SYNTHESIS AND CHARACTERIZATION OF BRANCHED POLYMERS

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BY

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DEDICATED TO MY PARENTS

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T.K. Bera

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DECLARATION

Certified that the work incorporated in this thesis " **Synthesis and characterization of branched polymers** " submitted by Mr. Tushar Kanti Bera was carried out by the candidate under my supervision. Such materials as has been obtained from other source has been duly acknowledged.

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GLOSSARY

MeOTS	Methyl-p-toluene sulfonate
2-PhOZO	2-Phenyl-2-oxazoline
Kp	Propagation rate constant
Ki	Initiation rate constant
PEI	Polyethylenimine
LPEI	Linear polyethylenimine
$LiAlH_4$	Lithium aluminium hydride
GTP	Group transfer polymerization
IBVE	Isobutyl vinyl ether
PIBVE	Poly (isobutyl vinyl ether)
MA	Methylacrylate
PMA	Poly (methylacrylate)
PMMA	Poly (methyl methacrylate)
EA	Ethyl acrylate
PEA	Poly (ethyl acrylate)
LDA	Lithium diisopropylamine
TMSCl	Trimethyl silyl chloride
Mn	Number average molecular weight
Mw	Weight average molecular weight
MWD	Molecular weight dispersity
DXL	1,3 Dioxolane
TMSI	Trimethyl silyl iodide

VE	Vinyl ether
TBO	2-Perbromomethyl-2-oxazoline
MeOXZ	2-Methyl-2-oxazoline
ROZO	2-Alkyl-2-oxazoline
DVB	Divinyl benzene
NBS	N-Bromosuccinimide
GPC	Gel permission chromatography
SEC	Size exclusion chromatography
DMF	Dimethyl formamide
PIP	Poly (isoprene)
PBd	Poly (butadiene)
THF	Tetrahydrofuran
$AgSbF_6$	Silver antimonate hexaflouride

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ABSTRACT

This thesis deals with the synthesis of a novel tribromo compound, namely, 2-perbromomethyl-2-oxazoline (TBO) and exploration of its synthetic utility as a trifunctional initiator for living polymerization and trifunctional terminator for the synthesis of three arm star polymer.

TBO was synthesized by the reaction of 2-methyl-oxazoline (MeOXZ) with N-bromosuccinimide in DMF at 25-27°C. The structure of TBO was established by a combination of spectroscopic technique.

TBO was used as a trifunctional initiator for the living ring opening cationic polymerization of MeOXZ. TBO smoothly initiated the polymerization of MeOXZ in refluxing acetonitrile. The living nature of this polymerization system was established. End group analysis by ion selective electrode titration and insitu proton nmr study showed that the polymer thus formed has a three arm star branch shaped structure. Also, it is evident from ^{1}H-NMR spectroscopy that initiation takes place stepwise. The initiation of first polymer arm is faster than the second polymer arm. The initiation of the third polymer arm is apparently slow. Thus, the relative length of the three arms of the resulting star shaped polymer are unequal. The presence of oxazoline group from initiator in the polymer chain was established by potentiometric titration. This established that every polymer chain has, on an average, one oxazoline group. Thus, under the present experimental conditions, the oxazoline group of the initiator does not undergo any ring opening reactions.

TBO was explored as a linking agent for the synthesis of three arm star polymer by termination method. Isoprene and butadiene were polymerized in toluene and THF at room temperature using n.BuLi as initiator. Linking reactions were carried out at room temperature as well as at 50°C. Formation of the three arm star polymer has been demonstrated in THF at room temperature and in toluene at 50°C. However, even under the best conditions, free arm content could not be reduced below 20%.

TBO in presence of ZnI_2 as coinitiator smoothly polymerized IBVE in dichloromethene as well as toluene between 25°C to -40°C. However, molecular weight distributions were broad in all cases. The tailing of the peak in SEC occurred at the lower Mn side. This is perhaps, due to the slow initiation. Interhalogen reaction with KI was attempted to improve the efficiency of the initiation. However, the results were not satisfactory. Therefore, it was concluded that TBO in presence of ZnI_2 as coinitiator does not initiate living cationic polymerization of IBVE.

CHAPTER 1

CHAPTER 1

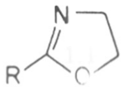
SECTION A

Synthesis of poly (N-acylethylenimine) by living cationic ring opening polymerization.

1.1:Introduction.

Living cationic ring opening polymerization of 2-methyl-2-oxazoline produces poly(N-acylethylenimine). 2-methyl-2-oxazoline is a cyclic imino ether. Cyclic imino ether compounds are those having -N=C-O- group in the cyclic molecule.

The following compounds have been used for the polymerization of cyclic imino ethers: a) 2-oxazolines. b) 5,6-dihydro-4H-1,3-oxazolines. c) 2-iminotetrahydrofurans. d) ethylene iminocarbonates. e) 2-imino-oxazolines.



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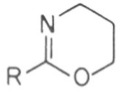

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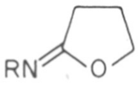

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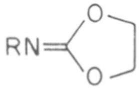

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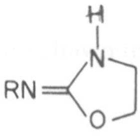


(e)

It is established that acid catalysed cleavage reaction of imino ethers proceeds by alkyl oxygen bond fission as shown in equation 1.1 in which the imino ether group (-N=C-O-) is isomerised to an amide group (-NH-C=O)[1].

$$R^1\text{-}N{=}C(R^2)\text{-}O\text{-}R^3 + HX \dashrightarrow [R^1\text{-}NH\text{-}C(R^2)\text{-}O\text{-}R^3]^+X^- \dashrightarrow R^1\text{-}NHCO(R^2) + R^3X \text{ ------}1.1$$

In a similar manner, polymerization of cyclic imino ether with a cationic initiator proceeds via ring opening through C-O bond cleavage in a SN_2 mode to produce a polymer with an amide structure[2]. It has been proven that cyclic imino ethers are inert to free radical and anionic initiators.

Polymerization of substituted 2-oxazoline, five membered cyclic imino ethers was first reported in 1965[3]. Poly(N-acylethylenimine (2) was obtained in good yield by a cationic ring opening polymerization of (1) as shown in scheme1.1.

(1)

(2)

Scheme 1.1 : Polymerization of 2-alkyl-2-oxazoline.

Various alkyl derivatives of 2-oxazolines have been polymerized and are shown in figure 1.1.

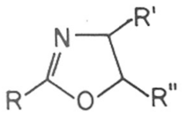
 (1)	R = (a) H, (b) CH_3, (c) C_2H_5, (d) n.C_3H_7, (e) i-C_3H_7, (f) n-C_4H_9, (g) i-C_4H_9, (h) ${}^tC_4H_9$, (i) n-C_5H_{11}, (j) ${}^tC_5H_{11}$, (l) n-C_6H_{13}, (m) n-C_7H_{15}, (n) n-$C_{11}H_{23}$, (o) n-$C_{17}H_{35}$, (p) Cyclo-C_6H_{11}, (q) $CHCl_2$, (r) CCl_3, (s) C_2F_5, (t) n-C_7F_{15}, (u) $CH{=}CCH_3$, (v) $CH_2{=}CH(CH_2)_8$, (w) $C_6H_5CH_2$, (x) C_6H_5, (y) p-$CH_3C_6H_4$, (z) p-ClC_6H_4, (ab) p-(OH)C_6H_4,(ac) B-$C_{10}H_7$, (ad) $CH_3OCOCH_2CH_3$,(ae) $CH_3CO_2(CH_2)_5$, (af) $CH_3CO_2CH_2$, (ag) $HO(CH_2)_5$.
(3)	R= Ph , R^1= Et , R^{11}= H
(4)	R= Ph , R^1= H , R^{11}= Me
(5)	R= Ph , R^1= Me_2 , R^{11}= H
(6)	R= Ph , R^1= H , R^{11}= Me_2
(7)	R= Me , R^1= H , R^{11}= Me
(8)	R= Me , R^1= Me , R^{11}= H
(9)	R= H , R^1= H , R^{11}= H
(10)	R= H , R^1= Me , R^{11}= H

Figure 1.1 : 2-Oxazoline monomer.

1.2: Initiators used for the living polymerization of 2-alkyl-2-oxazoline.

Various kinds of initiators have been examined for the polymerization of 2-oxazolines. They may be divided into four classes:

A a) Friedel-Craft Catalysts : $BF_3.O(C_2H_5)_2$, complexes of BF_3 with 2-oxazolines, SbF_6 and $SnCl_4$ b) Metal Chlorides : $SnCl_4$, $TiCl_4$, $AlCl_3$, and their stable salts[4-9]

B Strong protic acids and their oxazolinium salts : H_2SO_4[6], HI[5,7], toluene-p-sulphonic acid[6], $HClO_4$[9], H_3PO_4[9]

C Esters of sulfuric and sulfonic acids: Dimethyl sulfate[4,6], methyl toluene-p-sulfonate (MeOTs)[4,6].

D Alkyl iodide[8,10]. Methyl and n-butyl iodides are much more active than the corresponding bromide. n.Butyl chloride is inactive for the 2-oxazoline polymerization[10]. Benzyl halides $C_6H_5CH_2X$ (X: I, Br, Cl)[11].

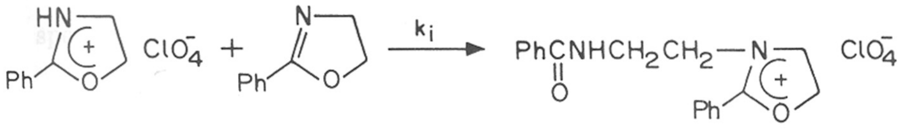
1.3: Kinetics and mechanism of polymerization .

A kinetic study on the 2-oxazoline polymerization was first reported by Tomalia and Sheetz[8]. The kinetic analysis was made by measuring the rate of monomer disappearance by IR spectroscopy. The relative polymerizability as measured by propagation rate constant was as follows.

2-phenyl->2-methyl->2,4-dimethyl->2,5-dimethyl-2-oxazoline

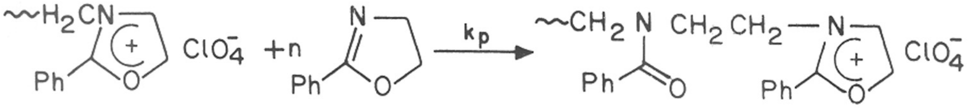
Kagiya et al also performed a kinetic study of 2-phenyl-2-oxazoline polymerization by IR technique[9,12-14]. The initiator was 2-phenyl-2-oxazolinium perchlorate. Based on the results they proposed the following mechanism (equation 1.2 and 1.3).

Initiation:

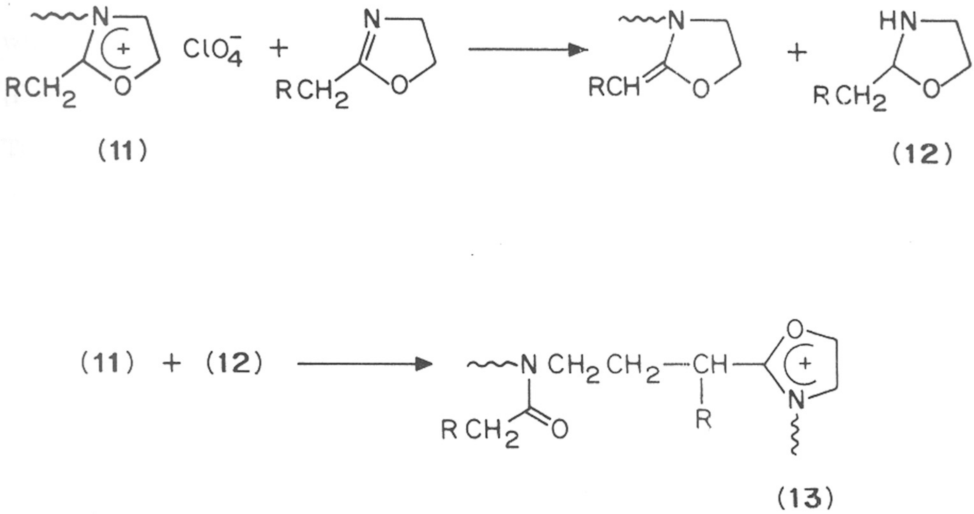


….. 1.2

Propagation:


..... 1.3

A kinetic study by Litt et al[15] gave a value of K_p=0.216 lit mol^{-1} s^{-1} for the polymerization of 2-heptyl-2-oxazoline initiated by 2-(p-chlorophenyl)-2-oxazoliniumperchlorate in butyro-lactone at 150^{0}C. Extensive chain transfer occurs as shown in scheme 1.2.



Scheme 1.2: Chain transfer process

The polymer molecules,**(12)**, formed by chain transfer has an enamine structure and hence very reactive. Therefore ,**(12)**,is repolymerized by the active species,**(11)**,to produce a branched polymer,**(13)**.

