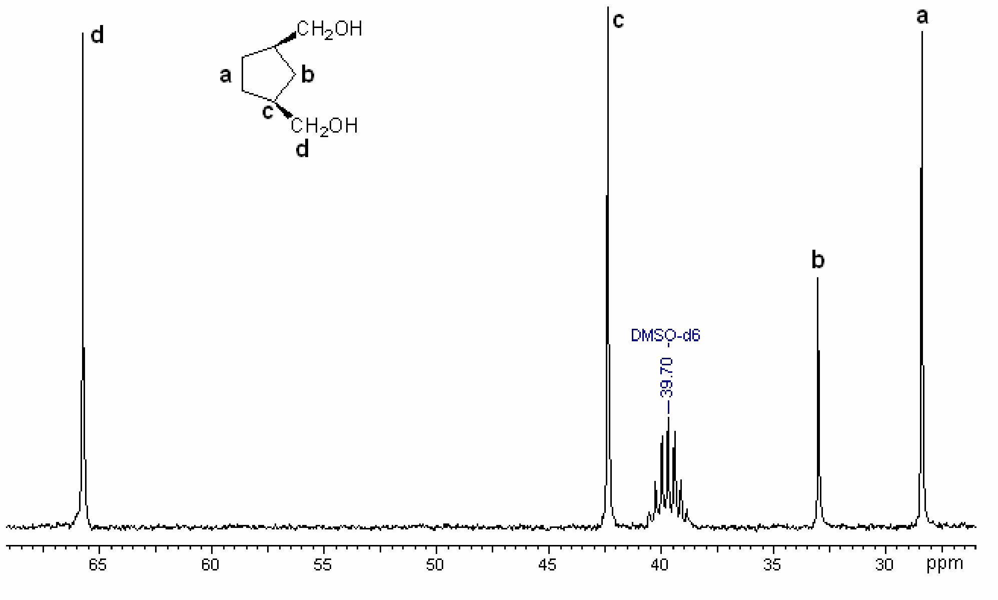


Figure 4.4 ^{13}C NMR of 1,3-bis(hydroxymethyl) cyclopentane (CPDM)

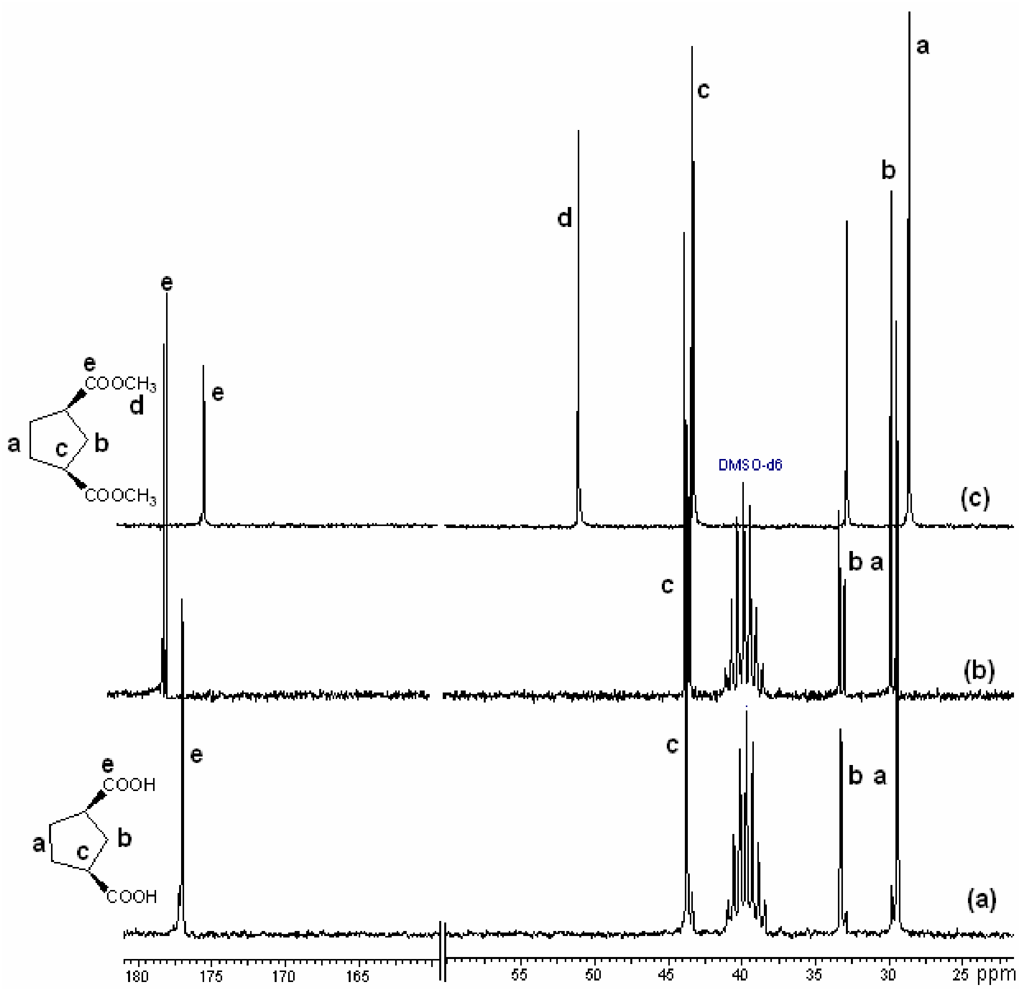


Figure 4.5 ^{13}C NMR of (a) cis-CPDA **(2)**, (b) *cis/trans*-CPDA **(2,3)** and (c) *cis*-CPDE **(4)**

CPDE **(4,5)**and CPDM **(6)** were purified by vacuum distillation and the purity was confirmed by GC and NMR. GC showed a single peak at 4.92 min for cis-CPDE and two peaks at 4.84 and 4.94 min for trans and cis CPDE and for CPDM at 7.8 min (**Figure 4.6**).

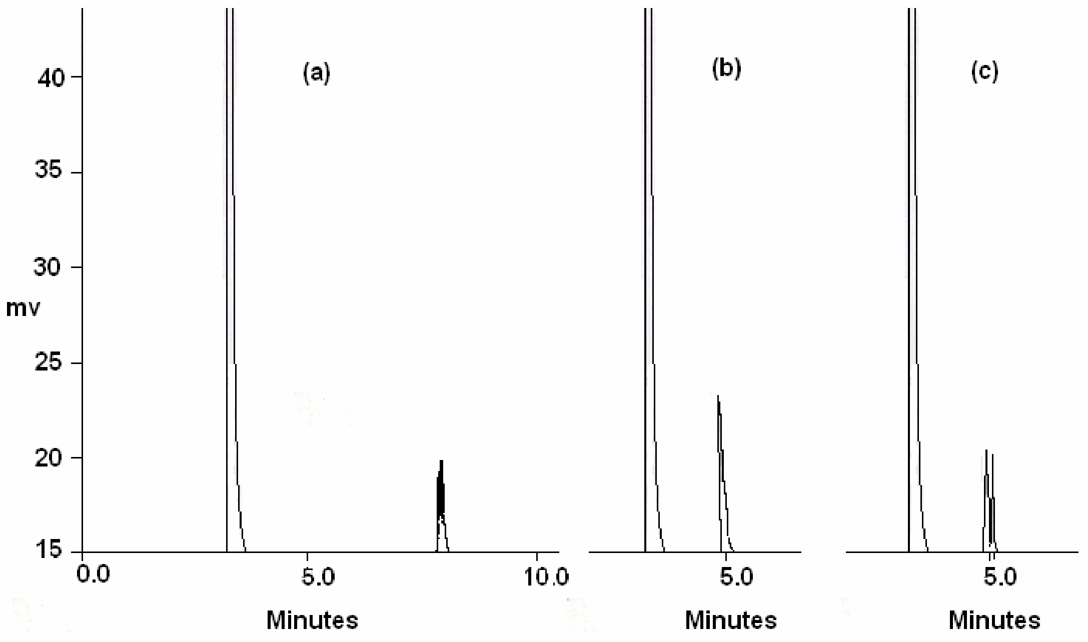
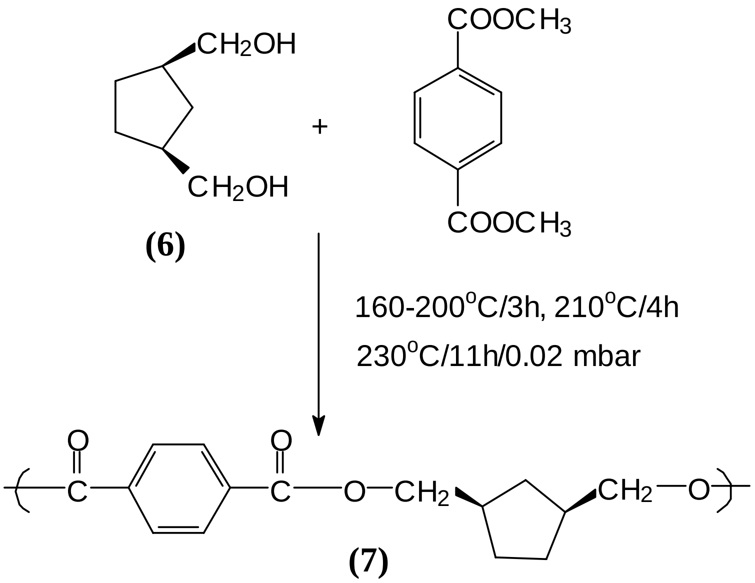


Figure 4.6 Gas chromatogram of (a) CPDM (b) CPDE and (c) cis/trans CPDE

4.4.2 Synthesis and properties of polyester and copolyesters containing cis-1,3-bis(hydroxymethyl cyclopentane) (CPDM)

4.4.2.1 Synthesis and structure of poly(cyclopentylene dimethylene terephthalate) (PCPDT)

A new polyester, poly (cyclopentylene dimethylene terepthalate) (PCPDT) **(7)** was synthesized by melt condensation of 1,3-bis hydroxymethyl cyclopentane and dimethyl terephthalate in presence of titanum isopropoxide catalyst as depicted in **Scheme 4.4** The transesterification reaction was carried out at 160-210°C and polycondensation at 230-250°C. The inherent viscosity of the polyester was found to be 0.8 dL/g (in phenol/TCE 60/40 w/w) and the M_n and M_w were found to be 43,500 and 69,100 respectively with a polydispersity of 1.6 (**Figure 4.9**).



Scheme 4.4 Synthesis of poly(cyclopentylene dimethylene terephthalate) (PCPDT)

The structure of the polyester was confirmed by ^{1}H and ^{13}C NMR. The ^{1}H NMR spectrum of PCPDT along with the NMR assignments is shown in **Figure 4.7**. The peak at 8.07 is due to the terephthalate proton resonance, H_e, the doublet peak at 4.26, 4.3 is due to the OCH_2 protons, H_d. The H_c protons appear at 2.46 ppm and the rest H_b and H_a

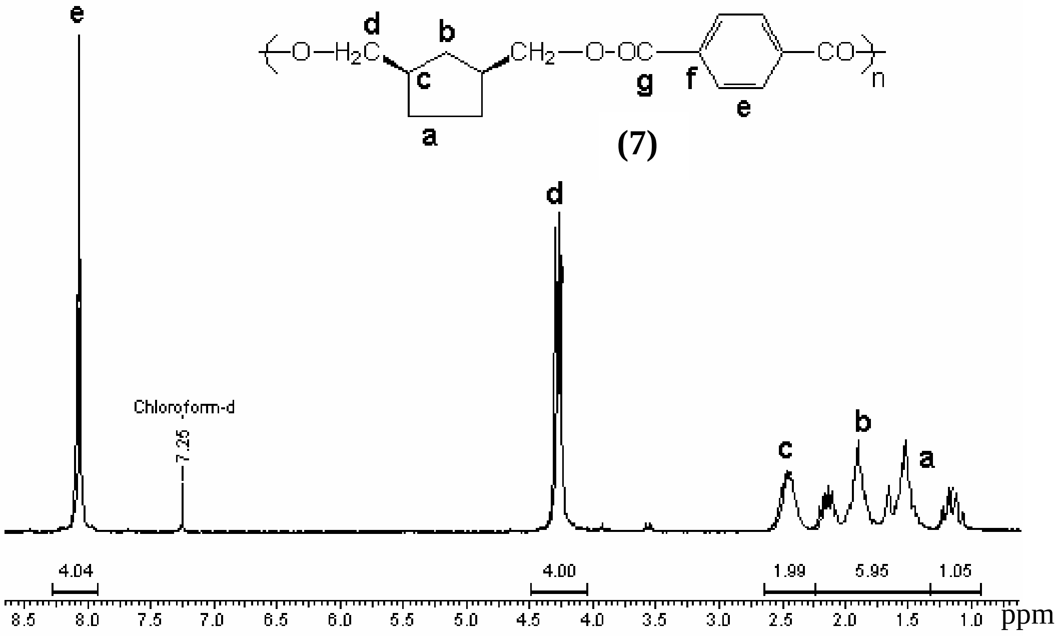


Figure 4.7 ^{1}H NMR spectrum of poly(cyclopentylene dimethylene terephthalate) (PCPDT)

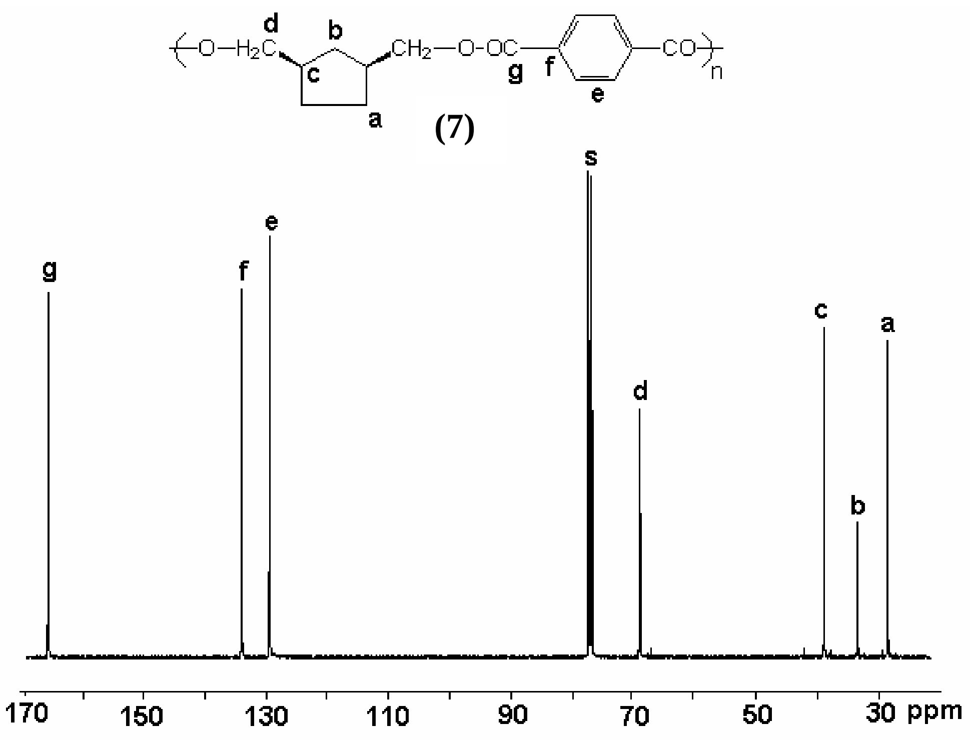
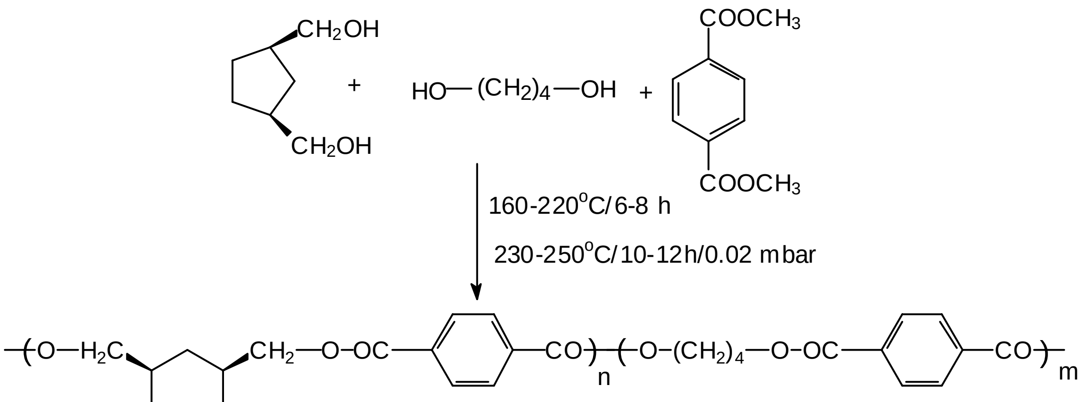

(7)

Figure 4.8 ^{13}C NMR spectrum of poly (cyclopentylene dimethylene terephthalate) (PCPDT)

appears at 1-2.14 ppm. The ^{13}C NMR is shown in **Figure 4.8.** The C_d carbon appears at 68.8 ppm, the quaternary carbon, $C_{f,}$ appears at 133.98, the four C_e carbons appear at 129.4 ppm and the carbonyl carbon, and C_g appears at 165.6 ppm.

4.4.2.2 Synthesis of poly (butylene terephthalate-co-cyclopentylene dimethylene terephthalate) (P(BT-co-CPDT)) copolyesters

Copolyesters of dimethyl terephthalate and 1,4-butanediol containing CPDM **(6)** were synthesized by melt condensation using titanium isopropoxide catalyst. The reaction scheme is depicted in **Scheme 4.5**. A series of copolyesters were synthesized by changing the molar ratio of BD/CPDM (90/10, 80/20, 50/50 and 20/80). The copolyesters containing more than 50 % CPDM, $PBT_{45}CPDT_{55}$ and $PBT_{15}CPDT_{85}$ were found to be soluble in chloroform, while the other two compositions were insoluble. The inherent viscosities were in the range of 0.5-1.03 dL/g. The M_n and M_w of $PBT_{45}CPDT_{55}$ were found to be 88,940 and 1,85,500 with a polydispersity of 2.08 (**Figure 4.9**).



(8)

Scheme 4.5 Synthesis of poly(butylene terephthalate-co-cyclopentylene dimethylene terephthalate) (P(BT-co-CPDT))

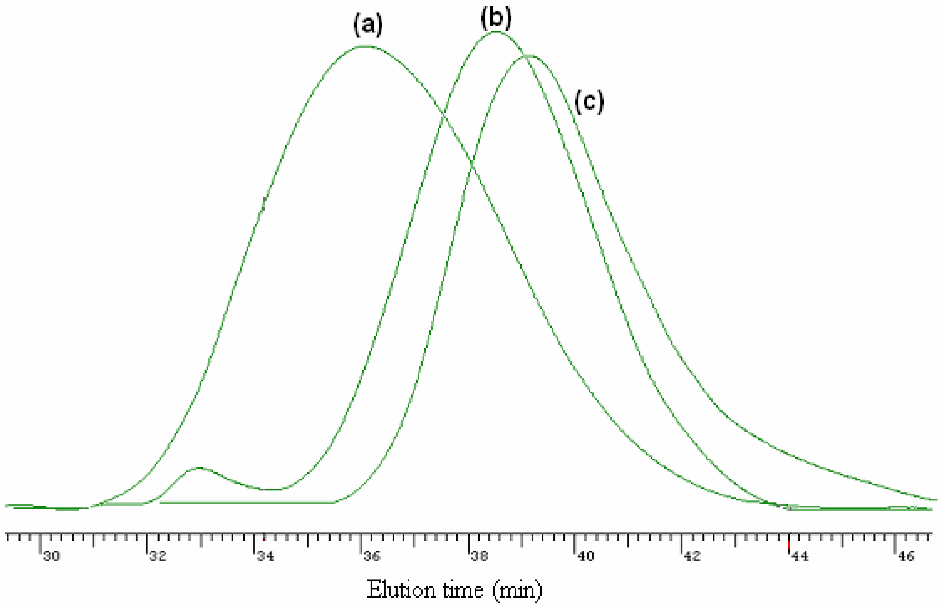
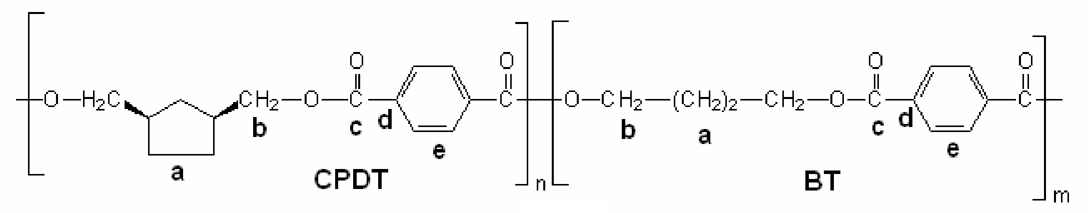


Figure 4.9 GPC curves of (a) $PBT_{45}CPDT_{55}$ (b) PCPDT (c) $PBT_{15}CPDT_{85}$

4.4.2.3 Composition and Microstructure of P (BT-co-CPDT) copolyesters

A typical ^1H NMR specta of poly(BT-co-CPDT) **(8)** copolyester with indication of the notation used in NMR assignments is shown in **Figure 4.10**, where CPDT is cyclopentylene dimethylene terephthalate unit and BT is butylene terephthalate unit. Signal assignment was accomplished by comparison of spectra obtained for different copolymer compositions. Chemical shifts of all peaks appearing in such spectra, together with their respective assignments are given in **Table 4.1**.



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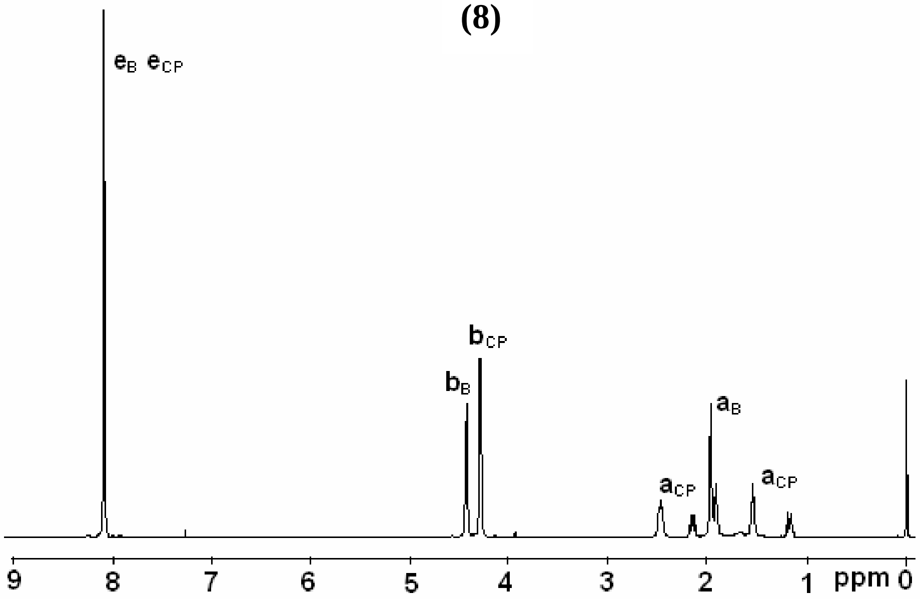


Figure 4.10 A typical ^{1}H NMR spectrum of poly(BT-co-CPDT) copolyester with its peak assignment.

Table 4.1 ^{1}H and ^{13}C NMR Chemical Shifts (δ in ppm) of PBT, PCPDT and poly(BT-co-CPDT) copolyesters

^{1}H Chemical shifts

	^BH_a	^BH_b	^BH_e	$^{CP}H_a$	$^{CP}H_b$	$^{CP}H_e$
PBT	2.02	4.5	8.12			
PCPDT				1.0-1.9, 2.1, 2.5	4.30, 4.26	8.07
$PBT_{45}CPDT_{55}$	1.96	4.4	8.07	1.0-1.8, 2.0-2.6	4.30, 4.26	8.07

^{13}C Chemical Shifts

	^BC_b	^BC_c	^BC_d	^BC_e	$^{CP}C_b$	$^{CP}C_c$	$^{CP}C_d$	$^{CP}C_e$
PBT	65.9	167.6	133.7	129.8				
PCPDT					68.86	165.66	133.98	129.41
$PBT_{45}CPDT_{55}$	66.0	167.8	133.9	129.89	70.2	167.7	133.78	129.89

The composition of the copolyesters could be determined from the areas of the glycolic proton resonances in the ^{1}H NMR spectra, and results are tabulated in **Table 4.2**. The signal at 4.4 ppm appearing as a singlet in the ^{1}H NMR spectra of the copolyester $PBT_{46}CPDT_{54}$ is due to PBT and the doublet at 4.3, 4.26 ppm is assigned to PCPDT.

The microstructure of the copolyesters was analyzed using ^{13}C NMR spectroscopy. The quaternary aromatic carbon resonances appeared to be sensitive to dyad sequence effects. The ^{13}C NMR spectra of the copolyester $PBT_{45}CPDT_{55}$ is shown in **Figure 4.11** and the peak assignments are given in **Table 4.1**.

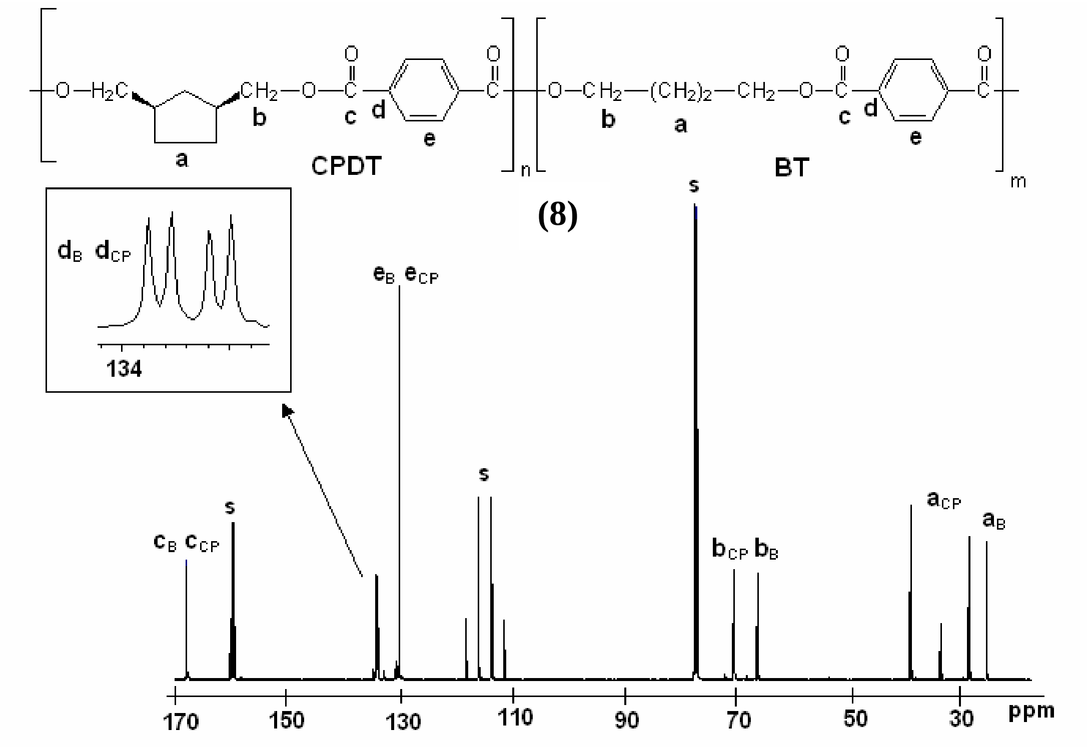

(8)

Figure 4.11 ^{13}C NMR spectrum of $PBT_{45}CPDT_{55}$

The quaternary carbon of the terephthalate (labeled as d) is split into four, BB (133.81), CPCP (133.94), CPB (133.98) and BCP (133.81) and is shown in **Figure 4.12.** The four different dyads possible in the copolymer repeat units are depicted in **Figure 4.13**. Molar fractions of butylene terephthalate (P_B) and cyclopentylene dimethylene terephthalate (P_{CP}) units were obtained from the relative intensities of the four kinds of signals in the NMR spectrum using equation **(4.1).**

$$P_B = \frac{f_{BCP} + f_{CPB}}{2} + f_{BB} \qquad P_{CP} = \frac{f_{BCP} + f_{CPB}}{2} + f_{CPCP} \qquad (4.1)$$

where, f_{BB}, f_{CPCP}, f_{BCP} and f_{CPB} correspond to the proportion of the integrated intensities of BB, CPCP, BCP and CPB to the total intensity of the butylene moieties respectively.

If one could inspect the units along the copolymer chain from one end to the other, the probability (P_{TCD} or P_{CDT}) of finding T (or CD) unit next to a CD (or T) unit would be

$$P_{BCP} = \frac{f_{BCP} + f_{CPB}}{2P_B} \qquad P_{CPB} = \frac{f_{BCP} + f_{CPB}}{2P_{CP}} \qquad (4.2)$$

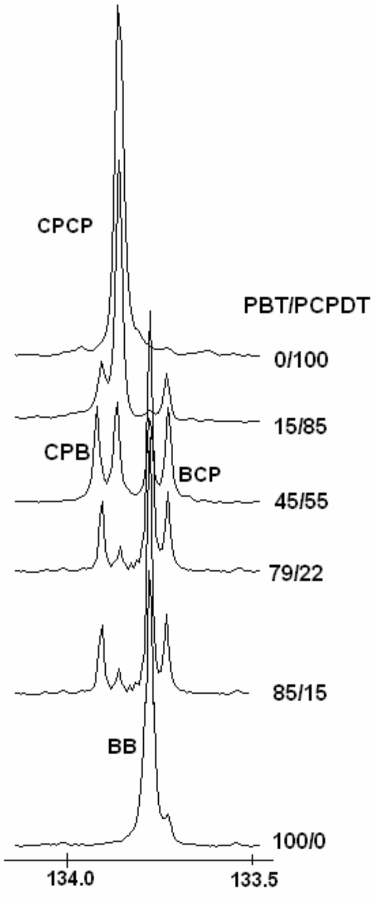


Figure 4.12 Expanded ^{13}C NMR of PBT, PCPDT and poly(BT-co-CPDT) copolyesters in the range of 133.5-134.5 ppm

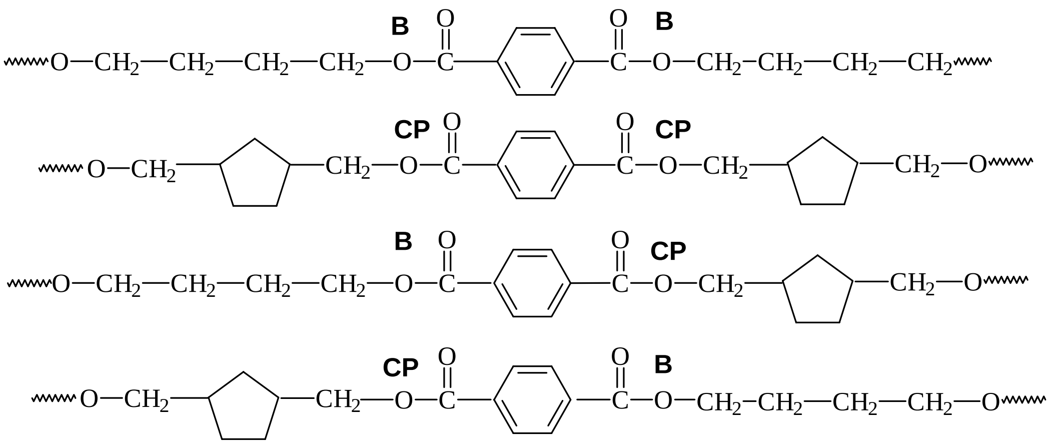


Figure 4.13 Possible dyad sequences for the quaternary carbon in the poly(BT-co-CPDT) copolyester

The number average sequence length of a butylene terephthalate (BT) unit and cyclopentylene dimethylene(CPDT) unit are given by

$$L_{nB} = \frac{2P_B}{f_{BCP} + f_{CPB}} \qquad L_{nCP} = \frac{2P_{CP}}{f_{BCP} + f_{CPB}} \qquad \textbf{(4.3)}$$

The degree of randomness (B) is defined by equation **(4.4)**

$$B = P_{BCP} + P_{CPB} \quad (4.4)$$

Table 4.2 summarizes the number average sequence and the degree of randomness of the copoyesters. The degree of randomness value close to unity shows that the copolyesters are all completely random in nature[8,9].

Table 4.2 Composition, Average sequence lengths and Randomness of poly(BT-co-CPDT) copolyesters

	Feed composition (mol %)		Copolymer composition[b] (mol %)		Average sequence length		Degree of randomness
Copolyester[a]	X_B	X_{CP}	X_B	X_{CP}	L_{nB}	L_{nC}	B
PBT	100	0	100	0	-	-	-
$PBT_{85}CPDT_{15}$	87	12	85	15	5.7	1.2	0.96
$PBT_{78}CPDT_{22}$	80	20	78	22	4.1	1.3	0.99
$PBT_{45}CPDT_{55}$	50	50	46	54	1.9	2.2	0.97
$PBT_{15}CPDT_{85}$	20	80	20	80	1.2	5.9	0.98
PCPDT	0	100	0	100	-	-	-

[a] calculated from 1H NMR, [b] calculated from ^{13}C NMR

4.4.2.4 Thermal properties

Thermal properties of PCPDT and the copolyesters were evaluated by DSC and TGA. PCPDT was found to be semi-crystalline polyester having a melting temperature of 207°C. Its glass transition temperature was 60°C and it crystallized at 140°C on cooling from the melt. The glass transition temperature (T_g), melting temperature (T_m) and heat of melting (ΔH_f) and crystallization temperature (T_c) from the first cooling cycles, are compiled in **Table 4.3.**

The glass transition temperature of the copolyesters increased with increasing CPDM mole fraction; from 40°C for pure PBT to 52°C for $PBT_{15}CPDT_{85}$. The copolyesters crystallized readily on cooling from the melt, but the copolyester at intermediate composition, $PBT_{45}CPDT_{55,}$ did not crystallize from the melt on cooling. However, on annealing above the Tg, the sample showed a very weak double melting peak.

The melting endotherms on heating and crystallization exotherms on cooling are shown in **Figures 4.14**.

Table 4.3 Thermal properties of poly(BT-co-CPDT) copolyesters

Polyester sample	η_{inh}[a] (dL/g)	T_g (°C)	T_m (°C)	ΔH (J/g)	T_c (°C)	ΔH (J/g)	IDT[d]
PBT	0.90	40	226	41	193	49	374
$PBT_{85}CPDT_{15}$	0.85	44	199	37	174	43	392
$PBT_{78}CPDT_{22}$	0.91	46	189	26	135	30	389
$PBT_{45}CPDT_{55}$	1.03	48	133[b]	12	[c]	[c]	392
$PBT_{15}CPDT_{85}$	0.50	52	186	33	105	27	395
PCPDT	0.80	60	207	45	140	51	385

[a] Measured in 60/40 phenol/TCE (w/w) at 30°C; [b]The copolyester sample was annealed at 100°C for 2 h. [c]copolyester did not crystallize on cooling; [d]Measured by TGA

Melting, crystallization and glass transition temperatures for poly(BT-co-CPDT) copolyesters are plotted in **Figure 4.15** as a function of CPDT mole fraction. The copolyesters showed melting endotherm on heating and crystallization exotherm on cooling over the entire composition range. The presence of clear melting and crystallization peak indicated cocrystallization behavior of the copolyesters over the entire range of composition. The melting and crystallization temperatures of the copolyesters showed eutectic behavior and the eutectic composition was $PBT_{45}CPDT_{55}$. The typical eutectic behavior indicated that the cocrystallizaion was isodimorphic in nature and monomer units of one type were included in the crystal lattice of the other type.