^{1}H NMR spectroscopy has proved to be a very useful method for kinetic analysis[16-19]. It is possible to determine the instantaneous concentration of monomer, initiator and propagating species by ^{1}H NMR. Based on equations 1.4 and 1.5, the rate equation of initiation and propagation are given in the following form.

$$-d[I]/dt = k_i\,[I]\,[M] \qquad \ldots\ldots \quad 1.4$$

$$\text{and} \quad -d[M]/dt = k_i[I][M] + k_p\,[P^*]\,[M] \qquad \ldots\ldots \quad 1.5$$

where K_i and K_p are rate constants of initiation and propagation, and [I], [M] and [P^*] represent the concentrations of initiator, monomer, and propagating species. The integrale forms are respectively,

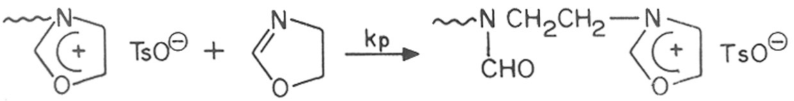
$$\ln\,[I^\circ]\,/\,[I] = k_i \int_0^t [M]\,dt \qquad \ldots\ldots\ldots \quad 1.6$$

$$\text{and} \quad \frac{\ln[M]_0/[M]}{\int_0^t [I]\,dt} = (k_i - k_p) + k_p\,\frac{[I]_0^t}{\int_0^t [I]\,dt} \qquad \ldots\ldots \quad 1.7$$

To obtain equation 1.7, the relationship [P^*] = $[I]_0$ - [I] was taken into account.

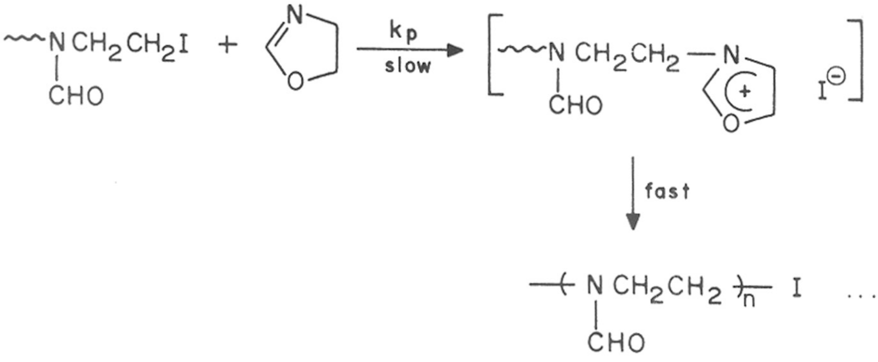
1.3.1: Effect of nucleophilicity of counter anion of initiator .

For the polymerization of unsubstituted oxazoline, two types of propagating species were identified. One is the ionic species of oxazolinium salt, which is found to be responsible for propagation in polymerization with methyl tosylate initiator[21] (equation 1.8).



..... 1.8

The other is the covalent species having an alkyl halide structure , which is responsible for the propagation in the case of polymerization with methyl iodide initiator[19] (equation 1.9)

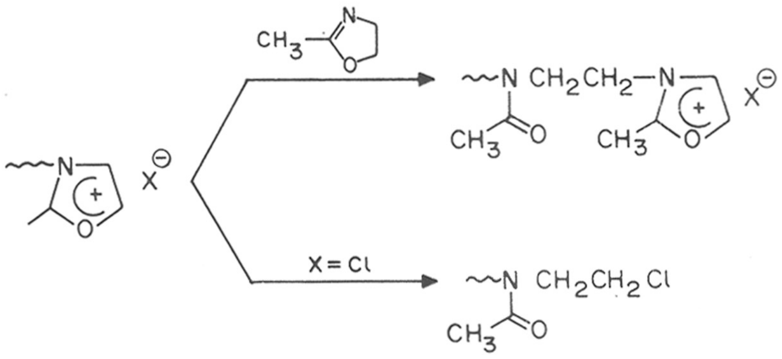


..... 1.9

The difference in the polymerization mechanism is well demonstrated by the activation parameters (table 1.1).

The rate constant, the type of propagating species and activation parameters for the polymerization of unsubstituted, 2-methyl and 2-phenyl-2-oxazoline are shown in table 1.1. With methyl tosylate as initiator, propagating species is always ionic in nature. With halide counter ions, the propagating species may be either ionic or covalent, or sometimes both.

In general the type of species is determined by the relative nucleophilic reactivities of the monomers and of the counter anion. The mechanistic difference is explained by the difference in nucleophilic reactivity between the two counter anions of tosylate and iodide. According to Swain-Scott formalism, the nucleophilic constant (n) of iodide (n= 5.04) is much higher than tosylate (n= 1.0). The strong nucleophilic iodide ion attacks the oxazolinium cation to produce alkyl halide, whereas the weak nucleophilic tosylate does not (scheme 1.2).



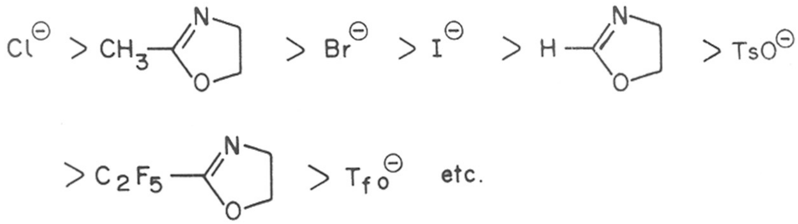
Scheme 1.2: The effect of nucleophilicity of counter anion.

The order of nucleophilicity of counter anion is as follows.[20]

Table 1.1 : Rate constant and activation parameters for the polymerization of three 2-oxazolines in CD_3CN at 40°C

Substituent	Initiator	$K_i x10^4$ (lit mol^{-1} s^{-1})	$K_p x10^4$ (lit mol^{-1} s^{-1})	type of propagating species	E_p (KJmol^{-1})	A_p (lit mol^{-1} s^{-1})
None	MeOTs	0.98	19	ionic	105	$7.5x10^{14}$
None	MeI	1.6	0.18	covalent	56.5	$5.0x10^{4}$
2-Me	MeOTs	1.8	1.17	ionic	80.0	$1.9x10^{9}$
2-Me	MeI	2.7	1.14	ionic	73.0	$1.7x10^{8}$
2-Me	$PhCH_2Br$	1.3^a	1.2	ionic	71.5	$1.1x10^{8}$
2-Me	$PhCH_2Cl$	0.01^a	0.03^a	covalent	62.0	$6.5x10^{4}$
2-C_6H_5	MeOTs	0.16^a	0.02^a	ionic	98.0	$7.2x10^{10}$
			12.5^b			
2-C_6H_5	MI	----	1.8^c	d	-----	-----

a) Calculated value from the experimental data.
b) At 100°C
c) At 100°C in nitro benzene.
d) Covalent species probably predominant at 100°C.

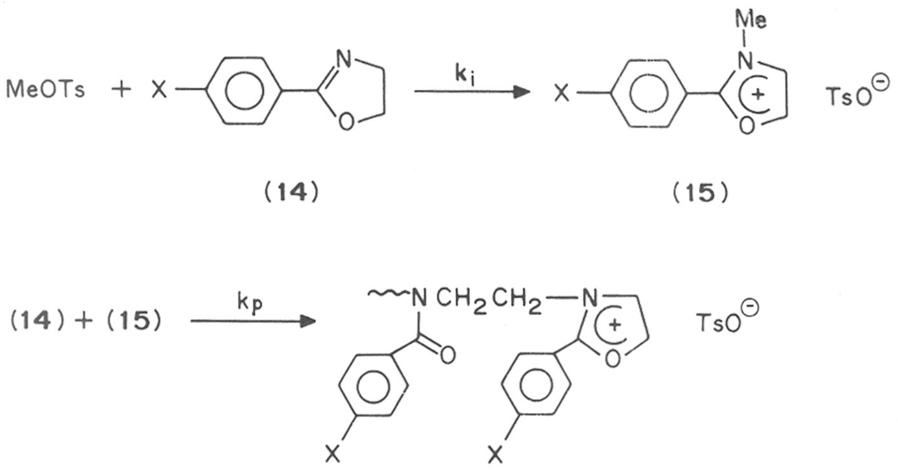


1.3.2 : Effect of ring substituents .

The effects of substituents at 2-position is remarkable. The nucleophillic reactivity of three monomers (Table 1.1) viz., unsubstituted, 2-methyl and 2-phenyl-2-oxazoline towards methyl tosylate is reflected in the k_i value which lie in the order $CH_3 > H > C_6H_5$, whereas the order of polymerizability is $H > CH_3 > C_6H_5$,

In general, electron withdrawing substituent at 2 - position reduces the nucleophilicity of the oxazoline ring and hence the rate of initiation. Similarly, electron releasing substituent at 2-position stabilize the propagating chain end i.e oxazolinium cation and hence increase the rate of propagation i.e polymerizability.

This was confirmed by studying the substituent effects using five 2-(p-substituted) phenyl-2-oxazolines,**(14)**[21](scheme 1.3). The k_i and k_p values were obtained with methyl tosylate initiator.



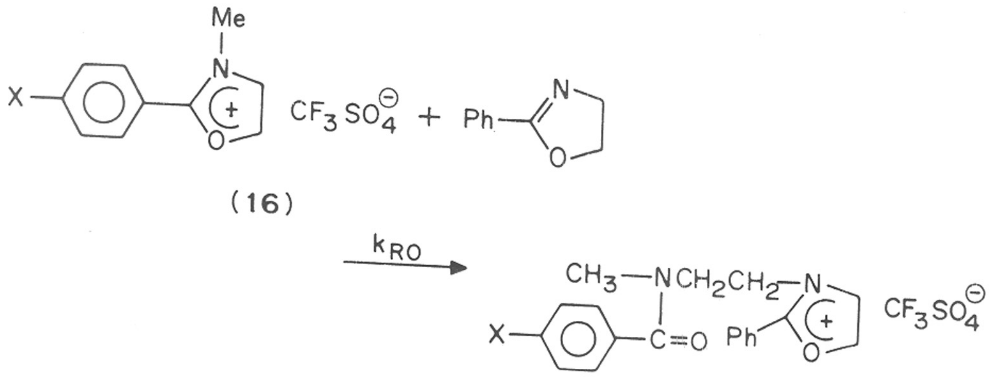
Scheme 1.3: Effect of ring substituents.

The nucleophilicity of monomers,**(14)**,with different X groups, towards electrophile MeOTs, as reflected by k_i values were in the following order with respect to X ; $CH_3O > H > Cl$. The order of polymerizability, as reflected by the k_p values was $Cl > H > CH_3O$.

An electron donating group CH_3O will increase the nucleophilicity of **(14)**, whereas such a group stabilizes the onium species **(15)** and hence reduce the ring opening tendency.

The ring opening reactivity (K_{RO}) of the propagating oxazolinium ion must be in the order of $Cl > H > CH_3O$.

This assumption was again examined by the model reaction (scheme 1.4), where five oxazolinium salts,**(16)**, were ring opened by the common monomer 2-phenyl-2-oxazoline.



Scheme 1.4: Effect of ring substituents.

The order of K_{RO} was NO_2> Cl> H> CH_3> CH_3O, which is the same as that of the polymerizability.

The Hammett plot of K_{RO} was better correlated with values (δ =0.729, correlation efficient R=0.997) than with values (δ =0.942, R=0.980), which is quite reasonable for the reaction of onium species,**(16)** (figure 1.2)[21].

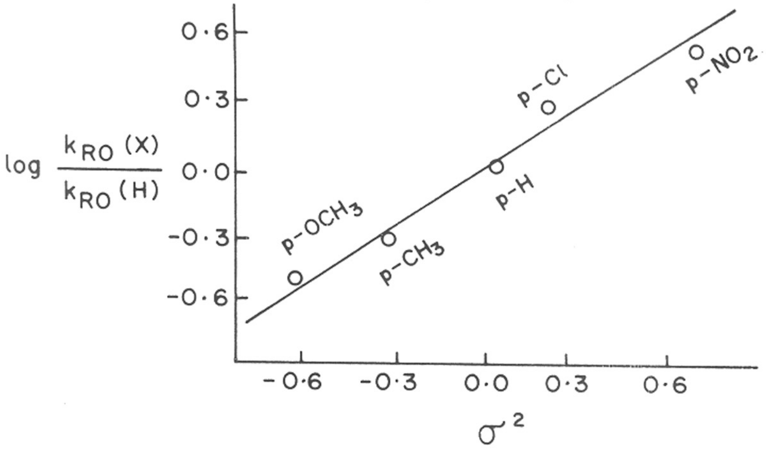


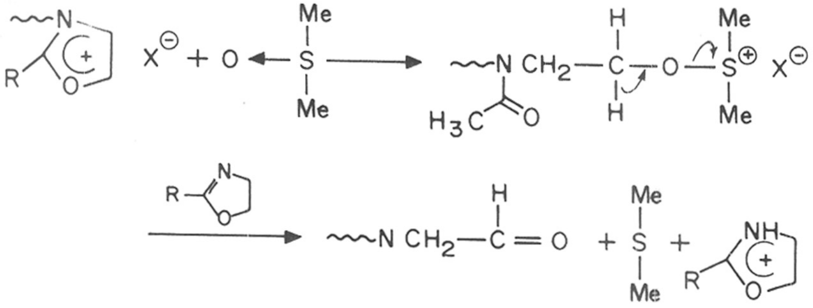
Figure 1.2: Hammett plot.

1.3.3: Effect of solvent.

The polymerization of 2-n-pentyl-2-oxazoline was carried out with oxazolinium perchlorate initiator in solvents containing various functional groups[22] such as sulphone, ester, ether and aromatic nitro compounds. Nitriles did not interfere with polymerization, whereas solvents with ketone, disulphide, and alcohol reacted with growing polymer chains by chain transfer. Compounds containing sulphoxide, phenol and carboxylic acid groups interfered strongly with polymerization. The mechanism (scheme 1.5) was proposed to explain the chain transfer phenomenon with DMSO.

Table 1.2 : Kinetic data for the 2-PhOZO polymerization initiated by the 2-PhOZO-HClO4 salt in various solvents.

sl.no	type of solvent	solvent	dielectric constant (δ ;25^{0}C)	nucleophilicity (η)/cm^{-1}	K$_p$ (120^{0}C) /l mol^{-1} min^{-1}	Δ E /Kcal mol^{-1}	Δ S / calK^{-1} mol^{-1}
1	Polar	nitro ethane	28.1	8	1.52	19.2	-16.8
2	Polar	nitrobenzene	34.8	21	0.82	19.1	-19.5
3	Polar	acetonitrile	37.5	49	0.71	23.1	-10.8
4	Polar	DMA	36.7	113	0.25	27.4	-2.0
5	Nonpolar	anisole	3.4	26	0.50	18.8	-22.4
6	Nonpolar	ethyl acetate	6.0	39	0.40	17.0	-27.4
7	Nonpolar	di-n-propyl ether	4.3	73	0.06	17.8	-29.0



Scheme 1.5 Chain transfer with DMSO.

The effect of solvent on the polymerization of 2-phenyl-2-oxazoline in which 2-phenyl-2-oxazoline-$HClO_4$ complex was used as initiator was studied by kinetic analysis. The results are summarized in table 1.2[23].

The K_p value is larger in polar than in nonpolar solvents. This means that dissociation of the propagating ion pair is promoted by solvents with high dielectric constant resulting in increase of the propagation rate.

On the other hand, the K_p value in both polar and nonpolar solvents is decreased with increase in the solvent nucleophilicity . It is argued that a solvent with large nucleophilicity coordinates strongly to the propagating oxazolinium ion preventing the coordination of the incoming monomer.

1.3.4 : Livingness of oxazoline polymerization.

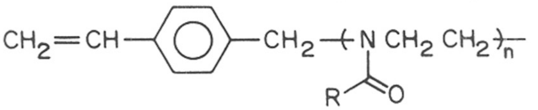
Although various initiators are reported for the polymerization of 2-alkyl-2-oxazoline (section 1.2), very few of them show the characteristic of living polymerization. For example, living polymerization was observed when methyl iodide[24], methyl p-toluenesulfonate[25], and benzyl bromide[26] was used as monofunctional initiator. Several bifunctional initiators such as α, ω-dodecamethylene bis (p-toluene sulfonate)[27], bis(oxazolinium tosylate)[28] and allylic dihalides such as 1,4-dibromo-2-butene and 3-iodo methyl-1-propene[29] have shown living characteristic. Even multifunctional initiators for example 1,3,5-(trisbromomethyl)-benzene[29], tetrakis(bromomethyl) ethylene[30] and hexakis[p-(bromomethyl)phenoxy] cyclotriphosphazene[31] have shown to induce living polymerization. Rate constant for these initiators are shown in table 1.3. In all cases rate of initiation is faster than rate of propagation confirming the livingness of the polymerization.

1.4: Synthetic approaches.

1.4.1: Synthesis of macromonomers and end functionalization.

When a polymer or an oligomer contains a polymerizable group, it is called a macromonomer. Macromonomers are extremely important for the preparation of graft copolymers with well defined structure[32].

A styryl type macromonomer of poly (N-acylethylenimine) **(17)** was prepared by initiating the 2-oxazoline polymerization with a p- or m- vinyl benzyl halide[33,34].

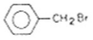
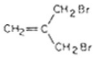
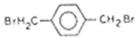
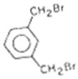
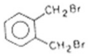


(17)

(Meth)acrylic type macromonomers (18) were prepared by the terminating of the 2-oxazoline propagating species with (meth)acrylate nucleophiles (direct method) or by the reaction of the isolated alcohol with (meth)acryloyl chloride (indirect method)[35,36].

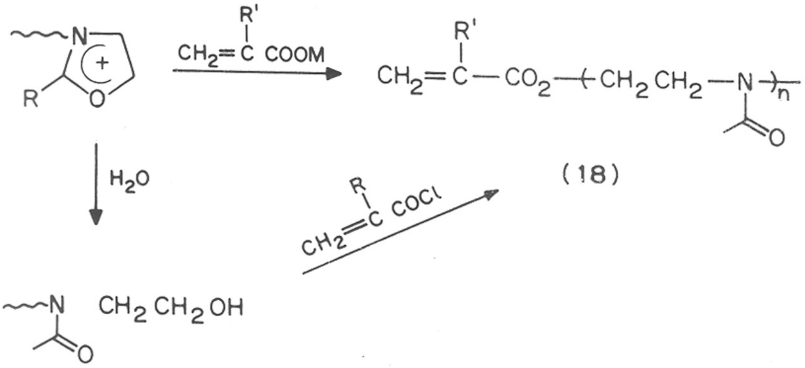
Table 1.3 : Rate constant of MeOZO polymerization in CD_3CN at 35^{0}C.

Rate constant, X10^{-4} L/mole. s

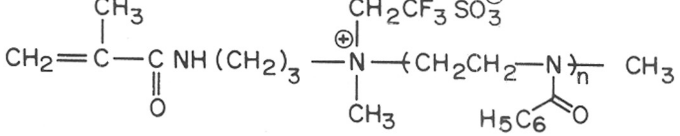
Initiator	k_{i1}	k_{i2}	k_i	k_p
MeI			0.98	0.47[a]
MeOTs			1.82	1.17[a]
			1.30	1.20[a]
$BrCH_2CH=CHCH_2Br$	1.2	1.0		0.81
 $CH_2=C(CH_2Br)_2$	1.5	2.1		0.76
	1.1	1.1		0.81
	0.90	0.89		0.81
	1.2	0.47		0.81
$CH_2=CHCH_2Br$			1.1	0.81

a) Temperature = 40^{0}C.

In the direct method, silver and ammonium (meth)acrylates gave **(18)** with higher functionality (functionality=0.9) than sodium, potasium or trimethylsilyl (meth)acrylates (functionality=0.5) . The direct termination can be achieved by adding (meth)acrylic acid followed by a tri alkylamine like triethylamine. A mixture of a hindered amine like 2,6 lutadine and the acid is also effective for the synthesis of **(18)**



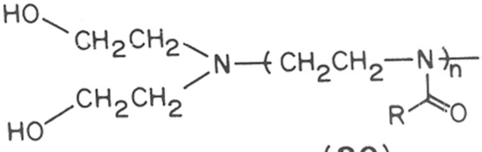
An ionic macromonomer of methacrylamide type is also reported[34] **(19)**.



$$CH_2=\overset{\displaystyle CH_3}{\overset{|}{C}}-\underset{\underset{\displaystyle O}{\|}}{C}NH(CH_2)_3-\overset{\displaystyle CH_2CF_3SO_3^{\ominus}}{\overset{\oplus|}{\underset{\underset{\displaystyle CH_3}{|}}{N}}}-(CH_2CH_2-\underset{\underset{\displaystyle H_5C_6\diagup C\diagdown O}{|}}{N})_n-CH_3$$

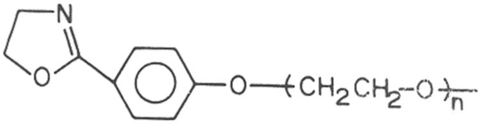
(19)

A glycol type macromonomer **(20)** was obtained by terminating the 2-oxazoline living species with diethanol amine[37].



(20)

A macromonomer with 2-oxazoline as a polymerizable group was reported[38,39,40] (**21-23**).



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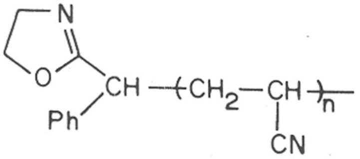

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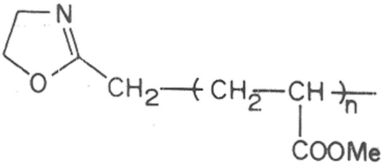
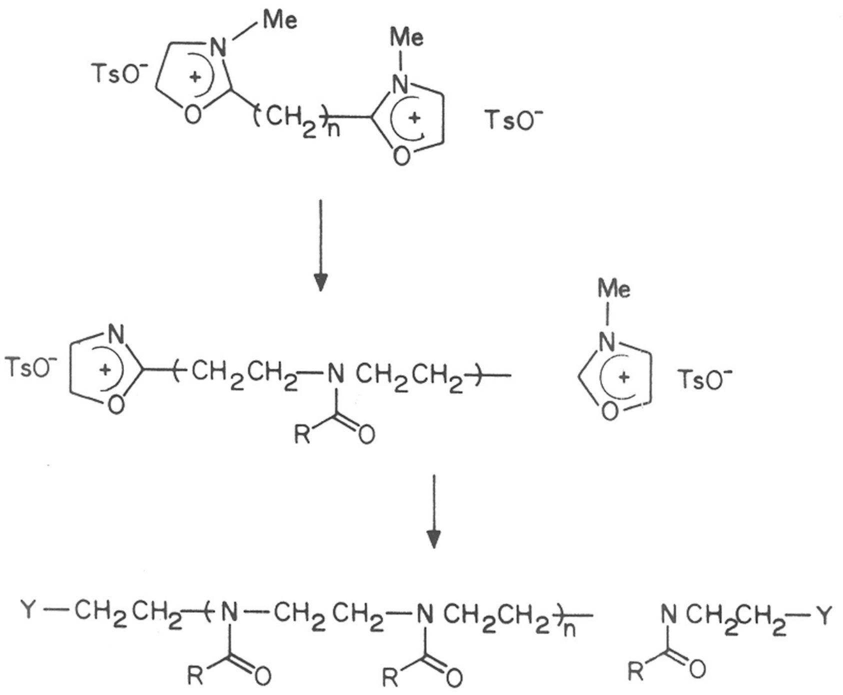


(23)

Starting from a bifunctional initiator, poly (N-acylethylenimine) telechelics with various functional groups have been obtained[36,41]. These telechelics e.g. Y=OH, are useful starting materials for preparing a segmented polyurethane via reaction with a diisocyanate[35](**24**).



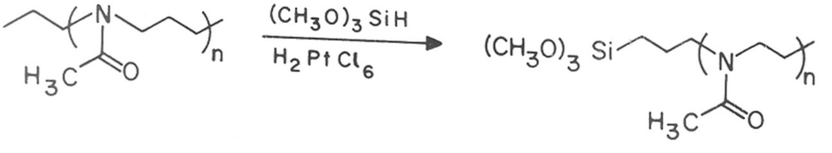
(24)

Y = OH, NH_2, n·PrNH, SH, N = N = S, $O_2CCCR' = CH_2$,

$O(CH_2)_m$ — COOH

A mono-telechelic polymer with a reactive silyl group is exemplified, which is used as a silane coupling agent[42].

These telechelics **(25,26)** were prepared via two methods; a) hydrosilylation b)direct termination of the living species. These telechelic can be used to modify the surface properties of silica gel to increase the hydrophilicity of the gel.



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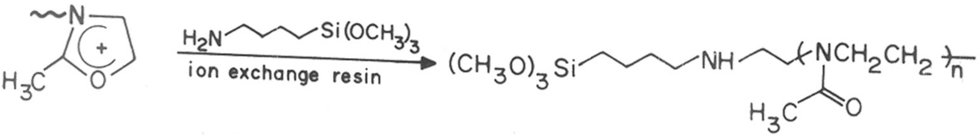


(26)

1.4.2 : Copolymerization.

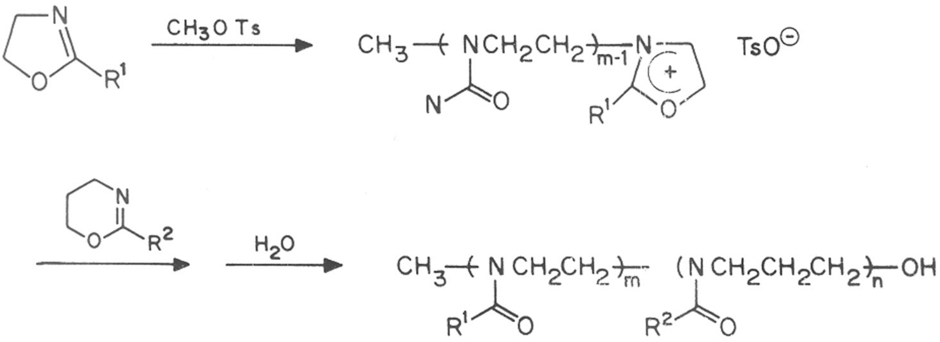
1.4.2.1:Statistical copolymers.