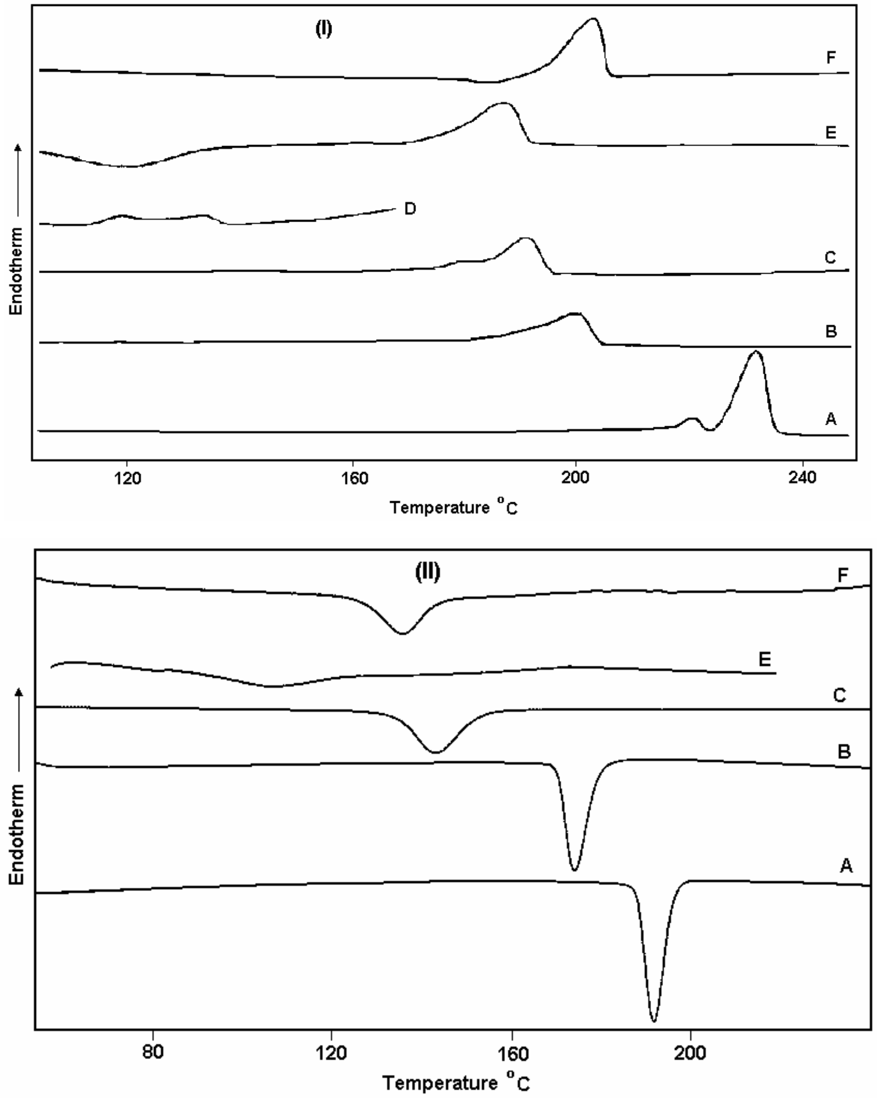


Figure 4.14 DSC scans of (I) second heat (II) cooling A) PBT, B) $PBT_{85}CPDT_{15}$, C) $PBT_{78}CPDT_{22}$, D) $PBT_{45}CPDT_{55}$, E) $PBT_{15}CPDT_{85}$, F) PCPDT at heating / cooling rate of 10°C / min

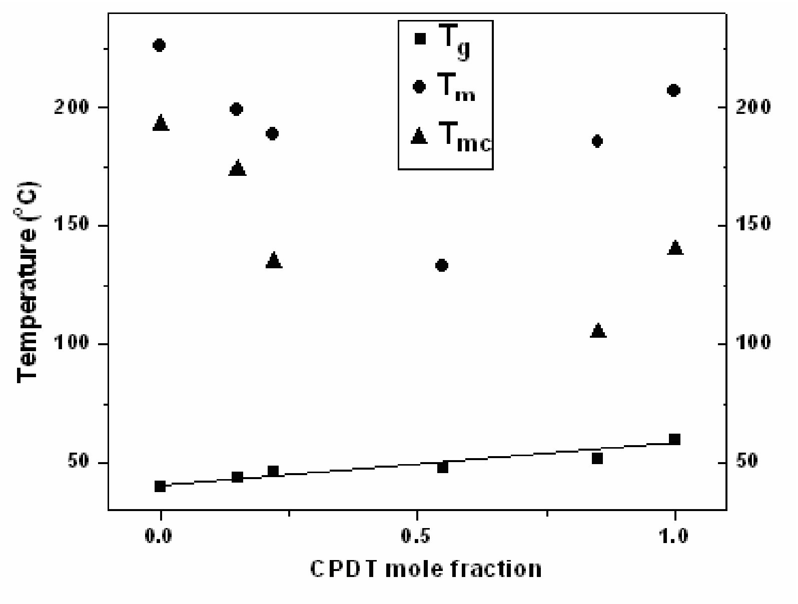


Figure 4.15 Glass transition (T_g), melting (T_m) and melt-crystallization temperatures (T_{mc}) of poly(BT-co-CPDT) copolyesters as a function of copolymer composition

4.4.2.5 Crystallization kinetics

PCPDT is a new semi-crystalline polyester synthesized for the first time and hence the crystallization properties are unknown. Detailed crystallization kinetics of PCPDT and few of the copolyesters was made and compared with that of PBT. The crystallization kinetics[10-14] of PCPDT, $PBT_{78}CPDT_{22}$ and $PBT_{15}CPDT_{85}$were determined from isothermal crystallization studies. **Figures 4.16 to 4.18** show the crystallization isotherms obtained for PCPDT, $PBT_{78}CPDT_{22}$ and $PBT_{15}CPDT_{85}$ respectively. The crystallization half time and Avrami exponent n obtained from the crystallization isotherms are given in **Tables 4.4 to 4.6** for PCPDT, $PBT_{78}CPDT_{22}$ and $PBT_{15}CPDT_{85}$ respectively. The crystallization half time $t_{1/2}$ as a function of crystallization temperature (T_c) is shown in **Figure 4.19.** PCPDT exhibited slower crystallization rate compared to PBT as evident from the higher crystallization half time values. Similar to PCCD (Chapter 3), PCPDT also exhibited a W shaped curve, however, it was less pronounced. The copolyester $PBT_{78}CPDT_{22}$showed lower crystallization temperatures compared with PBT but higher than the crystallization temperatures of PCPDT. However, the crystallization rate was too rapid to measure crystallization below 150°C. On the other hand, $PBT_{15}CPDT_{85}$composition showed slower crystallization rate and lower crystallization temperatures compared to both PBT and PCPDT. The Avarami exponent, “n”, calculated for various temperatures generally fall between 2 and 4, indicating normal crystallization kinetics for these samples.

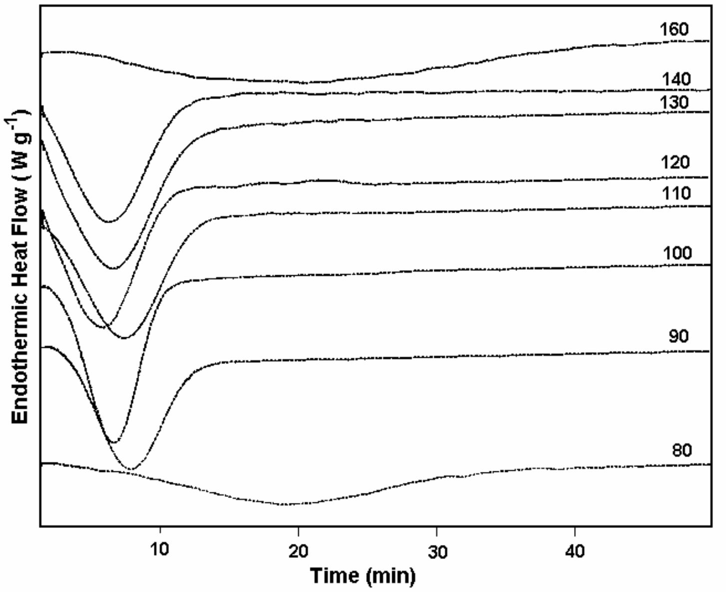


Figure 4.16 Isothermal DSC curves for crystallization of PCPDT at various crystallization temperatures

Table 4.4 Half time of crystallization and Avrami parameters for PCPDT

Crystallization temperature (°C)	Half time of Crystallization $t_{1/2}$ (min)	n	K (min^{-n})
80	19.0	3.2	5.4 x 10^{-5}
90	7.9	4.3	8.2 x 10^{-5}
100	6.6	4.5	1.4 x 10^{-4}
110	7.5	3.6	14.8 x 10^{-4}
120	6.5	3.3	1.5 x 10^{-3}
130	5.9	3.2	2.4 x 10^{-3}
140	6.7	3.0	2.2 x 10^{-3}
150	9.4	3.1	6.1 x 10^{-4}
160	21.5	2.8	1.3 x 10^{-4}
170	73.9	3.5	2.1 x 10^{-7}

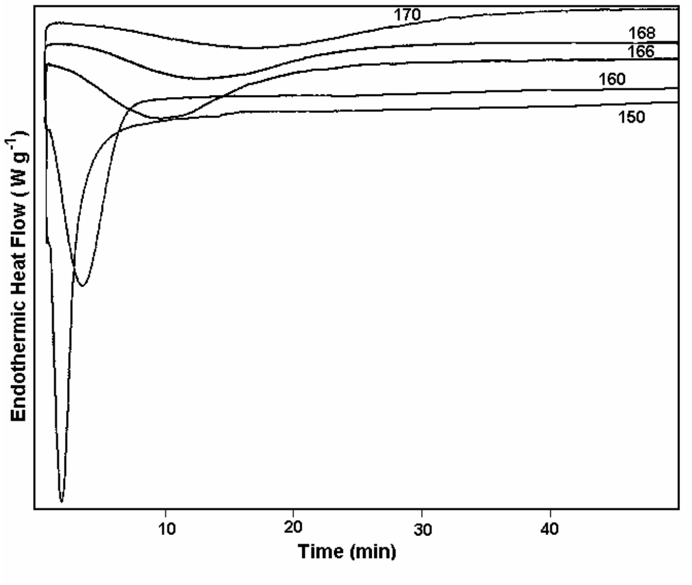


Figure 4.17 Isothermal DSC curves for crystallization of $PBT_{78}CPDT_{22}$ at various crystallization temperatures

Table 4.5 Half time of crystallization and Avrami parameters for $PBT_{78}CPDT_{22}$

Crystallization temperature (°C)	Half time of Crystallization $t_{1/2}$ (min)	n	K (min^{-n})
150	2.0	4.6	2.6×10^{2}
160	4.3	3.5	7.1×10^{3}
166	10.6	2.7	1.0×10^{3}
168	13.9	3.2	1.6×10^{-4}
170	17.7	3.0	1.3×10^{-4}
173	31.9	3.1	1.5×10^{-5}

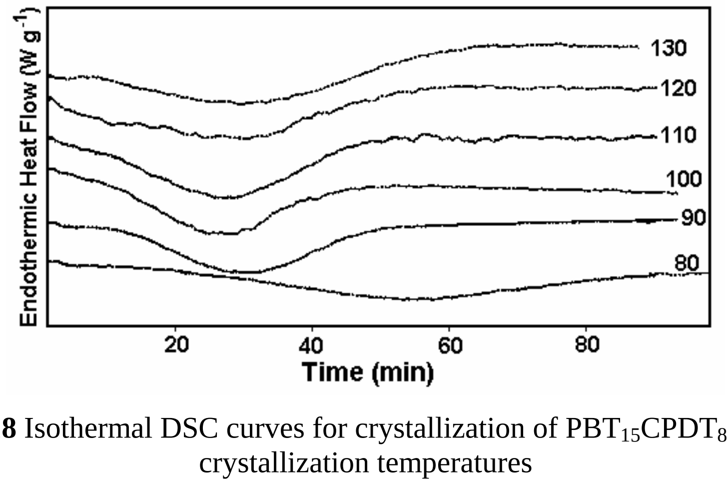


Figure 4.18 Isothermal DSC curves for crystallization of $PBT_{15}CPDT_{85}$ at various crystallization temperatures

Table 4.6 Half time of crystallization and Avrami parameters for $PBT_{15}CPDT_{85}$

Crystallization temperature (°C)	Half time of Crystallization $t_{1/2}$ (min)	n	K (min^{-n})
80	52.9	4.0	$1.0x10^{-7}$
90	30.1	4.1	$6.6x10^{-7}$
100	25.9	3.5	$8.7x10^{-6}$
110	26.8	2.8	$6.5x10^{-5}$
120	26.8	2.2	$4.9x10^{-4}$
130	32.2	-	

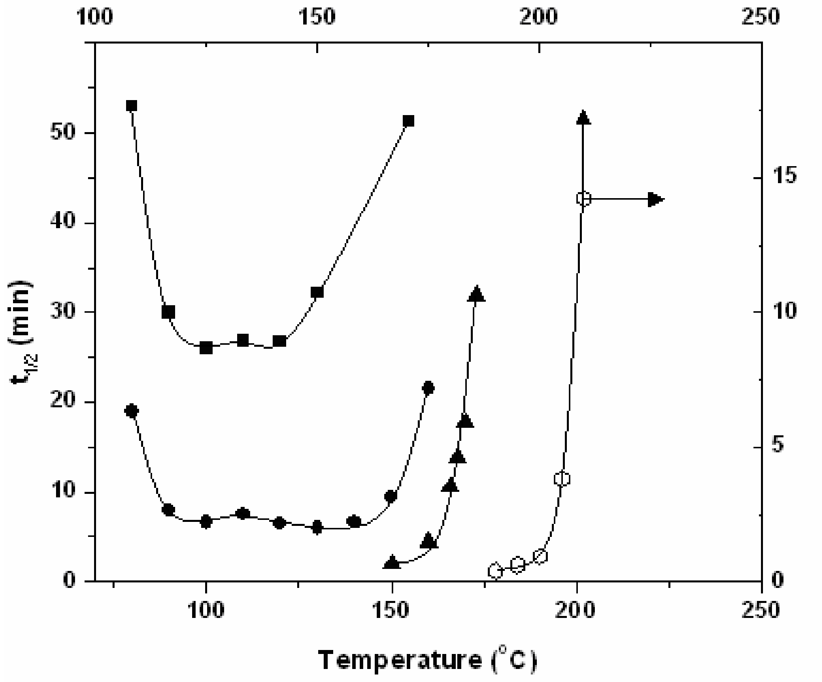
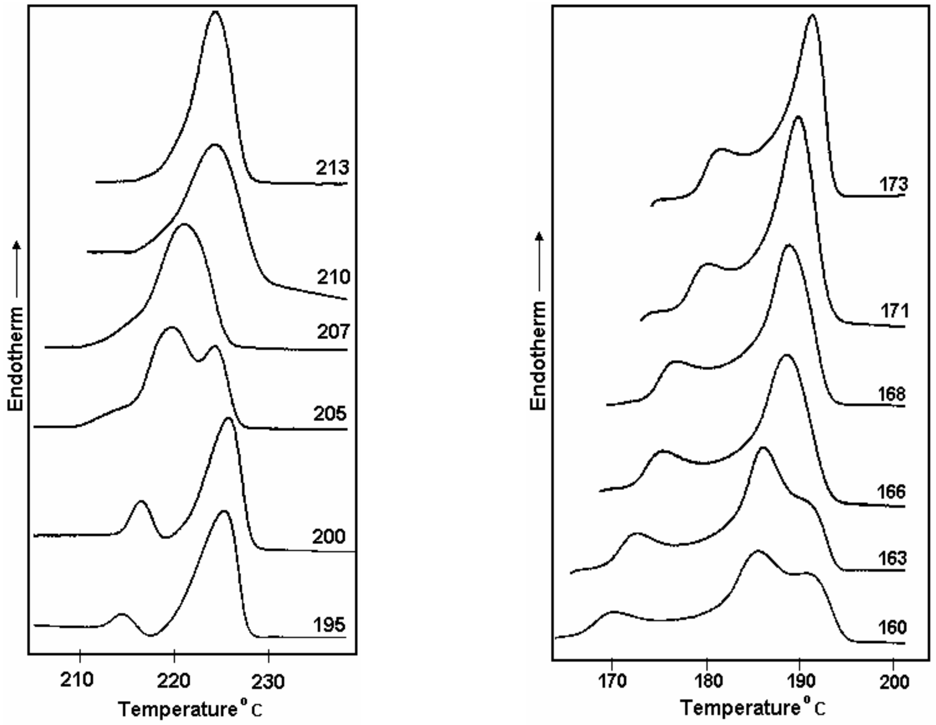


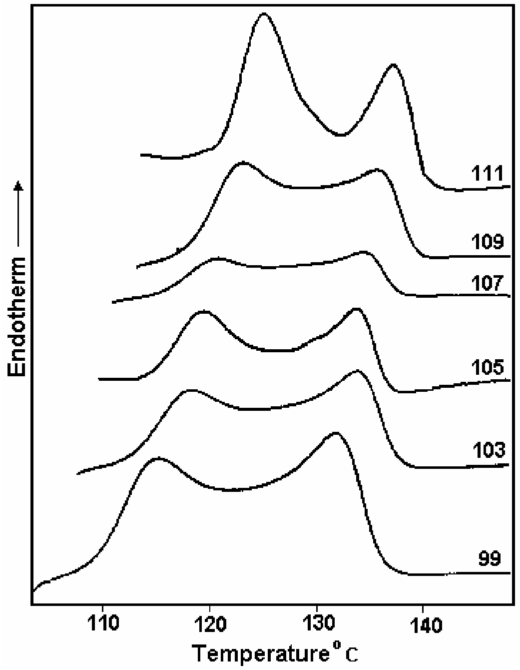
Figure 4.19 Crystallization half time of (v) PBT, (7) $PBT_{78}CPDT_{22}$, (!) $PBT_{15}CPDT_{85}$ and (,) PCPDT

4.4.2.6 Equilibrium melting temperature

The equilibrium melting temperatures of the copolyesters were determined from the melting temperatures of isothermally crystallized samples close to melting temperature and the procedure is outlined in chapter 3. **Figure 4.20** shows the melting endotherms of various samples crystallized at different temperatures. Similar to poly(BT-co-CT) copolyesters discussed in the chapter 3 all the samples showed double melting peaks (and will not be discussed in detail here). **Figure 4.21** shows the plot of observed melting

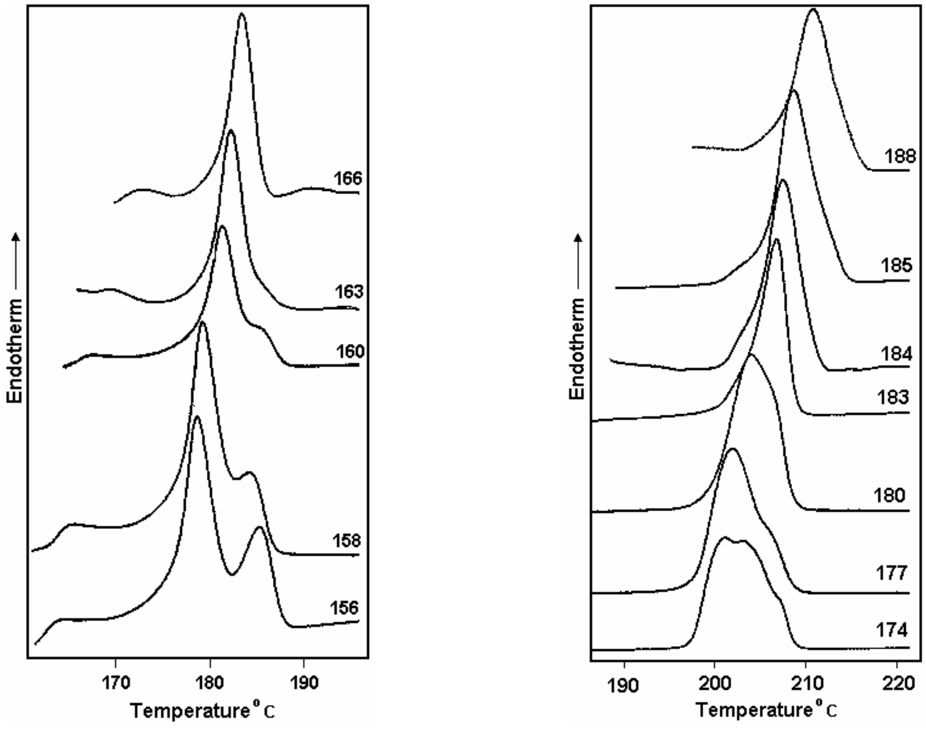


PBT **PBT$_{78}$CPDT$_{22}$**



PBT$_{45}$CPDT$_{55}$

Figure 4.20 DSC heating thermograms for samples crystallized at various temperatures (heating rate 10°C/min) contd........



$PBT_{20}CPDT_{80}$ **PCPDT**

Figure 4.20 DSC heating thermograms for samples crystallized at various temperatures (heating rate 10°C/min)

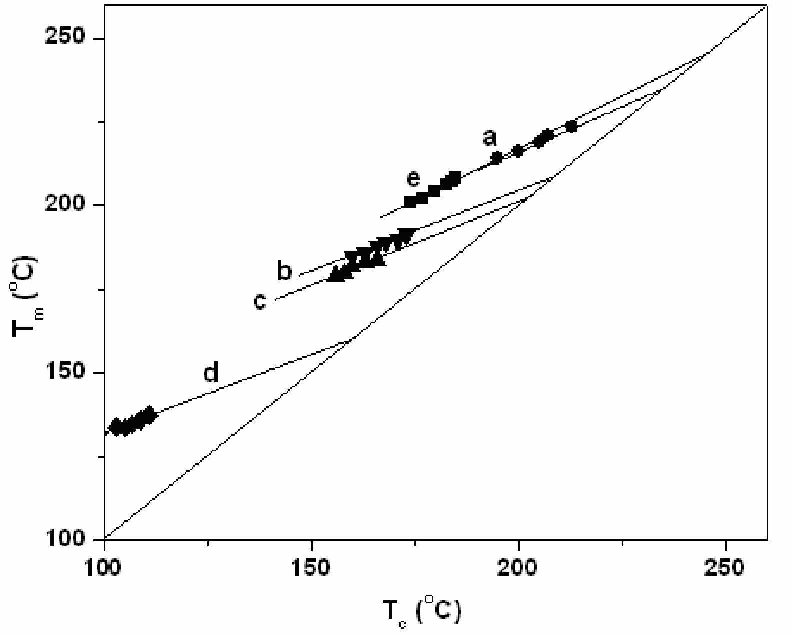


Figure 4.21 Hoffman-Weeks plots of first melting peak temperature (T_m) as a function of T_C for (a) PBT, (b) $PBT_{78}CPDT_{22}$ (c) $PBT_{45}CPDT_{55}$, (d) $PBT_{15}CPDT_{85}$, (e) PCPDT.

temperature and crystallization temperature according to Hoffman-Week plots[15]. The data are fitted by straight line: the intersections of these straight lines with the line $T_m=T_c$ gives the equilibrium melting temperature ($T°_m$) of the copolyesters. In **Figure 4.22** the $T_m°$ of copolymers and the homopolymer are plotted and the corresponding T_m are also shown for comparison. The PCPDT shows an $T_m°$ of 246°C which about 39°C higher than the observed T_m. The $T_m°$ also exhibits the eutectic behaviour similar to P(BT-co-CT) system and $PBT_{45}CPDT_{55}$ is the eutectic composition.

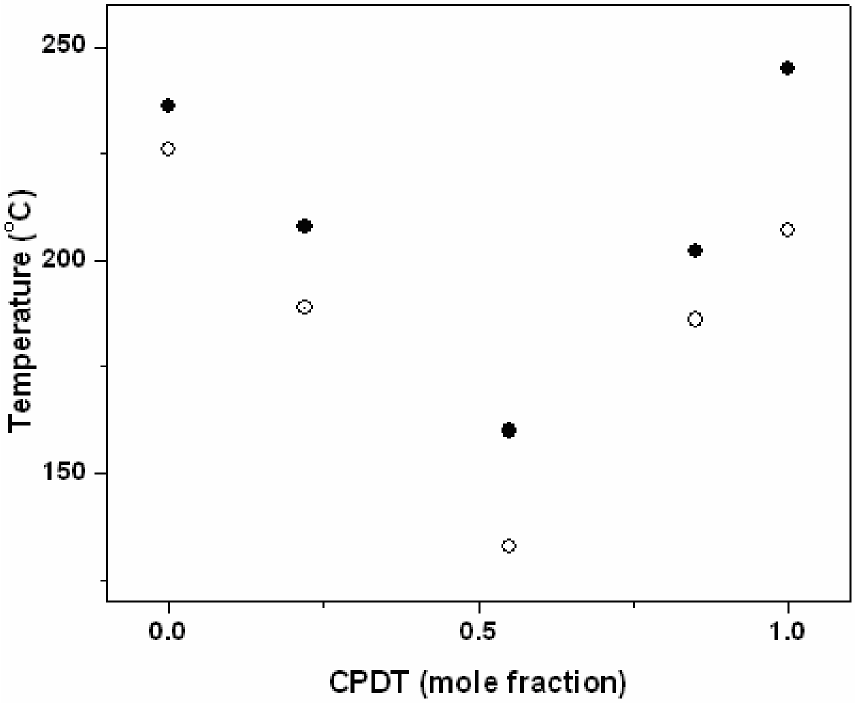


Figure 4.22 Equlibrium melting temperature ($T_m°$) (,) and T_m (–) as a function of copolymer composition

4.4.2.7 X-ray diffraction studies

The room temperature structure of the polyester PCPDT and the copolyesters P(BT-co-CPDT) were analyzed by WAXS. The diffraction patterns of the annealed samples are shown in **Figure 4.23**. It is known that the comonomer concentration in crystal lattice is strongly dependent on the copolymer composition in bulk and crystallization condition[16,17]. The extent of cocrystallization can be qualitatively be measured by the change of the lattice d-spacing in the WAXD pattern[17, 18].

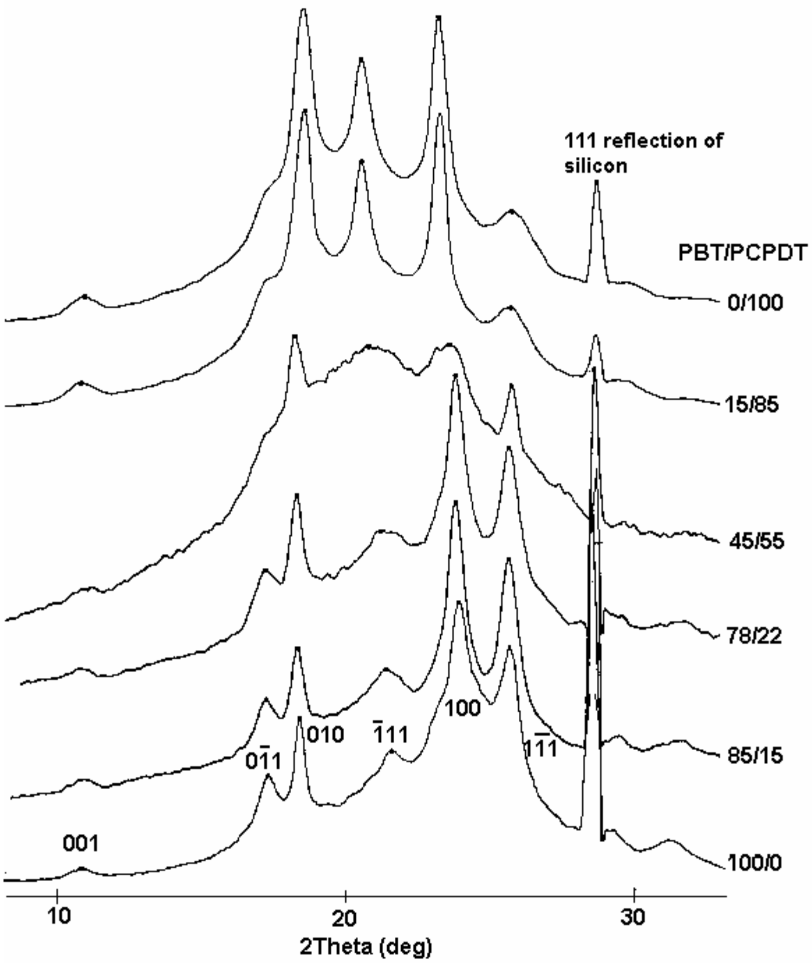


Figure 4.23 WAXD patterns of poly(BT-co-CPDT) copolyesters

The diffractogram of PCPDT **(7)** (**Figure 4.23**) was distinctly different from that of PBT indicating that PCPDT crystallizes into a different lattice. The data from the powder diffractogram was too limiting to determine the crystal structure of PCPDT. Nevertheless, from the diffractograms useful information were extracted. From the WAXD pattern it was noted that from 45 to 100 % BT content, PBT type crystal structure developed where as below 45 % BT content, PCPDT type crystal structure developed. As a consequence of comonomer inclusion, the d spacings of both crystal structures changed with the comonomer content. **Figure 4.24** shows the variation of d-spacing with composition and it shows a break in the region around 55 % PCPDT content. It is worth pointing out that in the case of poly(BT-co-CT) system the break occurred at a lower PCT content (26 %) and it has been argued that PCT controls the crystallization, which is attributed to its rigid structure (chapter 3). The length of CPDT units were calculated using conjugate gradient and Newton-Raphson method using Cerius 2 software was 1.29 nm which was 0.056 nm longer than the BT unit. The similar length of the BT and CPDT units made them cocrystallize even though the average sequence length was lower than the required length for crystallization to occur[19].

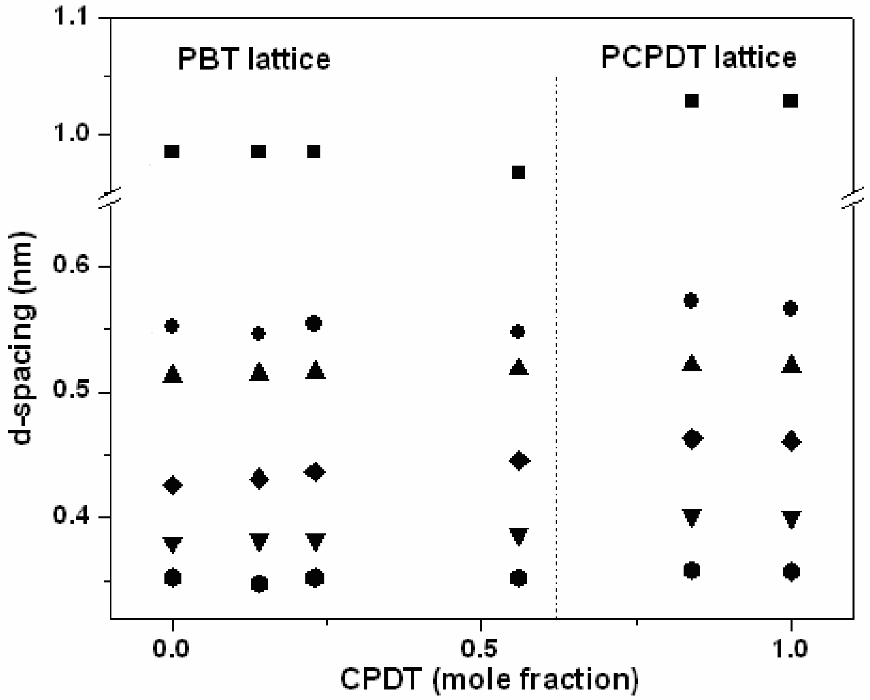
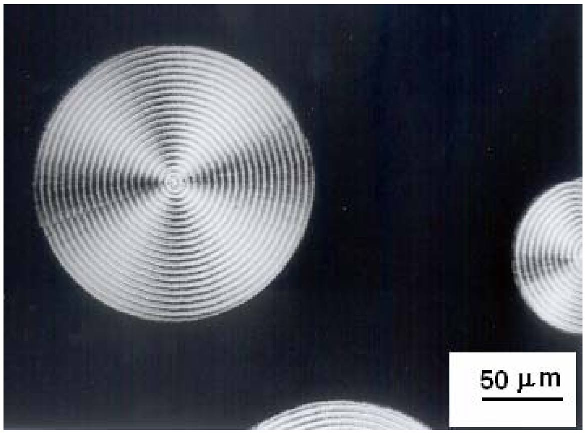


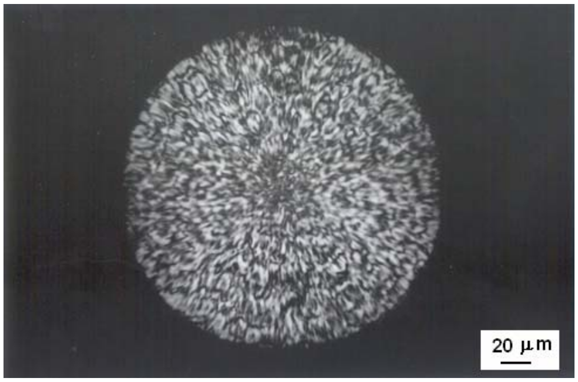
Figure 4.24 Changes of d-spacings for poly(BT-co-CPDT) copolymers as a function of copolymer composition (!) 001(along chain direction), (,) 0$\bar{1}$1, (7) 010, (Λ)$\bar{1}$11 (B)100 and (μ) 1$\bar{1}$1 reflections (based on PBT structure)

4.4.2.8 Polarized optical microscopy

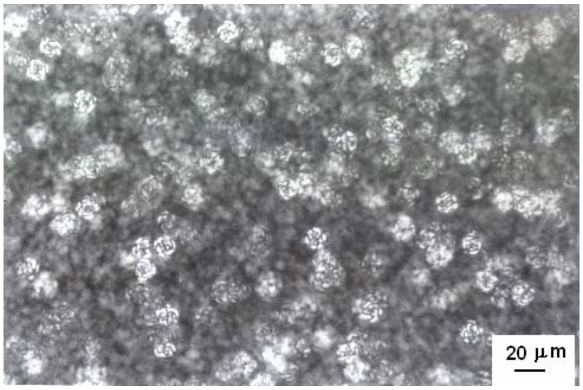
The crystallization and morphology of PCPDT **(7)** and the poly(BT-co-CPDT) **(8)** copolyesters were observed using a polarized optical microscope. The samples were completely melted in the hot-stage, and isothermally held at a temperature 15°C above the melting temperature for two minutes. The sample was then cooled to the crystallization temperature, which was about 20^{o}C lower than the melting temperature, and the growth of spherulitic morphology was monitored. **Figure 4.25** shows the spherultic morphology of PBT, PCPDT and the copolyesters. PCPDT was found to exhibit well-defined banded spherulites, which were highly bi-refringent. Banded spherulites were also observed in poly(trimethylene terephthalate) (PTT)[20,21]. The formation of banded spherulites was attributed to lamellar twisting. In the case of PTT, the banded spherulites grew in the lower half of the bell shaped curve (spherulitic growth rate vs. temperature)[22], however, in the case of PCPDT the spherulites were observed in the high temperature region, 140 to 175°C. Below 140°C, the nucleation density was too high to observe single spherulites.



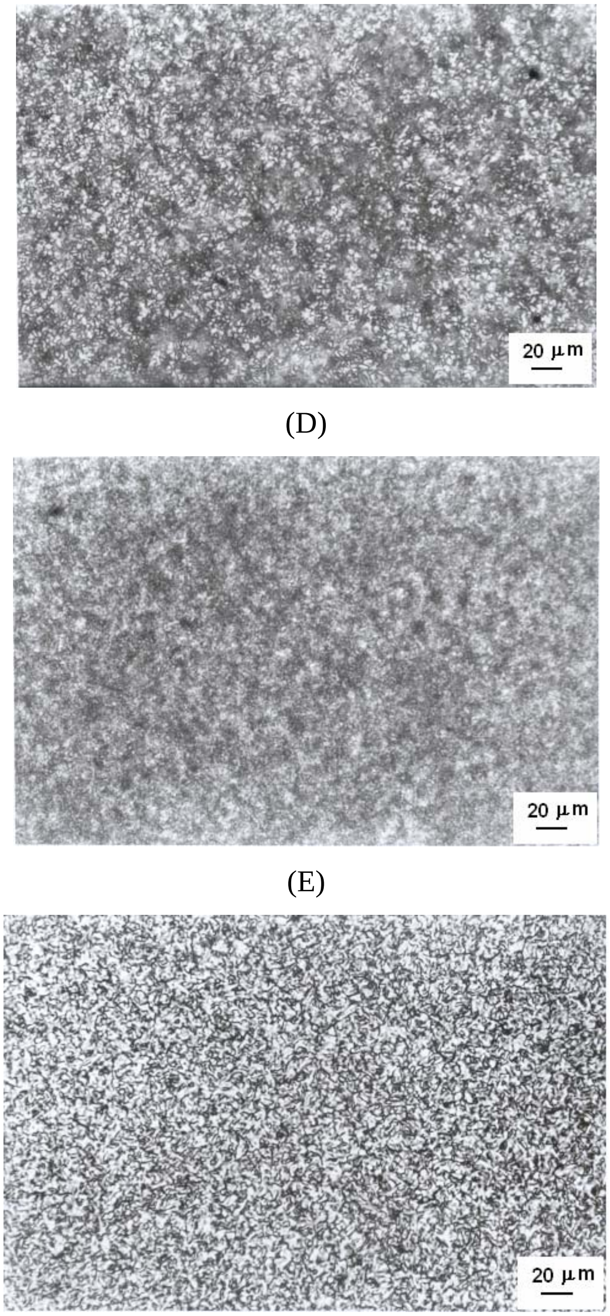
(A)



(B)



(C)



(D)

(E)

(F)

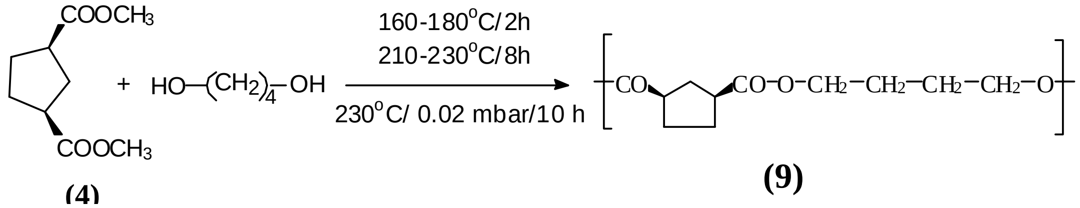
Figure 4.25 Polarized light micrographs of (A) PCPDT (B) $PBT_{15}CPDT_{85}$ (C) $PBT_{45}CPDT_{55}$ (D) $PBT_{78}CPDT_{22}$ (E) $PBT_{85}CPDT_{15}$ (F) PBT

The banded spherulite morphology changed with increasing comonomer content. When 20 % PBT was included as comonomer, the banded spherulitic morphology was highly distorted (**Figure 4.25 B**) apparently due to the disturbance in the sequence of CPDT units by BT units. Other specific features were lower growth rates and increased nucleation density. For the sample $PBT_{45}CPDT_{55}$, the banded structure (**Figure 4.25 C)** was extremely distorted and the excessive nucleation density reduced the size of spherulites also. The PBT rich blend, $PBT_{78}CPDT_{22}$ showed spherulitic morphology (**Figure 4.25 D)** similar to that of PBT (**Figure 4.25 E).**

4.4.3 Synthesis of polyester and copolyesters containing 1,3-cyclopentane dicarboxylate (CPDE)

4.4.3.1 Synthesis and structure of poly (butylene cyclopentane dicarboxylate) (PBCP)

PBCP was synthesized from both *cis* and *cis/trans*-CPDE and butanediol by melt condensation. **Scheme 4.6** depicts the synthesis of PBCP from the *cis*-ester. The polyesters were found to be light brown and rubbery in nature. The inherent viscosity and the GPC data are given in **Table 4.7**.



Scheme 4.6 Synthesis of poly(butylene cyclopentane dicarboxylate) (PBCP)

Table 4.7 Viscosity, Molecular weights and T_g of PBCP polyesters

Polyester	$\eta_{inh}{}^{a}$ dL/g	M_n	M_w	PDI	T_g (°C)	IDT[b]
Cis-PBCP **(9)**	0.66	57,100	1,51,300	2.6	-44	403
Cis/trans-PBCP **(10)**	0.82	36,200	1,70,600	4.7	-15	408

[a]Measured in $CHCl^3$ at 30°C; [b]Measured by TGA.

The structures of the polyesters were confirmed by ^1H and ^{13}C NMR spectra. **Figure 4.26** shows the ^1H spectra of *cis*-PBCP along with the chemical structure and assignments for NMR spectra. The peak at 4.08 was due to the OCH_2 protons, H_d, and the peak at 2.77 was due to the CH proton attached to the carbonyl, H_c. In the case of *cis/trans*-PBCP, two peaks at 2.86 (*cis*) and 2.97 (*trans*) in a ratio of 54/46 were seen (**Figure 4.27**).

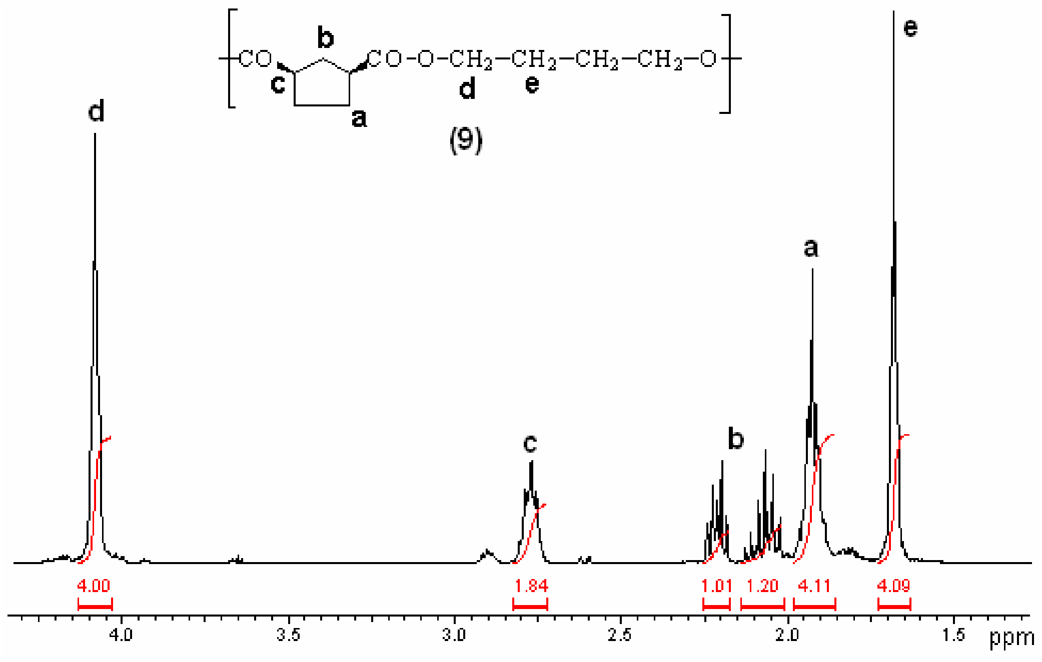


Figure 4.26 ^{1}H NMR spectrum of *cis*-poly(butylene cyclopentane dicarboxylate) (*cis*-PBCP)

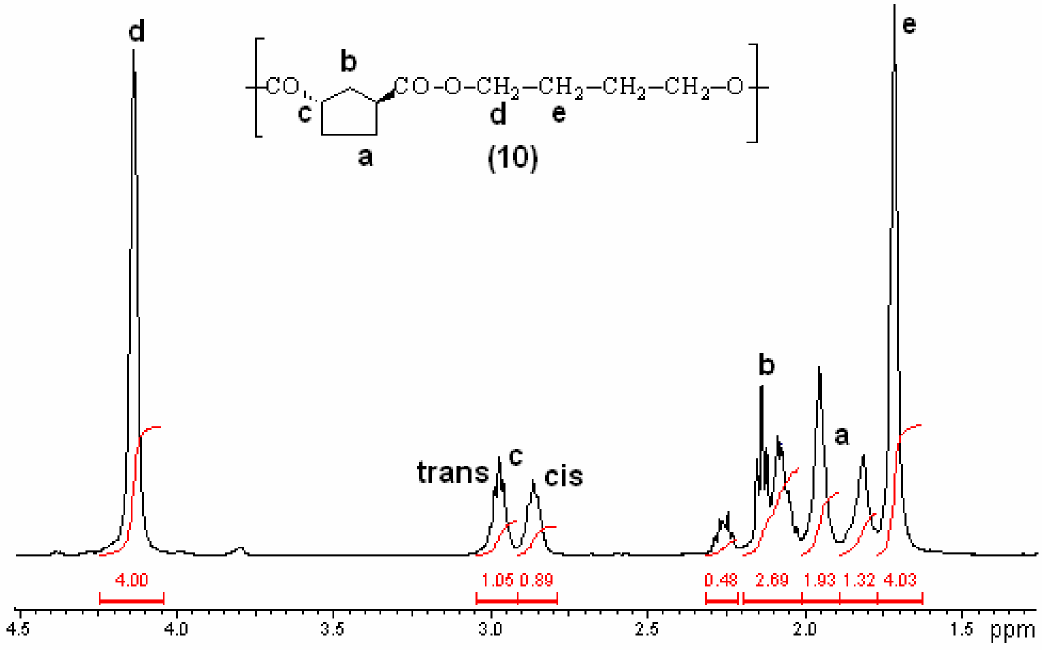


Figure 4.27 ^{1}H NMR spectrum of *cis/trans*-poly(butylene cyclopentane dicarboxylate) (*cis/trans*-PBCP)

The ^{13}C NMR of cis and cis/trans PBCP are shown in **Figures 4.28 & 4.29.** It can be seen that the carbonyl carbon appears at 174.97 for *cis*-PBCP **(9)** and at 177.2 (*cis*) and

177.57 (*trans*) for *cis/trans*-PBCP **(10)**. The C_a, C_b and C_c carbons also appear at different chemical shifts for *cis* and *trans* PBCP.

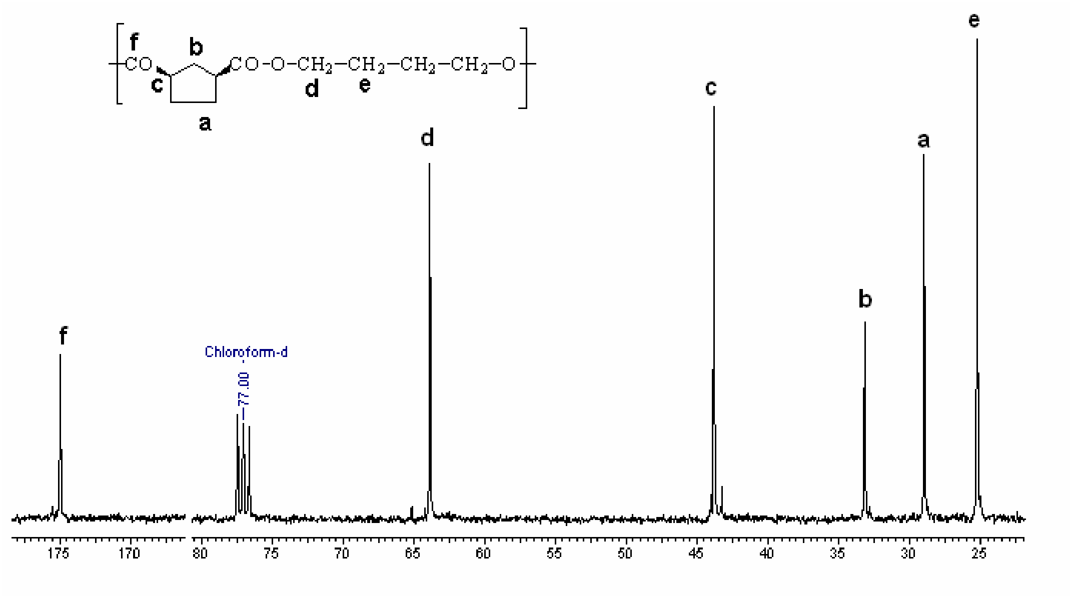


Figure 4.28 ^{13}C NMR spectrum of *cis*-poly(butylene cyclopentane dicarboxylate) (*cis*-PBCP)

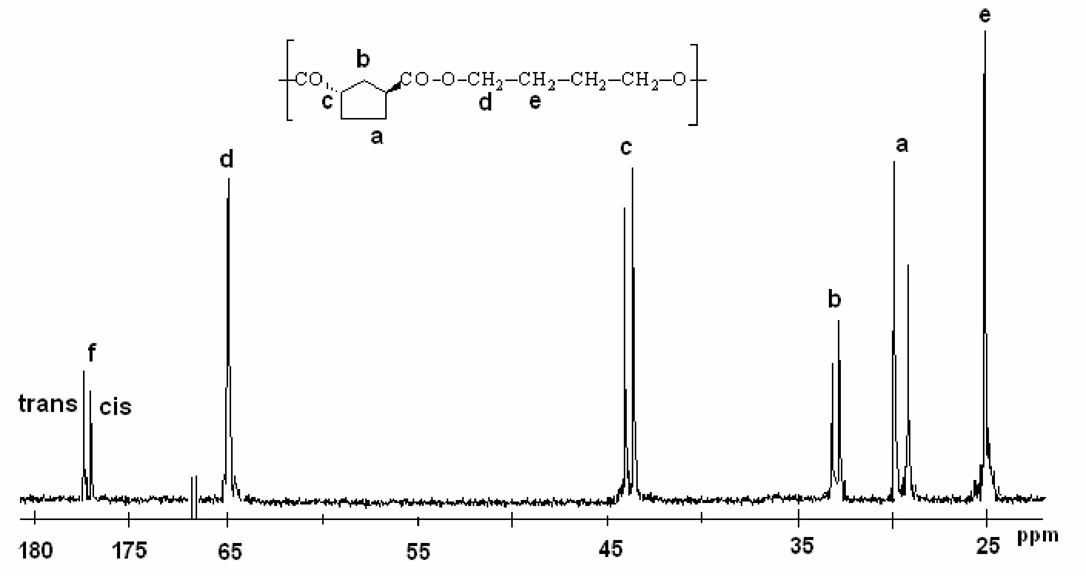
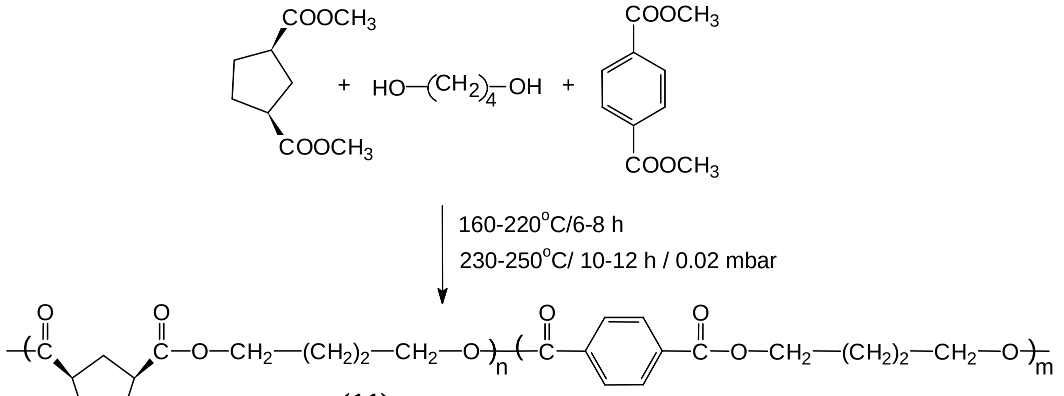


Figure 4.29 ^{13}C NMR spectrum of *cis/trans*-poly(butylene cyclopentane dicarboxylate) (*cis/trans*-PBCP)

4.4.3.2 Synthesis of poly (butylene terephthalate-co-butylene cyclopentane dicarboxylate) copolyesters

Copolyesters of dimethyl terephthalate and 1,4-butanediol containing dimethyl-1,3-cyclopentane dicarboxylate (CPDE) **(4)** were synthesized by melt condensation using titanium isopropoxide catalyst and the reaction scheme is depicted in **Scheme 4.7**. A series of copolyesters were synthesized by changing the molar ratio of DMT/CPDE (90/10, 80/20, 70/30 and 50/50). The copolyester $PBT_{55}BCP_{45}$ was found to be soluble in chloroform, while the other compositions were insoluble.



(11)

Scheme 4.7 Synthesis of poly (butylene terephthalate-co-butylene cyclopentane dicarboyxlate) (P(BT-co-BCP))

The inherent viscosities were in the range of 0.8-1.2 dL/g (**Table 4.10**). The M_n and M_w of $PBT_{55}BCP_{45}$ were found to be 49, 530 and 81,600 with a polydispersity of 1.65.

4.4.3.3 Composition and microstructure of poly(BT-co-BCP) copolyesters

The chemical structure of poly(BT-co-BCP) **(11)** along with the notations using for NMR assignments is given in **Figure 4.30**, where BCP is butylene cyclopentane dicarboyxlate unit and BT is the butylene terephthalate unit

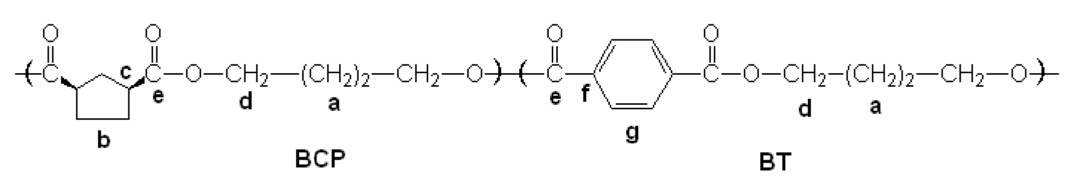


Figure 4.30 Chemical structure of poly(BT-co-BCP) copolyester with notations used for NMR assignments

The copolyester composition was determined from ^{1}H and ^{13}C NMR spectra using the H_d proton and C_d carbon respectively. The ^{1}H NMR spectrum of PBT, PBCP and $PBT_{56}BCP_{44}$ copolymer with assignments for each peak is shown in **Figure 4.31.** **Table 4.8** gives the peak positions of PBT, PBCP and $PBT_{56}BCP_{44}$ copolyester. The OCH_2 peak for PBT appears at 4.5 ppm and for PBCP appears at 4.08 ppm.

Table 4.8 ^{1}H and ^{13}C NMR Chemical Shifts (δ in ppm) of PBT, PBCP and poly(BT-co-BCP) copolyesters

				^{1}H Chemical shifts			
	^BH_a	^BH_d	^BH_g	$^{CP}{}_a$	$^{CP}{}_b$	$^{CP}H_c$	$^{CP}H_d$
PBT	2.02	4.5	8.12				
PBCP				1.68	1.8-2.3	2.77	4.08
$PBT_{56}BCP_{44}$	1.99	4.47	8.1	1.99	1.8-2.5	2.88	4.21
				^{13}C Chemical Shifts			
	^BC_d	^BC_e	^BC_f	^BC_g	$^{CP}C_d$	$^{CP}C_e$	$^{CP}C_c$
PBT	65.9	167.6	133.7	129.8			
$PBT_{56}BCP_{44}$	65.72	166.55	133.89	129.4	63.84	175.03	43.74
PBCP					63.85	174.99	43.79

In the ^{1}H NMR spectrum of the poly(BT-co-BCP) copolyester, the OCH_2 protons (H_d) was split into four. An expanded ^{1}H NMR spectrum in the range of 4.1- 4.5 ppm is shown in **Figure 4.33**, where the four peaks are assigned to BT/BT (4.47 ppm), BT/BCP (4.41ppm), BCP/BT (4.21 ppm) and BCP/BCP (4.15 ppm) dyads. The different possible environments for the copolyester: TT, TCP, CPT, CPCP, where T corresponds to terephthalate and CP corresponds to cyclopentane dicarboyxlate unit is shown in **Figure 4.32.** The relative concentrations of the four diads determined from the areas of four peaks, f_{TT}, f_{CPCP}, f_{TCP} and f_{CPT} correspond to the proportion of the integrated intensities of TT, CPCP, TCP and CPT units respectively. The number average sequence lengths (L_{nB} and L_{nCP}) and degree of randomness of the copolyesters were calculated and are summarized in **Table 4.9.** For random copolyesters B = 1. If B is less than unity, the units tend to cluster together in blocks of each unit and the value of B is zero in a mixture of homopolymers. A value of B = 2 implies alternating distribution.

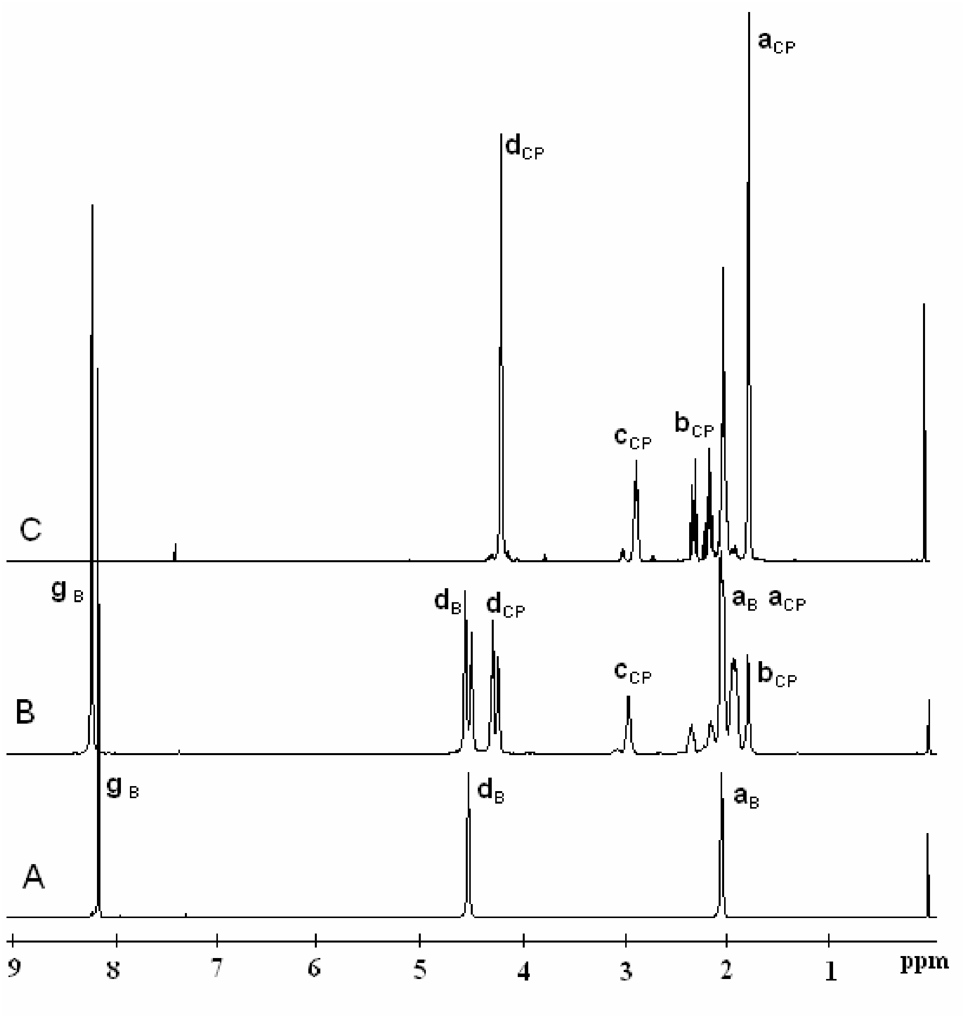


Figure 4.31 ^{1}H NMR spectrum of (A) PBT, (B) $PBT_{50}CP_{50}$, (C) PBCP and its peak assignment

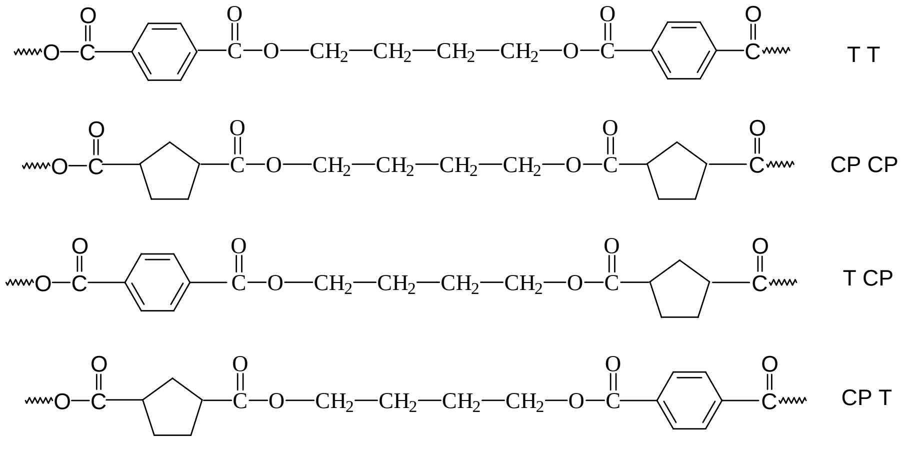


Figure 4.32 Different environments of methylene protons

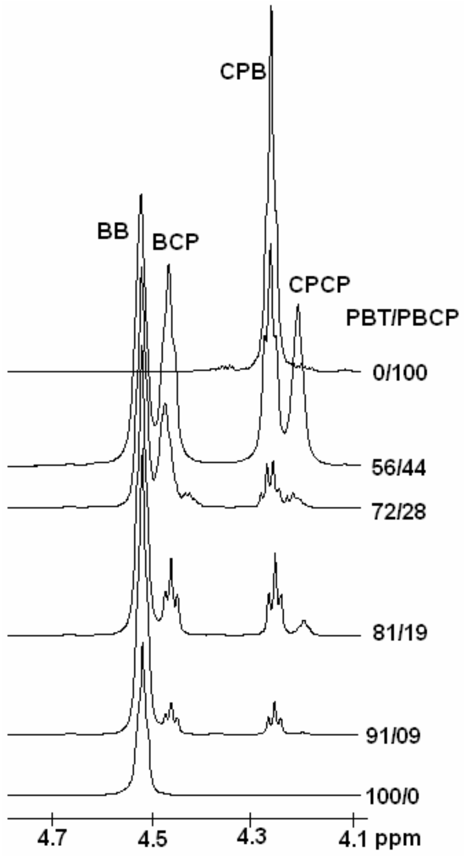


Figure 4.33 ^{1}H NMR spectra in the range of 4.0-4.8 ppm of PBT, PBCP and poly(BT-co-BCP) copolyesters

Table 4.9 Composition, Average sequence lengths and degree of randomness of poly(BT-co-BCP) copolyesters determined by ^{1}H NMR

Copolyester	Feed composition (mol %)		Copolymer composition[a] (mol %)		L_{nB}	L_{nCP}	B
	X_{DMT}	X_{CPDE}					
PBT	100	0	100	0	-	-	2
$PBT_{91}BCP_9$	90	10	91	09	10.69	10.8	1.01
$PBT_{81}BCP_{19}$	80	20	82	18	5.06	1.23	1.01
$PBT_{73}BCP_{27}$	70	30	72	28	3.65	1.36	1.00
$PBT_{56}BCP_{44}$	50	50	56	44	2.25	1.75	1.01
PBCP	0	100	0	100	-	-	2

[a] values were obtained from integration of OCH_2 peaks from ^{13}C NMR

A typical ^{13}C NMR spectrum of $PBT_{55}BCP_{45}$ copolymer with assignment of each peak is shown in **Figure 4.34**. The peaks at 65.72 and 63.84 are assigned to the d_B and d_{CP} carbons.

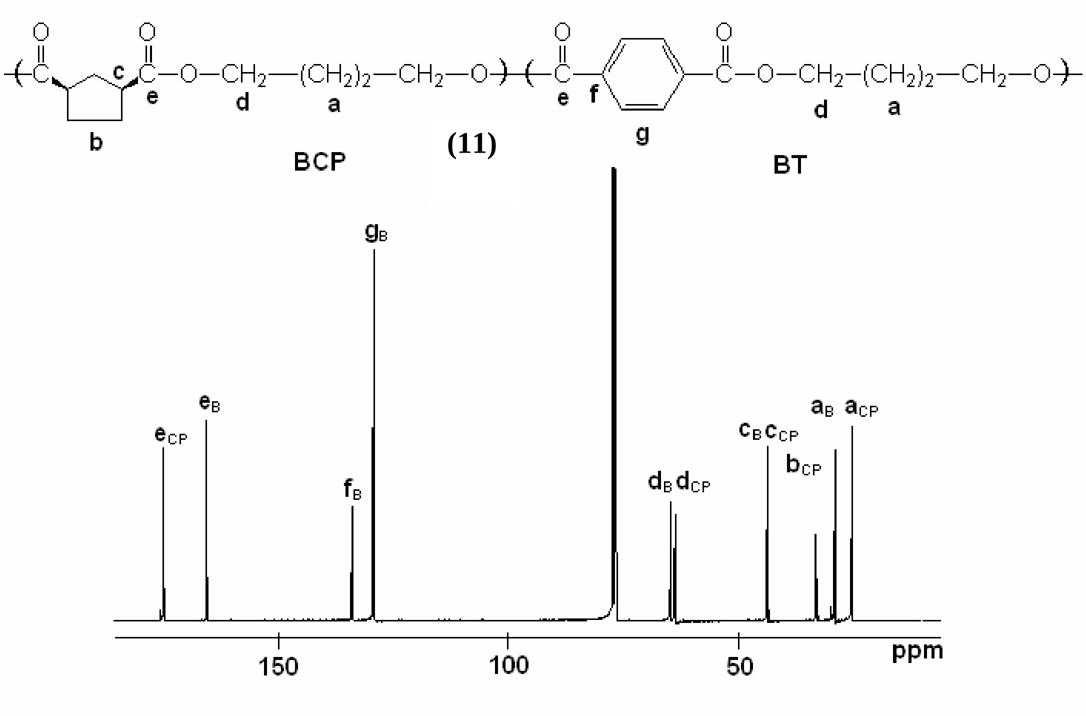


Figure 4.34 A typical ^{13}C NMR spectrum of poly(BT-co-BCP) copolyester with its peak assignment

4.4.3.4 Thermal properties

PBCP **(9)** is an amorphous polyester with a T_g of -44°C. The copolyesters of dimethyl terephthalate and 1,4-butanediol containing CPDE (4), were found be semicrystalline up to 50% CPDE incorporation. The T_g, T_m and T_c values are summarized in **Table 4.10.** The melting endotherms on heating and cooling exotherms of the copolyesters are shown in **Figure 4.35.**

The melting, crystallization and glass transition temperatures show linear relationship with composition (**Figure 4.36**) and in the composition range where the copolymers crystallize do not show eutectic behavior. The absence of eutectic composition indicates that the cocrystallizaion is isomorphic in nature and monomer units of one type are included in the crystal lattice of the other type.

Table 4.10 Thermal properties of poly(BT-co-BCP) copolyesters

Polyester	η_{inh}[a]	T_g (°C)	T_m (°C)	ΔH_m (J/g)	T_{mc} (°C)	ΔH_c (J/g)	IDT[b]
PBT	0.90	40	222	41	193	49	374
$PBT_{91}CP_{09}$	1.20	34	207	30	161	35	c
$PBT_{81}CP_{19}$	0.99	31	196	24	147	31	c
$PBT_{72}CP_{28}$	0.80	14	180	32	123	30	c
$PBT_{56}CP_{44}$	0.80	-9	130	20	64	21	390
PBCP	0.66	-44		Amorphous			403

[a] Measured in 60/40 phenol/TCE (w/w) at 30°C; [b] Measured by TGA; [c] Not determined

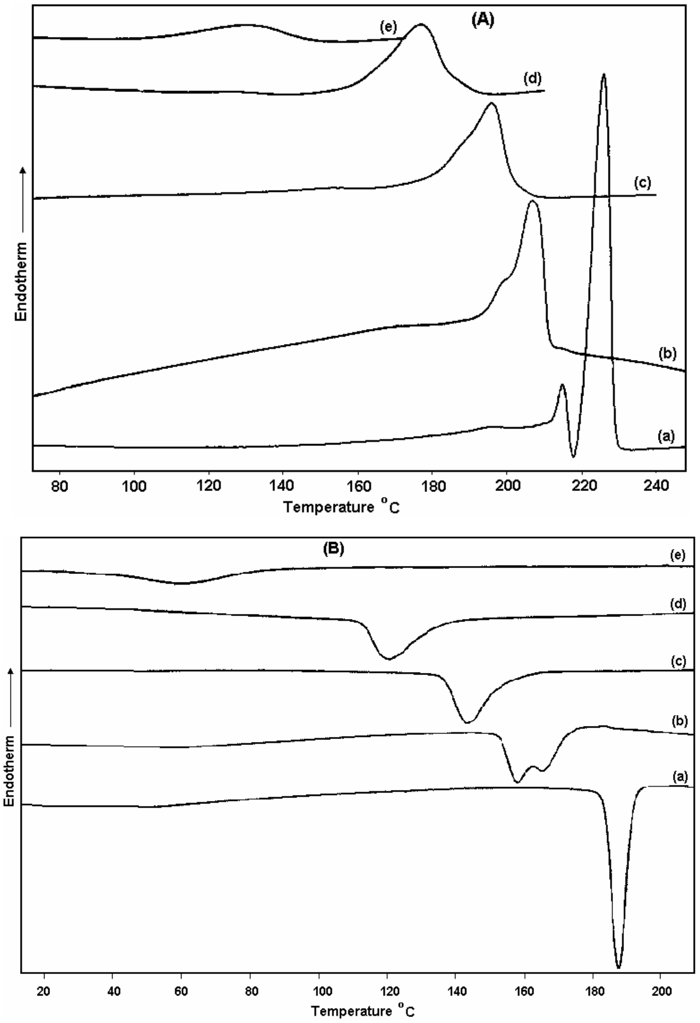


Figure 4.35 DSC scans of (a) PBT (b) $PBT_{91}CP_{09}$ (c) $PBT_{81}CP_{19}$ (d) $PBT_{72}CP_{28}$ (e) $PBT_{56}CP_{44}$ copolyesters (A) second heat (B) first cooling

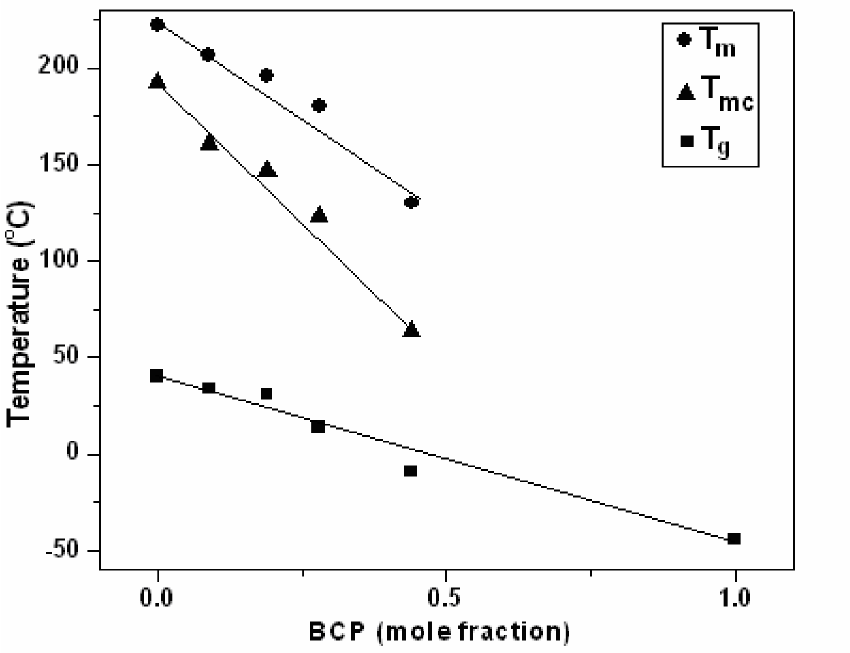


Figure 4.36 Melting, melt-crystallization and glass transition temperatures of poly(BT-co-BCP) copolyesters as a function of copolymer composition

4.4.3.5 X-ray diffraction studies

The WAXD patterns of poly(BT-co-BCP) **(11)** copolyesters are shown in **Figure 4.37**. All samples were annealed for 2 h at temperature10°C below their T_m to sharpen the diffraction patterns. The diffraction patterns of the copolymers appear similar to that of PBT indicating that all the copolyesters crystallized in PBT lattice. Copolyesters having more than 50% incorporation of BCP component do not crystallize, as PBCP is amorphous polymer. The d-spacings calculated from the patterns are shown in **Figure 4.38.** It is interesting to observe that PBCP on its own cannot arrange into a lattice but BCP units can get into the lattice along with PBT. The incorporation of BCP unit in the PBT lattice was apparent from the 001 spacing. The 001 d-spacing, which was less susceptible to variation to structure and morphology, showed marginal decrease with increase in BCP content and was in agreement with the BCP unit’s length 1.04 nm (calculated using conjugate gradient and Newton-Raphson method using Cerius 2 software), which was lower than the length of BT unit (1.234 nm).

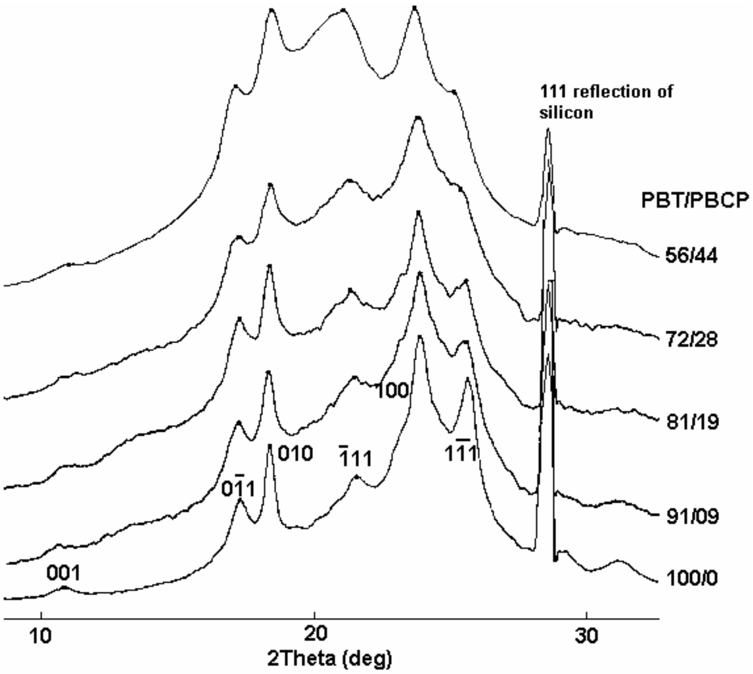


Figure 4.37 WAXD patterns of poly(BT-co-BCP) copolyesters

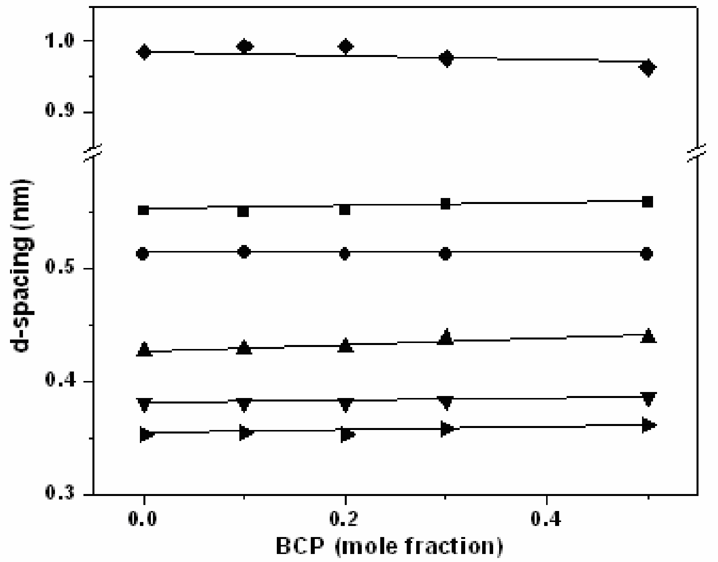


Figure 4.38 Changes of d-spacings for poly(BT-co-BCP) copolymers as a function of copolymer composition (Λ) 001(along chain direction), (!) 0$\bar{1}$1, (,)010, (7)$\bar{1}$11 (B)100 and (β) 1$\bar{1}$1 (based on PBT structure)

4.5 Conclusions

A new family of copolyesters of dimethyl terephthalate and 1,4-butanediol containing 1,3-bishydroxy methyl cyclohexane **(6)** and 1,3-dimethyl cyclopentane dicarboxylate **(4)** were synthesized by melt condensation for the first time. NMR spectroscopic analysis indicated that the poly(BT-co-CPDT) **(8)** and poly(BT-co-BCP) **(11)** copolyesters were statistically random irrespective of the composition. Homopolyester of DMT with 1,3-bishydroxy methyl cyclohexane (PCPDT) **(7)** was a semicrystalline polyester with a T_g of 60 °C and T_m of 208 ^oC. PCPDT showed well defined banded spherulites. PCPDT showed lower crystallization rate compared to that of PBT. Copolyesters of DMT and 1,4-butanediol with 1,3-bishydroxy methyl cyclohexane were synthesized with different monomer ratios. The thermal analysis and XRD studies showed that these copolymers could crystallize in all compositions. The poly(BT-co-CPDT) copolymers exhibit typical eutectic behaviour in melting and crystallization and the eutectic composition was $PBT_{45}CPDT_{55}$, which indicated iso-dimorphic cocrystallization behavior. The spherulitic morphology of poly(BT-co-CPDT) copolymers showed systematic changes with change in composition. PCPDT showed well defined banded spherulites. Addition of 15 % PBT in PCPDT changed the reqular banded structure into a highly distorted banded spherulite structure. Further increase in PBT comonomer changed the structure into a fine grain structure similar to that of PBT homopolymer.