The copolymerization of 2-isobutyl-2-oxazoline with 2-(5-hydroxy phenyl)-2-oxazoline, with an oxazolinium perchlorate initiator produced cloudy, brittle crystalline solid, which was proved to be a statistical copolymer[43]. Copolymerization of 2-phenyl-2-oxazoline (M_1) with 2-methyl, 2-isopropenyl, and 2-benzyl-2-oxazoline (M_2) gave three sets of monomer reactivity ratios: r_1=0.07, r_2=7.9, r_1=0.02, r_2=10.2, r_1=0.01, r_2=12.2, respectively[44].

2-phenyl-2-oxazoline macromonomer having poly(ethylene oxide) chain is believed to copolymerize in a statistical manner with 2-phenyl-2-oxazoline[38]. Copolymerizations involving a zwitterion mechanism however, yield statistical copolymers, if the sequence regulation is not controlled. Such examples are copolymerizations of 2-methyl or 2-ethyl-2-oxazoline with phthalic anhydride[45,46].

1.4.2.2: Block coploymers:

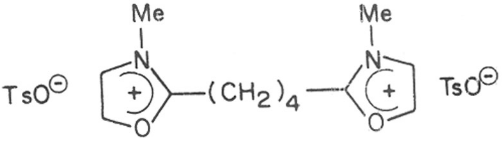
Because of the living nature of cationic ring opening polymerization of cyclic imino ethers, Litt et al[47], synthesized AB type block copolymers **(27)** in the following way;



(27)

A new class of non ionic surfactant was prepared by block copolymerization of cyclic imino ethers[49]. The resultant AB (orBA) and ABA (orBAB) type block copolymers, in which A denotes a hydrophilic segment and B denotes a lipophilic segment, were all soluble in water. These block copolymers are good surfactant of the non ionic type.

A bifunctional initiator, e.g. **(28)**, produced BAB type block copolymers via one pot two stage copolymerization.

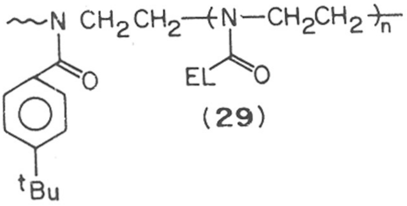


(28)

A similar block copolymerization was carried out by using 2-(perfluoroalkyl)-2-oxazolines for the construction of hydrophobic blocks[49].

A nonionic polymer surfactant block copolymer(**29**) was prepared and its emulsifying effectiveness was examined[50,51].

In the emulsion polymerization of n-butyl acrylate (5% in water), a stable latex was obtained in presence of 0.1 wt% of (**29**).

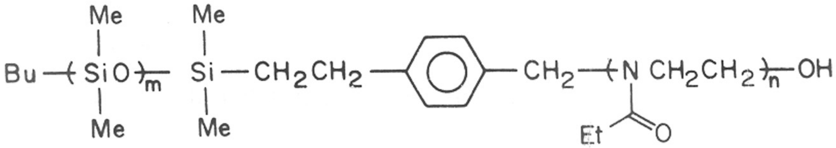


(29)

Triblock copolymers of the BAB type were more effective inverse emulsifiers than the corresponding diblock copolymers of the AB type in the polymerization of styrene in water using $K_2S_2O_4$ initiator.

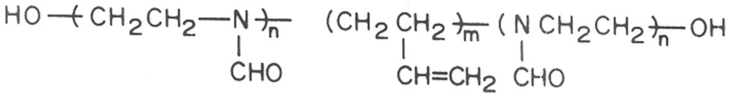
By using 2-phenyl- and 2-undecyl-2-oxazolines, AB diblock, ABA triblock, and three arm star block copolymer were prepared and their properties as surface modifiers and adhesives were examined[52].

A polysiloxane containing block copolymer(**30**) was prepared[53,54,,55] i.e.,



(30)

An ABA type block copolymer(**31**) was prepared by initiating the 2-oxazoline polymerization with polybutadiene ditosylate.



$$HO\!-\!(CH_2CH_2-\underset{CHO}{N})_n\;(CH_2\underset{CH=CH_2}{CH_2})_m(\underset{CHO}{N}CH_2CH_2)_n\!-\!OH$$

(31)

Poly(styrene-block-2-methyl-2-oxazoline) has been prepared[56]. Polymers having terminal alkyl halide groups were used to initiate the 2-methyl-2-oxazoline polymerization for the preparation of diblock copolymers of isobutyl vinyl ether and of styrene oxide respectively[57,58].

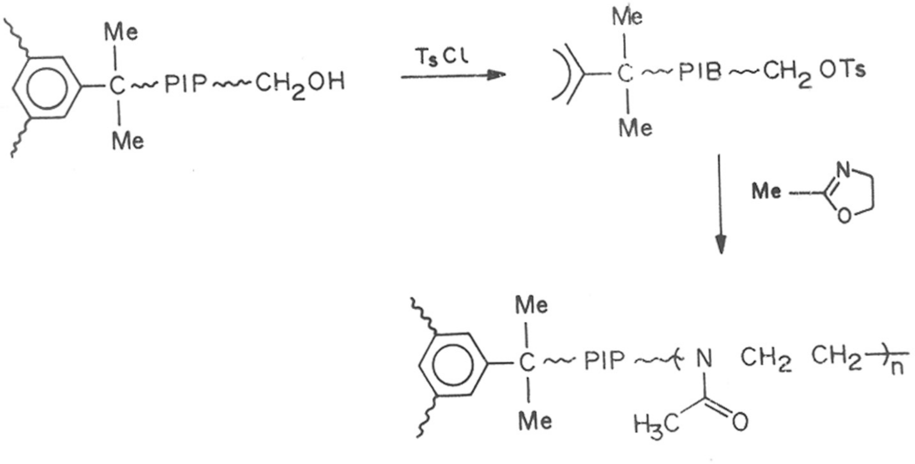
A copolymer composed of poly (N-acyl ethylenimine) as A block[59] and poly (ethylene oxide) as B block[60] is quite compatible with nylon 6 and shows good antistatic properties when blended with nylon 6.

A similar ABA type block copolymer was prepared by terminating the living ends of 2-methyl-2-oxazoline with poly (oxyethylene) dicarboxylic acid[61].

Living species from tetrahydrofuran polymerization initiated with CF_3SO_3Et or $(CF_3SO_2)_2O$ were used to induce the 2-oxazoline polymerization, giving rise to AB or ABA type of block copolymer respectivily. These block copolymers are good surfactants, in which the polytetrahydrofuran chain behaves as a lipophilic segment and the oxazoline chain as a hydrophilic segment[62].

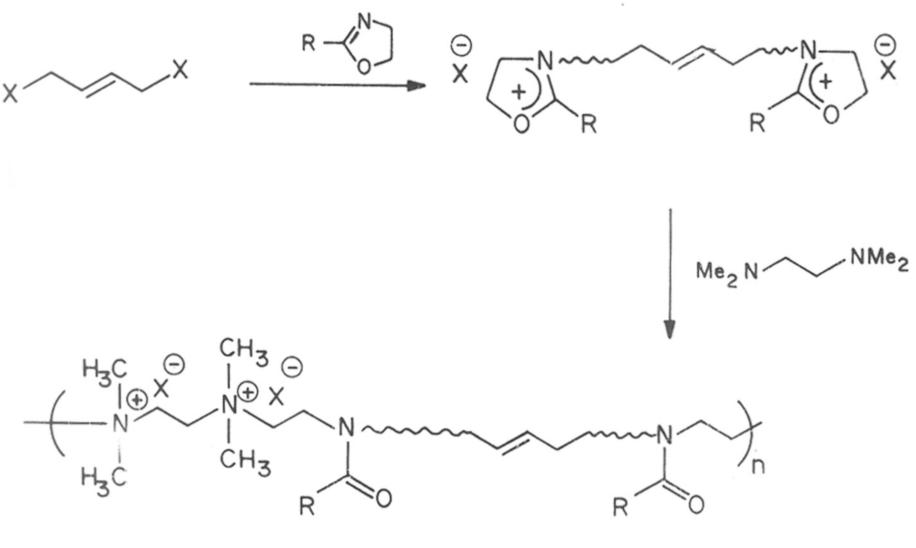
An ABC type of block copolymer of poly (styrene-block-tetrabydrofuran-block-2-methyl-2-oxazoline) was synthesized. They are starting materials for charge mosaic membranes with chemical modifications[63].

Three arm star polymers**(32)** containing isobutylene and N-acetylethylenimine blocks were prepared via the following procedure[64].



(32)

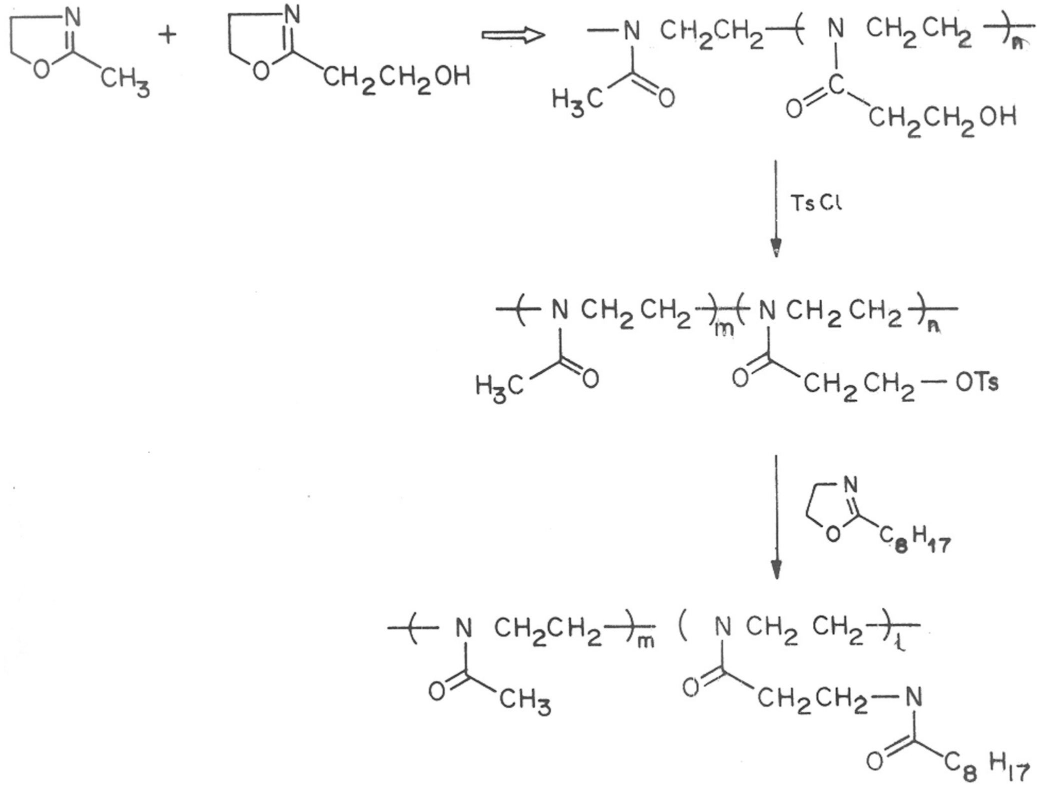
A novel bifunctional initiator of the allylic dihalide type also gave a living system[65]. The living ends were subjected to reaction with a diamine to yield an ionene-polymer **(33)**, which followed typical polyelectrolysis viscosity behaviour[66].



(33)

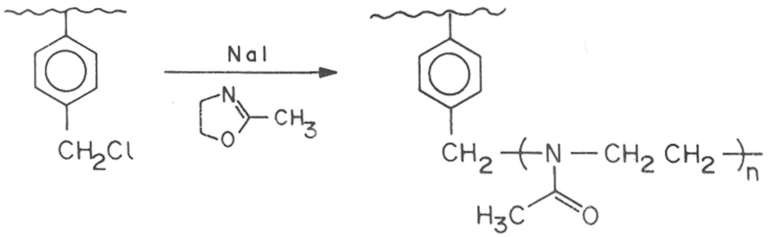
1.4.2.3: Graft copolymers.

Graft coplymers between 2-oxazoline monomers were first obtained in the following manner[67] 2-methyl-2-oxazoline and 2-hydroxyalkyl-2-oxazoline were copolymerized to constitute the main chain. Then, the hydroxy group was tosylated and this tosylated alkyl group induced the polymerization of the other 2-oxazoline monomer to give a graft copolymer(**34**), e.g.



(34)

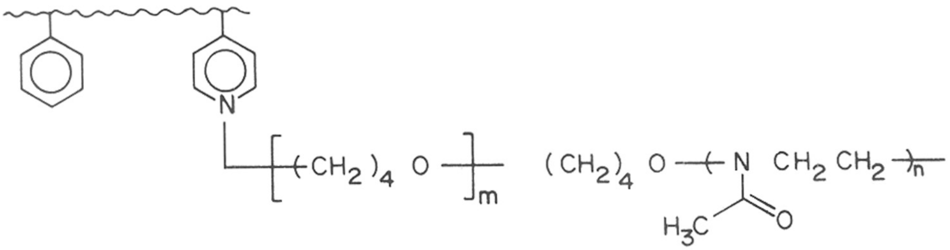
The poly(styrene-graft-(N-acylethylenimine)) has been prepared by chloromethylated polystyrene which was employed as initiator to induce the polymerization of 2-methyl-2-oxazoline yielding the first example of graft copolymer from a cyclic iminoether[68]**(35)**.