PBCP **(9)** is a new amorphous polyester with T_g of –45^oC and the copolyesters with PBT component more than 50% were semicrystalline. In the composition range where the copolyesters crystallized, the samples showed isomorphic crystallization and did not show eutectic behaviour in melting and crystallization. The glass transition temperature showed linear dependency on composition in these copolymers.

Copolyesters based on cyclopentane ring exhibited crystallization behaviour similar to the copolyesters based on cyclohexane ring discussed in Chapter 3, which can be related to the monomer structure. Incorporation of cyclopentane dimethanol, the diol component, as a comonomer, resulted in copolymers in which the T_c and T_m followed a eutectic behaviour. These copolyesters had a T_g higher than that of PBT. While incorporation of 1,4-cyclopentane dicarboyxlate comonomer, which is the ester component, resulted in copolyesters which have T_g lower than PBT, the T_m did not show eutectic behaviour.

II. Synthesis and properties of aliphatic polyesters containing cyclohexane and cyclopentane rings

4.6 Introduction

Aliphatic or cycloaliphatic polyesters are used in applications which require UV resistance since the aromatic polyesters absorb strongly in the UV region resulting in chain scission and subsequent degradation. Poly(1,4-cyclohexylenedimethylene-1,4-cyclohexane dicarboxylate) (PCCD) is a linear cycloaliphatic polyester made from dimethyl-1,4-cyclohexane dicarboxylate (DMCD) and 1,4-cyclohexane dimethanol. PCCD is characterized by advantageous properties such as crystallinity and weathering under conditions of exposure to ultraviolet radiation[23]. However, the crystallinity of PCCD is not as high as commercially available polyesters such as PBT. The melting temperature (T_m) is in the range of 220-235°C and the temperature of crystallization from the melt (T_c) is in the range of 152-171°C, which leads to slow crystallization. The *cis* to *trans* ratio of cycloaliphatic moiety in the polymer chain is an important factor and can greatly effect thermal and crystallization behavior. Polyesters with high *trans* content are usually semi-crystalline and those with a high *cis* content are amorphous, or have much lower T_m and T_g.

The present study deals with the synthesis of PCCD from *a,e/e,e*-1,4-cyclohexane dicarboxylate (67/33) and *a,e/e,e*-1,4-cyclohexanedimethanol (75/25) and a study of the influence of *a,e/e,e* isomer ratio on the polyester properties. The thermal and crystallization properties were compared with the commercial PCCD, which contains >90 % *e,e*-1,4-cyclohexane dicarboxylate content. It was also of interest to synthesize completely cycloaliphatic polyester similar to PCCD, from 1,3-bishydroxymethyl cyclopentane and dimethyl-1,3-cyclopentane dicarboxylate and study the properties.

4.7 Experimental

4.7.1 Synthesis of poly(cyclohexane dimethylene cyclohexane dicarboyxlate) (PCCD) (12)

1,4-CHDM (1.82 g, 0.0126 mol), dimethyl cyclohexane-1,4-dicarboxylate (2.5 g, 0.0125 mol) and titanium isopropoxide (0.1 wt%) were taken in a two neck round bottom flask equipped with a N_2 gas inlet, magnetic stirring bar, air condenser and a vacuum control assembly. The reaction mixture was heated at 160-220°C for 6 h and the temperature raised to 250°C. The pressure was gradually reduced to 0.02 mbar over 20 min and heated at 250-260°C for 10 h. The flask was cooled to room temperature under vacuum and the polymer recovered by breaking the flask and cutting into pieces. Yield = 3.34 g (93 %).

η_{inh} (phenol/TCE 60/40 w/w = 1.3 dL/g

GPC ($CHCl_3$) - M_n = 72,900 M_w = 2,17,600 (M_w/M_n - 2.9)

^{1}H-NMR ($CDCl_3$) δ: 0.7-2.1 (18H, m, ring), 2.45, 2.25 (2H, s, CH), 3.86, 3.95 (4H, d, CH_2O)

^{13}C-NMR ($CDCl_3$) δ: 25.17, 25.94, 27.97, 28.74 (CH_2), 34.4 (CH), 36.97 (CH), 40.65 (*cis* CH), 42.45 (*trans* CH), 66.85(*cis* CH_2O), 69.05 (*trans* CH_2O), 174.89 (*cis* carbonyl), 175.36 (*trans* carbonyl)

4.7.2 Synthesis of poly (cyclopentane dimethylene cyclopentane dicarboxylate) (PCPCPD) (13)

4.7.2.1 From *cis*-CPDE (4)

Cis-dimethyl-1,3-cyclopentane dicarboxylate **(4)** 3.77 g (0.02 mol), 1,3-bishydroxymethyl cyclopentane 2.86 g (0.02 mol) and titanium isopropoxide (0.1 wt % diester) were taken in a two neck round bottom flask fitted with N_2 inlet, air condenser and spiral trap. The reaction mixture was heated at 160-230°C for 7 h when methanol distilled out. The pressure was gradually reduced to 0.02 mbar over 30 min and continued at 230-280°C for 10 h. The flask was cooled under vacuum. The resulting polymer was found to be rubbery. Yield 5.03 g (98 %).

η_{inh} ($CHCl_3$). = 0.5 dL/g

GPC ($CHCl_3$) - M_n= 35,600, M_w= 1,17,800 (M_w/M_n - 3.3)

^{1}H NMR ($CDCl_3$) δ: 0.7-1 (1H, m, ring proton), 1.15-1.5 (2H, m, ring proton), 1.56-2.4 (12H, m, ring protons), 2.6-3 (2H, CH), 3.91, 3.94 (4H, d, CH_2O)

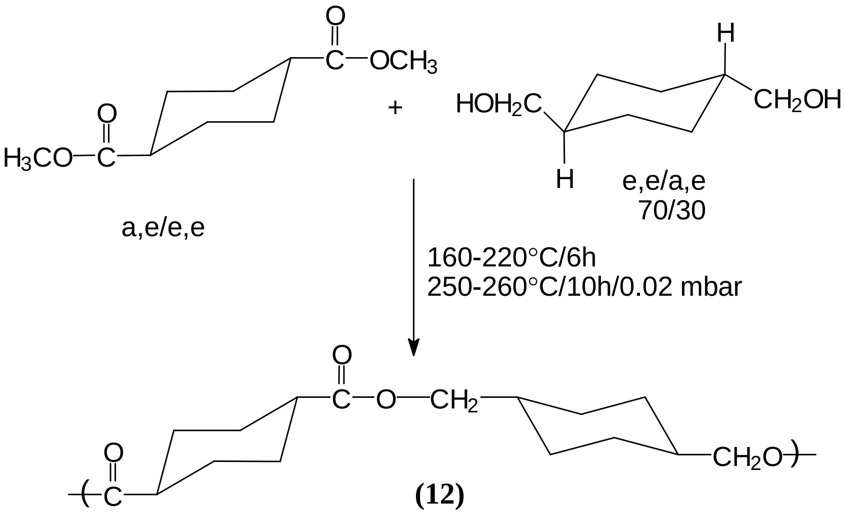
4.7.4.2 From cis/trans CPDE (4,5)

Dimethyl-1,3-cyclopentane dicarboxylate **(4,5)** (cis/trans 50/50) (1.86 g, 0.01 mol), 1,3-bishydroxymethyl cyclopentane 1.3 g (0.01 mol) and titanium isopropoxide (0.1 wt % diester) were taken in a two neck round bottom flask fitted with N_2 inlet, air condenser and spiral trap. The reaction mixture was heated at 160-230°C for 7 h under a constant stream of N_2 gas when methanol distilled out. The pressure was gradually reduced over 30 min to 0.02 mbar and reaction was continued at 230-280°C for 10 h. The flask was cooled under vacuum. The resulting polymer was found to be rubbery and was insoluble in $CHCl_3$ and phenol/TCE mixture. Yield 2.33 g (92 %).

4.8 Results and Discussion

4.8.1 Synthesis and structure of PCCD (12)

The ^{1}H NMR of DMCD showed that the *cis* and *trans* isomer ratio was 67/33. PCCD was synthesized by melt condensation from 1,4-CHDM and DMCD containing 67% *cis*-isomer. The scheme for synthesis is shown in **scheme 4.8.**



(12)

Scheme 4.8 Synthesis of poly (cyclohexylene dimethylene cyclohexane dicarboyxlate) (PCCD)

The inherent viscosity was found to be 1.3 dL/g (phenol/TCE 60/40 w/w). The number average molecular weight was found to be 72,900 and the weight average molecular weight to be 2,17,600 with a polydispersity of 2.9.

The ^{1}H and ^{13}C NMR spectra are shown in **Figure 4.32 and 4.33**. The *cis/trans* isomer ratio of cyclohexane dicarboxylate was calculated from H_c proton and ratio is 67/33. The $-OCH_2-$ of CHDM, H_a, splits into a doublet and the *cis/trans* isomer ratio of CHDM in PCCD was 20/80. The carboxyl carbon, C_a, appeared at 174.89 for the *cis*- isomer and at 175.36 for the *trans*- isomer in the ^{13}C-NMR spectrum. The $-CH_2-O-$ carbon, C_c appeared at 66.85 and 69.05 ppm for the *cis*- and *trans*- isomers of CHDM respectively.

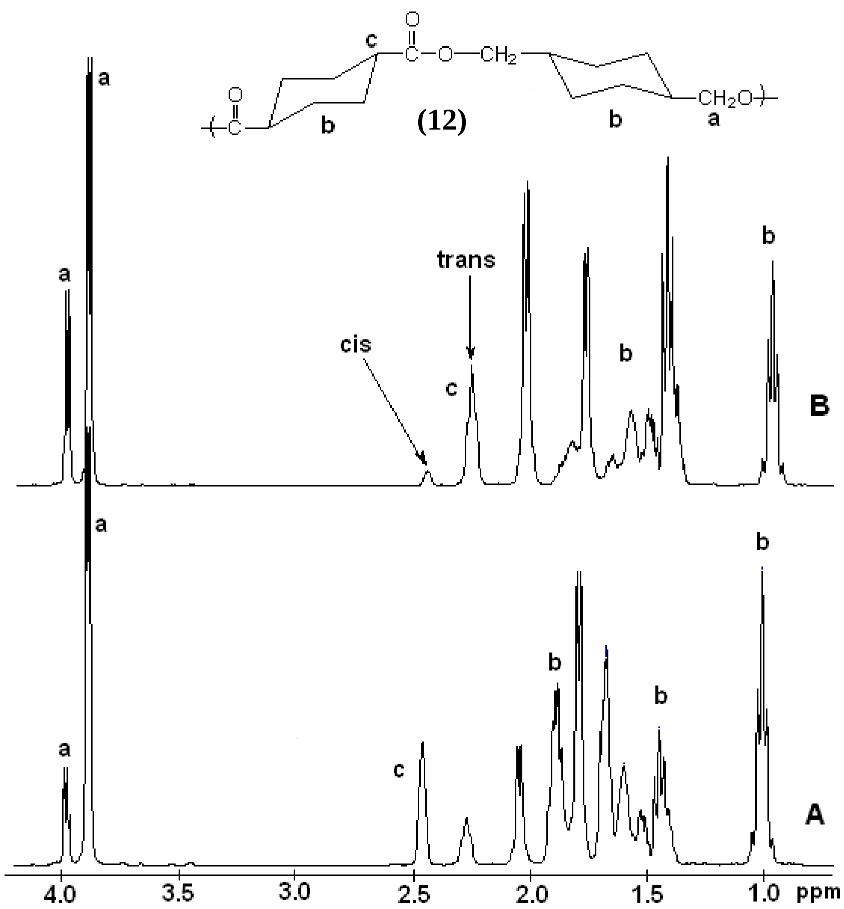


Figure 4.39 ^{1}H NMR specta of poly(cyclohexanedimethylene cyclohexane dicarboxylate) (PCCD) (A) Synthesized (B) Commercial

Commercial PCCD has an η_{inh} of 0.8 dL/g and number average molecular weight of 47,860 and weight average molecular weight of 85,900. The ^{1}H and ^{13}C-NMR spectra of the commercial PCCD are shown in **Figure 4.32 and 4.33**. The *a,e/e,e* isomer ratio was calculated from the H_c peak (**Figure 4.32**) and was found to be 91% *e,e* isomer.

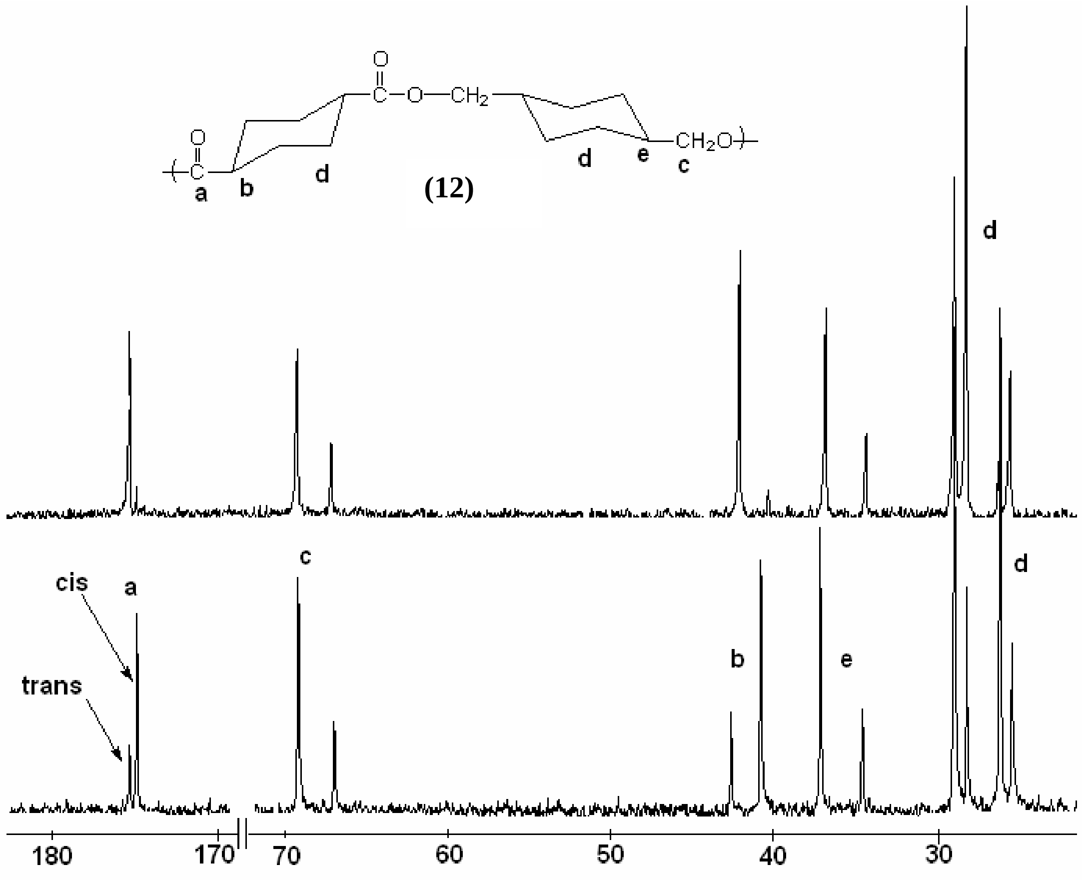


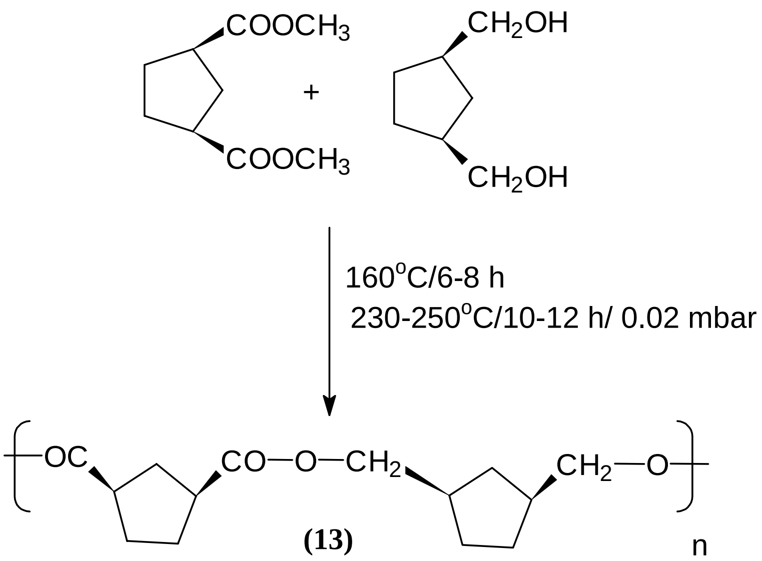
Figure 4.40 ^{13}C NMR spectra of poly(cyclohexanedimethylene cyclohexane dicarboxylate) (PCCD) (A) Synthesized (B) Commercial

4.8.2 Thermal properties

The T_g of PCCD **(12)** synthesized from DMCD containing 67% cis isomer was 50°C and found to be amorphous. The T_g of commercial PCCD containing 91 % trans isomer was 70°C, 20°C higher than the synthesized PCCD containing 67% cis isomer. The melting temperature was 223°C and the crystallization temperature on heating was 116°C as shown in **Figure 3.25**. The melt crystallization temperature T_{mc} (on cooling from melt at 2 °C/min) was 141°C.

4.8.3 Synthesis and structure of poly(cyclopentylenedimethylene cyclopentane dicarboxylate) (PCPCPD) (13)

Cycloaliphatic polyester was synthesized from *cis* and *cis/trans*-CPDE and CPDM by melt condensation using titanium isopropoxide catalyst as depicted in **Scheme 4.9**.



(13)

Scheme 4.9 Synthesis of poly(cyclopentylene dimethylene cyclopentane dicarboyxlate) (PCPCPD)

The molecular weights determined from GPC and viscosity data are given in **Table 4.11**. PCPCPD synthesized from cis/trans-CPDE was insoluble in chloroform. The structure of the polyester was confirmed by ^{1}H NMR and is shown in **Figure 4.35**. The peaks at 3.95, 3.99 were assigned to the OCH_2 peaks.

Table 4.11 Molecular weight, viscosities and T_g of PCPCPD polyester

Polyester	η_{inh} dL/g	M_n	M_w	PD	T_g (°C)
Cis-PCPCPDT	0.50	35,600	1,17,800	3.3	-24
Cis/trans-PCPCPDT		Insoluble			0

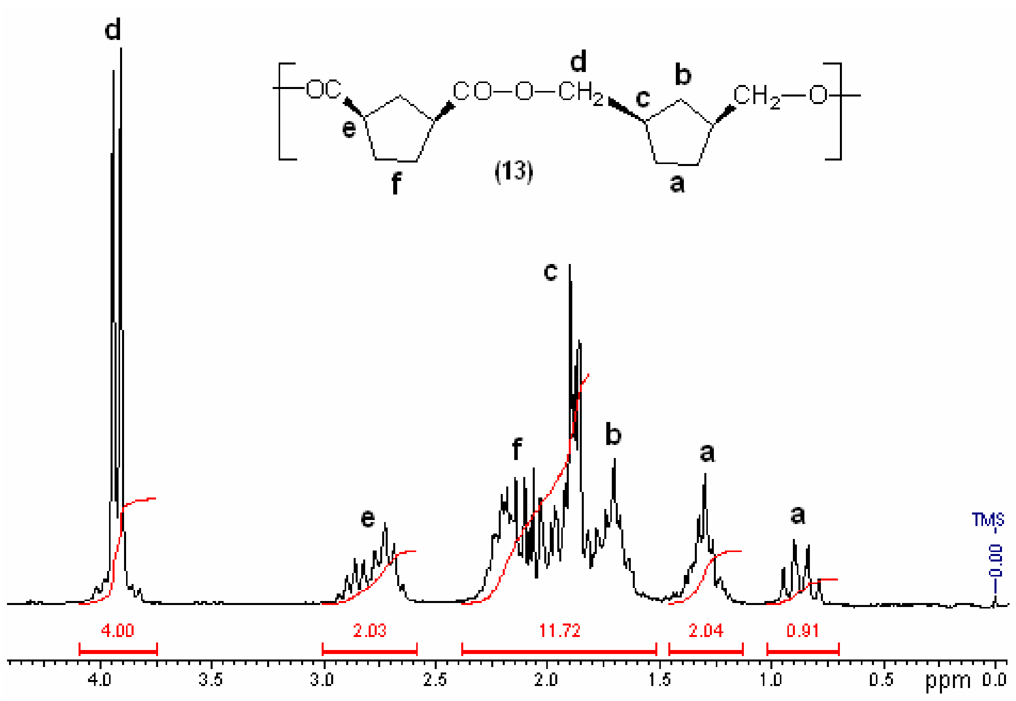


Figure 4.41 ^{1}H NMR spectrum of PCPCPD **(13)**

The polyester synthesized from cis-CPDE was found to be rubbery with a T_g of -24°C while the polyester synthesized from cis/trans-CPDE had a T_g of 0°C.

4.9 Conclusion

PCCD synthesized by melt condensation from DMCD containing 70 % *cis* isomer was found to be amorphous and had a T_g of 50°C, while the commercial PCCD was a semi-crystalline polyester. The aliphatic polyester synthesized from CPDM and *cis*-CPDE was found to be a amorphous polyester with a T_g of -24°C and the polyester synthesized from *cis/trans*-CPDE had a T_g of 0°C. The *cis/trans* isomer ratio of the starting diester governed the thermal and crystallization properties of the polyester. The *trans* isomer yielded the polyester with higher T_g.

4.10 References

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Chapter 5: I. Synthesis and characterization of polyesters and copolyesters containing norbornane ring in the chain

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5.1 Introduction

Rigid thermally stable alicyclic diols are potentially useful comonomers for improving the properties of polyesters. Norbornane ring containing diesters and diols are readily available whose potentials in polymers have not been fully exploited. Wilson et al[1] prepared polyesters from norbornane condensed diesters and dimethanols. Polyesters of norbornane and norbornane condensed diesters and dimethanols have high glass transition temperature (T_g >100°C) and exhibit little tendency to crystallize. The synthesis of copolyesters of PET containing 10-30 % 2,3-norbornane dimethanol have been reported for applications in hollow fibers having good hardness[2]. Copolyesters synthesized from dimethyl-e,e-1,4-cyclohexane dicarboyxlate, dimethyl perhydro-1,4:5,8-dimethano naphthalene-2,3-dicarboxylate and perhydro-1,4:5,8-dimethanonaphthalene-2,3-dimethanol having excellent transparency and T_g >100°C, which are used in optical applications[3].

This chapter discusses the synthesis of copolyesters containing norbornane ring in the chain. Norbornane ring containing diol and diester, namely, 2-exo, 3-endo bis(hydroxymethyl) bicyclo [2.2.1] heptane, dimethyl bicyclo[2.2.1]heptane 2-exo,3-endo dicarboxylate and 2-exo, 3-exo-dimethyl bicyclo[2.2.1]heptane-2-endo,3-endo-dicarboxylic acid dimethyl ester were synthesized by Diels-Alder reaction. Copolyesters of dimethyl terephthalate and 1,4-butanediol containing 2,3-bis(hydroxymethyl)bicyclo[2.2.1] heptane and dimethyl bicyclo[2.2.1] heptane 2,3-dicarboxylate were synthesized by melt polymerization. The copolyesters were characterized by ^{1}H and ^{13}C NMR spectroscopy. The thermal properties were analyzed by DSC and TGA and crystallization behavior by WAXD.

5.2 Experimental

5.2.1 Materials

Dimethyl fumarate, palladium on carbon 5 wt % and 10 wt %, 2-butene-1,4-diol, lithium perchlorate, 2,3-dimethyl maleic anhydride, terephthalic acid 1,4-dimethyl terephthalate (DMT) (99+%), 1,4-butanediol (BD), Titanium(IV) isopropoxide and N-methyl pyrollidone (NMP) were obtained from Sigma-Aldrich Inc, USA. Dicyclopentadiene was obtained from Fluka, Switzerland. Thionyl chloride, ethanol, diethyl ether, toluene, hexane, methanol and ethyl acetate were obtained from s.d. fine- chem. Limited, Mumbai.

5.2.2 Reagents and purification

DMT was recrystallized from methanol. BD was distilled and stored over molecular seives. Terephthaloyl chloride (TPC) was prepared from terephthalic acid (TPA). TPA was refluxed with freshly distilled thionyl chloride and the excess thionyl chloride was distilled out. TPC was recrystallized twice from dry hexane and distilled under vacuum. NMP was stirred overnight over calcium hydride and distilled under vacuum and stored over molecular sieves.

Diethyl ether was kept overnight over calcium chloride, distilled and was refluxed over sodium. The solvent was distilled prior to use. Methanol was stirred over calcium hydride and distilled prior to use. 2,3-dimethyl maleic anhydride was purified by vacuum sublimation under high vacuum.

Cyclopentadiene was obtained by thermal cracking of dicyclopentadiene. 200 mL of paraffin oil was taken in a 250 mL three neck round bottom flask equipped with magnetic stirring bar, addition funnel, a 40 cm long fractionating column wound with asbestos tape, distillation condenser and a receiver flask cooled in ice. The paraffin oil was heated to 180-200°C and dicyclopentadiene was added dropwise under vigorous stirring. Cyclopentadiene distilled out at 40°C and was collected in a flask cooled in an ice bath and used immediately.

5M lithium-perchlorate in diethyl ether solution was prepared as follows: Commercially available lithium perchlorate was dried under high vacuum at 160°C for 24 h. The anhydrous lithium perchlorate (27g) and diethyl ether (50 mL) were cooled in an ice bath separately under N_2 atmosphere and then ice-cold ether was added to $LiClO_4$ through syringe. The dissolution was highly exothermic. The solution was used immediately after preparation.

5.2.3 Synthesis of monomers

5.2.3.1 Synthesis of dimethyl bicyclo[2.2.1]heptane 2-exo,3-endo dicarboxylate (dimethyl 2-exo,3-endo norbornane dicarboxylate) (NBDE)

A 100 mL glass ampoule equipped with a magnetic stirring bar was charged with dimethyl fumarate **(2)** (20 g, 0.139 mol) and freshly distilled cyclopentadiene **(1)** (12 g, 0.182 mol). The ampoule was immersed in liquid nitrogen in a N_2 atmosphere and

vacuum was applied for 30 min. The ampoule was sealed under vacuum and heated at 170-180°C for 18 h with stirring. The ampoule was cooled to room temperature and broken. The reaction mixture was then hydrogenated using Pd on carbon (5 wt %) in ethanol at 80°C and H_2 pressure of 1000 psi. The reaction mixture was filtered several times to remove the Pd on carbon completely and concentrated to give 31 g of the diester. The diester was purified by vacuum distillation to give 11.43 g (40%) of pure diester **(3)**.
b.p. 66°C/0.01 mbar (lit[1].114°C/0.3 mm)
GC Retention time – 6.27 min
IR (neat) – 1733(C=O), 1433, 1297 (C-O), 1185, 1120, 1051cm^{-1}
^{1}H NMR ($CDCl_3$) δ: 1-1.6 (6H, m, CH_2 ring protons), 2.4-2.6 (2H, m, CH ring protons) 2.7 (1H, m, bridgehead CH_2), 3.08 (1H, m, bridgehead CH_2), 3.55, 3.57 (6H, d, OCH_3)
^{13}C NMR ($CDCl_3$) δ: 23.92 (CH_2), 28.44(CH_2), 37.74(CH_2), 39.84 (CH), 41.38(CH), 48.29 (CH), 49.06 (CH), 51.27, 51.42 (OCH_3), 173.38, 174.56 (CO)

5.2.3.2 Synthesis of 2-endo, 3-endo bis(hydroxymethyl) bicyclo [2.2.1]heptane (2-endo, 3-endo norbornane dimethanol) (NBDM)

Cyclopentadiene **(1)** (42.4 g, 0.64 mol), 2-butene-1,4-diol **(5)** (42.5 g, 0.48 mol) and 30 mL ethanol were charged into a 300 mL stainless steel Parr reactor. The reactor was purged three times with N_2 and pressurized with 100 psi N_2 and heated to 175°C and reaction continued for 10 h. The reactor was cooled to room temperature and 0.9 g of 5% Pd on carbon was added to the reaction mixture. The reactor was purged with H_2 and pressurized to 300 psi H_2 pressure and heated to 170°C. The reaction was continued until H_2 absorption ceased. The reaction mixture was filtered several times to remove Pd on carbon and concentrated. The semisolid material obtained was purified by vacuum distillation to get 16.4 g of NBDM. b. p. 90°C/0.09 m bar. The NBDM was further purified by recrystallization from toluene/hexane mixture. m.p. 55-57°C (lit.[4] 57-60°C)
GC - 4.29 min (isothermal at 250°C/10 min).
Elemental analysis found (Calcd.) - C: 69.94 (69.23) H: 10.59 (10.25)
Mass (m/z) – 156, 138, 120, 109, 91, 79(100)
^{1}H NMR ($CDCl_3$) δ: 1.2-1.55 (6H, m, ring CH_2), 2.25 (4H, m, bridegehead CH_2), 3.64(4H, m, CH_2), 3.93 (2H, t, OH)
^{13}C NMR ($CDCl_3$) δ: 22.49 (CH_2), 39.86 (CH_2), 40.50, 42.94 (CH), 61.31 (OCH_2)

5.2.3.3 Synthesis of 2-exo, 3-endo bis(hydroxymethyl) bicyclo [2.2.1] heptane (2-exo,3-endo-NBDM)

A three-neck 500 mL round bottom flask equipped with magnetic stirring bar, addition funnel, reflux condenser and a three-way vacuum adapter was flame dried under vacuum. To lithium aluminum hydride (3.4 g, 0.09 mol) in dry THF (180 mL) was added dimethyl bicyclo[2.2.1]heptane 2-exo, 3-endo dicarboxylate **(3)** (10 g, 0.047 mol) in THF (180 mL) drop wise over 1hr with vigorous stirring. The reaction mixture was heated under reflux in N_2 atmosphere for 24 h, cooled to room temperature and treated successively with 3.4 mL H_2O, 3.4 mL of 15% NaOH and 10.2 mL of H_2O. The precipitate was filtered and the solvent evaporated. The crude yield of 2-exo,3-endo--2,3-bis(hydroxymethyl) bicyclo [2.2.1] heptane (2-exo,3-endo-NBDM) was found to be 11.15 g. The 2-exo,3-endo-NBDM was purified by vacuum distillation to obtain 6.9 g (94 %) of the pure diol. b. p. 100-104°C/ 0.02 mbar.

G C – 5.52 min (150 for 5 min to 250°C at 10°C/min)

Elemental (found) – C: 69.25 (67.28), H: 10.25 (10.72)

Mass- 157, 174, 313 (M^+)

^1H NMR ($CDCl_3$) δ: 1.2-1.8 (8H, m, CH_2 and CH ring protons) 2.01, 2.26 (2H s, bridgehead CH_2), 3.22(2H, t, OCH_2), 3.46 (2H, t, OH)

^{13}C NMR ($CDCl_3$) δ: 22.37, 30.17, 37.45 (CH_2), 38.95, 39.18, 48.9, 50.49(CH), 64.01, 65.74 (OCH_2)

5.2.3.4 Synthesis of 2-exo, 3-exo-dimethyl bicyclo[2.2.1]heptane-2-endo,3-endo-dicarboxylic acid dimethyl ester (DMNBDE)

A two-neck 100 mL round bottom flask equipped with magnetic stirring bar and a vacuum adapter was flame dried under vacuum and 2,3-dimethyl maleic anhydride **(7)** (3.5 g, 0.028 mol) was added and cooled to 0°C. 50 mL 5M LPDE (lithium perchlorate in diethyl ether) was added slowly with syringe under stirring. Stirring was continued till all the anhydride was completely dissolved. The contents of the flask were cooled to 0°C and freshly distilled cyclopentadiene (10 mL, 0.124 mol) was added slowly. The reaction mixture was allowed to stir for 48 hrs, diluted by the addition of DCM followed by addition of water. The organic and aqueous layers were separated and the organic layer was washed several times with water. The organic layer was dried over anhydrous sodium sulphate and evaporated to give 5.9 g of 2-exo-3-exo-dimethyl bicyclo [2.2.1] hept-2-ene-2-endo-3-endo-dicaboxylic anhydride. The anhydride was further washed with cyclohexane to remove unreacted cyclopentadiene to give 4.0 g (75%) of 2-exo-3-exo-dimethyl bicyclo [2.2.1] hept-2-ene-2-endo-3-endo-dicaboxylic anhydride. The anhydride was hydrogenated in ethyl acetate using 10 wt % Pd on C at 700 psi H_2 pressure until H_2 absorption ceased. The reaction mixture was filtered to remove the Pd/C and evaporation of ethyl acetate gave 2.7g (50%) of 2-exo-3-exo-dimethyl bicyclo [2.2.1] heptane-2-endo-3-endo-dicaboxylic anhydride (DMNBDA) **(8)**. m.p. 198-200°C (lit[6]. 198-200°C)

IR (neat)- 2963 (CH_3), 2888, 1850 (anhydride C=O), 1772 (anhydride C=O), 1246, 1219, 980

GC - 7.68 min (150 for 5 min to 250°C at 10°C/min)

Elemental (found) – C: 68.04 (68.34), H: 7.2 (7.89)

Mass- 195, 167, 149 (M^+), 130

^1H NMR ($CDCl_3$/) δ: 1.32 (6H, s, OCH_3), 1.4-1.93 (6H, m, ring protons), 2.38 (2H, m, bridehead CH_2)

^{13}C NMR ($CDCl_3$) δ: 17.82 (CH_3), 25.39, 37.63, 48.59 (CH_2), 56.89 (CH), 175.73 (CO)

DMNBDA **(8)** (1.5 g, 7 mmol) and 40 mL of dry methanol were taken in a 100 mL round bottom flask equipped with a magnetic stirring bar and a reflux condenser. Thionyl chloride (5 mL) was added slowly under cooling through syringe with rapid stirring. After the addition was complete the reaction mixture was refluxed for 96 hrs. The reaction mixture was cooled to room temperature and DCM was added and washed with water, sodium bicarbonate and again water, the organic layer dried over anhydrous sodium sulphate and evaporated to give a mixture of DMNBDA and DMNBDE **(9)**. The mixture of anydride was difficult to separate. The mixture was heated in dilute bicarbonate solution when the anhydride dissolved and on cooling the ester crystals were obtained. This was done several times to get pure DMNBDE. The final yield of DMBNDE is 1.4 g (76 %). m.p. 52-55°C (lit.[6] 57-59°C)

IR (neat) – 2950 (CH_3), 2883, 1733 (C=O ester), 1536, 1438, 1250, 1119 cm^{-1}

GC - 6.45 min (150 for 5 min to 250°C at 10°C/min)

^1H NMR ($CDCl_3$) δ: 1.29 (1H, m, CH_3), 1.29 (6H, s, ring CH_2), 1.35-1.5 (2H, m, CH), 1.5-1.95 (3H, m,), 2.13 (2H, m, bridgehead CH_2), 3.62 (6H, s, OCH_3)

^{13}C NMR ($CDCl_3$) δ: 22.34 (CH_3), 25.03, 35.71, 48.92 (CH_2), 51.09(OCH_3), 55.09 (CH), 175.94 (CO)

5.2.4 Synthesis of polyester and copolyesters containing *2-endo,3-endo*-NBDM (6)

5.2.4.1 Synthesis of poly (2,3-norbornane dimethylene terephthalate) (PNBDT) (10)

5.2.4.1.1 Melt condensation

DMT (2.5 g, 0.013 mol), *2-endo,3-endo*--2,3-bis(hydroxymethyl) bicyclo[2.2.1]heptane (NBDM) **(6)** (3.01 g, 0.019 mol) and titanium isopropoxide (0.1 wt % w.r.t DMT) were taken in a two neck round bottom flask equipped with a magnetic stirring bar, N_2 inlet, air condenser and spiral trap to collect distillate. The flask was heated to 170°C under N_2 atmosphere when methanol distilled out. The reaction was continued at 160-180°C for 2 h and further at 220°C for 4h and the pressure was gradually reduced over 30 min to 0.02 mbar and reaction was continued for 2 h at 240°C. Polymerization reaction did not proceed and the reaction mixture underwent charring.

5.2.4.1.2 Solution polycondensation of terephthaloyl chloride and norbornane dimethanol

2-endo,3-endo--NBDM **(6)** (2.56 g, 10 mmol) and 5 mL of NMP were taken in a 50 mL two neck round bottom flask equipped with a N_2 inlet and magnetic stirring bar. The reaction flask was kept under a constant stream of N_2 with stirring till the NBDM completely dissolved in NMP. Terephthaloyl chloride (2 g, 10 mmol) was dissolved in 5 mL of NMP and added to the flask. The reaction mixture was stirred at room temperature. When no more heat was generated and the contents began to solidify, the reaction mixture was heated at 180°C for 2 h. The reaction flask was cooled and precipitated in methanol. The polymer was filtered, washed several times with methanol to remove the trapped NMP and dried at 100°C. Yield = 2.6 g (92 %).

η_{inh} (chloroform) – 0.2 dL/g

GPC ($CHCl_3$) - M_n = 6,700 M_w = 14, 900 (M_w/M_n - 2.2)

^1H NMR ($CDCl_3$) δ: 1.52 (6H,m,), 2.44, 2.53 (4H, m,) 4.49 (4H, m,), 8.05 (4H, s,)

5.2.4.1.3 Solid state polymerization

The PNBDT **(10)** oligomer (0.2 dL/g) was dried in vacuum oven. The oligomer was powdered and suspended in toluene, 0.01 wt % titanium isopropoxide in toluene was added. The toluene was stripped off at reduced pressure. The dried oligomer powder was subjected to solid state polymerization at 150°C for 6 h under reduced pressure (0.02 mbar). There was no change in viscosity after SSP.

5.2.4.2 Synthesis of copolyester from dimethyl terephthalate, 1,4-butanediol and 2-endo, 3-endo norbornane dimethanol

5.2.4.2.1 Melt condensation of DMT, BD and 2-endo, 3-endo norbornane dimethanol

DMT (5.0 g, 0.026 mol), BD (2.06 g, 0.023 mol), (2-endo, 3-endo norbornane dimethanol) (NBDM) **(6)** (1.14 g, 9 mmol) and DBTO (0.05 wt % w.r.t DMT) were taken in a two neck round bottom flask equipped with a magnetic stirring bar, N_2 inlet, air condenser and spiral trap to collect distillate. The flask was flushed with N_2 and heated to 167°C under a constant stream of N_2 when methanol distillation started. Reaction was continued at 160-200°C for 6 h and at 220°C for 2h and the pressure was gradually reduced to 0.02 mbar and reaction was continued for 2 h at 230°C. The reaction flask was cooled under vacuum and the polymer was recovered. Yield = 5.4 g (83 %).

η_{inh} (chloroform)- 0.16 dL/g

1H NMR ($CDCl_3$) δ: 1.54 (4H, m, ring CH_2), 2.02 (4H, s, CH_2), 2.4-2.7 (6H, m, ring protons), 4.02 (4H, s, OCH_2 of NBDM), 4.5 (4H, s, OCH_2 of BD), 8.12 (8H, d, aromatic)

5.2.4.2.2 Melt condensation of poly(BT-co-NBDT) oligomer, DMT and BD

DMT (2.5g, 0.013 mol), BD (1.87 g, 0.02 mol), PNBDT oligomer (1 g) and titanium isopropoxide (0.1 wt % w.r.t DMT) were taken in a two neck round bottom flask equipped with a magnetic stirring bar, N_2 inlet, air condenser and spiral trap. The flask was purged with N_2 and heated to 190°C and reaction was continued for 7 h. The pressure was gradually reduced to 0.02 mbar and reaction continued at 250-260°C for 3 h. The flask was cooled under vacuum and polymer was recovered. Yield = 3.6 g.

η_{inh} (chloroform)- 0.5 dL/g

^{1}H NMR ($CDCl_3/CF_3COOD$) δ: 2.02 (4H, s, CH_2), 4.50 (4H, s, $C\underline{H}_2O$) 8.12 (4H, s, aromatic protons)

5.2.4.3 Synthesis of poly(2,3-norbornane dimethylene terephthalate) (PNBDT)

DMT (2.5 g, 0.013 mol), 2-exo, 3-endo bis(hydroxymethyl) bicyclo [2.2.1] heptane (norbornane dimethanol) (NBDM) **(4)** (2.15 g, 0.014 mol) and titanium isopropoxide (0.1 wt % w.r.t DMT) were taken in a two neck round bottom flask equipped with a magnetic stirring bar, N_2 inlet, air condenser and spiral trap. The flask was heated to 160°C under of N_2 atmosphere when methanol distilled out. The reaction was continued at 160-180°C for 3 h and further at 220°C for 4 h and the pressure was gradually reduced over 30 min to 0.02 mbar and reaction was continued for 6 h at 230°C. The reaction flask was cooled under vacuum and the polymer was recovered. Yield = 3.54 g (96 %).

η_{inh} (phenol/TCE 60/40 w/w)- 0.33 dL/g

GPC ($CHCl_3$) - M_n = 18,300, M_w = 32,800 (M_w/M_n = 1.8)

^{1}H NMR ($CDCl_3$) δ: 1.1-1.8 (8H, m, ring protons) 2.27, 2.42 (2H, d, bridgehead), 4.23, 4.43 (4H, m, OCH_2), 8.10 (4H, s, aromatic)

^{13}C NMR - 22.15, 29.55, 36.82, 38.33, 39.18(CH_2), 43.43, 45.38 (CH), 66.91, 68.51 (OCH_2), 129.7, 133.82 (aromatic), 166.71, 166.74 (CO)

5.2.4.4 Synthesis of copolyesters containing dimethyl terephthalate, 1,4-butanediol and 2-exo, 3-endo bis(hydroxymethyl) bicyclo [2.2.1] heptane (norbornane dimethanol) (NBDM)

DMT, 1,4-BD, *2-exo,3-endo-bis(hydroxymethyl) bicyclo [2.2.1] heptane*-NBDM **(4)** and titanium isopropoxide (0.1 wt % w.r.t DMT) were taken in a two neck round bottom flask equipped with magnetic stirring bar, N_2 inlet, short path vacuum distillation adapter, spiral trap and a vacuum control assembly. A 1:1.15 ratio of DMT to diol was used in all polymerization and BD/NBDM ratio was varied (90/10, 80/20 and 50/50). The reaction was carried out at 160-220°C for 6-8 h. The pressure was gradually reduced to 0.02 mbar over 20 min and reaction continued at 230-250°C for 10-11 h. The flask was cooled under vacuum and polymer was recovered.

5.2.5 Synthesis of polyester and copolyesters containing dimethyl 2-exo, 3-endo norbornane dicarboxylate (NBDE)

5.2.5.1 Synthesis of poly (butylene-2,3-norbornane dicarboxylate) (PBNB)

NBDE **(3)** (2.12 g, 0.01 mol), BD (1.89 g. 0.02 mol) and titanium isopropoxide (0.1 wt % w.r.t NBDE) were taken in a two neck round bottom flask equipped with magnetic stirring bar, N_2 gas inlet, air condenser and spiral trap. The reaction mixture was heated at 160-180°C for 3 h when methanol distilled out and the reaction was continued at 210-260°C for 5 h. The pressure was gradually reduced to 0.02 mbar and reaction continued at 260°C for 4 h. The flask was cooled under vacuum. The polymer was found to be rubbery. Yield = 2.1 (92 %) g.

η_{inh} ($CHCl_3$) - 0.6 dL/g

GPC ($CHCl_3$) - M_n = 37,000 M_w = 98,800 (M_w/M_n = 2.6)

^1H NMR ($CDCl_3$) δ: 4.11 (4H, m, OCH_2), 3.22 (1H, m, CH), 2.82 (1H, m, CH)) 2.64, 2.56 (1H, m, bridgehead), 1.71 (4H, m, CH_2), 1.2-1.65 (6H, m, ring protons)

^{13}C NMR ($CDCl_3$)- 24.11, 25.27, 28.78, 37.93, 40.13, 41.75(CH_2), 48.62, 49.29 (CH-CO), 63.88, 64.0 (OCH_2), 173.2, 174.39 (CO)

5.2.5.2 Synthesis of poly (butylene terephthalate-co-butylene-2,3-norbornane dicarboxylate) (P(BT-co-BNB))

DMT, NBDE, BD and titanium isopropoxide (0.1 wt % w.r.t ester) were taken in a two neck round bottom flask equipped with magnetic stirring bar, N_2 inlet, short path vacuum distillation adapter and a spiral trap. A 1:1.5 ratio of diester to diol was used in all the polymerization reactions and DMT/NBDE ratio was varied (90/10, 80/20, 70/30 and 50/50). The reaction mixture was heated at 160-220°C for 6-8 h under a constant stream of N_2 gas. The pressure was gradually reduced over 1h to 0.02 mbar, as the excess butanediol distilled out and reaction was continued at 230-250°C for 10-12 h. The flask was cooled under vacuum and polymer was recovered by breaking and cutting into pieces. The viscosity and thermal properties of the copolyesters are given in the results and discussion section.

5.2.6 Synthesis of poly (butylene-2,3-dimethyl-2,3-norbornane dicarboxylate

DMNBDE **(9)** (1.0 g, 4 mmol), BD (0.6 g, 6.6 mmol) and titanium isopropoxide (0.1 wt % w.r.t DMNBDE) were taken in a two neck round bottom flask equipped with magnetic stirring bar, N_2 gas inlet, air condenser and spiral trap. The reaction mixture was heated at 160-180°C for 3 h and the reaction was continued at 210-260°C for 4 h. The reaction did not proceed. ^1H NMR shows same spectrum as that of DMNBDE.

5.3 Analysis

5.3.1 Monomer Characterization

^1H and ^{13}C NMR were recorded in $CDCl_3$ or DMSO-d_6 on a Bruker AC-200 NMR spectrometer. The IR spectrums were recorded as neat or in chloroform on FTIR 16 PC Perkin Elmer spectrophotometer. Elemental analysis was done on CHNS-O, EA1108-Elemental Anlyser, Carlo-Erba Instruments, Italy. Gas chromatography was done using a BP1 Column. The temperature program used was: Oven - 150°C (5 min) to 250°C at 10°C/min, injector - 260°C and detector 270°C.

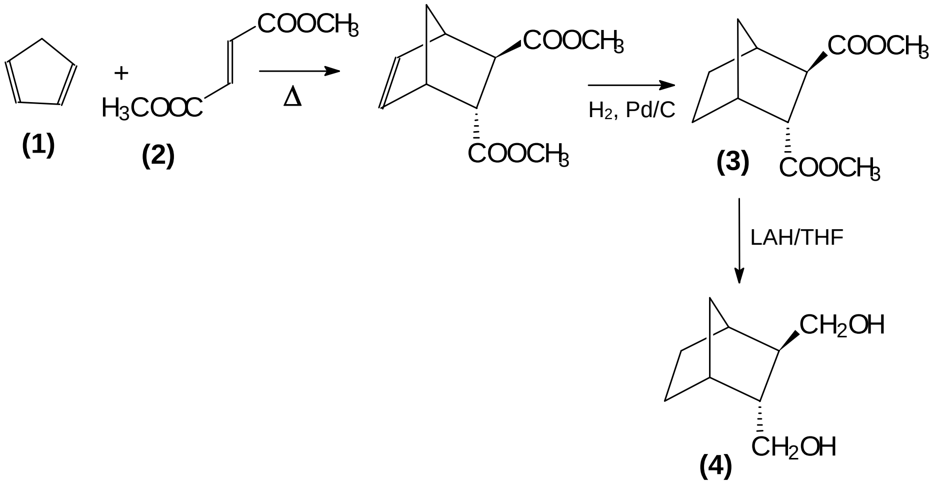
5.3.2 Polymer characterization

Inherent viscosities were measured at 30°C in an automated Schott Gerate AVS 24 viscometer, using an Ubbelohde suspended level viscometer in phenol/1,1’,2,2’-tetrachloroethane (TCE) (60:40 wt/wt) or $CHCl_3$ at a polymer concentration of 0.5 wt%. Other characterizations are discussed in Chapter 3.

5.4 Results and discussion

5.4.1 Monomer synthesis

Dimethyl bicyclo[2.2.1]heptane 2-exo, 3-endo dicarboxylate (NBDE) **(3)** was synthesized by Diels Alder reaction[1]. The first step is reaction of cyclopentadiene **(1)** with dimethyl fumarate **(2)** and subsequent reduction using palladium-on-carbon as catalyst which leads to the formation of dimethyl bicyclo[2.2.1]heptane2-exo, 3-endo dicarboxylate **(3).** 2-exo, 3-endo -bis(hydroxymethyl) bicyclo [2.2.1] heptane **(4)** was synthesized from NBDE by LAH reduction. The synthetic scheme is illustrated in **Scheme 5.1** and the 1H and 13C NMR is shown in **Figures 5.1** and **5.2**.



Scheme 5.1 Synthesis of dimethyl bicyclo[2.2.1]heptane-2-exo,3-endo-dicarboxylate (NBDE) and 2-exo,3-endo-bis(hydroxymethyl) bicyclo [2.2.1] heptane (2-exo,3-endo-NBDM)

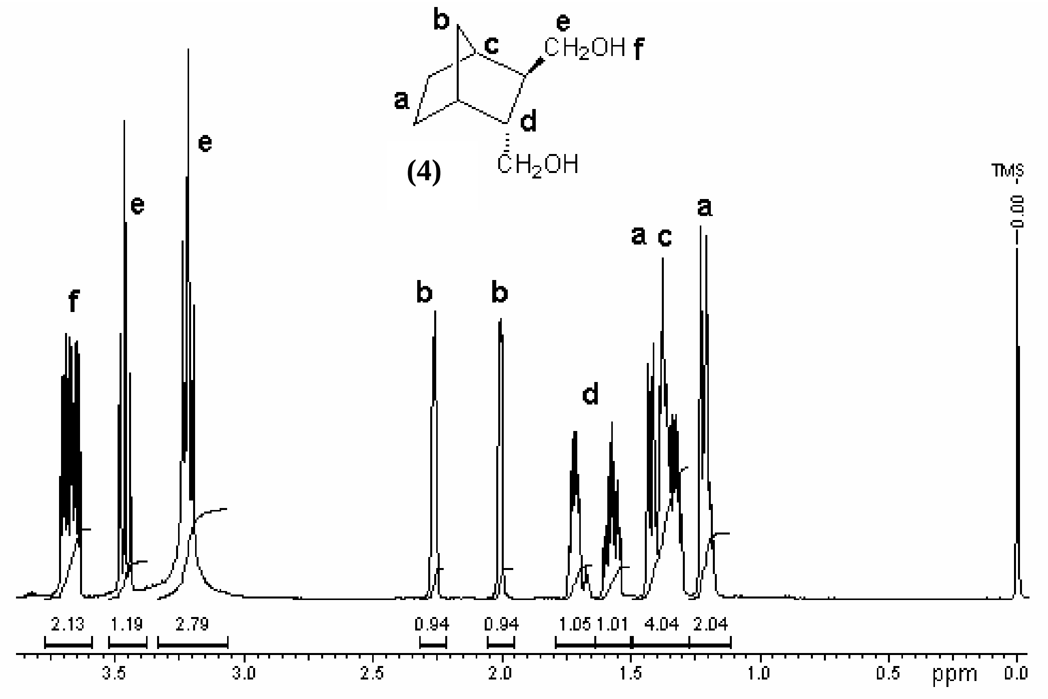


Figure 5.1 ^{1}H NMR spectrum of 2-exo,3-endo-bis(hydroxymethyl) bicyclo [2.2.1] heptane (2-exo,3-endo-NBDM)

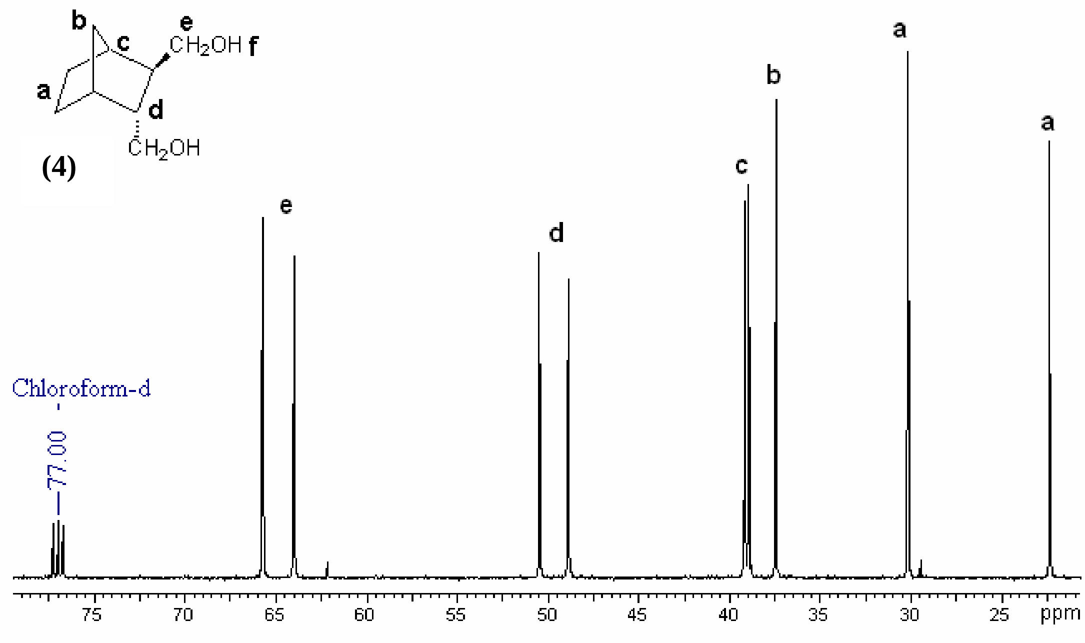
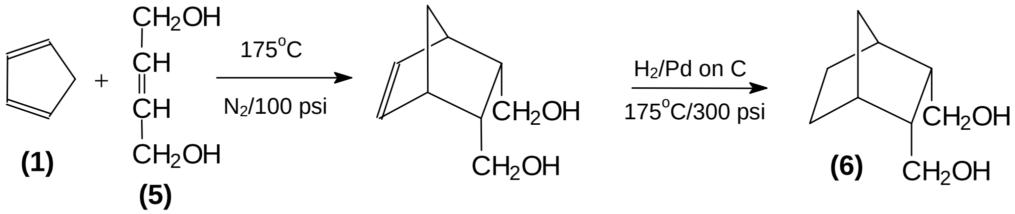


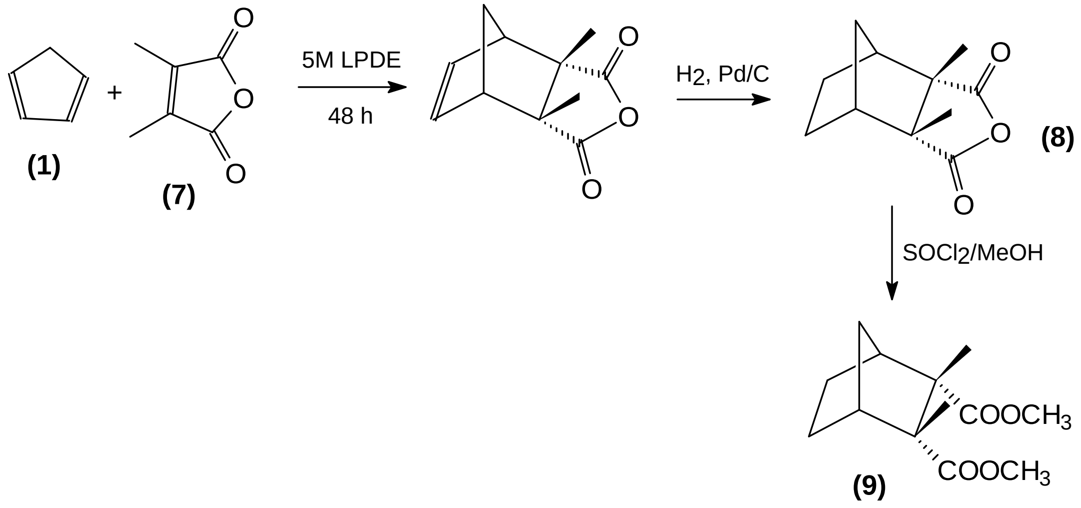
Figure 5.2 ^{13}C NMR spectrum of 2-exo, 3-endo-bis(hydroxymethyl) bicyclo [2.2.1] heptane (2-exo,3-endo-NBDM)

Literature describes a one pot synthesis of 2-endo,3-endo-bis(hydroxy methyl)bicyclo[2,2,1] heptane **(6)** starting from 2-butene-1,4-diol **(5)**, which is a weak dienophile[4]. Hence the reaction was done under pressure, which lead to the formation of the *endo-endo* isomer. The Diels-Alder reaction of cyclopentadiene **(1)** with *cis*-2-butene-1,4-diol was done under nitrogen pressure followed by reduction with Pd on C to give the 2-endo,3-endo bis(hydroxymethyl) bicyclo [2.2.1]heptane **(6)** as given in **Scheme 5.2**.



Scheme 5.2 Synthesis of 2-endo,3-endo-bis(hydroxymethyl) bicyclo [2.2.1]heptane (2-endo,3-endo-NBDM)

Kreiser et al[6] synthesized of 2-exo,3-exo-dimethyl bicyclo[2.2.1]heptane-2-endo,3-endo-dicarboxylic anhydride **(8)** by Diels Alder reaction of cyclopentadiene and dimethyl maleic anydride **(7)** at 90°C for 12 h in benzene with a yield of 55 %. The anhydride was further hydrolyzed using sodium methoxide-dimethyl sulphate to get 2-exo,3-exo-dimethyl bicyclo[2.2.1]heptane-2-endo,3-endo-dicarboxylic acid-dimethyl ester **(9)** with a yield of 82 %. The two methyl groups in dimethyl maleic anydride makes it a weak dienophile which makes Diels Alder reaction sluggish. The synthetic procedure follwed by Kreiser et al[6] is very tedious involving repeated reactions of the reaction mixture with cyclopentadiene **(1)**. The yields and rate of Diels Alder reaction are known to show improvement when 5 M lithium perchlorate in diethyl ether (5M LPDE) solution[5]. The reaction of cyclopentadiene and 2,3-dimethyl maleic anhydride **(7)** was, therefore, performed in 5M LPDE at room temperature followed by subsequent reduction with Pd on carbon gave the norbornane anhydride **(8)** with a yield of 50 %. (**Scheme 5.3**). The anhydride could not be hydrolyzed by the method of Kreiser et al[6]. Hence it was converted to the ester by refluxing with thionyl chloride in presence of methanol which gave a mixture of anhydride and diester **(9)**. The diester was separated from anhydride by dissolving in hexane. Evaporation of hexane gave a white crystalline solid with a yield of 76 %. The separation of the anhydride from the diester was monitored by IR and GC. IR shows carbonyl peak for DMNBDA at 1850, 1830 (doublet) and for ester at 1733 cm^{-1}. GC shows the peak for DMNBDA at 7.68 min and DMNBDE at 6.45 min. The IR specturm of the ester (DMNBDE) (**9**) is shown in **Figure 5.3.** The ^{1}H and ^{13}C NMR of DMNBDE **(9)** is shown in **Figures 5.4** and **5.5**.



Scheme 5.3 Synthesis of 2-exo,3-exo-dimethyl bicyclo[2.2.1]heptane-2-endo,3-endo-dicarboxylic acid-dimethyl ester (DMNBDE)

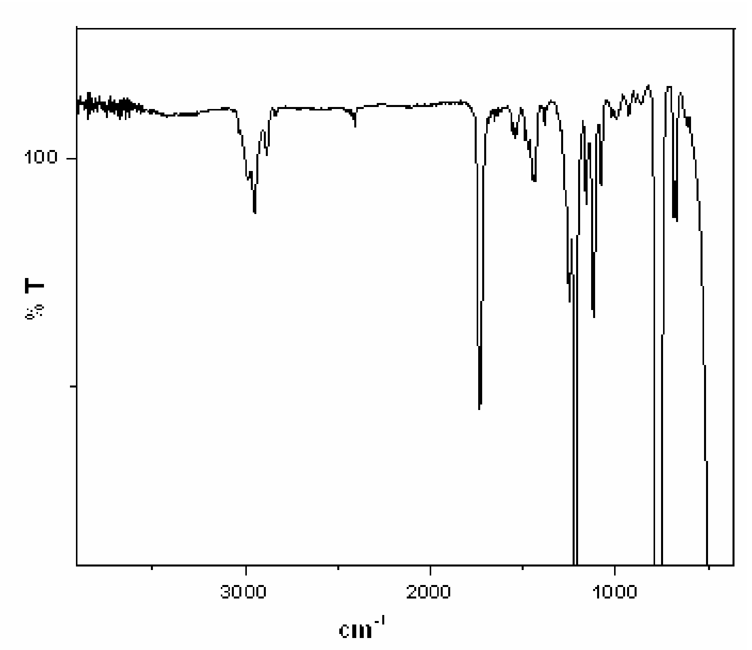


Figure 5.3 IR spectrum of 2-exo,3-exo-dimethyl bicyclo[2.2.1]heptane-2-endo,3-endo-dicarboxylic acid-dimethyl ester (DMNBDE)

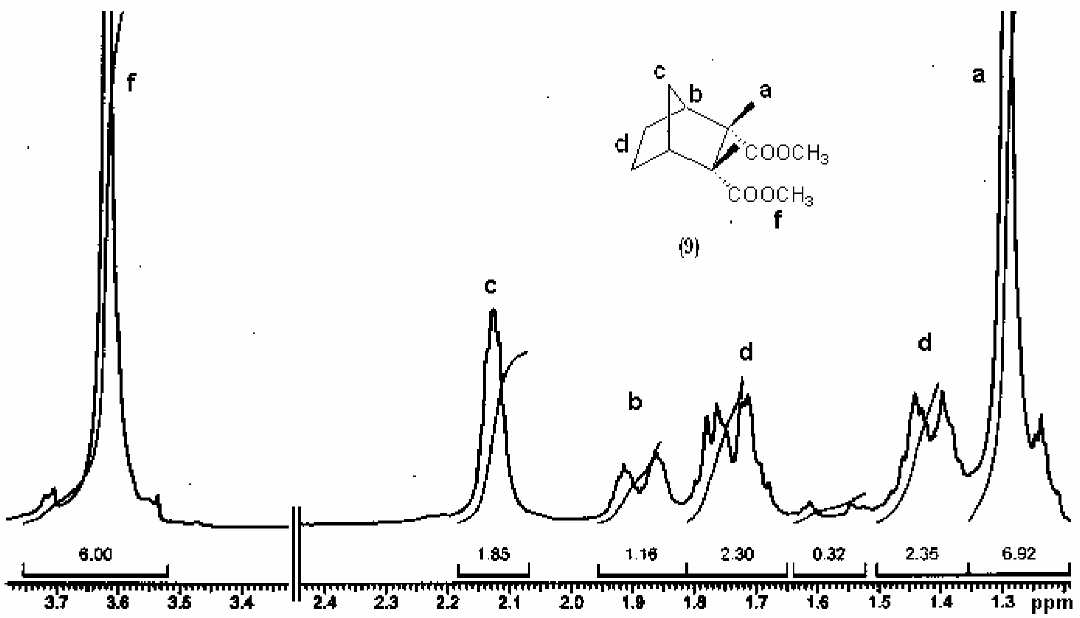


Figure 5.4 ^{1}H NMR spectrum of 2-exo,3-exo-dimethyl bicyclo[2.2.1]heptane-2-endo,3-endo-dicarboxylic acid-dimethyl ester (DMNBDE)

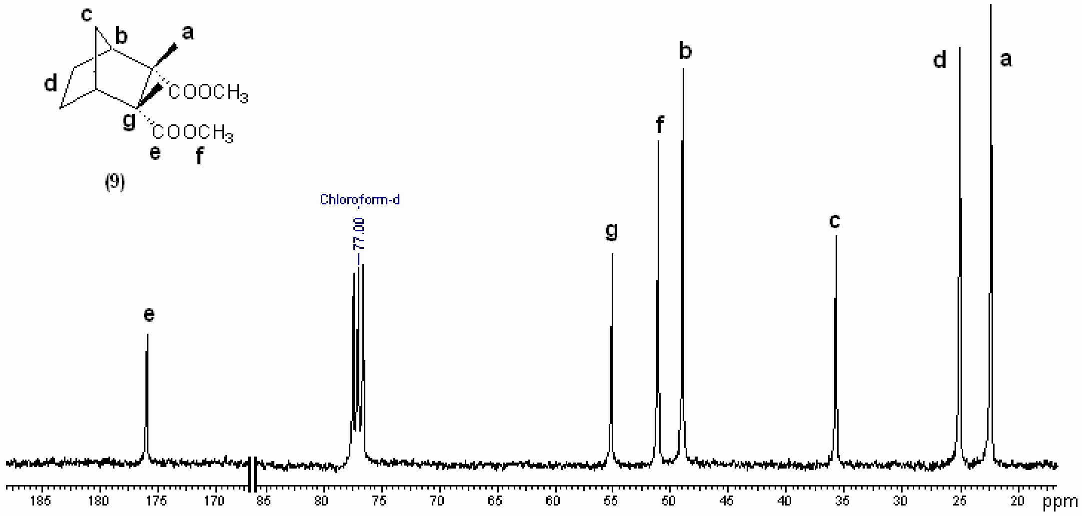
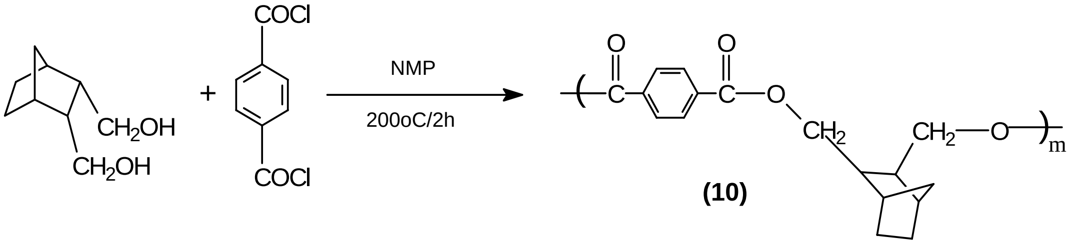


Figure 5.5 ^{13}C NMR spectrum of 2-exo,3-exo-dimethyl bicyclo[2.2.1]heptane-2-endo,3-endo-dicarboxylic acid-dimethyl ester (DMNBDE)

5.4.2 Synthesis and structure of polyester and copolyesters containing NBDM

5.4.2.1 Synthesis of poly (2,3-norbornane dimethylene terephthalate) (PNBDT) and copolyesters from 2-endo,3-endo-NBDM

2-endo,3-end-NBDM **(6)** did not undergo melt polymerization with DMT. High temperature solution polymerization (**Scheme 5.4**) of NBDM with terephthaloyl chloride in NMP at 200°C gave a semicrystalline polymer with an inherent viscosity of 0.2 dL/g. There was no improvement in molecular weight after solid state polymerization.



(10)

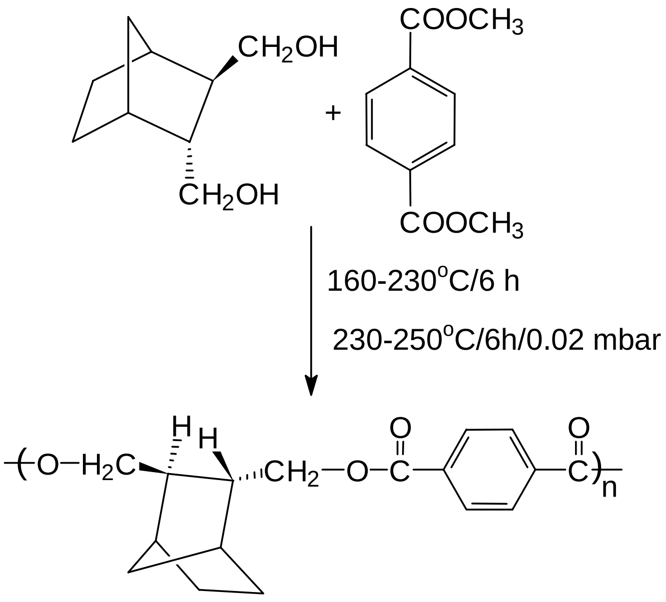
Scheme 5.4 Synthesis of poly (2,3-norbornane dimethylene terephthalate)(PNBDT) from 2-endo,3-endo-NBDM by solution polymerization

Melt copolymerization of DMT, BD and *2-endo,3-endo*--NBDM gave polymer with inherent viscosity of 0.16 dL/g and there was no further increase in molecular weight. Melt condensation of the oligomer (obtained by solution polymerization) with BD and DMT gave the homopolymer, PBT.

5.4.2.2 Synthesis and structure of poly (2, 3-norbornane dimethylene terephthalate) (PNBDT) from 2-exo, 3-endo-NBDM

PNBDT **(11)** was synthesized from 2-exo, 3-endo bis(hydroxymethyl) bicyclo [2.2.1]heptane **(4)** and DMT by melt condensation using titanium isopropoxide catalyst and the synthesis is illustrated in **Scheme 5.5**. The polyester was found to be soluble in chloroform. The inherent viscosity of the polyester was found to be 0.33 dL/g and the number average and weight average molecular weights were found to be 18,300 and 32,700 respectively. There was no improvement in molecular weight by melt and solid state polymerization.

The structure of the polyester was confirmed by ^1H and ^{13}C NMR spectroscopy. **Figure 5.6** shows the ^1H NMR of PNBDT **(11)** along with the assignments for the peaks. The peak at 8.1 is assigned to the terephthalate protons, H_f, and the OCH_2 protons, H_e, appears at 4.2-4.4. ppm



(11)

Scheme 5.5 Synthesis of poly (2,3-norbornane dimethylene terephthalate) (PNBDT)

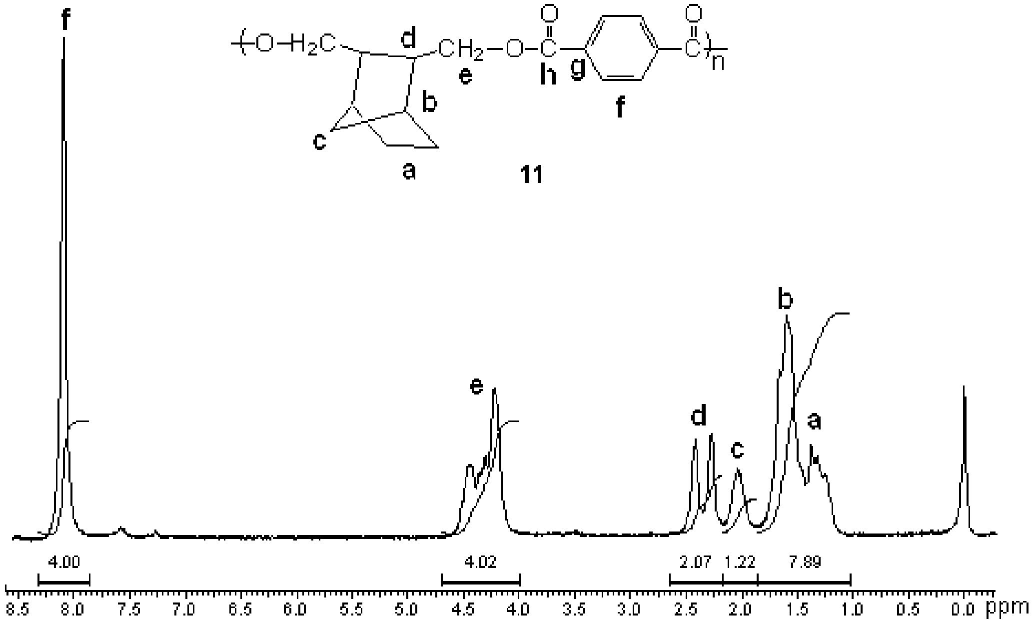


Figure 5.6 ^{1}H NMR spectrum of poly (butylene 2,3- norbornane dimethylene terephthalate) (PNBDT)

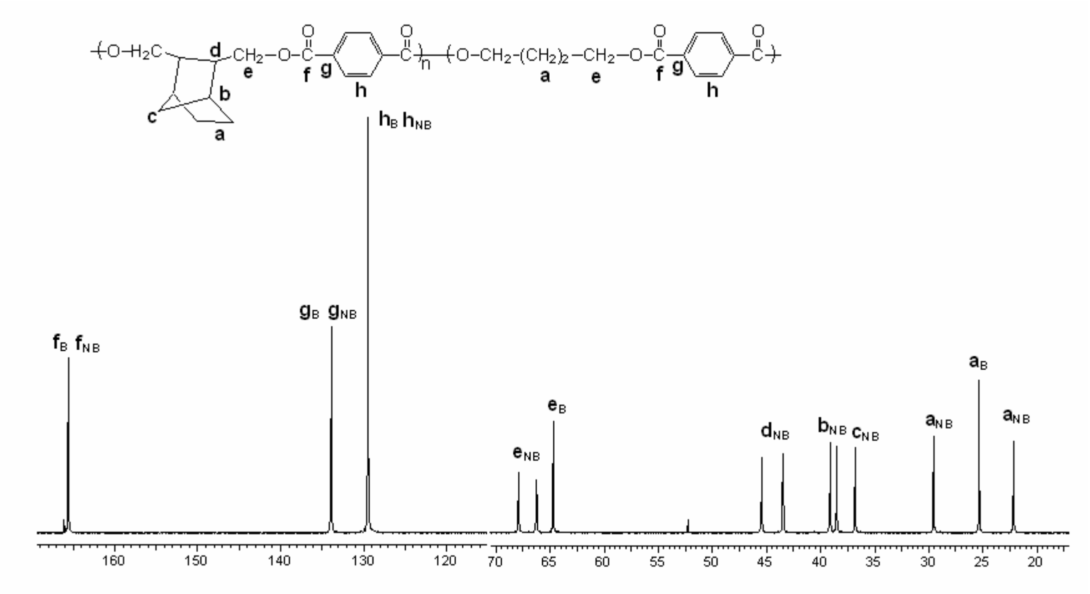


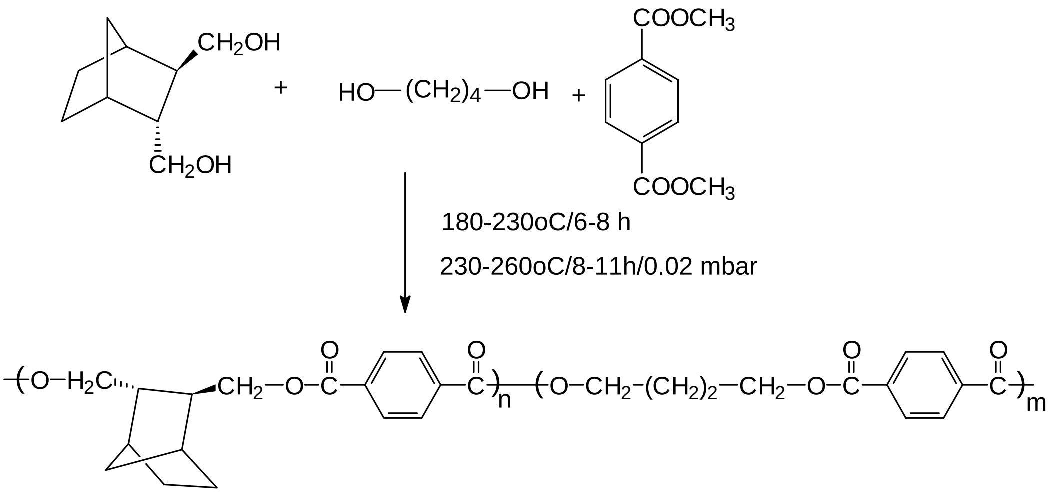
Figure 5.7 ^{13}C NMR spectrum of poly (butylene 2,3- norbornane dimethylene terephthalate) (PNBDT)

The ^{13}C NMR spectrum of PNBDT **(11)** and the peak assignments is shown in **Figure 5.7**. The carbonyl carbon, C_h, appears at 166.71 and 166.74 ppm; the C_e carbons at 68.5 and 66.9 ppm.