(35)

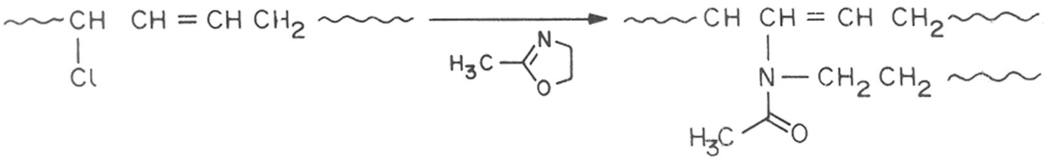
A polystyrene containing amine groups was used to terminate the living propagating ends of the 2-oxazoline polymer to produce graft copolymer[69].

A three component graft copolymer **(36)** from styrene, tetrahydrofuran and 2-methyl-2-oxazoline was prepared for use in charge mosaic membranes[63].



(36)

A copolymer of 1-chloro-1,3-butadiene and butadiene contains reactive alkylic chloride groups. These induced 2-oxazoline polymerization to give poly (butadiene-graft-(N-acetylethylenimine)[70] **(37)**.

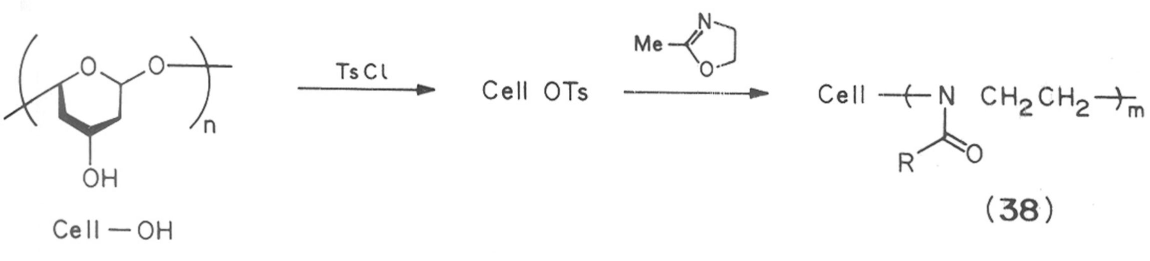


(37)

Poly(vinyl chloride) also contains low concentration of allylic chloride groups. The chloride site can be utilized for grafting 2-methyl-2-oxazoline with KI or AgO_3SCF_3 as coinitiator to produce poly(vinyl chloride-graft-2-methyl-2-oxazoline). The graft copolymer was thermally less stable than poly(vinylchloride) and could be molded. It exhibited greater flexural moduli but lower heat distortion temperatures than poly(vinyl chloride)[71].

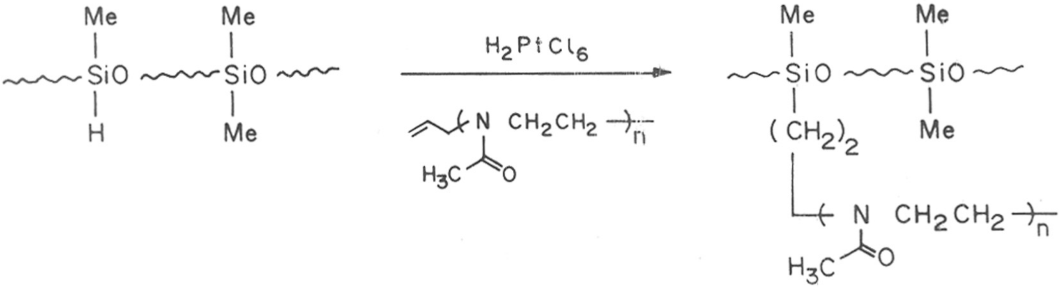
N-Acylethylenimine chains were introduced into an ethylene-vinyl acetate copolymer. The films from the resulting graft copolymers having N-acetyl side chains showed enhanced antithrombogenic properties[72].

Cationic graft copolymerization of 2-oxazoline on to cellulose and its derivatives has been achieved [73,74] (38).



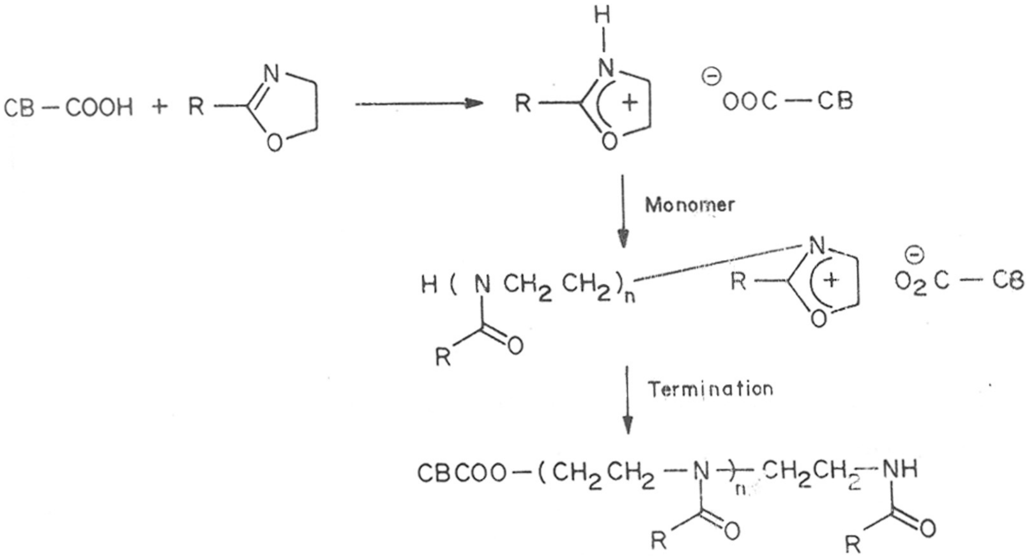
(38)

A hydrosilylation reaction was utilised to prepare a polysiloxane with an N-acylethylenimine graft chain(**39**) in the following way.[42]



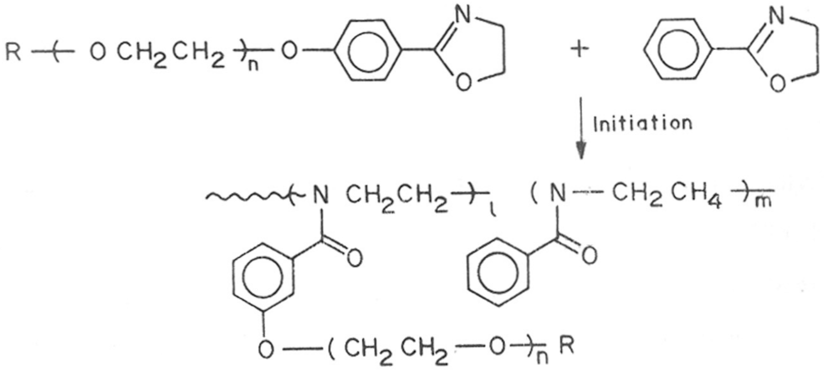
(**39**)

Carbon black (CB) have carboxylic acid groups on the surface initiated the polymerization of 2-oxazoline at elevated temperatures (100°C) to give CB with poly(N-acylethylenimine) chains grated on the surface(**40**). The carboxylic acid groups are responsible for both initiation and termination.[75]



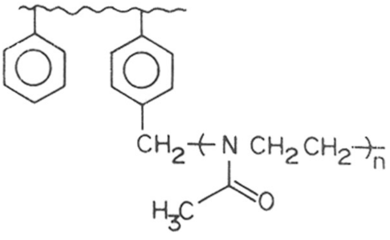
(**40**)

Poly(N-benzoylethylenimine-graft-ethylene oxide) was obtained by cationic copolymerization of a ring opening polymerizable macromonomer with phenyl-2-oxazoline(**41**)).[38]



(**41**)

A graft copolymer of **(42)** is an amphiphilic polymer.



(42)

(42) is soluble in chloroform and almost soluble in benzene and in water/methanol. In the ^1H NMR spectra in these three solvents all signals were seen in chloroform. However only signals due to the polystyrene chain appeared in benzene and only signals due to the N-acetyle ethylenimine chain were seen in water/methanol[76]. **(42)** can also be used for the surface modification of polystyrene e.g. a small amount (<1 wt %) of **(42)** was added to polystyrene and a film was prepared from the mixture by casting in glass. The glass side of the remelting film was very unstable by water. The contact angle of a water droplet was 38°, in comparison with 90° for polystyrene.[76]

1.4.3: Star branched polymers. See chapter 3 in secton 3.1.

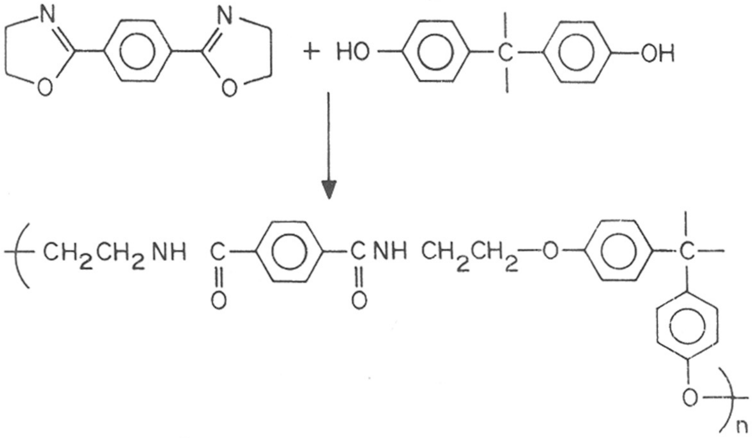
1.5: Properties of poly(N-acylethylenimine) and application.

The homopolymer is a polymeric analog of dimethyl acetamide, a familiar, dipolar aprotic solvent. The polymer too possesses similar characteristic. The poly(N-acyl ethylenimine) structure is miscible with PVC, polystyrene and PVF_2. This has led to the synthesis of new composition of polymers which show application as "compatibilising agents"[77]. Besides the surface active properties in block and graft copolymers bearing poly(N-acylethylenimine) segments have found application in resins,[78] gelling agents,[79] thickening agents,[80] adhesives,[81,82] surface coatings,[83] antieletrostatic agents,[84,85] thermosetting rubber blocks,[86] surfactants,[87] suspension stabilizers for PVC, coin exchangers and coagulents,[88] fire retardants,[89] textile colorants[90] and complexing agents with phenolics in waste water[91].

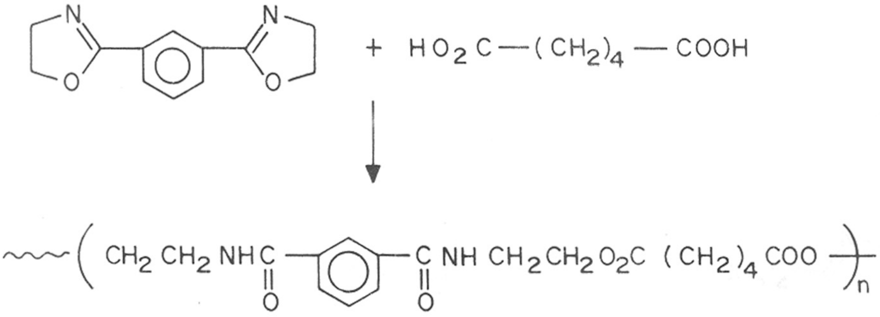
A styryl type macromonomer **(17)** was used as a comonomer as well as an emulsifies in soap-free emulsion copolymerization with styrene[92]. Copolymerization with potassium persulphate initiator at 70^0C for 8h under argon gave polymer particles whose contours were observed by scanning electron microscopy. The particle size was in the submicron range and relatively monodisperse. The poly(N-acyl ethylenimine) chain was locally present on the particle surface from ESCA analysis.

The dispersion polymerization of styrene was carried out in ethanol in the 2,2-azobis(2,4-dimethyl valeronitrile) initiator in the presence of poly(N-propionyl ethylenimine) of different molecular weights as a stabilizer.[93] The remelting polymer precipitates were spherical particles of relatively monodisperse size. The styryl type macromonomer **(17)** was also usable as a stabilizer as well as a comonomer in copolymerization with styrene in ethanol.