5.4.2.3 Synthesis and structure of poly (butylene terephthalate-co-norbornane dimethylene terepthalate) copolyesters (P(BT-co-NBDT))

Copolyesters of dimethyl terephthalate and 1,4-butanediol containing *2-exo,3-endo*-NBDM **(4)** were synthesized by melt condensation (**Scheme 5.6**). A series of copolyesters were synthesized by changing the molar ratio of BD/NBDM (90/10, 80/20 and 50/50). The transesterification reactions were carried out at 180-230°C for 6-8 h followed by polycondensation at 230-260°C for 8-11h. The viscosities of the polyesters were in the range of 0.3-0.4 dL/g.

The structure of the copolyester was confirmed by ^{1}H and ^{13}C NMR spectroscopy. The ^{1}H NMR spectrum of $PBT_{52}NBDT_{48}$ copolymer with assignments for each peak is shown in **Figure 5.8. Table 5.1** gives the peak positions of PBT, PNBDT and $PBT_{55}BCP_{45}$ copolyester. In the ^{1}H NMR spectrum of the P(BT-co-NBDT) **(12)** copolyester, the OCH_2 protons (H_d) is splits into four peaks. The copolyester compositions were calculated from the ^{1}H MNR spectra and are given in **Table 5.2**.



(12)

Scheme 5.6 Synthesis of poly (butylene terephthalate-co-norbornane dimethylene terephthalate) (P(BT-co-NBDT))

Table 5.1 ^{1}H and ^{13}C NMR chemical Shifts (δ in ppm) of PBT, PBNB and poly(BT-co-NBDT) copolyesters

^{1}H Chemical shifts

	$^{B}H_{a}$	$^{B}H_{e}$	$^{B}H_{h}$	$^{NB}H_{a,b}$	$^{NB}H_{c}$	$^{NB}H_{d}$	$^{CP}H_{e}$	$^{NB}H_{g}$
PBT	2.02	4.5	8.12					
PtNBDT				1.1-1.8	2.27	2.42	4.23, 4.43	8.10
$PBT_{55t}NBDT_{45}$	1.97	4.43	8.09	1.2-1.7	2.3	2.4	4.31, 4.22	8.09

^{13}C Chemical Shifts

	$^{T}C_{e}$	$^{T}C_{h}$	$^{T}C_{d}$	$^{T}C_{g}$	$^{NB}C_{d}$	$^{NB}C_{e}$	$^{NB}C_{g,h}$	$^{NB}C_{f}$
PBT	65.9	129.8	133.7	167.6				
$PBT_{55}NBDT_{45}$					45.44, 43.49	67.9, 66.2, 64.7	133.90, 129.44	166.55
PNBDT					43.43, 45.38	66.9, 68.5	133.8, 129.7	166.74, 166.71

An expanded ^{1}H NMR spectrum in the range of 4-5 ppm is shown in **Figure 5.9**, where the four peaks are assigned to BB (4.43 ppm), BNB (4.41ppm), NBB (4.32 ppm) and NBNB (4.22 ppm) diads. The peaks arising due to the BB and BNB diads could not be separated. Hence, the copolyester sequence length and randomness could not be calculated.

Table 5.2 Composition of poly(BT-co-NBDT) copolyesters determined by ^{1}H NMR

Copolyester	Feed composition (mol %)		Copolymer composition[a] (mol %)		η_{inh}[b] dL/g
	BT	NBDT	BT	NBDT	
PBT	100	0	100	0	0.9
$PBT_{91}NBDT_9$	90	10	91	09	0.30
$PBT_{83}NBDT_{17}$	80	20	83	17	0.25
$PBT_{52}NBDT_{48}$	50	50	52	48	0.27
PNBDT	0	100	0	100	0.33

[a]Calculated from 1H NMR; [b]Measured in 60/40 phenol/TCE (w/w) at 30°C;

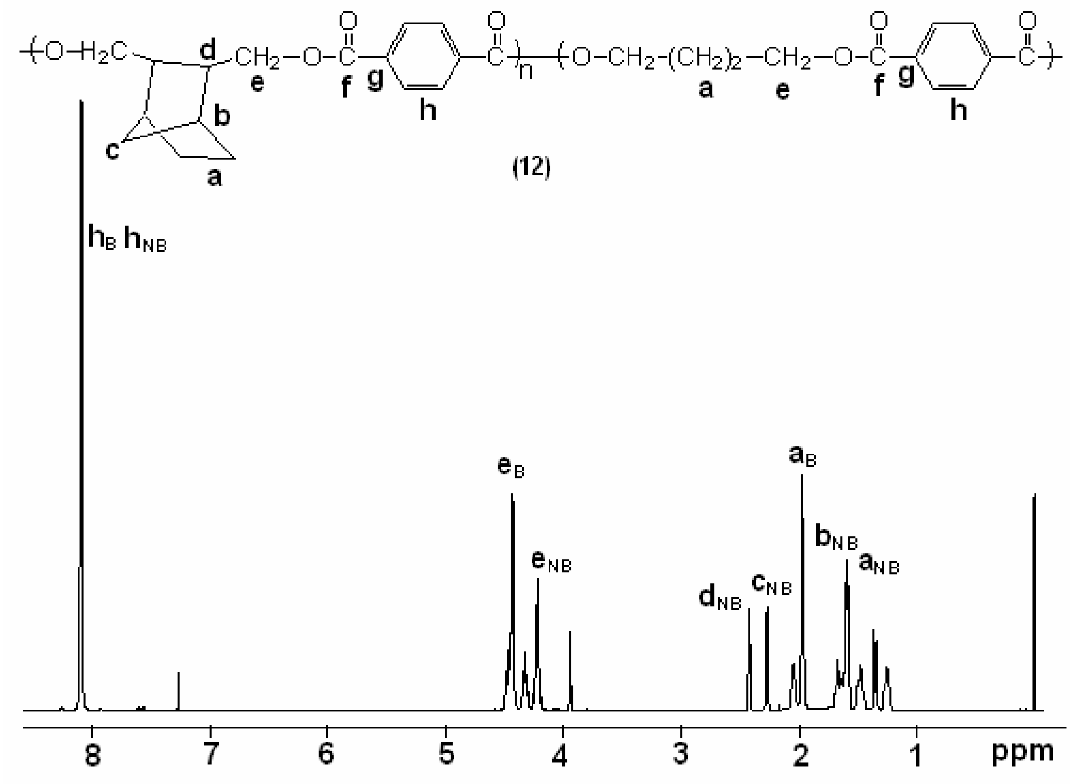


Figure 5.8 ^{1}H NMR spectrum of $PBT_{52}NBDT_{48}$ and its peak assignment

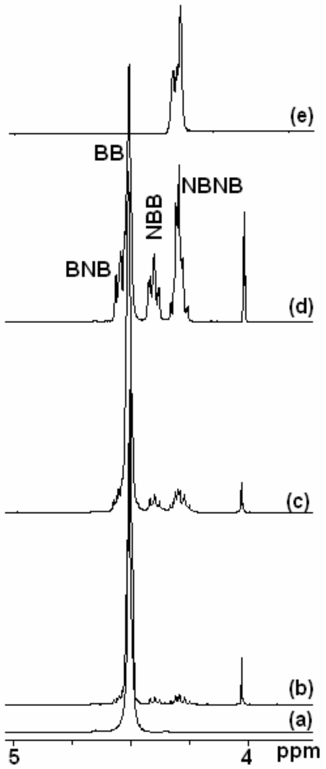


Figure 5.9 ^{1}H NMR spectra in the range of 4.0-5.0 ppm of (a) PBT, (b) PBT$_{91}$NBDT$_{9}$ (c) PBT$_{83}$NBDT$_{17}$ (d) PBT$_{52}$NBDT$_{48}$ (e) PNBDT

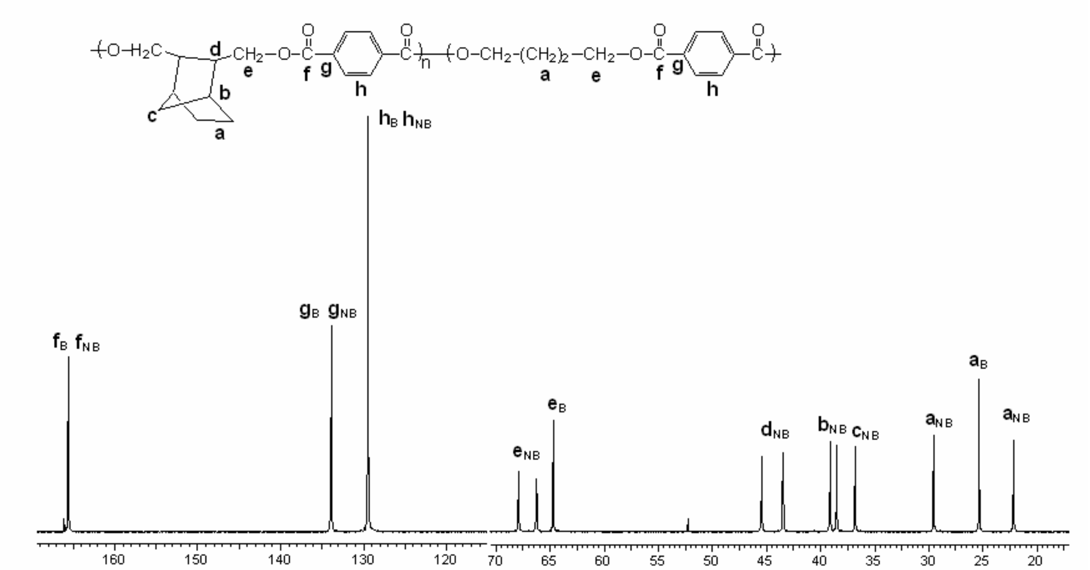


Figure 5.10 ^{13}C NMR spectrum of PBT$_{52}$NBDT$_{48}$

The ^{13}C NMR spectrum of PBT$_{52}$NBDT$_{48}$ is shown in **Figure 5.10**. The quaternary carbon of the terephthalate, C$_g$, appears as a singlet at 133.90 ppm. In the case of the poly(BT-co-NBDT) **(12)** copolyesters the quaternary carbon does not split into four signals as in the case of poly(BT-co-CT) and poly(BT-co-CPDT) copolyesters.

5.4.2.4 Crystallization and melting behavior

PNBDT **(10)** synthesized by solution polymerization exhibits melting endotherm at 214°C on heating in DSC. However it does not crystallize on subsequent cooling or on heating. It appears that the PNBDT underwent solvent induced crystallization during the course of precipitation. The sample shows a T_g of 123°C. On the other hand the polyester synthesized from 2-exo,3-endo--NBDM, namely, PNBDT **(11)** has a T_g of 113°C and is found to be amorphous. The copolyesters were synthesized from 2-exo,3-endo- NBDM. Copolyesters rich in PBT show distinct melting endotherm indicating their ability to crystallize. When the PNBDT composition increases above 20% the copolyesters lose their ability to crystallize. **Figure 5.11** shows the thermograms of the crystallizable samples during heating and subsequent cooling. The melting temperature, heat of fusion, crystallization temperature and the heat of crystallization for the copolyesters are given in **Table 5.3**. The rapid decrease in T_m and T_c is indicative of eutectic crystallization behavior but only a small portion of the range is realized. The T_g on the other hand exhibits a linear change from 40 to 113°C with increase in PNBDT composition.

Table 5.3 Thermal properties of poly(butylene-co-norbornane dimethylene terephthalate) (poly(BT-co-NBDT)) copolyesters

Polyester sample	η_{inh} [a] (dL/g)	T_g (°C)	T_m (°C)	ΔH_m (J/g)	T_{mc} (°C)	ΔH_c (J/g)	IDT[b]
PBT	0.60	40	226	41	193	49	374
$PBT_{91}NBDT_9$	0.30	47	211	36	175	43	385
$PBT_{83}NBDT_{17}$	0.25	58	190	28	143	40	380
$PBT_{52}NBDT_{48}$	0.27	75	Amorphous				380
PNBDT	0.33	113	Amorphous				395

[a] Measured in 60/40 phenol/TCE (w/w) at 30°C; [b] Measured by TGA

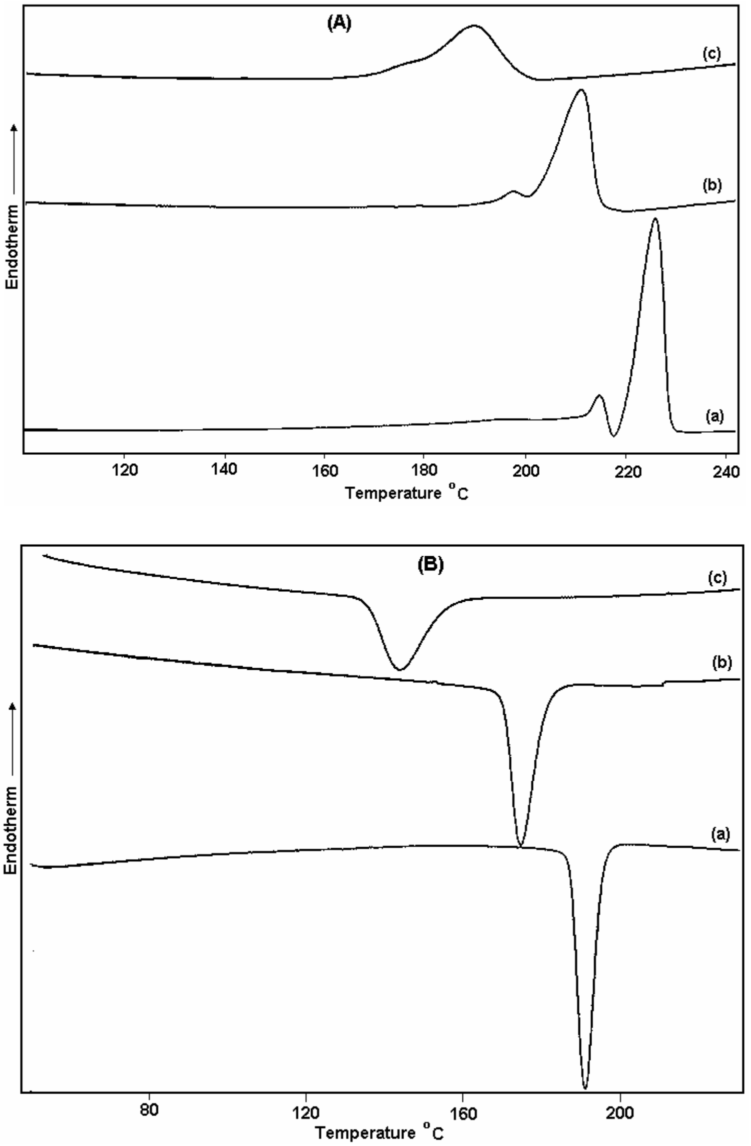


Figure 5.11 DSC heating (A) and cooling (B) thermograms of (a) PBT, (b) $PBT_{91}NBDT_9$ (c) $PBT_{83}NBDT_{17}$copolyesters.

The WAXD patterns (**Figure 5.12)** shows that the copolyesters with PNBDT compositions higher than 20% are amorphous. The copolyesters that crystallize clearly display diffraction pattern similar to that of PBT. The d-spacings of the reflections plotted in **Figure 5.13** show little variation indicating that the copolyesters crystallized in the PBT lattice. Detailed sequence analysis could not be performed on these copolyesters, but based on the results obtained on other copolyesters studied in the chapters 3 and 4, it is assumed that these copolyesters are also random in nature and have similar sequence length. The length of NBDT units were calculated using conjugate gradient and Newton-

Raphson method using Cerius 2 software was 1.22 nm which was 0.034 nm shorter than the BT unit. The compositions crystallized are rich in PBT and have PBT sequence length

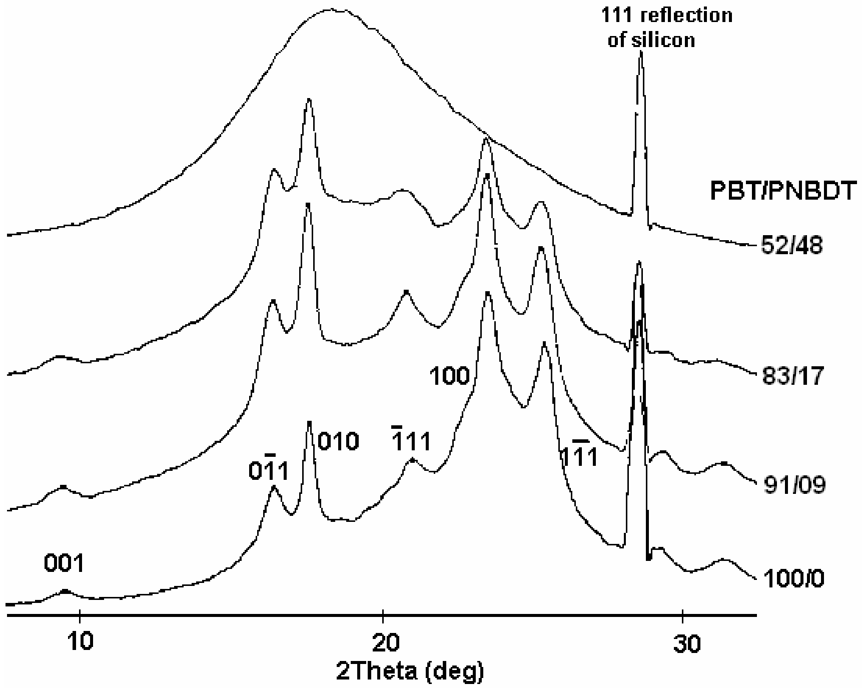


Figure 5.12 WAXD patterns of poly(BT-co-NBDT) copolyesters

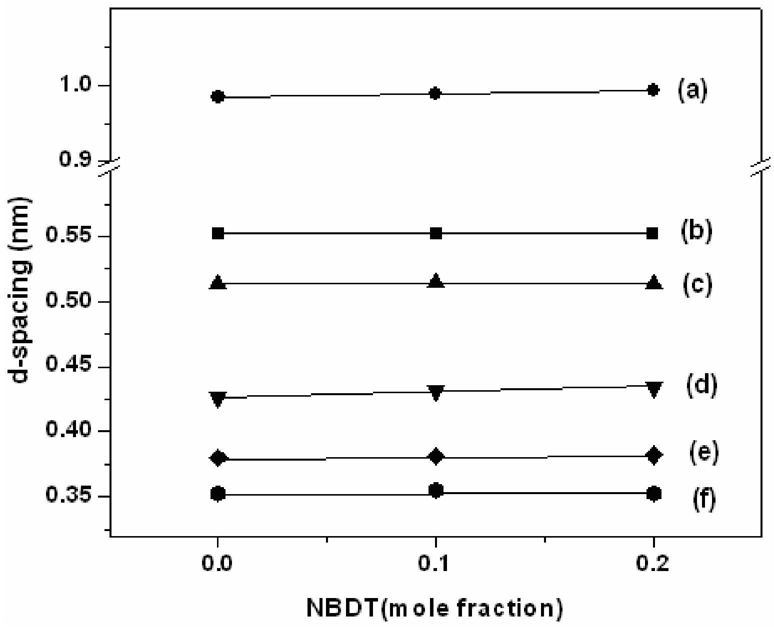


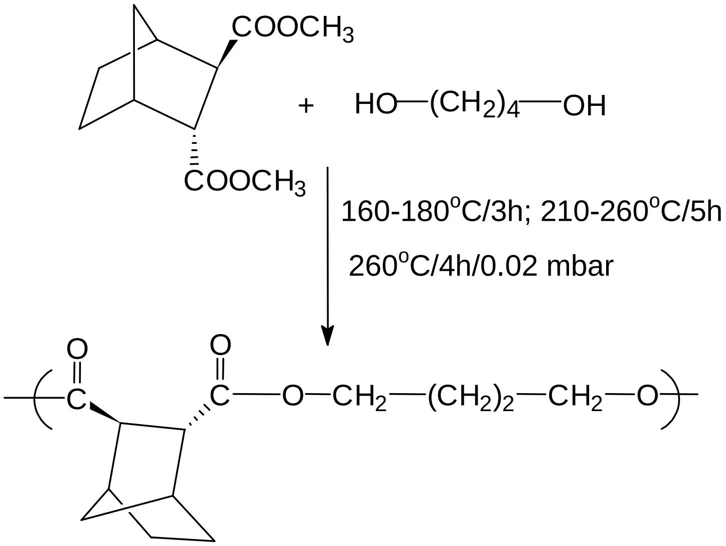
Figure 5. 13 Changes of d-spacings for poly(BT-co-NBDT) copolymers as a function of copolymer composition (a) 001(along chain direction), (b) $0\bar{1}1$, (c) 010, (d) $\bar{1}11$ (e)100 and (f) $1\bar{1}1$ reflections (based on PBT structure)

greater than 3 (Chapter 3 Table 3.3, Table 3.6). Hence, PBT sequence can crystallize with the rejection of PNBDT to the amorphous phase. The compositions in which NBDT composition was more than 25 %, the sequence length was less than 3 and could not crystallize.

5.4.3 Synthesis and characterization of polyester and copolyesters containing NBDE

5.4.3.1 Synthesis and structure of poly (butylene-2,3-norbonane dicarboyxlate) (PBNB)

Poly (butylene-2,3-norbornane dicarboxylate) (PBNB) **(13)** was synthesized from dimethyl bicyclo[2.2.1]heptane 2-exo,3-endo dicarboxylate (NBDE) **(3)** and butanediol by melt condensation. The synthetic scheme is illustrated in **Scheme 5.7**. The transesterification reaction was carried out at 160-180°C for 3 h and polycondensation at 210-260°C for 5 h. The polyester was found to be rubbery. The inherent viscosity was found to be 0.6 dL/g and the number average and weight average molecular weights were found to be 37, 000 and 98,800 respectively, with polydispersity 2.65.



(13)

Scheme 5.7 Synthesis of poly (butylene-2,3-norbornane dicarboyxlate) (PBNB)

The structure of the polyester was confirmed by ^{1}H and ^{13}C NMR spectra.

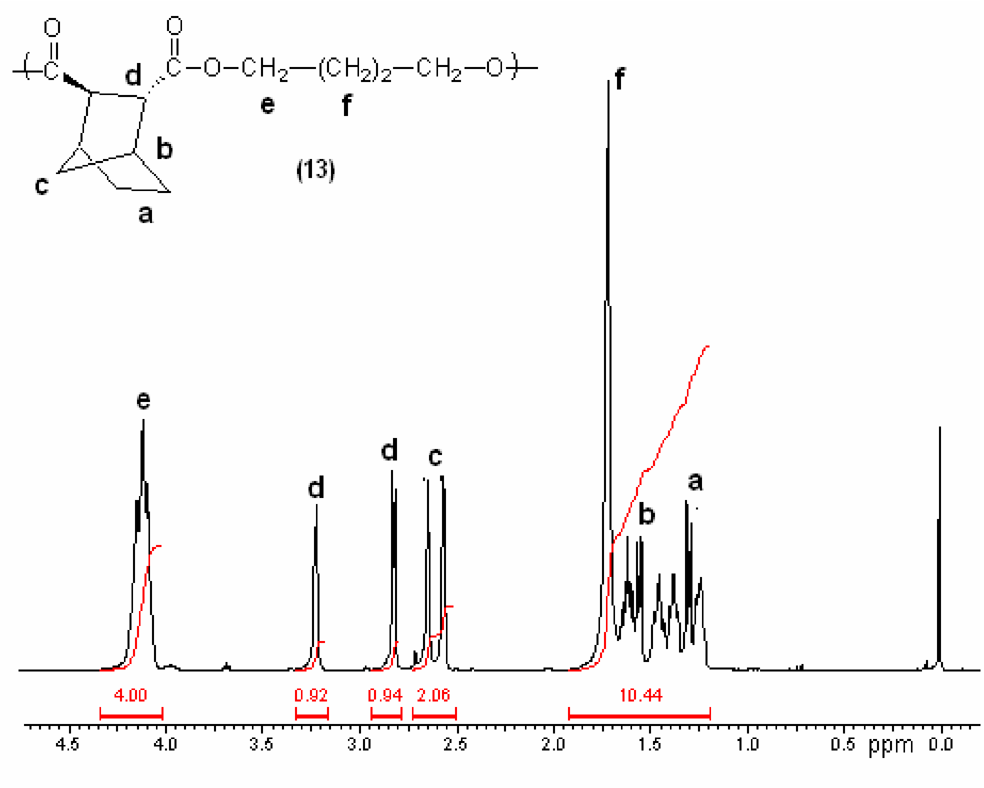


Figure 5.14 ^{1}H NMR spectrum with peak assignments of poly (butylene norbornane dicarboyxlate) (PBNB)

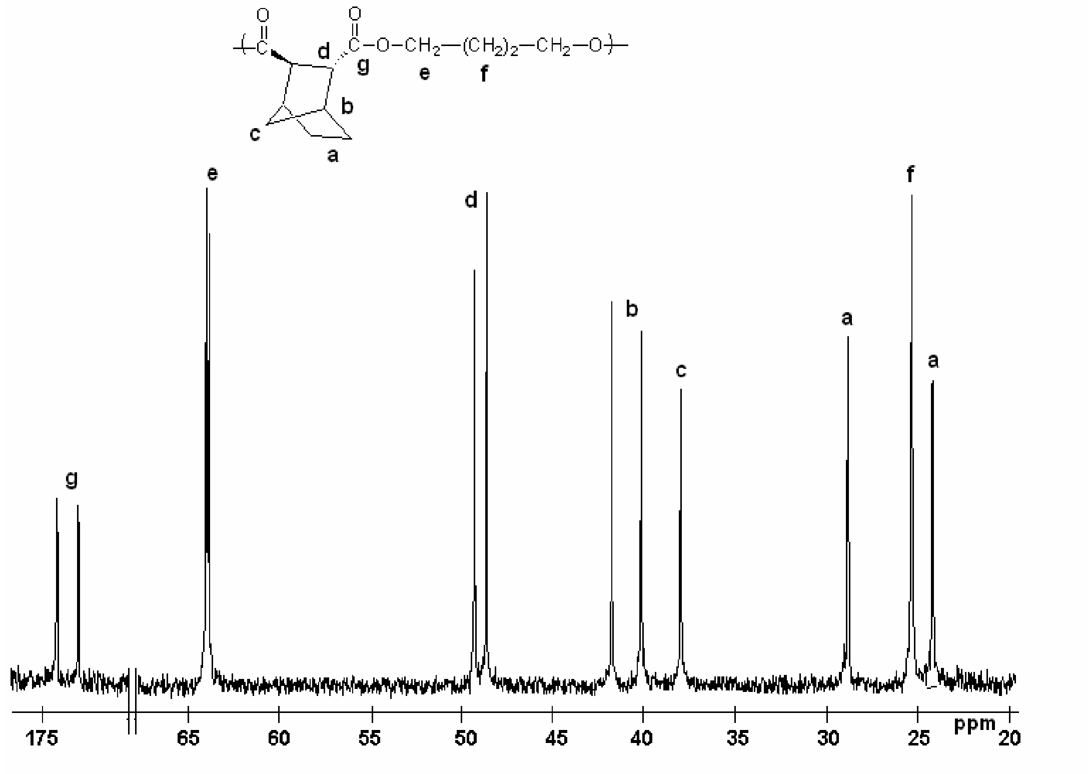
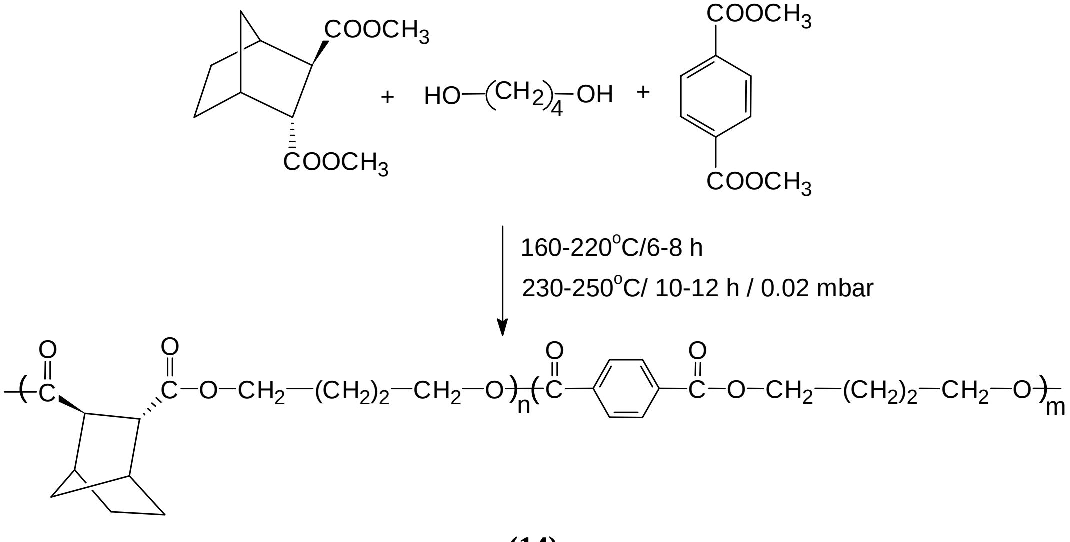


Figure 5.15 ^{13}C NMR spectrum of poly(butylene norbornane dicarboxylate) (PBNB)

The ^1H NMR spectrum of PBNB **(13)** and the repeat units along with the assignments is shown **Figure 5.14**. The peak at 4.11, H_e, is assigned to the OCH_2 protons. The peaks at 3.22 and 2.82, H_d, to the CH protons attached to the carbonyl group. The bridgehead protons, H_c, are non-equivalent and appear at 2.64 and 2.56 ppm. The chemical shifts are given in **Table 5.4**. In the ^{13}C NMR spectrum of PBNB (**Figure 5.15**), the carbonyl carbon, C_g, appears at 173.2 and 174.39 (trans carbonyl). The carbon attached to oxygen, C_d, appears at 63.88 and 64.0 ppm.

5.4.3.2 Synthesis and structure of poly (butylene terephthalate-co-2,3-norbornane dicarboxylate) (Poly(BT-co-BNB)) copolyesters

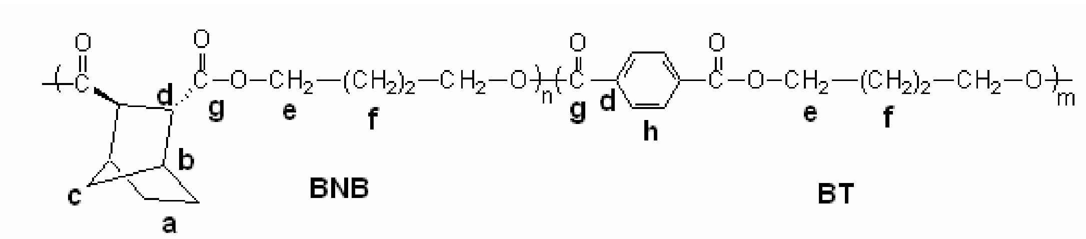
Copolyesters of dimethyl terephthalate and 1,4-butanediol containing NBDE were synthesized by melt condensation (**Scheme 5.8**). A series of copolyesters were synthesized by changing the molar ratio of DMT/NBDE (90/10, 80/20, 70/30 and 50/50). The copolyesters containing upto 30% PBNB were found to be insoluble in chloroform, whereas the copolyester containing 50% PBNB was to be soluble. The inherent viscosities were in the range of 0.8 - 1.4 dL/g. The M_n and M_w of $PBT_{50}NB_{50}$ were found to be 51,700 and 88,900 with a dispersity of 1.7.



(14)

Scheme 5.8 Synthesis of poly (butylene terephthalate-co-butylene-2,3-norbornane dicarboxylate) (P(BT-co-BNB))

The structure and the composition of the copolyesters were confirmed by ^1H and ^{13}C NMR spectra. **Figure 5.16** shows the chemical structure of the copolyester along with the notations used for assigning the NMR chemical shifts. **Table 5.4** summarizes the ^{1}H and ^{13}C NMR chemical shift values of PBT, PBNB and poly(BT-co-BNB) copolyesters. The ^{1}H NMR spectra of PBT, PBNB and PBT$_{50}$NB$_{50}$ are shown in **Figure 5.17**. The OCH$_2$ protons, H$_e$, for PBT appears at 4.5 ppm and for PBNB appears at 4.11 ppm. In the case of the copolyesters the OCH$_2$ protons are split into four corresponding to the different diads possible: TT, TNB, NBT and NBNB, where T is the terepthalate moiety and NB is the norbornane dicarboxylate moeity.



(14)

Figure 5.16 Chemical structure of poly(BT-co-BNB) copolyester with notations used for NMR assignments

Table 5.4 ^{1}H and ^{13}C NMR Chemical Shifts (δ in ppm) of PBT, PBNB and poly(BT-co-BNB) copolyesters

^{1}H Chemical shifts

	$^{B}H_{a}$	$^{B}H_{d}$	$^{B}H_{g}$	$^{NB}H_{a,b}$	$^{NB}H_{f}$	$^{NB}H_{c}$	$^{NB}H_{d}$	$^{NB}H_{e}$
PBT	2.02	4.5	8.12					
PBNB				1.2-1.9	1.7	2.64, 2.56	3.22, 2.82	4.11
PBT$_{50}$NB$_{50}$	2.0	4.41, 4.47	8.11	1.2-1.7	1.7-2.1	2.59, 2.67	3.24, 2.85	4.07-4.3

^{13}C Chemical Shifts

	$^{T}C_{e}$	$^{T}C_{h}$	$^{T}C_{d}$	$^{T}C_{g}$	$^{CP}C_{b}$	$^{NB}C_{d}$	$^{NB}C_{e}$	$^{NB}C_{g}$
PBT	65.9	129.8	133.7	167.6				
PBT$_{50}$NB$_{50}$	64.74	129.4	133.93	165.57	40.14, 41.75	48.57, 49.25	63.92, 64.04	173.2, 174.48
PBNB					40.13 41.75	48.62, 49.29	63.88 64.0	173.2 174.39

In the ^{1}H NMR spectrum, the peak for TT, ie the repeat unit in which both OCH$_2$ are attached to terephthalate appears at 4.47. The TNB peak appears at 4.41. As the peaks for NBT and NBNB appear as a broad multiplet from 4.1-4.26 ppm, they could not be resolved. Hence the diad distriubutions for the copolyesters could not be calculated.

Table 5.5 Composition of poly(BT-co-BNB) copolyesters determined by ^{1}H NMR

Copolyester[a]	Feed composition (mol %)		Copolymer composition[a] (mol %)		η_{inh}[b] (dL/g)
	BT	BNB	BT	BNB	
PBT	100	0	100	0	0.90
$PBT_{90}NB_{10}$	90	10	90	10	0.82
$PBT_{78}NB_{22}$	76	24	78	22	0.96
$PBT_{71}NB_{29}$	71	29	71	29	1.42
$PBT_{50}NB_{50}$	50	50	50	50	0.80
PBNB	0	100	0	100	0.66[c]

[a]calculated from ^{1}H NMR. [b] Measured in 60/40 phenol/TCE (w/w) at 30°C; [c] measured in chloroform

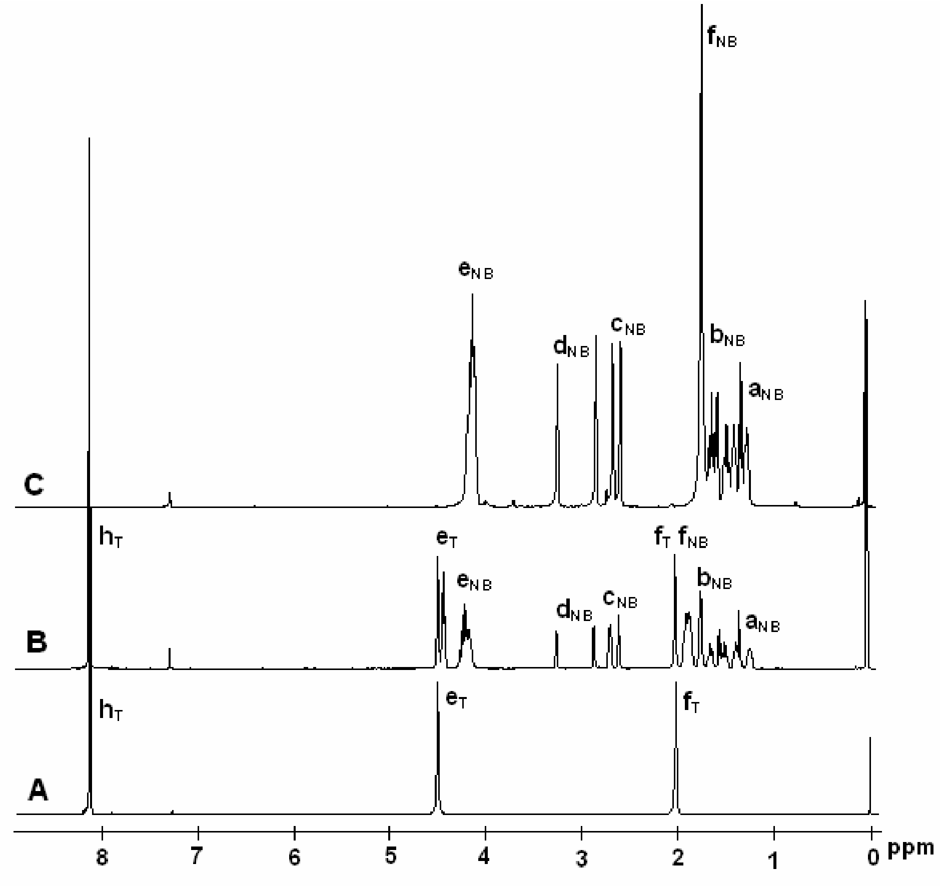


Figure 5.17 ^{1}H NMR spectra of (A) PBT, (B) $PBT_{50}NB_{50}$, (C) PBNB

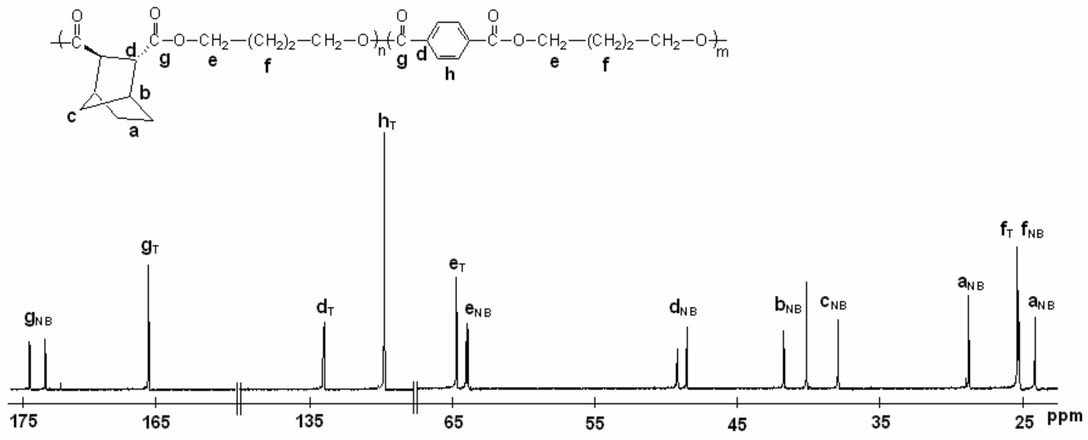


Figure 5.18 ^{13}C NMR spetrum poly (butylene terepthalate-co-butylene norbornane dicarboyxlate) (PBT$_{50}$NB$_{50}$)

The ^{13}C NMR spectrum of PBT$_{50}$NB$_{50}$ is shown in **Figure 5.18**. The peak for carbonyl carbon of the norbornane dicarboxylate, C$_g$, appears at 174.29 and 174.48 ppm and that for terephthalate appears at 165.57 ppm. The peak for OCH$_2$ carbon, C$_e$, attached to terephthalate appears at 64.74 and that attached to norbornane dicarboxylate appears at 63.92 and 64.04 ppm.