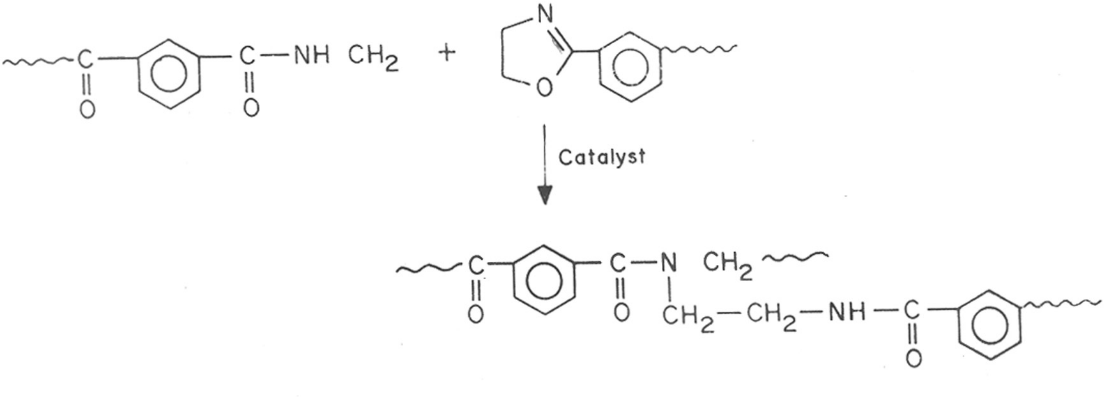
Copolymers of 2-propyl-and 2-isopropyl-2-oxazoline[93] and of 2-propyl and 2-methyl-2-oxazoline[94] were claimed to be efficient stabilizers for the suspension polymerization of vinyl chloride. Polycations derived from poly(N-acylalkyl enimines) by hydrolysis that is linear poly (trimethyl enenimine) were found to lower the serum choresterol level.[95] These polymers which is a cationic polymer under physiological conditioned that is p^H 7.3 increased host survival of Ehrlich Ascites and Ehrlich Carcinoma-bearing mice when injected either before or after tumor transplants.[96] Polycations may inhibit tumor growth, may stimulate immune reactivity or may allow negatively charged lymphocytes to over come an electrochemical barrier. Various functional groups can be introduced into PEI for biological or pharmacological purposes. LPEI contains meleic acid base like adenine or thymine as grafted pendent groups were prepared as model polymers of polynucleotides[97,98]. Similarly,2-(thymin-1-yl) propionyl and 2-(adenin-9-yl) propionyl graft PEI and PEI with corresponding optically active graft components[99-102] were synthesized. Two classes of thermoplastic resins have been developed on the basis of the ring opening addition of a phenol group or a carboxylic acid group to a 2-oxazoline group. These are poly(ester-amides).[103-105] The former is synthesized by the following way.



The poly(ester-amide) production reaction involves two steps,e.g (i) ring opening polymerization

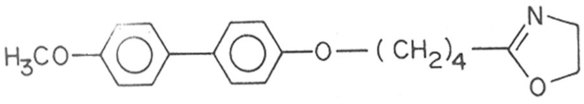


(ii) Crosslinking via ring-opening addition on to the amide group

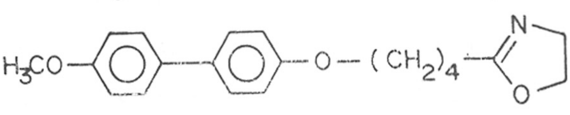


Linear poly(N-methylethylenimine) was used as a model polymer for N,N,N,N-tetramethylenediemine. The polymer forms an insoluble complex with $LiAlH_4$. This complex is a good reducing agent for aldehydes, ketones and esters in which the reaction takes place in a heterogeneous phase.[106]

From the following two monomers(**43**), (**44**) and (**45**) thermotropic liquid crystaline, poly(N-acylethylenimines) were obtained via cationic ring opening polymerization.



(43) :n =4
(44) :n =6



(45)

SECTION B

Synthesis of star shaped polymer by living polymerization techneques.

1.6: Introduction.

Multiarmed polymers are interesting macromolecules with unique shapes and have been synthesised by addition polymerization techniques primarily by three methods.

(i) Living polymerization with a multifunctional initiator

(ii) Coupling reaction of linear living polymers with a multifunctional coupling agent (termination)

(iii) the linking reaction of linear living polymers with a difunctional vinyl compound through microgel formation.

The occurrence of branching in polymer in a random fashion is common. Chain transfer reactions can cause short and long chain branching in polymerization such as the high pressure polymerization of ethylene. Branching can also be introduced intentionally by the use of a polyfunctional monomers in end linking polymerizations. Similar branching can be produced in addition polymerization by the use of a small amount of difunctional monomer, e.g. divinyl benzene. Branching can be accomplished by graft polymerization by which long chain branches can be introduced onto a backbone which is a different polymer from the backbone.

The properties of branched polymers can be quite different from those of linear polymers of the same molecular weight. For examples, bulk viscosities as well as concentrated and dilute solution viscosities can be lower for branched polymers than for a linear polymers of equivalent molecular weight. As an example, the melt processing behaviour of polymers can be manipulated by alternations in the average molecular weight, molecular weight distribution and the frequency and length of long branches in the molecules. Thus, there is an obvious need to correlate and characterize the type and degree of branching in a polymer with its effect on the physical properties in solution or melt.

In all of the above examples of branching there is a mixture of branched and unbranched polymers. The branched and unbranched polymers can have wide range of molecular weight distribution, as can the branches themselves. Also, the frequency of branches and the segment lengths between branch points can vary.

Hence, the physical properties of such materials represent an average of the properties of all the different species present. Such great diversity poses a problem with regard to the quantitative interpretation of the effects of branching. Theoretical models can be set up for simple branched architectures. However, calculations involving even these structures can be quite complex, and thus the attempt to describe a system of a mixture of complicated branched polymers is a burden that is best avoided.

The true test of any theory dealing with branched polymers is, of course, dependent upon its success in predicting or explaining the physical parameter in question. However, for fair evaluation the exact nature of the experimental polymer must be known.

Thus, it is desirable to test a theory with the simple possible system. For branched polymers, a macromolecules with a single branching point with all the branches being of equal molecular weight, i.e., a star branched polymer is the simplest possible system. The first successful attempt of model star-branched polymer synthesis was that of Schaefgen and Flory[107] in 1948.

They were able to synthesise four and eight armed polyamide stars by condensation polymerization with either a tetrabasic (cyclohexanone tetrapropionic) or an octabasic (dicyclo hexanone octa-propionic) acid as the multifunctional reactant.

The Mw/Mn ratio for these star branched materials was calculated to be between 1.2 and 1.37. These polymers exhibited lower viscosities both in the melt and in dilute solution than the equivalent linear materials.

1.7: Synthesis of star shaped polymers by termination method.

1.7.1:Living anionic polymerization technique.

The preparation of star-branched polymers by the use of polyfunctional chlorosilanes in conjunction with anionic polymerization was first shown to be a feasible concept by Morton, Helminaik, Gadkary, and Bueche[108] in 1962. Using methyltrichlorosilane and tetrachlorosilane in conjunction with polystyryllithium in benzene, they were able to prepare both three and four armed polystyrene stars. As a consequence of the termination free nature[109] of this anionic polymerization system, these star branched polystyrenes, possessed relatively narrow molecular weight distribution.

The polymerizations involving the lithium counterion are suitable for star-branched polymer formation since organolithium reagents readily undergo metathesis with the electronegatively substituted silanes, e.g.

$$SiX_4 + 4RLi \text{ ------> } SiR_4 + 4LiX.$$

Thus, if properly performed, this synthesis should allow the predetermined manipulation of molecular architecture with control over molecular weight and molecular weight distributions. This general reaction was subsequently extended to polybutadiene[110,111,112]. Roovers and coworkers[113-118] synthesised a series of four and six armed polystyrene and polyisoporene stars using 1,2-bis (dichlorosilyl)- and 1,2-bis (trichlorosilyl) ethane.

Polymers with upto 56 arms have been synthesised (table 1.4).

It is clear from table 1.4 that the synthesis of well defined star branched polymers involving a controlled linking reaction have followed two lines.

Table 1.4 : Synthesis of branched polymers.

Monomers	Initiator	Solvent[a]	Linking agent	f[b]
Styrene	n.BuLi	Benzene	Silicon tetrachloride	3 and 4
	n-BuLi	Benzene/THF	1,2,4-tris(chloro-methyl) benzene	3
	n-BuLi	Benzene/THF	1,2,-bis(trichlorosilyl) ethane	3 and 4
	n-BuLi	Benzene/THF	cyclic trimer of Phosphonitrilic chloride	2,4,6
	n-BuLi	Benzene/THF	1,2,4,5-tetra (chlromethyl)benzene	2-11
	n-BuLi	Benzene/THF	hexa[p-(chloromethyl) benzene	6
	Cumylpotassium	THF,Toluene/THF	2,4,6-tri (allyloxy) triazine	3

Continuted.......

	Cumylpotassium	THF	1,1,4,4-tetraphenyl 1,4-bis(diallyloxy triazine butane	4
	-Phenyl ethyl Potassium	THF	1,2,4,5-tetra(chloro methyl) benzene	3 and 4
	n-BuLi	Benzene/THF	Silicon tetrachloride	3 and 4
	S-BuLi	Benzene	1,2-bis(dichloromethyl silyl) ethane, 1,2-bis (trichlorosilyl) ethane	4 and 6
	S-BuLi	Benzene	p- and m-Divinyl benzene	6-15.5
	Cumyl potassium	Benzene/THF	p- and m-Divinyl benzene	6.15.5
Butadiene	n-BuLi	Cyclohexane	Silicon tetrachloride	4
	n-BuLi	Cyclohexane	Methyl trichlorosilane	3

Continued.......

	n-Buli	Benzene	Silicon tetrachloride	4
	n-BuLi	Hexane	Silicon tetrachloride	4
	n-BuLi	Hydrocarbon	Tin tetra chloride	4
Isoprene	S. BuLi	Cyclohexane	Methyl trichloride silane	3
	S.BuLi	Benzene	Silicon tetrachloride	3
	S. BuLi	Benzene	Octa- and dodeca- chlorosilanes	8-12
	S. BuLi	Benzene	Divinyl benzene	10-56
Styrene diene^{d}	S.BuLi	Benzene	Divinyl benzene	6-30
	n-BuLi	Benzene	Silicon tetrachloride	3 and 4

Continued.......

n-BuLi	Toluene	Silicon tetrachloride	4
S.BuLi	Hydrocarbon	Dimethyl phthalate	2.9
S.BuLi	Hydrocarbon	Phosphorous trichloride	2.9
S. BuLi	Hydrocarbon	Divinyl benzene	7-14

a) THF=tetrahydrofura

b) Degree of branching.

c) The polystyrene lithium was reacted with isoprene (about 3 units per active chain end). This served to reduce steric hindrance which retards the linking reaction.

d) Block copolymers.

(a) the reaction of polyfunctional linking agents with monocarboanionic polymers and

(b) the application of an anionic sequential polymerization involving a difunctional monomer. This latter generates a microgel link point by polymerization. Both procedure lead to star-branched polymers containing various number of arms.

Steric considerations can influence the extent and efficiency of the linking reactions involving the chlorosilanes. It was noted[108] that the reaction between polystyryllithium and silicon tetrachloride yield a mixture of three and four branch material along with coupled and uncoupled linear chains. Similar results were obtained for polystyryllithium when the linking agent was 1,2-bis (trichlorosilyl) ethane[114,119]. The maximum degree of branching obtained was four. It has also been found[120] that poly (isoprenyllithium) will not react completely with silicon tetrachloride when the latter is present in near stoichiometric amount. Tri chain material predominates. However, it has been found that the butadienyllithium chain end will react qualitatively with silicon tetrachloride.[110,111,112,121,122] The validity of these observations is demonstrated by preparing four arm star branch polystyrene[123] and polyisoprene,[120] both of which were synthesized by adding few units of butadiene prior to reacting with silicon tetrachloride.

For polyisoprene it seems that the methyl group in the 1,4 chain end[124,125] is sufficiently large to retard complete reaction with silicon tetrachloride. It should be noted that a quantitative reaction occurs[120] when poly (isoprenyllithium) reacts with methyltrichlorosilane.

It thus appears that the steric effects of the polystyrene and polyisoprene chain ends can be overcome by resorting to the technique of capping these chain ends with several units of butadiene. This method has also proven effective for the synthesis[126] of eight and twelve armed polyisoprene stars using octa- and dodeca chlorosilanes.

A potential side reaction which can effectively hinder star branched polymer formation is that of metal halogen exchange. Although apparently not a serious problem when chlorosilanes[127] are used as linking agents, this side reaction is observed for species involving halogen-carbon bonds. For example, in table 1.4, tetrafunctional 1,2,4,5-tetra(chloromthyl benzene)[128] led to couple linear material and branched polystyrene species containing upto eleven arms. These findings can be explained on the basis of halogen metal interchange reactions. Reaction of this type[129] and others[130] if they occur concurrently with the bimolecular displacement step, can lead to star branched polymers of higher and lower functionalities than desired.

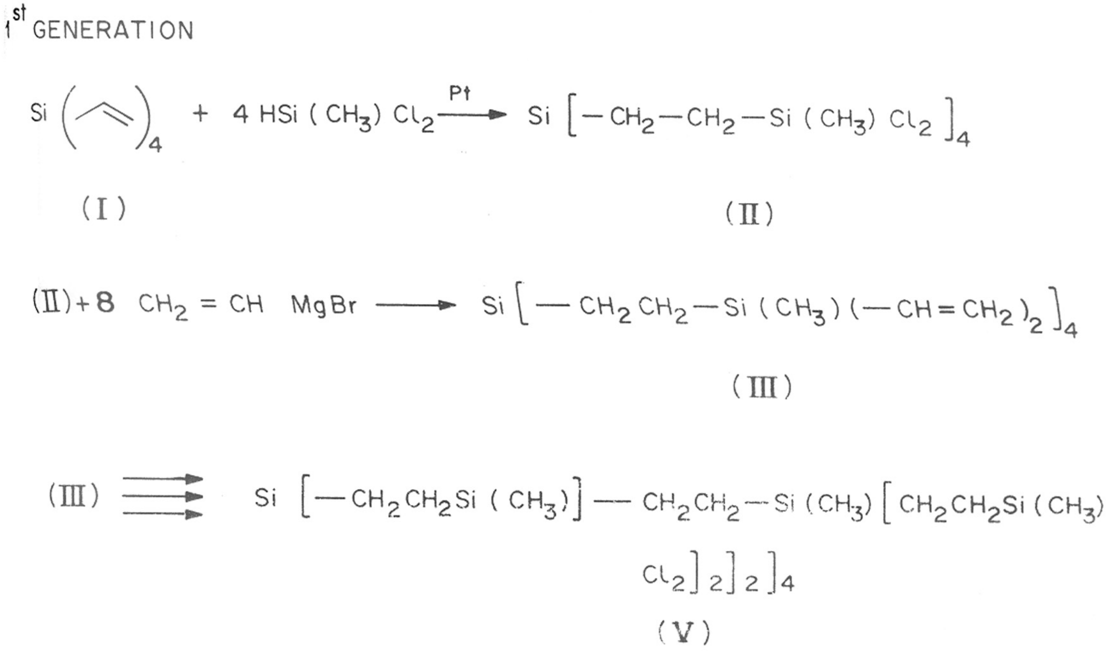
From a practical stand point, the interchange and displacement reactions can be considered to be competing reactions. Several attempts have been made to maximize the displacement reaction at the expense of the interchange step. Wenger and Yen[131] found that for the lithium counter ion a solvent mixture of benzene and tetrahydrofuran and elevated temperature favoured the displacement reaction relative to the interchange step. Yen[116] has found that the use of potassium, rather than lithium, counter ion will achieve the same effect. A third method involves the addition of a dilute solution of the linking agent to the excess of the active chain ends. This concept was based on the fact that high functionality star results from the metal halogen interchange followed by the reaction of the metallated linking agents with another linking molecule to yield a species of higher functionality than desired. The probability of this occurring is expected to be minimized if an excess of active chain ends is maintained during the linking reaction. This process was found effective for the poly (styryllithium)- 1,2,4,5 -tetra (chloromethyl) benzene system at 50°C for a 50/50 benzene- tetrahydrofuran mixture when the linking agent added over several hours.

However, it clearly demonstrates that the reactions involving carbon lithium chain ends and chlorosilanes represent a more efficient linking process than the poly functional halogenated hydrocarbon. As a rule the chlorosilanes do not exhibit the detrimental metal chlorine exchange reactions. Their reactivity is complicated only by steric factors involving the chain ends of polystyrene and, to a lesser extent, of polyisoprene. This problem, though, is easily avoided by converting these chain ends to the butadiene species. Thus chlorosilanes possess atleast five other beneficial features :

(a) ease of purification, (b) ease of analysis (c) ease of handling under vacuum conditions (d) long term stability under vacuum, and (e) the wide range of functionalities with which they can be prepared. In regard to this latter point, tri, tetra-, hexa-, octa- and dodecachlorosilanes have been used successfully for star branched polymer formation. In principle, the penta-, nona-, and decachlorosilanes can also be prepared by established hydrosilation procedure[132-134] as can species with functionalities greater than twelve.

The synthesis of more complex multifunctional silicon chloride coupling agents led to the preparation of 8-, 12 and 18- arm polyisoprene[135,136] in the year of 1980.

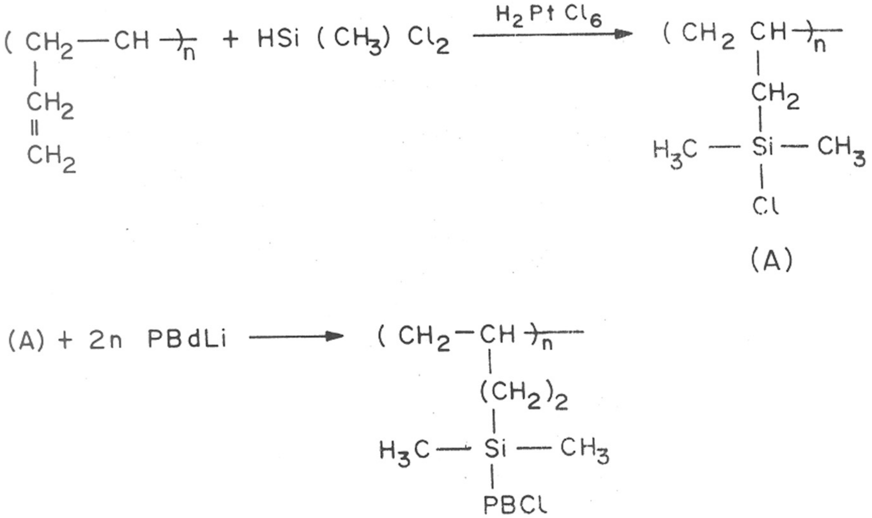
More than 10 years elapsed before higher functionality coupling agents became available. The insights gained in the synthesis of dendritic molecules[137] were used to prepare carbosilane dendrimers with 32 silicon chloride bonds for the preparation of 32 arm star polybutadienes.[138] The preparation of the coupling agent is shown in scheme 1.6.



Scheme 1.6: Preparation of carbosilane dendrimers with 32 silicon chloride bonds.

Living polybutadienyl lithium was prepared with sec BuLi in benzene at room temperature (10% solution). Prior to addition of (v) to the parent arm, a sample of the parent arm was removed and terminated with MeOH. The coupling reaction was left for 3 weeks. Using the same method, preparation of 64- and 128 arm star polymers were also reported.[139]

Stars with 200 and 270 arms have been prepared by coupling the living polymer with a low molecular weight perhydrosylated 1,2-polybutadiene as shown in scheme 1.7.[140]



Scheme 1.7: Preparatrion of star polymer with 200 and 270 arms.

Star copolymers with different arms of the A_2B, A_2B_2, AnBn or ABC type have been prepared and called miktoarm (from the Greek work meaning mixed) star copolymers.

Pennisi and Fetters,[141] using chlorosilane method, have prepared narrow molecular weight distribution in three arm polystyrene (PS) and polybutadiene (PBd) stars, where one of the three arms differs in molecular weight from the remaining two.

Mays[142] employed the same approach to prepare a near monodisperse mixed 3-arm star copolymers of the A_2B type, where A was polyisoprene (PI) and B was PS.

Teyssie and coworkers[143] by using naphthalene terminated polymers have also prepared mixed star copolymers of A_2B type, where A is poly oxirane and B is poly (p-tert-butylstyrene), PS or PI.

Quirk and coworkers[144] using 1,1-diphenyl ethylenes[145] have prepared mixed stars of the A_2B_2 type, where A is PS and B is PI. Finally, Rempp and coworkers[146] by using the divinyl method[147] have prepared mixed stars of AnBm type where n=3-12, A is PS and B is poly (n-butyl methacrylate). These methods generally give polymers with a higher polydispersity than the chlorosilane route.

The chlorosilane approach has also been extended for the preparation of a new type of model polymer i.e. the miktoarm star terpolymer, an ABC type where A is PI, B is PS and C is PBd by Hadjichristidis and coworkers[148]. Synthetic approach for the synthesis of ABC type miktoarm star ter-polymer is shown in the scheme 1.8.

$$\mathrm{PILi + Excess\ CH_3SiCl_3 \longrightarrow PISi\,(Cl_2)\,CH_3 + LiCl + CH_3SiCl_3}$$

$$\mathrm{PISi\,(Cl_2)\,CH_3 + PSLi \longrightarrow (PI)\,(PS)\,SiClCH_3 + LiCl}$$

$$\mathrm{PI\,(PS)\,SiClCH_3 + Excess\ PBdLi \longrightarrow (PI)\,(PS)\,(PBd)\ SiCH_3 + LiCl}$$

Scheme 1.8 : Synthesis of miktoarm star ter-polymer.

Takano et al.[149], using anionic polymerization techniques and a block copolymer having a multifunctional linking agent at one end, prepared a miktoarm star copolymer of the AnB type where n=13, A is polystyrene, and B is poly (vinyl- β -naphthalene). This method suffers from the disadvantage that the number of arms is difficult to control precisely and that a large amount of unreacted double bonds remains.

Fujimoto et al.[150] have prepared a 3-miktoarm star terpolymer with three different arms, i.e. poly(dimethyl siloxane), polystyrene, and poly(tert-butyl methacrylate). The synthetic approacch involves the reaction of PSLi with a diphenylethylene-terminated poly (dimethyl siloxane), followed by polymerization of tert-butyl methacrylate with the formed $-CH_2C(Ph_2)Li$ group. The weak point of this method is that fractionation is needed after each step.

Naka[151] using complexation of bipyridinyl terminated polymers with an Ru(11) ion, was able to prepare 3-miktoarm star copolymers of the A_2B type, where A is poly (oxyethylene) and B is polyoxazoline. Unfortunately only limited characterization was given in this communication.

Chlorosilane approach has also been applied to prepare (a) a new type of model polymer i.e. the 4-miktoarm star quarterpolymer of the ABCD type where A is PS, B is PBd, C is PI and D is poly(4-methylstyrene) and (b) a 4-miktoarm star copolymer of the A_2B_2 type by Hadjichristidin and coworkers.[152]

Synthesis of star polymer of polar monomers for example, poly(alkylmethacrylates) presented, however, several additional difficulties over nonpolar monomer by this termination method. The high electron affinity of the methacrylates diminishes their reactivities with electrophilic reagents which are used for coupling. Also, most of the alkyl methacrylate carbanions are stable only in polar solvents at temperatures below -60^0C[153]. Working at these low temperature decreases even further the reaction rate for linking, thus making the system highly susceptible to impurities and side reactions.

Attempts to prepare three and four arm star poly (methyl methacrylate) have been reported[154]. Starting with low molecular weight oligocarbanions (Mn=1000), the yield of the star polymers was poor even after 24h of coupling reaction with 1,3,5-tris (bromomethyl) benzene or with 1,2,4,5- tetrakis (bromomethyl) benzene. The yeild can be improved if it is possible to increase the rate constant for nucleophilic substitution, e.g. by raising the reaction temperature with out destroying the carbanion site. Using this concept, Nguyen and Kausch[155] have reported the synthesis of three arm star poly (tert-butylmethacrylate) by coupling poly (tert-butylmethacrylate) carbanions with 1,2,3-tris (bromomethyl) benzene at $+15^0$C. The yield of star polymer was approx. 80%. PMMA endcapped with few units of tert-butylmethacrylate was made to couple at $+15^0$C and similar result was observed.

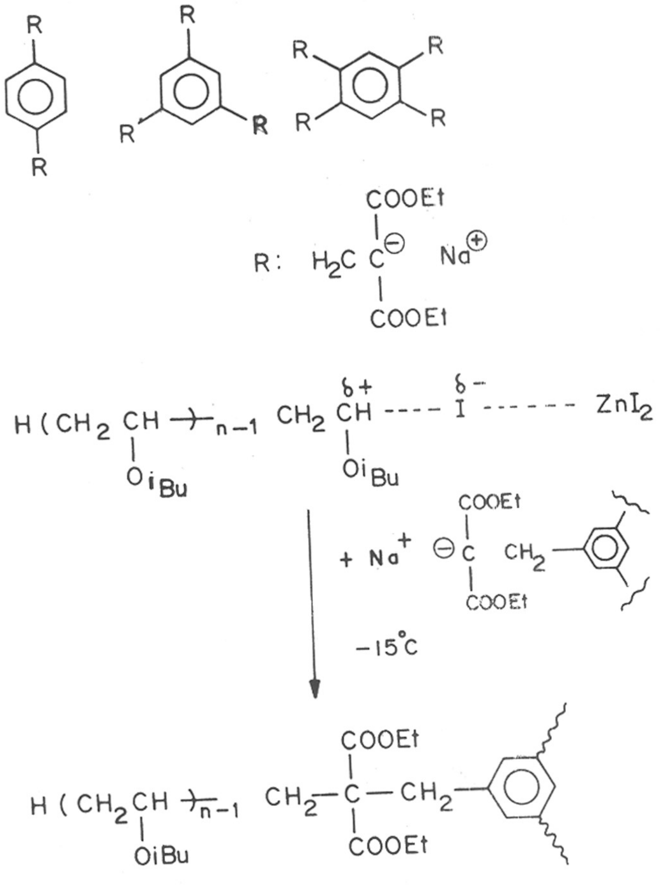
An alternative method of star-branched polymer formation involves the sequential polymerization of the monomer (or monomers) used for the arm, followed by the addition of divinyl benzene. The polymerization of this difunctional monomer produces a microgel nodule which serves as the branched point for the star shaped polymer. The application of this procedure has led for example, to the formation of star branched polyisoprenes containing upto a 56 weight average number of arms[156]. This method of star branched polymer formation was adumbrated by Milkovich[157] in 1965. However, Rempp and coworkers[158-160] were the first to exploit this concept successfully; in this case for the synthesis of star branched polystyrenes. A latter extension[156,161,162] of this procedure led to the synthesis of multiarmed star-branched polyisoprene homopolymers and polystyrene-polydiene block copolymers.