5.4.3.3 Thermal properties

Poly (butylene norbornane dicarboxylate) (PBNB) **(13)** is an amorphous polyester with a T$_g$ of 15°C. Among the copolyesters only the PBT rich compositions crystallize and the thermograms during heating and cooling are shown in **Figure 5.19.** The parameters extracted from the thermograms are given in **Table 5.6.** The T$_m$, T$_c$ and T$_g$ are plotted in **Figure 5.20** and all exhibit a linear change with composition. The heat of fusion and crystallization also decrease indicating the difficulty in crystallizing with increase in PBNB content.

Table 5.6 Thermal properties of poly(BT-co-BNB) copolyesters.

Polyester	η_{inh}[a]	T_g (°C)	T_m (°C)	ΔH_m (J/g)	T_c (°C)	ΔH_c (J/g)	IDT[b]
PBT	0.90	40	226	41	193	49	374
PBT$_{90}$NB$_{10}$	0.82	38	205	23	157	29	384
PBT$_{78}$NB$_{22}$	0.96	34	175	13	113	25	384
PBT$_{72}$NB$_{28}$	1.42	28	162	29	93	24	386
PBT$_{50}$NB$_{50}$	0.80	22	120	10	does not crystallize		375
PBNB	0.66	15	Amorphous				389

[a] Measured in 60/40 phenol/TCE (w/w) at 30°C; [b] Measured by TGA

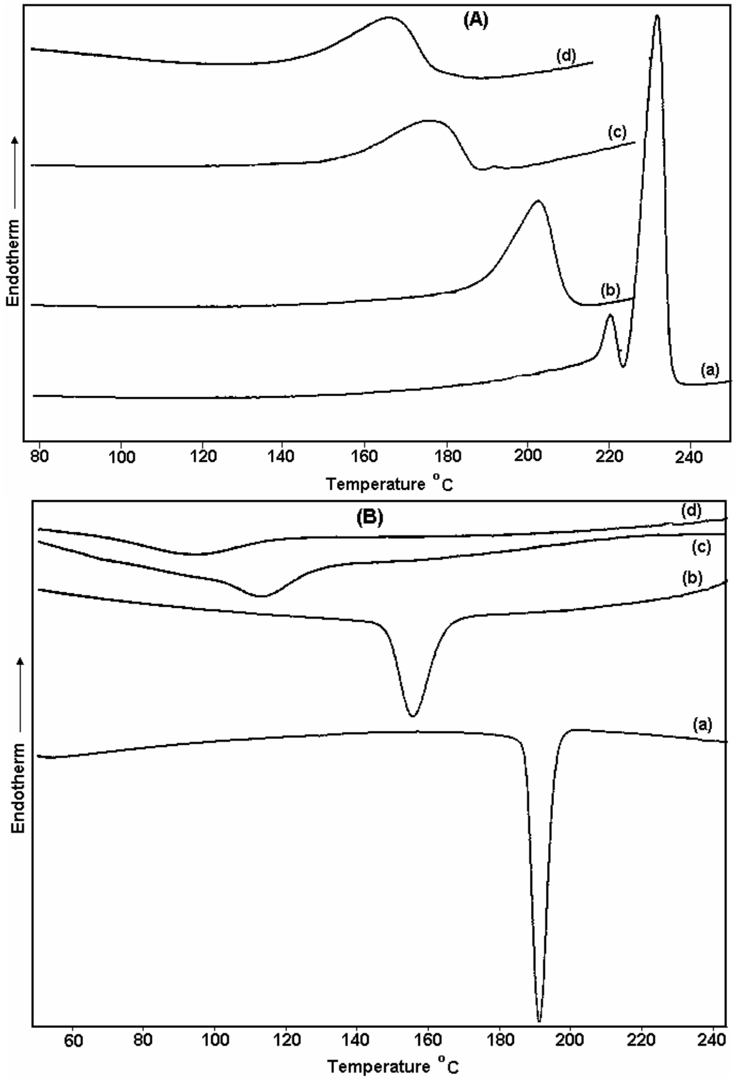


Figure 5.19 DSC heating (A) and cooling (B) thermograms of (a) PBT, (b) PBT$_{90}$BNB$_{10}$, (c) PBT$_{78}$NB$_{22}$, (d) PBT$_{71}$NB$_{29}$ (e) PBT$_{50}$BCD$_{50}$

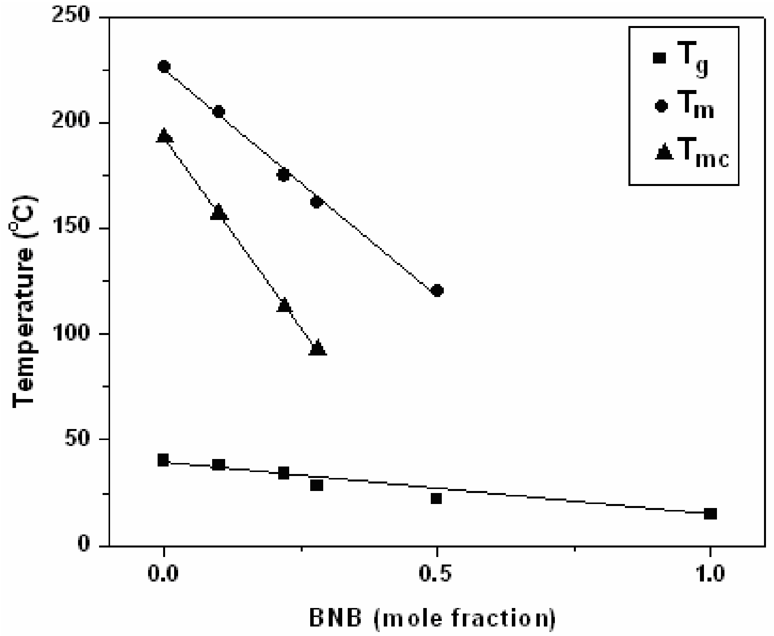


Figure 5.20 Melting, melt-crystallization and glass transition temperatures of poly(BT-co-BNB) copolyesters as a function of copolymer composition

5.4.3.4 X-ray diffraction studies

The WAXS patterns of the copolyesters are shown in **Figure 5.21.** PBNB **(13)** is amorphous polyester and is indicated by the broad amorphous pattern (not shown in the Figure). All the compositions with PBT 50% or more show well defined peaks due to crystalline fraction. The composition $PBT_{50}NB_{50}$ shows weak diffraction pattern only after annealing at 100°C for about 2 hours. The weak diffraction pattern displayed by $PBT_{50}NB_{50}$ composition is indicative of cocrystallization, as the sequence length of PBT is less than 3 it cannot crystallize on its own. The PBNB segment cocrystallizes with PBT in the PBT lattice. The incorporation of BNB unit in the PBT lattice was apparent from the 001 spacing. The 001 d-spacing, which was less susceptible to variation to structure and morphology, showed marginal decrease with increase in BNB content and was in agreement with the BNB unit's length 1.02 nm (calculated using conjugate gradient and Newton-Raphson method using Cerius 2 software), which was lower than the length of BT unit (1.234 nm). The definite but small change in the d-spacing of the reflections **(Figure 5.22)** also points to the cocrystallization behavior. The experimental data is a little limiting to conclude the nature of the cocrystallization behavior. Nevertheless, based on the behavior of d-spacing and results obtained in the Chapter 3and 4, it may be concluded that the crystallization is isomorphic in nature.

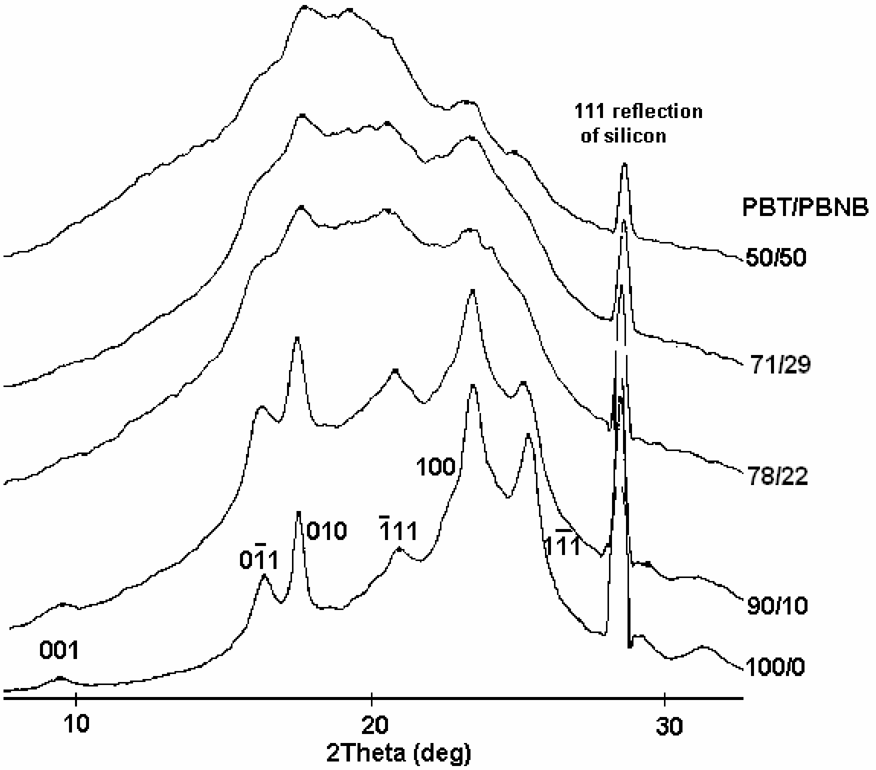


Figure 5.21 WAXD patterns of poly(BT-co-BNB) copolyesters

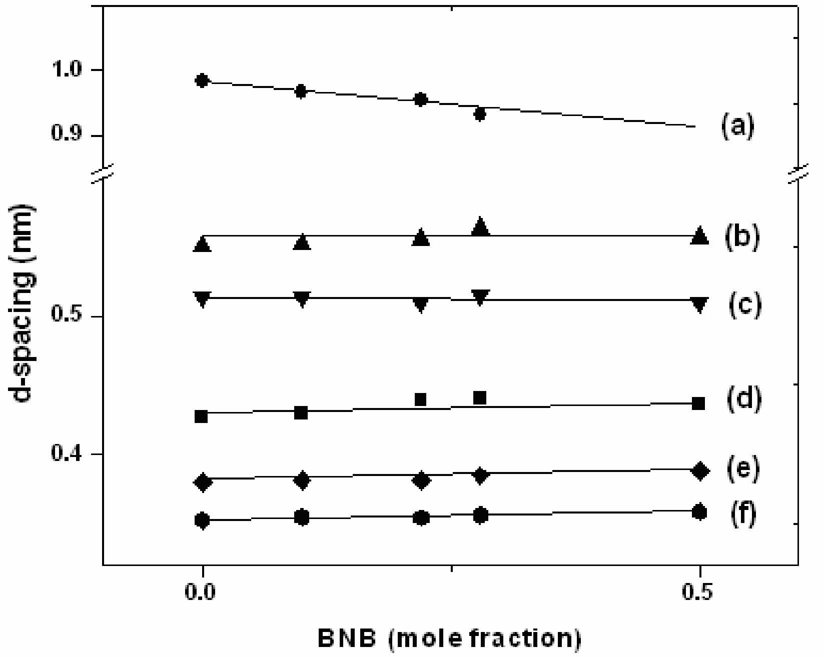


Figure 5.22 Changes of d-spacigs for poly(BT-co-BNB) copolymers as a function of copolymer composition (a) 001(along chain direction), (b) 0$\bar{1}$1, (c)010, (d)$\bar{1}$11 and (e)100 (f) 1$\bar{1}$1 reflections (based on PBT structure)

5.5 Conclusions

A series of poly(butylene terephthalate-co-2,3-norbornane dimethylene terephthalate) (poly(BT-co-NBDT)) **(12)** and poly (butylene terephthalate-co-2,3-norbornane dicarboyxlate) (poly(BT-co-BNB)) **(14)** copolymers with various NBT and BNB contents were synthesized by melt condensation. The NMR spectroscopic analysis indicates that the coploymers are random. The thermal analysis and XRD studies shows that the PNBDT **(11)** is an amorphous polyester with a T_g of 113°C. The Poly(BT-co-NBDT) copolyesters could crystallize in compositions upto 20 % NBDT content, while the composition having 50 % NBDT is amorphous. On the other hand, PBNB **(13)** was found to be an amorphous polyester with a T_g of 15°C. The poly(BT-co-BNB) copolyesters showed isomorphic crystallization and did not show eutectic behaviour in melting and crystallization. The glass transition temperature showed linear dependency on composition in these copolymers.

The copolyesters of dimethyl terephthalate and 1,4-butanediol exhibit a wide range of melting temperature and glass transition temperature. Incorporation of NBDM as a comonomer, which has a rigid norbornane ring increases the T_g of PBT. While incorporation of 2,3-norbornane dicarboyxlate comonomer, which is the ester component, results in copolyesters, which have T_g, lower than PBT and the T_m does not show eutectic behavior.

II. Synthesis and characterization of copolyesters containing 2,2,4,4-tetramethyl-1,3-cyclobutane diol

5.6 Introduction

Polyesters of 2,2,4,4-tetramethyl-1,3-cyclobutanediol (TMCBD) reported[7,8,9] are primarily high melting, semicrystalline materials. Melting points for the polyesters from dimethyl terephthalate and TMCBD, are 316-319°C (38/62 *cis/trans)*[8], 296-308°C (*cis*) and >350°C (*trans*)[10] and the T_g is 174°C. The synthesis of aliphatic polyester containing TMCBD having superior weathering properties has been described[10]. Polyesters synthesized from TMCBD 1,4-cyclohexanedicarboxylic acid are reported to possess improved weatherability[11]. The aliphatic copolyesters synthesized from 1,4-CHDA, CHDM and TMCBD have T_g >100°C and improved UV resistance.

This chapter discusses the synthesis and properties of aliphatic copolyesters of TMCBD with cycloaliphatic diesters and a straight chain diol.

5.7 Experimental

5.7.1 Materials

1,4-Dimethyl terephthalate (DMT), (99+%) 1,4-butanediol (BD), ruthenium on carbon and isobutyryl chloride were obtained from Sigma-Aldrich Inc, USA. Triethyl amine, diethyl ether and toluene, were obtained from s.d. fine- chem Limited, Mumbai.

5.7.2 Reagents and purification

DMT was recrystallized from methanol. BD was distilled and stored over molecular sieves. Triethyl amine was stirred over calcium hydride and distilled and stored on KOH. Diethyl ether was kept overnight over calcium chloride, distilled and was refluxed over sodium.

5.7.3 Synthesis of 2,2,4,4-tetramethyl-1,3-cyclobutane diol (TMCBD)

Triethyl amine (120 mL, 0.8 mol) and 160 mL anhydrous diethyl ether were taken in a 1000 mL round bottom flask and cooled in an ice salt mixture. Isobutyryl chloride **(15)** (52 mL, 0.5 mol) in 80 mL anhydrous diethyl ether was added slowly over 1 h under vigorous stirring. The reaction mixture was brought to room temperature and allowed to stir for 21 days. The reaction mixture was filtered using a sintered funnel and washed several times with diethyl ether. Evaporation of ether gave yellow colored crude 2,2,4,4-tetramethyl cyclobutane dione **(16)** which was purified by vacuum sublimation to give 10.37 g (60 %) of white crystalline dione. 2,2,4,4-tetramethyl cyclobutane dione (14.9 g, 0.1 mol), 0.9 g of ruthenium on carbon and 50 mL of methanol were charged into a 300 mL stainless steel Parr reactor. The reactor was purged with hydrogen gas and pressurized to 1000 psi of H_2. The reactor was heated to 125°C when hydrogen absorption started. The reaction was continued till there was no more absorption of H_2. The reaction mixture was cooled to room temperature and filtered off to remove ruthenium. Evaporation of methanol gave 14.5 g of TMCBD **(17)**. TMCBD was recrystallized from hot toluene to yield 12.8 g of white crystalline TMCBD. m. p. 124°C (lit[12] 129-150°C).

Elemental, found (calcd.): C - 66.1(66.66), H -11.58 (11.11)

IR (neat) – 3312 (O-H), 2900, 2860, 1490, 1390, 1041, 960, 850 cm^{-1}.

GC-7.13, 7.31 min, 45:55 cis/trans ratio.

^{1}H NMR (chloroform) δ: 0.9(12H, t, CH_3), 3.15, 3.25(2H, dd CH), 4.5(2H, t, OH)

^{13}C NMR (chloroform) δ: 78.4, 77.03 (CH-OH), 42.12, 40.29 (quarternary C), 29.3, 22.9, and 15.78 (CH_3).

5.7.4 Synthesis of copolyester containing TMCBD, BD with DMT

A 100 mL two-neck round bottom flask equipped with a magnetic stirring bar, nitrogen inlet, air condenser and spiral trap was charged with DMT (2.5 g 0.013 mol), TMCBD **(17)** (1.19 g, 0.008 mol) and dibutyl tin dioxide (DBTO) (0.1 wt % w. r. t DMT). The flask was degassed with N_2 and heated in an oil bath at 160-210°C for 7 h under N_2 atmosphere (closed condition to avoid sublimation of DMT and TMCBD) when methanol distilled out. The reaction flask was subsequently cooled to room temperature. BD (0.76 g, 8 mmol) and titanium isopropoxide (0.05 wt % w.r.t. DMT) were added to the reaction flask and degassed again. The reaction mixture was heated at 230-250°C for 12 h under a constant flow of N_2. The pressure was gradually reduced to about 0.02 mbar over 30 min and reaction continued at 250-260°C for 6 h. The flask was cooled under vacuum and polymer was dissolved in methylene chloride and precipitated in methanol. The polymer was filtered, washed with methanol and dried in a vacuum oven. The polymer was found to be fluffy (powder). Yield = 3g (90 %).

η_{inh} (chloroform) - 0.5 dL/g

^{1}H NMR ($CDCl_3$) δ: 1.33 (12H, t, CH_3), 2.00 (4H, s, CH_2), 4.46 (4H, s, CH_2O) 4.66, 4.81 (2H, d, CH-O), 8.15 (8H, s, aromatic)

^{13}C NMR ($CDCl_3$) δ: 16.86, 22.72 (CH_3), 25.39 (CH_2), 28.44 (CH_3), 40.47, 41.79 (quarternary C), 64.77 (OCH_2), 80.58, 81.54 (O-CH), 129.45, 129.56, 133.71, 133.87, 133.94, 134.08 (aromatic), 165.26, 165.58 (CO).

5.7.5 Synthesis of copolyester containing TMCBD, BD with DMCD

A 100 mL two-neck round bottom flask fitted with a magnetic stirring bar, nitrogen inlet, air condenser and spiral trap was charged with DMCD (5.01 g 0.025 mol), TMCBD (2.24 g, 0.016 mol) and dibutyl tin dioxide (DBTO) (0.1 wt % w. r. t DMCD). The flask was degassed with N_2 and heated in an oil bath at 200-230°C for 11 h under N_2 atmosphere when methanol distilled out. And then the reaction flask was cooled to room temperature. BD (1.42 g, 0.0157 mmol) and titanium isopropoxide (0.05 wt % w.r.t. DMCD) were added to the reaction flask and degassed again. The reaction mixture was heated at 230-250°C for 4 h under a constant flow of N_2. The pressure was gradually reduced to about 0.02 mbar over 30 min and reaction continued at 250-260°C for 13 h. The flask was cooled under vacuum and the polymer recovered. Yield = 6.2 g (98 %).

η_{inh} (chloroform) – 0.65 dL/g

GPC ($CHCl_3$) Mn - 42, 200 M_w - 80,000 (M_w/M_n -1.9)

^1H NMR ($CDCl_3$) δ: 1.10 (12H, t, CH_3), 1.3-2.6 (26H, m, ring), 4.10, (4H, s, OCH_2), 4.27, 4.41 (2H, s, CH-OH)

^{13}C NMR ($CDCl_3$) δ: 16.65, 16.75, 22.5, 22.6, 25.23, 25.91, 27.91, 28.04, 28.36, 39.82, 40.55, 41.16, 42.57, 63.95, 79.43, 79.56, 80.28, 80.44, 174.54, 174.77, 174.96, 175.24.

5.7.6 Synthesis of copolyester containing TMCBD, BD with CPDE

A 100 mL two-neck round bottom flask fitted with a magnetic stirring bar, nitrogen inlet, air condenser and spiral trap was charged with CPDE (3.74 g, 0.02 mol), TMCBD (1.87 g, 0.013mol) and dibutyl tin dioxide (DBTO) (0.1 wt % w. r. t CPDE). The flask was degassed with N_2 and heated in an oil bath gradually from 100-180°C for 4 h under N_2 atmosphere when methanol distilled out. The reaction mixture was further heated at 180-200°C for 8 h. The reaction flask was cooled to room temperature, BD (1.29 g, 0.014 mol) and titanium isopropoxide (0.05 wt % w.r.t. CPDE) were added to the reaction flask and degassed again. The reaction mixture was heated at 230-250°C for 4 h under a constant flow of N_2. The pressure was gradually reduced to about 0.02 mbar over 30 min and the reaction was continued at 240-250°C for 8.5 h. The polymer was found to be rubbery. Yield = 4.4 g (92 %).

η_{inh} (chloroform) – 1.23 dL/g

^1H NMR ($CDCl_3$) δ: 1.10 (12H, t, CH_3), 1.71 (4H, s, CH_2), 1.8-2.4 (12H, m, ring), 2.7-3.1 (4H, m, ring), 4.11(4H, s, CH-OH), 4.28, 4.43 (2H, d, OCH_2)

^{13}C NMR ($CDCl_3$) δ: 16.45, 22.29 (CH_3), 24.88 (CH_2), 28.14 (CH_3), 29.17, 29.90, 32.62, 33.10, 40.10, 41.42, 43.56, 44.14, 43.99, 65.43 (CH_2-OH), 80.95, 81.85 (CH-OH), 177.73, 178.07, 178.49 (CO).

5.7.7 Synthesis of copolyester containing TMCBD, BD with NBDE

A 100 mL two-neck round bottom flask equipped with a magnetic stirring bar, nitrogen inlet, air condenser and spiral trap was charged with NBDE (4.19 g, 0.0.02 mol), TMCBD

(2.2 g, 0.015 mol) dibutyl tin dioxide (DBTO) (0.1 wt % w. r. t NBDE). The flask was degassed with N_2 and heated in an oil bath at 120-200°C for 6 h under N_2 atmosphere (closed condition to avoid sublimation of TMCBD) when methanol distilled out. The reaction was further continued at 200-220°C for 12 h. The reaction flask was cooled to room temperature, BD (1.35 g, 0.015 mol) and titanium isopropoxide (0.05 wt % w.r.t. NBDE) were added to the reaction flask and degassed again. The reaction mixture was heated at 230-250°C for 4 h under a constant flow of N_2. The pressure was gradually reduced to about 0.02 mbar over 30 min and reaction continued at 250-260°C for 11 h. The flask was cooled under vacuum and polymer was recovered. Yield = 4.98 g (96 %).

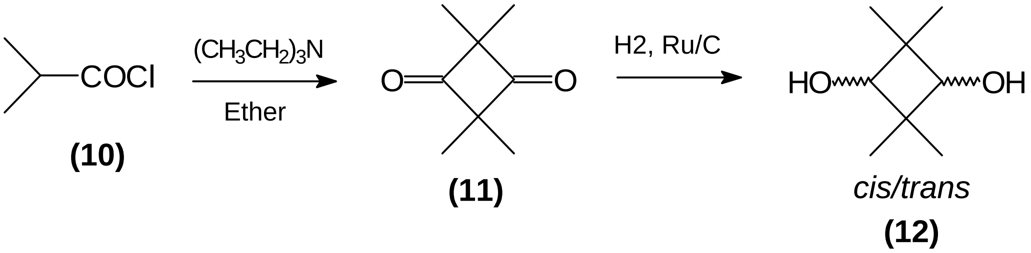
η_{inh} (chloroform) – 0.6 dL/g

^{1}H NMR ($CDCl_3$) δ: 0.8-1.9 (28H, m, CH_3 and ring protons), 2.46-3.0 (6H, m, bridgehead), 3.21 (2H, m, CH-O), 4.11 (4H, s, OCH_2), 4.24-4.45 (2H, dd, CH-OH)

5.8 Results and discussion

5.8.1 Monomer synthesis

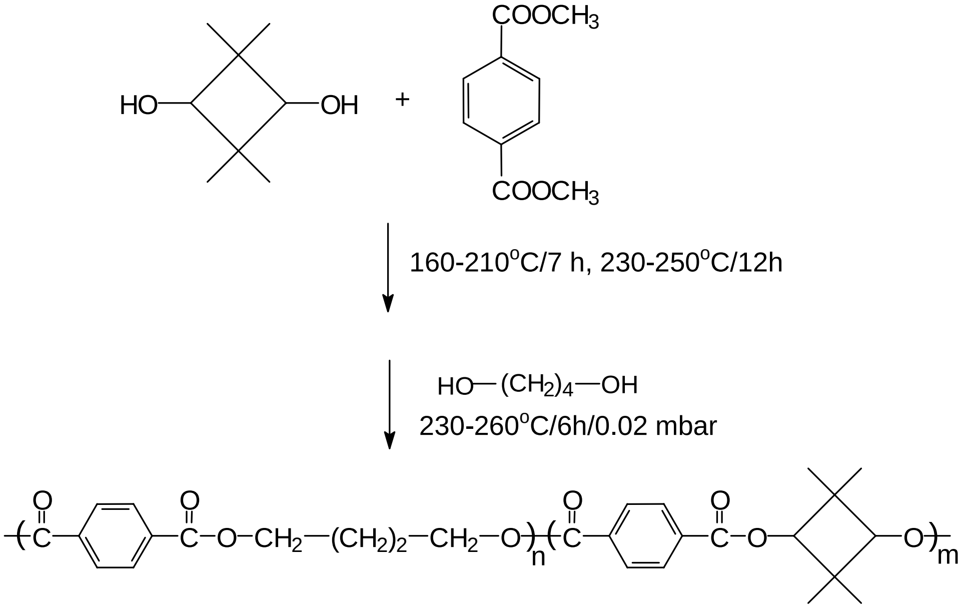
TMCBD was synthesized[13] from isobutyryl chloride (10), which dimerizes to form dimethyl ketene in presence of triethyl amine base, which spontaneously dimerizes to cyclic diketone (11), a molecule known since 1906[14,15] (**Scheme 5.9**). Hydrogenation of ketone in presence of ruthenium catalyst gives *cis/trans*-TMCBD (12).



Scheme 5.9 Synthesis of 2,2,4,4-tetramethyl-1,3-cyclobutane diol (TMCBD)

5.8.2 Synthesis and structure of TMCBD /BD terephthalate copolyester

The copolyesters of dimethyl terephthalate and 1,4-butanediol containing cyclobutane diol were synthesized by melt polymerization in two stages (**Scheme 5.10**). The first stage involved the transesterification of TMCBD with DMT in presence of dibutyltin oxide catalyst. The initial stages of transesterification was carried out under closed conditions instead of a constant stream of N_2 gas as both DMT and TMCBD underwent sublimation. It has been reported that the tin compounds are good catalysts for trans-esterification with TMCBD [3]. Since the TMCBD hydroxyl groups are secondary and sterically hindered by adjacent methyl groups, they require longer reaction times. The methanol byproduct was formed after 4-5 h of reaction time at 160-210°C. During the second trans-esterification stage, BD was added and melt polymerization carried out in the presence of titanium isopropoxide as catalyst. The excess diols were removed by heating at 230-260°C under high vacuum to increase the molecular weight. The polymer was dissolved in methylene chloride, precipitated in methanol and filtered.



(18)

Scheme 5.10 Synthesis of TMCBD /BD terephthalate copolyester

The ^1H NMR spectrum is shown in **Figure 5.23**. The TMCBD /BD molar ratio in the final polymer was calculated from the H_h (4.44) and H_d (4.66, 4.81) protons and was found to be the same as the TMCBD /BD ratio in the monomer feed. The NMR of the copolymer also showed the same cis/trans ratio as in the feed. The ^{13}C NMR spectrum of the copolyester is shown in **Figure 5.24**. The peak for carbonyl carbon appears at 165.58 and 165.26 for terephthalate attached to BD and TMCBD respectively. The C_h carbon appears at 64.77 and C_d carbon appears at 80.58 and 81.54 for the *cis* and *trans* isomers. The tetra methyl groups show peaks at 16.86 and 28.44 for the *cis* isomer and at 22.72 for the *trans* isomer.

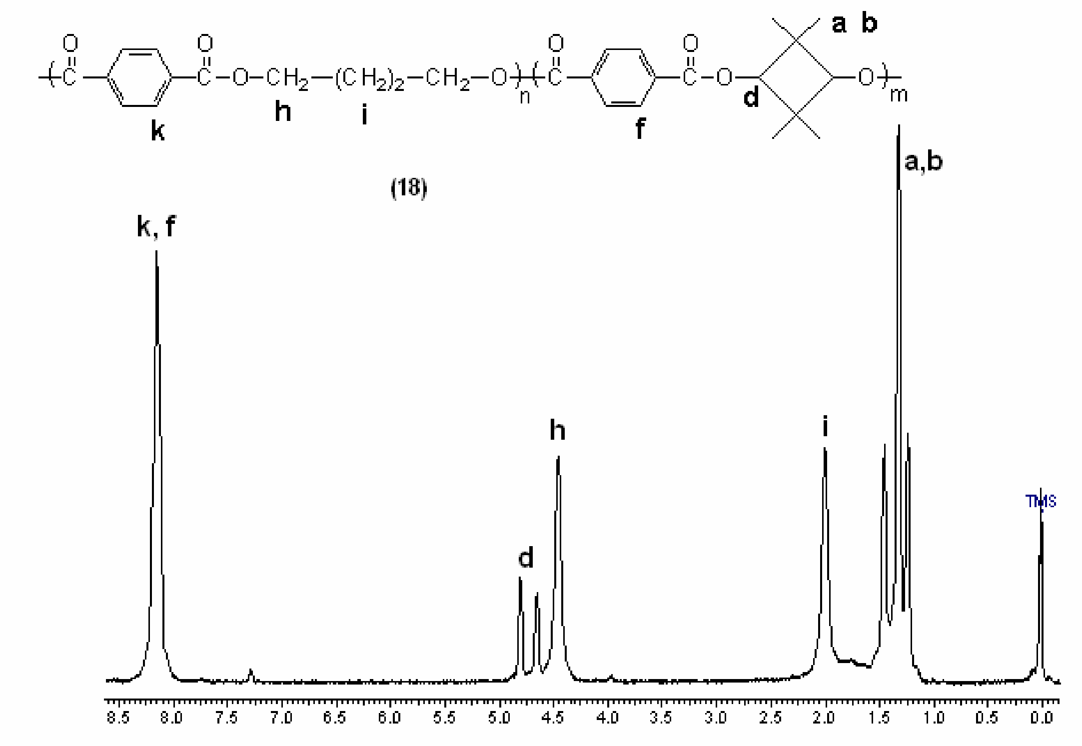


Figure 5.23 ^{1}H NMR spectrum of TMCBD /BD terephthalate copolyester

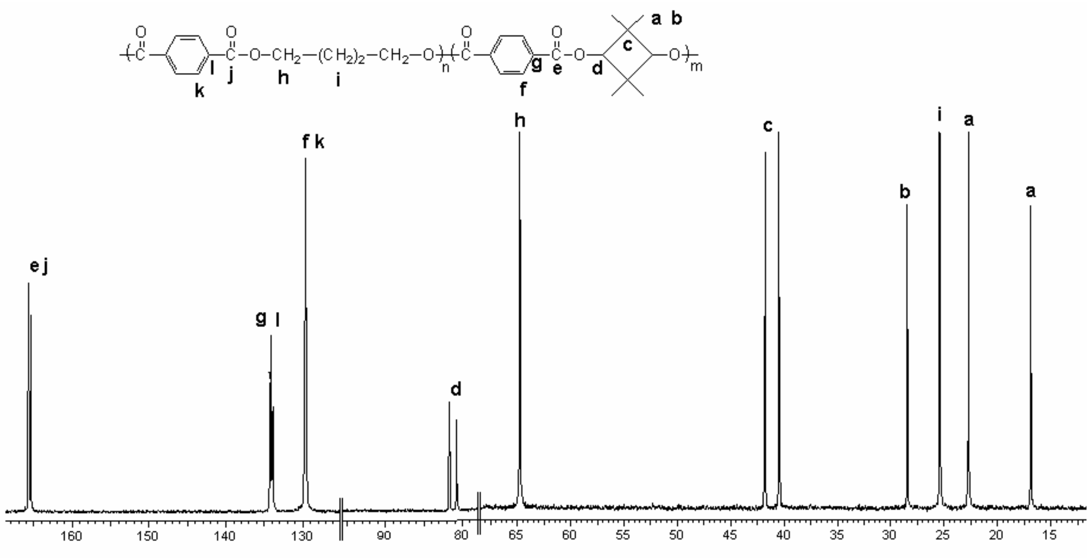
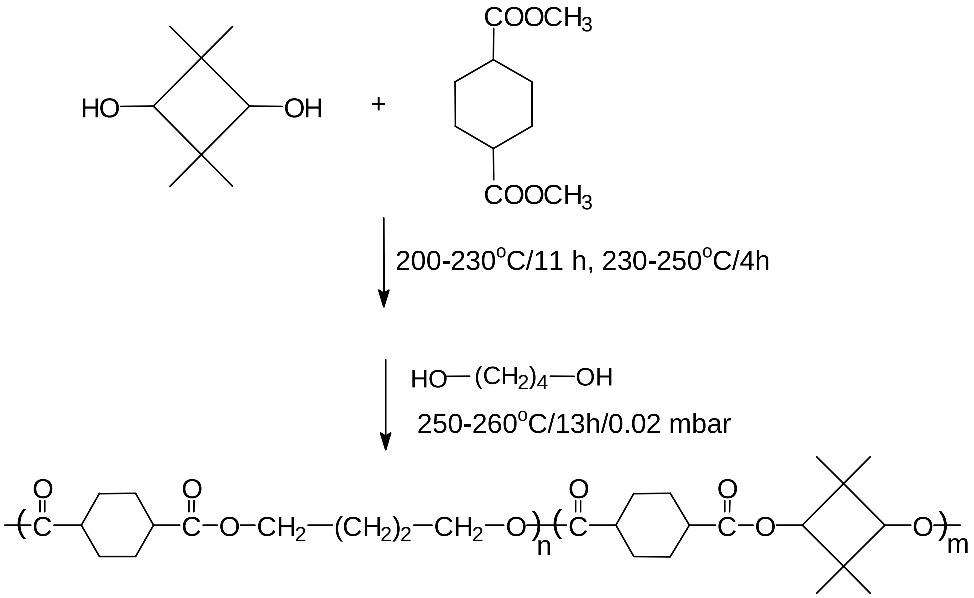


Figure 5.24 ^{13}C NMR spectrum of TMCBD /BD terephthalate copolyester

5.8.3 Synthesis of TMCBD /BD cyclohexane dicarboxylate copolyester

Aliphatic cyclohexane dicarboxylate copolyester containing TMCBD /BD was synthesized from dimethyl-1,4-cyclohexane dicarboxylate, BD and TMCBD by melt polymerization using dibutyltin oxide and titanium isopropoxide as catalysts in two stages (**Scheme 5.11**). The amorphous copolyester was transparent and slightly yellow in color when cooled from the melt to room temperature. The inherent viscosity of the copolyester was found to be 0.65 dL/g and the M_n and M_w were found to be 42,200 and 80,000 respectively.



(19)

Scheme 5.11 Synthesis of TMCBD/BD cyclohexane dicarboxylate copolyester

The TMCBD/BD ratio in the copolyester was calculated from the h (4.10 ppm) and d (4.27, 4.41 ppm) proton resonance (^{1}H NMR spectra **Figure 5.25**). The ratio of TMCBD/BD was found to be 50/50 the same as in the feed. The ^{13}C NMR spectrum along with the assignments is shown in **Figure 5.26**. The NMR spectrum shows peak for the h carbons at 63.65 and d carbons at 80.28 and 80.44 ppm.

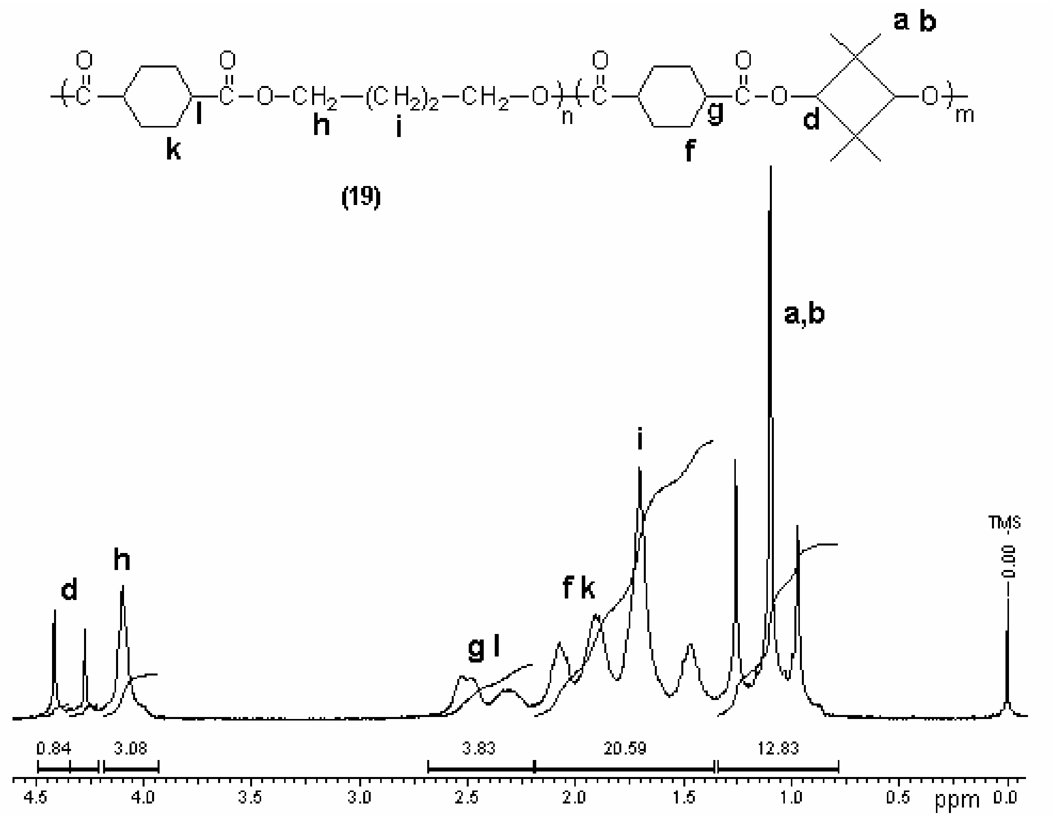


Figure 5.25 ^{1}H NMR spectrum of TMCBD/BD cyclohexane dicarboxylate copolyester

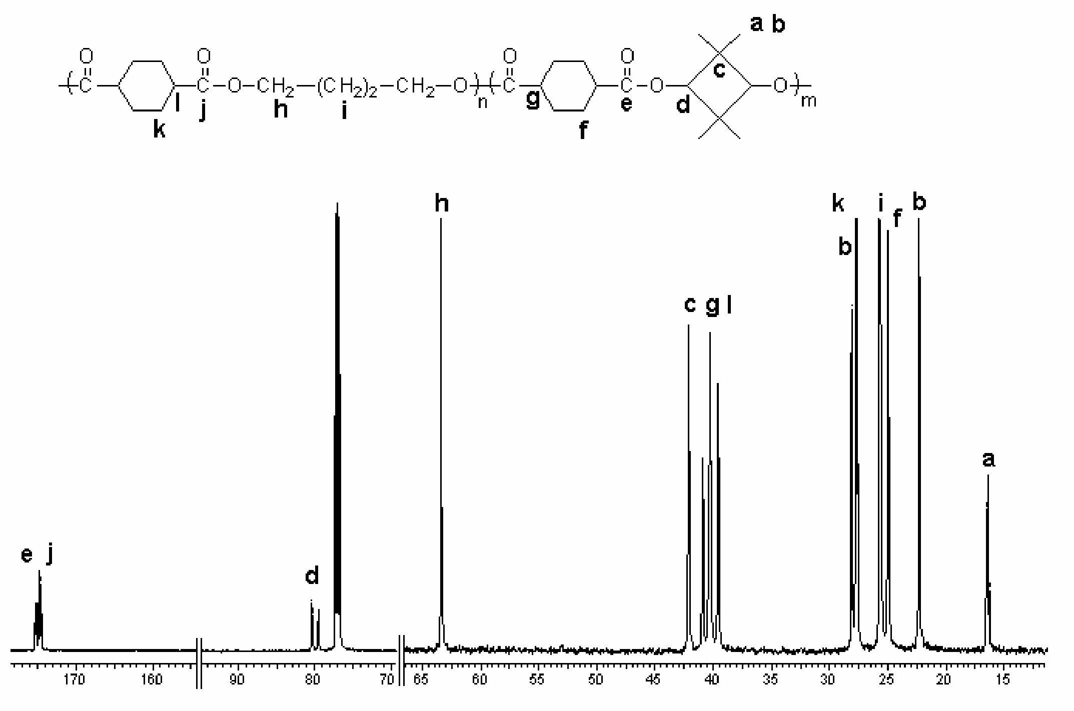
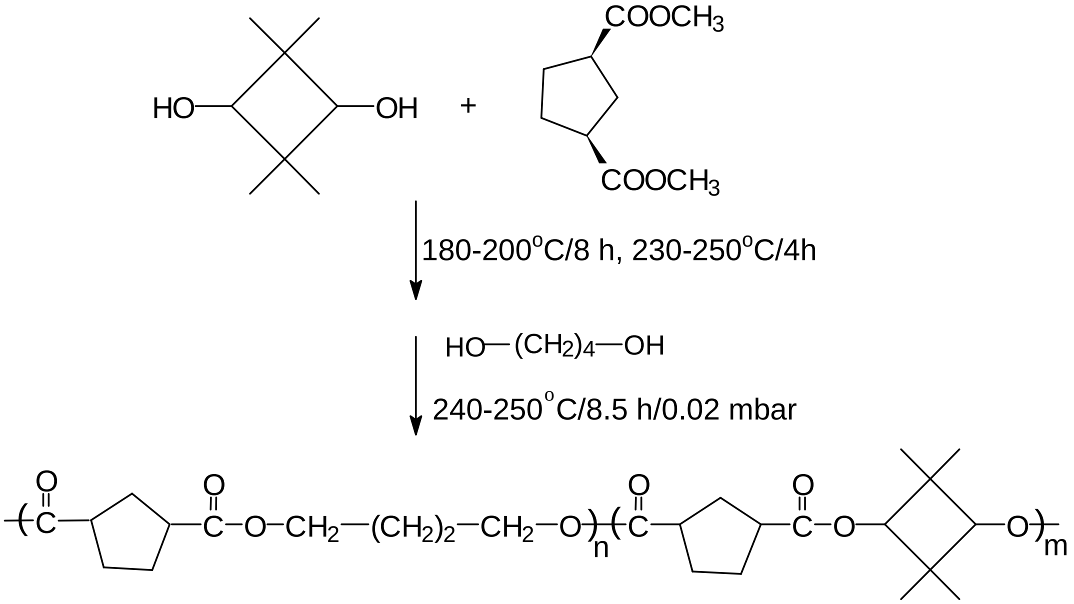


Figure 5.26 ^{13}C NMR spectrum of TMCBD/BD cyclohexane dicarboxylate copolyester

5.8.4 Synthesis and structure of TMCBD/BD cyclopentane dicarboxylate copolyester

TMCBD/BD copolyester of cylopentane dicarboxylate was synthesized from dimethyl-1,3-cyclopentane dicarboxylate, BD and TMCBD by melt polymerization using a combination of catalyts, DBTO and titanium isopropoxide (**Scheme 5.12**). The copolyester was found to be brown colored and rubbery. The inherent viscosity of the copolyester was found to be 1.23 dL/g.



(20)

Scheme 5.12 Synthesis of TMCBD/BD cyclopentane dicarboxylate copolyester

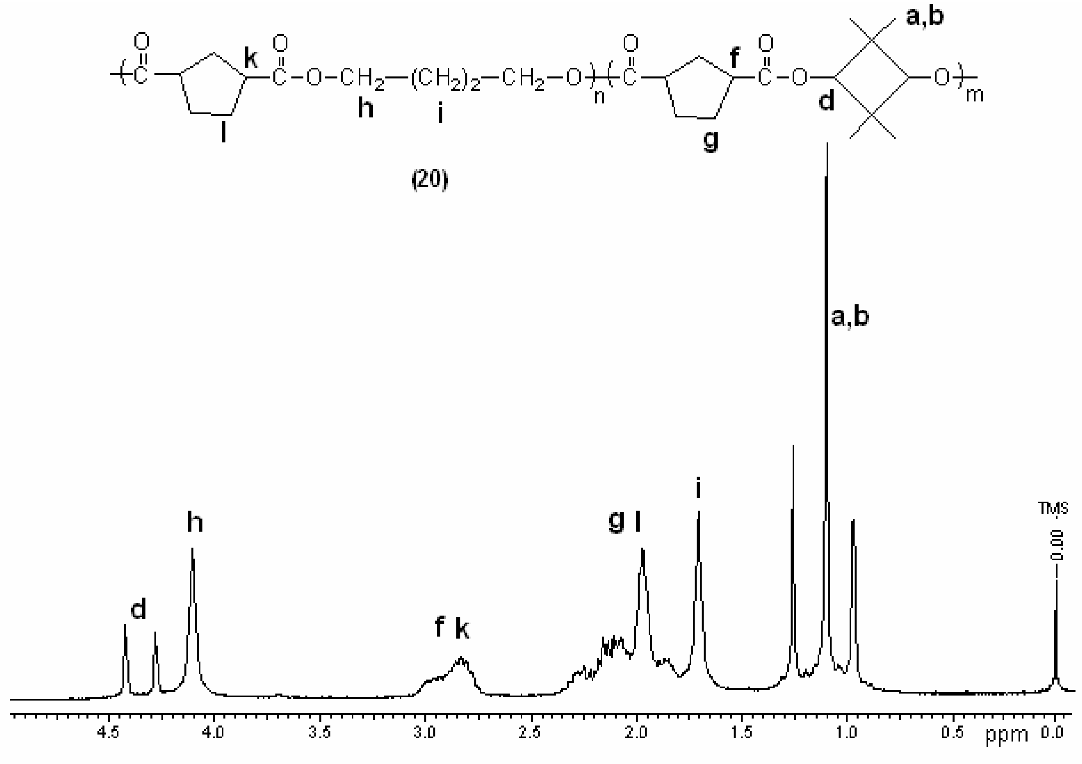


Figure 5.27 ^{1}H NMR spectra of TMCBD/BD cyclopentane dicaboxylate copolyester

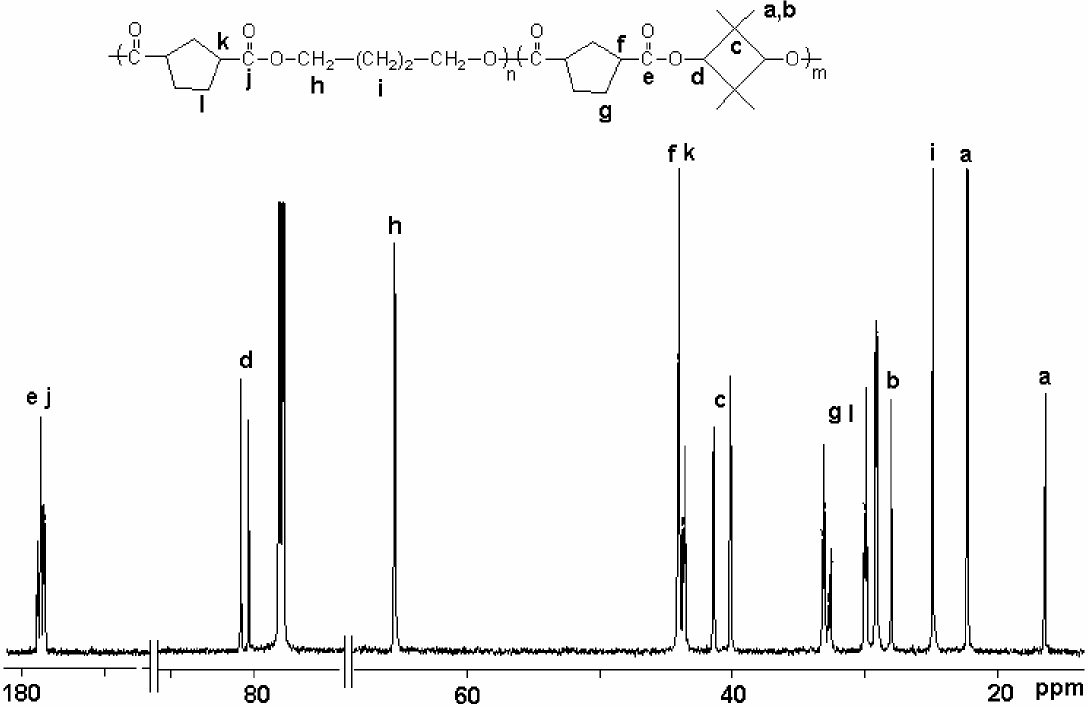
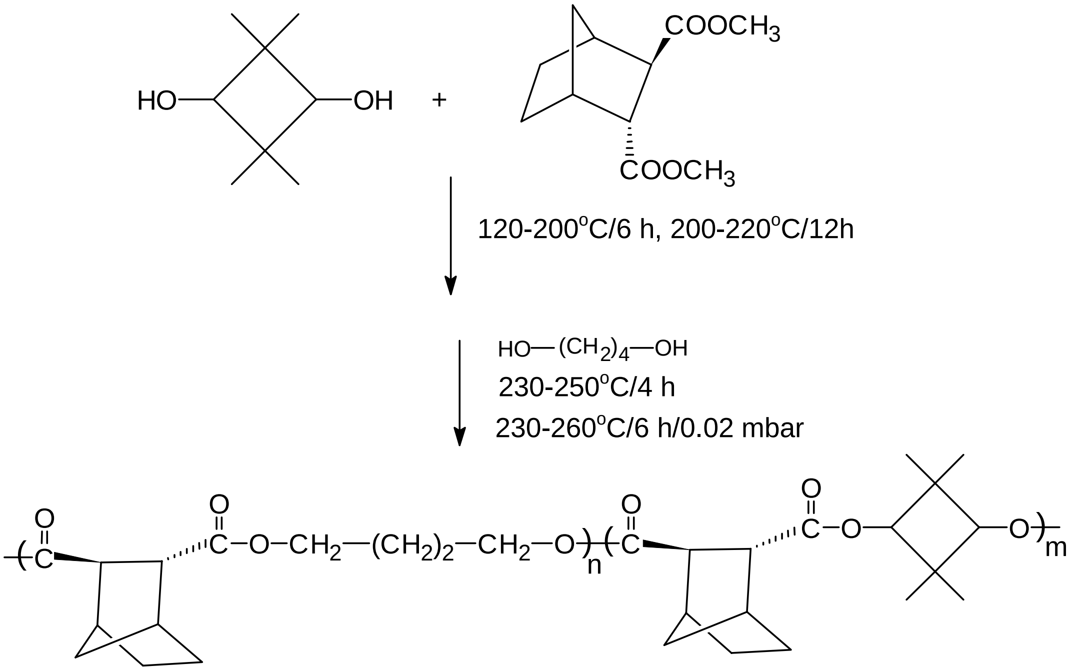


Figure 5.28 ^{13}C NMR spectrum of TMCBD/BD cyclopentane dicaboxylate copolyester

The TMCBD/BD ratio in the copolyester was calculated from the h (4.11) and d (4.28, 4.43) proton resonances (**Figure 5.27**) and was found to be 50/50. ^{13}C NMR spectrum (**Figure 5.28**) shows peaks for h carbons at 65.43 and d carbons at 80.05 and 81.85 ppm.

5.8.5 Synthesis and structure of TMCBD/BD norbornane dicarboxylate copolyester

TMCBD/BD copolyester of norbornane dicarboxylate was synthesized from NBDE, BD and TMCBD by melt polymerization using a combination of catalyts, DBTO and titanium isopropoxide (**Scheme 5.13**). The copolyester was found to be brown colored. The inherent viscosity of the copolyester was found to be 0.6 dL/g.



(21)

Scheme 5.13 Synthesis of TMCBD/BD norbornane dicarboxylate copolyester

Figure 5.29 shows the ^{1}H spectrum of the copolyester. The TMCBD/BD molar ratio in the copolyester was calculated from the h and d proton resonances and was found to be 50/50, same as in the feed.

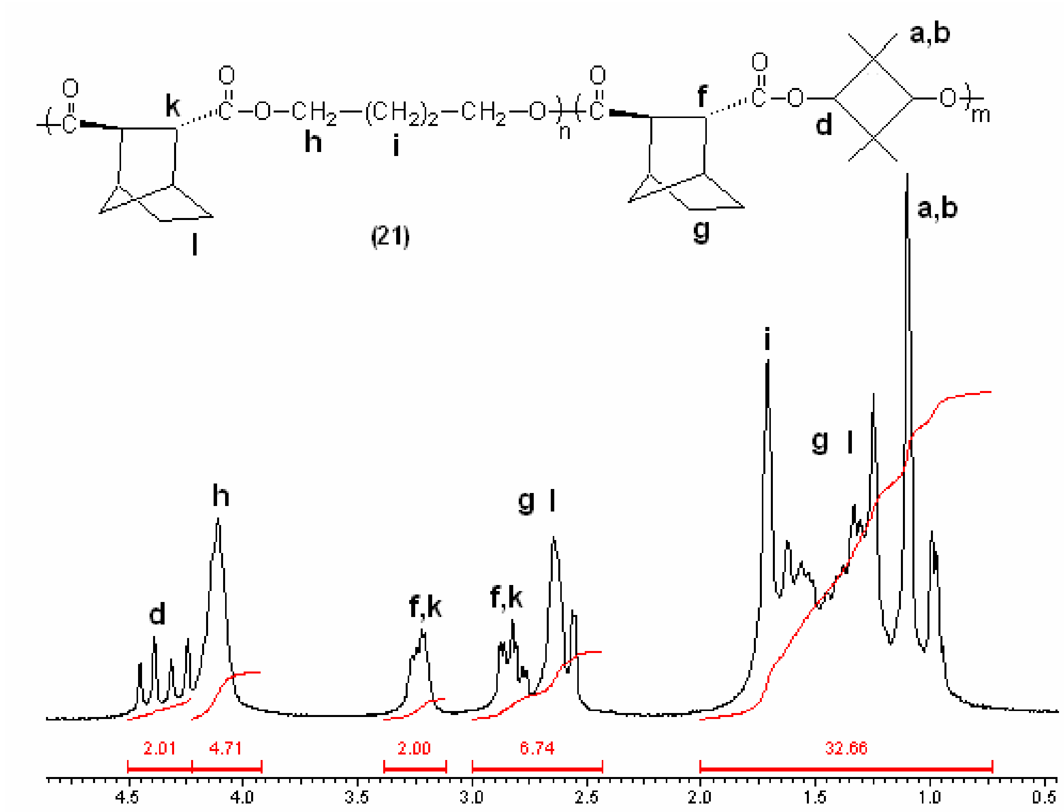
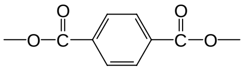
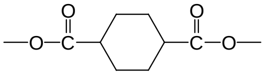
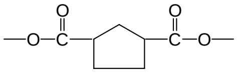
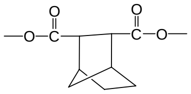


Figure 5.29 ^{1}H NMR spectrum of TMCBD/BD norbornane dicarboxylate copolyester

5.8.6 Thermal properties

All the copolyesters were found to be amorphous and had good thermal stability. The TMCBD/BD terephthalate copolyester has a T_g of 86°C. TMCBD/BD terephthalate copolyester has been synthesized by Kelsey et al[7]. The T_g of the copolyesters having 78/22, 72/28 and 64/36 compositions is 145, 129 and 119 respectively. Using Flory Fox equation[16] the T_g for the TMCBD/BD terephthalate (50/50) copolymer would be 92 °C. In the case of the other copolyeters containing cyclopentane, cyclohexane and norbornane dicarboxylates, incorporation of rigid TMCBD group increases the T_g by 46°C. The T_g and the initial decomposition temperature values are given in **Table 5.7.**

Table 5.7 Thermal properties of TMCBD/BD copolyesters

Diester component	TMCBD/BD mole ratio	T_g	IDT[a]
	50/50	86	394
	0/100	40	
	50/50	37	406
	0/100	-10	
	47//53	-12	392
	0/100	-44	
	47//53	52	398
	0/100	15	

[a]Calculated from TGA

5.9 Conclusions

Aliphatic copolyesters based on cyclobutane diol and butane diol containing, dimethyl terephthalate, 1,4-cyclohexane dicarboxylate, 1,3-cyclopentane dicarboxylate and 2,3-norbornane dicarboxylate were synthesized and found to be amorphous. The incorporation of the rigid cyclobutane diol in the copolymer backbone boosts the T_g by about 40°C compared to the corresponding homopolymers.

5.10 References

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Chapter 6: Summary and conclusions

6.1 Summary

The key findings and conclusions of the present thesis are summarized below:

A series of poly(butylene terephthalate-co-1,4-cyclohexylene dimethylene terephthalate)s (P(BT-co-CT)) and poly(butylene terephthalate-co-1,4- cyclohexane dicarboxylate)s (P(BT-co-BCD)) copolymers with various CT and BCD contents were synthesized by melt polycondensation. The NMR spectroscopic analysis indicates that the copolymers are statistically random, irrespective of the composition. The thermal analysis and XRD studies showed that these copolymers crystallize in all range of compositions, a feature not commonly observed in such polymers. The poly(BT-co-CT) copolymers exhibited typical eutectic behavior in melting and crystallization with a eutectic composition corresponding to $PBT_{75}CT_{25}$ indicating iso-dimorphic cocrystallization behavior. On the other hand, poly(BT-co-BCD) copolyesters showed isomorphic crystallization but did not show eutectic behavior in melting and crystallization. The glass transition temperature showed linear dependency on composition in these copolymers.

A detailed crystallization kinetics study of PCT and PCCD was performed and compared with PBT. PCT is a rapidly crystallizing polymer like PBT and has short crystallization half time (less than 0.5 minute over wide range of temperature from 110 to 275°C). PCCD, on the other hand, crystallizes slowly and shows unique minimum crystallization half time at two different temperatures.

Monomers containing a cyclopentane ring, such as, 1,3-bis(hydroxymethyl) cyclopentane and dimethyl-1,3-cyclopentane dicarboxylate are synthesized. The homopolyester of 1,3-bis (hydroxy methyl) cyclopentane and DMT (PCPDT) is found to be a semicrystalline polyester. PCPDT has lower crystallization rate compared to PBT and shows well defined banded spherulitic morphology. The homopolyester of dimethyl-1,3-cyclopentane dicarboxylate with DMT (PBCP) is found to be an amorphous polyester. Random copolyesters of PBT with 1,3-bishydroxy methyl cyclohexane and dimethyl-1,3-

cyclopentane dicarboxylate, namely, poly(BT-co-CPDT) and poly(BT-co-BCP) were synthesized. The thermal analysis and XRD studies show that poly(BT-co-CPDT) copolymers also crystallize in all compositions. The poly(BT-co-CPDT) copolymers exhibit typical eutectic behavior in melting and crystallization and iso-dimorphic cocrystallization.

The poly(BT-co-BCP) copolyesters containing upto 50 % BCP component are found to be semicrystalline. In the composition range where the copolyesters crystallized, the samples show isomorphic crystallization but do not show eutectic behaviour in melting and crystallization. The glass transition temperature exhibits linear dependency on composition in these copolymers.

Two aliphatic polyesters, namely, poly(cyclohexanedimethylene cyclohexanedicarboxylate) (PCCD) and poly (cyclopentane dimethylene cyclopentane dicarboyxlate) (PCPCPD) are synthesized and characterized. The PCCD synthesized contains 67 % axial,equatorial-cyclohexane dicarboxylate and is an amorphous polymer. PCPCPD is found to be an amorphous rubbery polymer with a T_g below room temperautre.

A series of poly(butylene terephthalate-co-2,3-norbornane dimethylene terephthalate) (P(BT-co-NBDT)) and poly (butylene terephthalate-co-2,3-norbornane dicarboyxlate) (P(BT-co-BNB)) copolymers with various NBT and BNB contents are synthesized by melt condensation. The NMR spectroscopic analysis indicates that the copolymers are random. The thermal analysis and XRD studies show that the PNBDT is an amorphous polyester with a T_g of 113°C. The poly(BT-co-NBDT) copolyesters could crystallize in compositions upto 20 % NBDT content, while the composition having 50 % NBDT is amorphous.

On the other hand, PBNB was found to be an amorphous polyester with a T_g of 15°C. The poly(BT-co-BNB) copolyesters show isomorphic crystallization but did not show eutectic behaviour in melting and crystallization.

Copolyesters of TMCBD/BD containing, dimethyl terephthalate, 1,4-cyclohexane dicarboxylate, 1,3-cyclopentane dicarboxylate and 2,3-norbornane dicarboxylate were synthesized and found to be amorphous. The incorporation of the rigid cyclobutane diol increases the T_g by about ~ 45°C compared to the corresponding homopolymers.

6.2 Conclusion

- A series of poly(BT-co-CT) and poly(BT-co-CPDT) copolyesters with various CT and CPDT contents were synthesized for the first time. *These polyesters exhibit isodimorphic crystallization behavior and show typical eutectic melting behavior and the eutectic compositions are* $PBT_{74}\ CT_{26}$ *and* $PBT_{45}CPDT_{55}$. These copolymers, in general, have higher T_g than PBT.

- Poly(cyclopentylene dimethylene terephthalate) (PCPDT) is a newly synthesized semicrystalline polymer and exhibits banded spherulites. *The Tg of the new polymer is 60°C and the melting temperature is 207°C.*

- A series of poly(BT-co-BCD), poly(BT-co-BCP) and poly(BT-co-BNB) copolyesters with various BCD, BCP and BNB contents, respectively, were synthesized and characterized. *These coplyesters show isomorphic crystallization and melting behavior.* These copolymers have lower T_g than PBT.

- Poly(butylene cyclopentane dicarboyxlate) (PBCP) synthesized from dimethyl-*cis*-1,3-cyclopentane dicarboxylate and dimethyl *cis/trans*-1,3-cyclopentane dicarboxylate (50/50), namely, *cis*-PBCP and *cis/trans*-PBCP are found to be amorphous polymers. *The glass transition temperature of cis-PBCP and cis/trans-PBCP are –44°C and -15°C respectively.* The polyester poly(butylene 2-exo,3-endo-norbornane dicarboxylate) (PBNB) synthesized is an amorphous polyester with a T_g of 15°C.

- The crystallization behaviour of the polyesters depends on the molecular structure. *The faster crystallization behavior of PCT compared with PCCD may* *be attributed to their structures, i.e. planar benzene ring structure of PCT vis-à-vis the non-planar cyclohexane ring of PCCD. The non-planar nature of the cyclohexane ring inhibits the quick packing of the chains in the lattice leading to slower crystallization rates. Similarly, PCPDT exhibits lower crystallization rate than PCT due to the non-planar cyclopentane structure.*

Perspectives:

Aliphatic poly(ester)s are attracting increasing attetion in view of their potential application as materials with biodegradability. In this context an understanding of the structure-property relationship in aliphatic polyesters is of significant contempery interest. There is a need to vastly expand the range of material properties that can be obtained from aliphatic poly(ester)s. The present work, thus, opens up newer opportunities to talilor the polymer property by appropriate choice of comonomers.

The copolymer synthesised as part of this work and reported in this thesis is based on terephthalates. It should be interesting to synthesize poly(ester)s and copoly(ester)s based on naphthalate and study their crystallization behaviour.

The present work has focused on the synthesis and thermal characterization of the copolymers. Studies using dynamic mechanical analysis (DMA) will give useful information on the sub T_g relaxation behaviour, which controls the impact characteristics of the copolymers.

PBT is shown to exhibit crystal to crystal transition during drawing because of conformational changes ocurring in the methylene segments. It will be interesting to study the effect of comonomer on the crystalline transition in these coploymers.

The 1,3-bis(hydroxymethyl) cyclopentane synthesized and used in the present work is predominantly the *cis* isomer. The *trans* isomer is optically active and sythesis of polyesters and copolyesters from trans isomer could lead to optically active poly(ester)s.

Synopsis

"Synthesis and characterization of aliphatic-aromatic polyesters"

Introduction

Aliphatic aromatic polyesters are a class of thermoplastic polyesters with a broad range of properties including high heat distortion, high rigidity and hardness, good mechanical strength and toughness, excellent surface appearance, good chemical resistance, stable electrical-insulation properties etc[1]. The principal polymers of this class are the poly (ethylene terephthalate), poly (butylene terephthalate) and poly (ethylene naphthalate)s.

Aliphatic-aromatic polyesters are obtained from aliphatic glycols and aromatic dicarboxylic acids or esters. Poly (ethylene terephthalate) was introduced commercially in 1953 as a textile fibre. It is a major industrial polymer used extensively in the form of fibres, films and as molding material. Poly (butylene terephthalate) was introduced in 1970 and grew rapidly as it found utility in various high volume automotive, electrical and other engineering applications[2].

PBT is one of the most successful thermoplastic polyester[3]. It belongs to the class of semicrystalline polymers. It has a high melting temperature (222-224°C) depending on degree of crystallization and annealing conditions and the heat of fusion is about 140 J/g. The glass transition temperature of PBT varies with crystallinity, annealing and method of measurement. Although the Tg value is reported between 30 and 50°C, the crystallization of quenched samples occurs as low as 20°C. Totally amorphous PBT has a Tg of 15°C, estimated by extrapolation. It is a fast crystallizing polymer and hence well suited for extrusion and injection molding applications. Properties of PBT (especially above Tg) are influenced by the degree and nature of crystallization and on the morphology of the material i.e., the way in which the polymer chains are arranged in the amorphous and crystalline domains in the material[4]. At Tg (40°C) the mobility of the polymer chains in the amorphous regions increases considerably, resulting in decrease in stiffness. Hence PBT is not suitable for applications involving high heat[5].

The properties of PBT can be modified in many ways to meet the requirements of specific fields of application. Copolymerization, blending with other polymers and addition of additives are different ways to modify the properties of PBT.

It is well known that aromatic groups impart molecular rigidity, which contributes to improved properties of semicrystalline polymers. Cyclo-aliphatic diols also impart molecular rigidity.

Polyester derived from 1,4-cyclohexane dimethanol (CHDM), poly (cyclohexane dimethylene terepthalate) (PCT) has a high Tm ranging from 250-305°C depending on the cis/trans ratio[6,7]. The Tg likewise increases from 60° (cis) to 90°C (trans). Cycloaliphatic diols such as CHDM have been used for the purpose of improving the performance of polyesters[8,9]. The improved impact properties of copolyesters of PET/PCT has been attributed to the conformational flexibility of the cyclohexane rings and its influence on chain mobility[10, 11, 12].

Polyesters of norbornane and norbornane condensed diesters and dimethanols[13] have high second order transition temperature (Tg) and exhibit little tendency to crystallize. Varying the point of substitution in the norbornane moiety has little effect on the glass transition temperatures of the polyesters. Increasing the number of norbornane residues as polymer side chains results in a linear increase in the Tg.

Polyesters prepared from substituted 1,1-norbornane dimethanol[14, 15] has a Tg of 118°C. These polyesters can be used to prepare hard and transparent materials that neither crystallize nor are brittle. The polyesters containing norbornane moiety have not only high Tg but also possess excellent dimensional stability.

Polyesters of 2,2,4,4-tetramethyl-1,3-cyclobutanediol (TMCBD) reported[16,17,18] are primarily high melting, semicrystalline materials. Melting points for the polyesters from dimethyl terephthalate and TMCBD, are 316-319°C (38/62 cis/trans), 296-308°C (cis) and >350°C (trans)[19] and the Tg is 174°C. The properties of random copolyesters of TMCBD with small chain aliphatic diols over a range of compositions were studied by Kelsey et al[16]. The new family of terephthalate-based copolyesters were found to exhibit high impact resistance combined with good thermal properties, ultraviolet stability, optical clarity, and low color[20,21,22]. The copolymers were amorphous when the TMCBD contents was about 40-90 mol% of the total diol.

Objectives of the present work

A. One of the objective of the present work is to systematically examine a series of aliphatic-aromatic polyesters with a view to understand the structure relationship between monomer and polyester properties.
B. To synthesize various cycloaliphatic diols and diesters with varying degrees of molecular rigidity.
C. To synthesize a series of copolyesters of dimethyl terephthalate with different cycloaliphatic diols and diesters.
D. To synthesize aliphatic polyesters containing cycloaliphatic diols and diesters
E. To study the thermal and dynamic mechanical properties of the polyesters and copolyesters.
F. To study the crystallization behavior and the crystallization kinetics of the copolyesters.

The thesis has been divided into the following chapters:

Chapter 1 : Introduction

A general literature background is presented on the influence of comonomer structure on the properties of aliphatic-aromatic copolyesters, with particular reference to thermal properties and crystallization phenomena.

Chapter 2: Scope and objectives of the present work.

This chapter discusses the scope and objectives of the present work.

Chapter 3: Synthesis and chracterization of poly (alkylene terephthalate)s containing cyclohexane ring.

This chapter describes the following

a) Synthesis of polyesters and copolyesters of dimethyl terephthalate, 1,4-butanediol and 1,4-bis(hydroxymethyl) cyclohexane.
b) Sequence analysis of the copolyesters and thermal properties.
c) Crystallization behavior and crystallization kinetics of the copolyesters.

Chapter 4: Synthesis and characterization of polyesters and copolyesters containing cyclopentane ring

This chapter describes the following

a) Synthesis of monomers, dimethyl-1,3-cyclopentane dicarboxylate and 1,3-bis(hydroxy methyl) cyclopentane.

b) Synthesis of homopolyester and copolyesters of dimethyl terephthalate, 1,4-butanediol and 1,3-bis(hydroxy methyl) cyclopentane.
c) Synthesis of polyester and copolyesters of dimethyl terephthalate, 1,4-butanediol and dimethyl-1,3-cyclopentane dicarboxylate.
d) Synthesis of polyester from 1,3-bis(hydroxy methyl) cyclopentane and dimethyl-1,3-cyclopentane dicarboxylate.
e) Sequence distribution analysis and thermal properties.
f) Crystallization behavior of the copolyesters.

Chapter 5: Synthesis and characterization of polyesters and copolyesters containing norbornane ring

This chapter describes the following

a) Synthesis of monomers, dimethyl bicyclo([2,2,1] heptane 2,3-dicarboxylate, 2,3-bis(hydroxymethyl)bicyclo[2,2,1] heptane and dimethyl-2,3-dimethyl bicyclo[2,2,1]heptane-2,3-dicarboxylate.
b) Synthesis of homopolyester and copolyesters of dimethyl terephthalate, 1,4-butanediol and dimethyl bicyclo[2,2,1] heptane 2,3-dicarboxylate
c) Synthesis of polyester and copolyesters of dimethyl terephthalate, 1,4-butanediol and 2,3-bis(hydroxymethyl)bicyclo[2,2,1] heptane
d) Synthesis of polyester and copolyesters of dimethyl terephthalate, 1,4-butanediol and dimethyl-2,3-dimethyl bicyclo[2,2,1]heptane-2,3-dicarboxylate.
e) Sequence distribution analysis and thermal properties
f) Crystallization behavior of copolyesters.

Chapter 6: Summary ad conclusion

This chapter summarizes the results and conclusion of the work.

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List of Publications

1. Copolyesters based on Poly (butylene terephthalate)s containing cyclohexyl group: Synthesis, structure and crystallization

   T. E. Sandhya, C. Ramesh and S. Sivaram

   Macromol. Symp. 2003, **199**, 467-482.

2. Copolyester based on Poly(butylene terephthalate)s Part 1: Containing cyclopentane: Synthesis, crystallization behavior and morphology

   Macromolecules (To be communicated)

3. Copolyester based on Poly(butylene terephthalate)s Part 2. Containing cyclohexane and cyclopentane: Synthesis and crystallization behavior and morphology

   Macromolecules (To be communicated)

4. Studies on the Crystallization behavior of PBT, PCT and PCCD

   Polymer (To be communicated)

5. Studies on the Crystallization behaviour of poly (butylene terephthalate-co-cyclopentylene dimethylene terephthalate) copolyesters

   Polymer (To be communicated)

6. Copolyester based on Poly(butylene terephthalate)s Part 1: Containing norbornane ring: Synthesis and characterization

   J. Polym Sci. Polym. Chem. (To be communicated)

7. Structure property relationship in aliphatic-aromatic polyesters

   J. Macrmol. Sci. Reviews (To be communicated)