The success of this "polymerization" linking process is dependent upon the relative rates of the cross over reaction and the subsequent "homopolymerization" of the divinyl benzene (meta- and/or para-) vinyl groups. If all limitations imposed by polarity, steric and mechanistic requirements (.e.g., chain end "self"- and cross association) are ignored, it is clear that j molecules of divinyl benzene isomer could, in principle, link together (j+i) polymer chains. That the linking efficiency is in actuality smaller than predicted has been shown for the linking reactions involving polystyrene[158-160,163] or polydiene[161,162] branches.

1.7.2: Living Cationic Polymerization Techniques.

Synthesis of star shaped polymers by termination method using living cationic polymerization techniques became possible only after the discovery of living cationic polymerizations of vinyl ethers and styrene.[54].

The first attempt to prepare star branched polymers by the use of polyfunctional terminator with living cationic polymerization was shown to be feasible concept by Fukui, Sawamoto, Higashimura[55] in 1993. In this study they employed bis to tetrakis (malonate) anion for coupling living poly(vinyl ethers) initiated with hydrogen iodide/Zinc iodide as shown in Scheme 1.9.

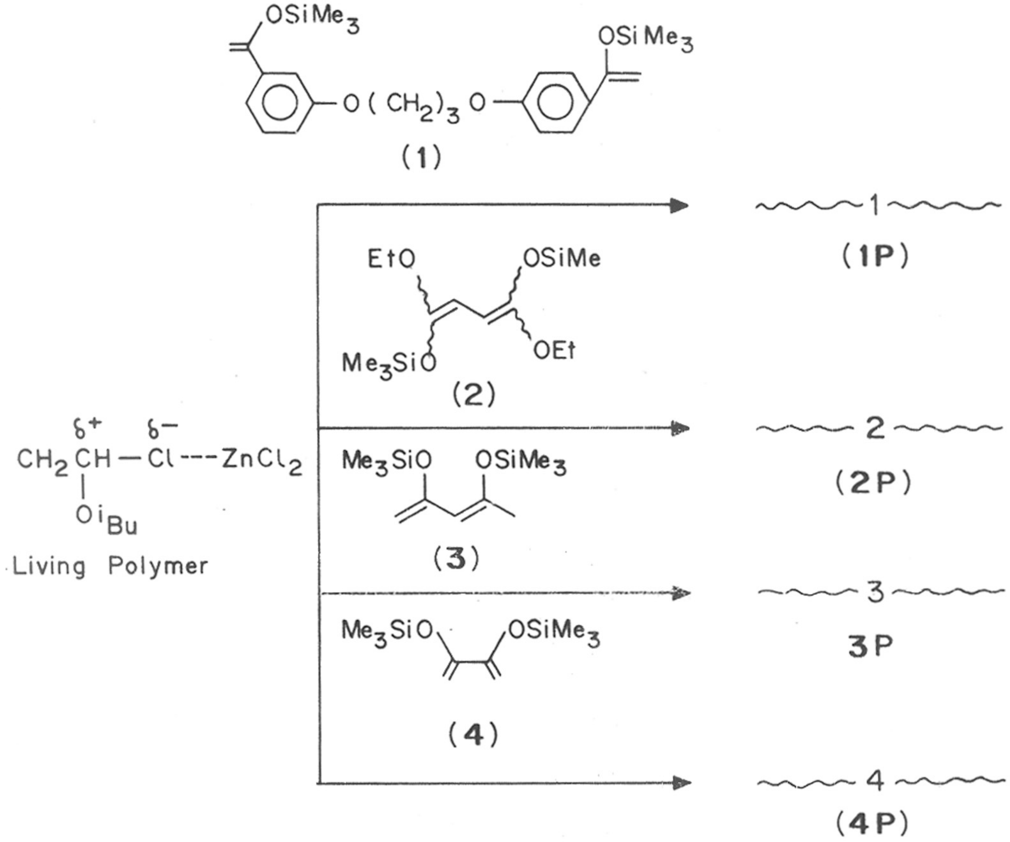


Scheme 1.9 : Coupling reaction of living poly (vinyl ether) with malonate anion.

In contrast to their monofunctional counterpart [$(Na^+\ ^-CH(COOEt)_2$] these multiple anions are less soluble in polymerization solvent such as toluene and methylene chloride and thus require precise control of reaction conditions for quantitative coupling to proceed. For example the bis (malonate) anion had to be dissolved in tetrahydrofuran containing a crown ether to form a solution in which a clean, fast, and quantitative coupling occurred. Even under these conditions, the tri- and tetra anion (Scheme 1.9) are less efficient coupling agents, probably because of low solubility and sterically hindered coupling sites. Thus, the synthesis of tri- and tetra-armed polymers is incomplete.

Latter,the same group[165] explored "non-ionic" nucleophiles, which are expected to be soluble in organic solvents and to be more efficient multiple coupling agents for living cationic polymers.

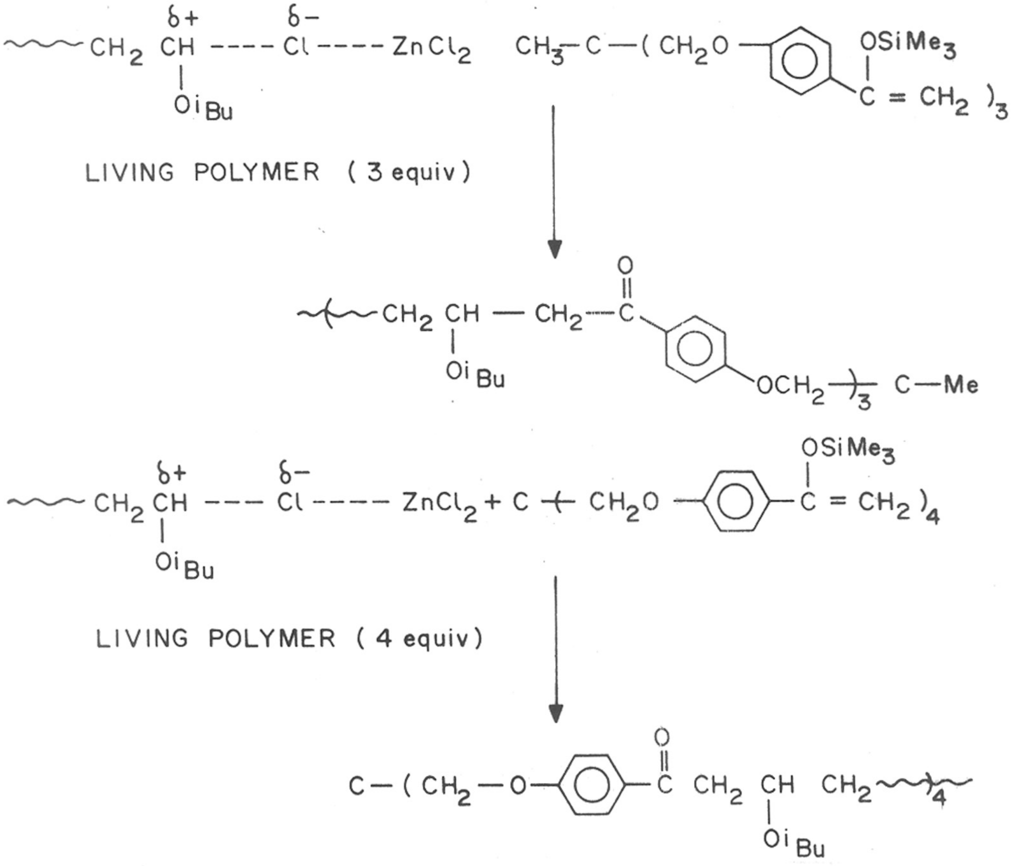
McGrath and Riffle used a silyl enol ether to terminate the HI/ZnI_2 initiated living poly(vinyl ether)[166]. Based on this observation silyl enol ethers was used as nonionic nucleophiles that would undergo quantitative coupling reactions in living cationic polymerization (scheme 1.10)



Scheme 1.10: Coupling reaction of poly (vinyl ether) with silyl enol ethers.

Bifunctional silyl enol ethers (1-4) proved efficient coupling agents for the HCl/$ZnCl_2$ initiated living poly (1BVE). The effectiveness of the silyl enol ethers in general, originates from their high solubility in organic solvents and from the high affinity of the silicon towards the chloride counteranion of the living end.

These findings were extended to the synthesis of tri armed and tetra armed polymers using multifunctional sinyl enol ethers (scheme 1.11) as terminators by the same group.[167]



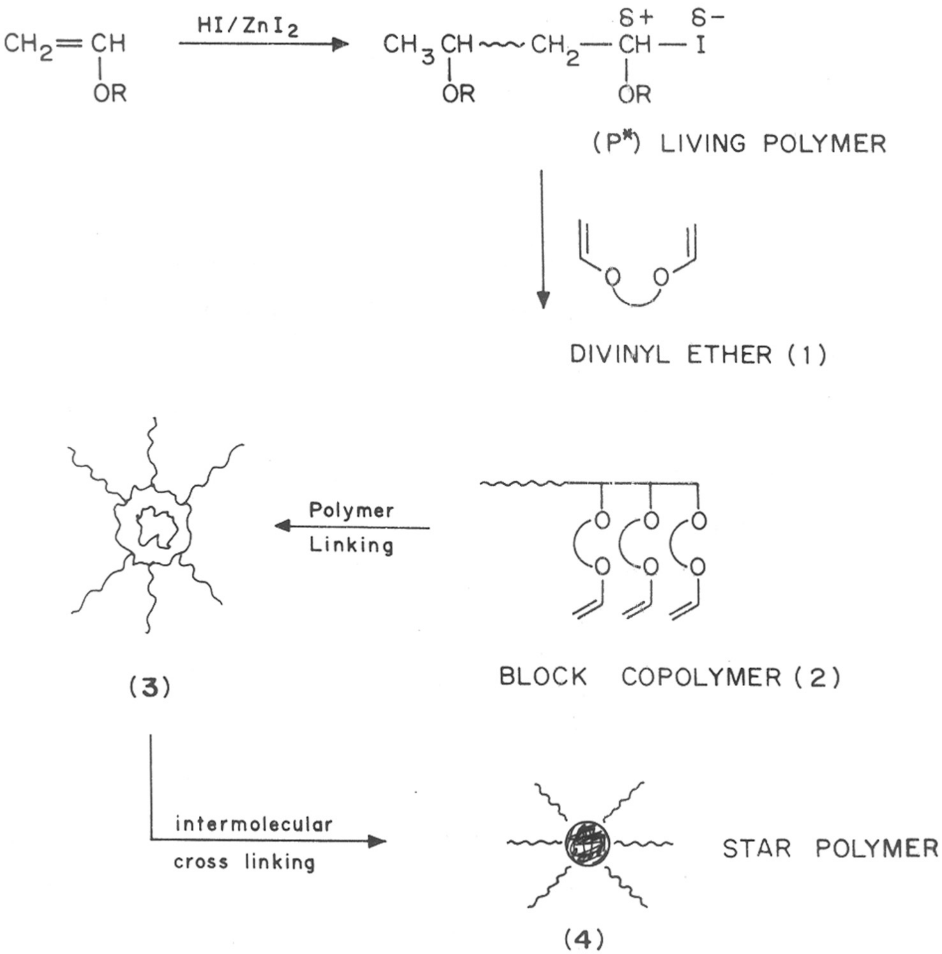
Scheme 1.11 : Coupling reaction of living poly (vinyl ether) with multifunctional silyl enol ethers.

The tri- and tetrafunctional silyl enol ethers are found to be soluble and efficient coupling agents for the living poly (1BVE) initiated with HCl/$ZnCl_2$. For short living chains, the coupling reactions were nearly quantitative to afford three armed and four armed star polymers with uniform arm lengths and narrow molecular weight distribution. Thus, as multifunctional coupling agents, the silyl enol ethers are superior to the corresponding malonate anions which suffer from much lower yields of multiarmed polymers.

Another alternative method for synthesising star polymer by living cationic polymerization involves a reaction for a linear living polymer with a small amount of divinyl compound. This method is particularly suited to prepare star polymers with many arms. The polymerization of this divinyl compound produces a microgel nodule which serves as a branching point.

The application of this procedure was first successfully carried out by Higashimura and coworkers[168] in 1991 (scheme 1.12).

A living polymer (P^*) of a vinyl ether (VE) was reacted with a small amount of a divinyl ether **(1)** to form a block copolymer **(2)** in which a short segment (scheme 1.12) of **(1)** was attached to the end of the living chain. Subsequent intermolecular reactions of the pendant vinyl groups of **(2)** with P^* or with the living ends of 2 resulted in polymer linking (into **(3)** for example, followed by intramolecular crosslinking that produced a star shaped polymer **(4)**.



Scheme 1.12: Synthesis of star poly (vinyl ether) through microgel formation.

It was demonstrated that[168] star shaped polymers of alkyl vinyl ethers with 3-59 arms per molecule can be synthesised in cationic polymerization, though the reactions (scheme 1.12) of these living polymers with appropriate divinyl ethers was carried out under dilute conditions. To increase the arm number of the star shaped polymers, the following factors should be fulfilled : (a) a short arm length (b) a high feed ratio of the divinyl ether to the living end and (c) a high concentration, (P^*) of the living end.

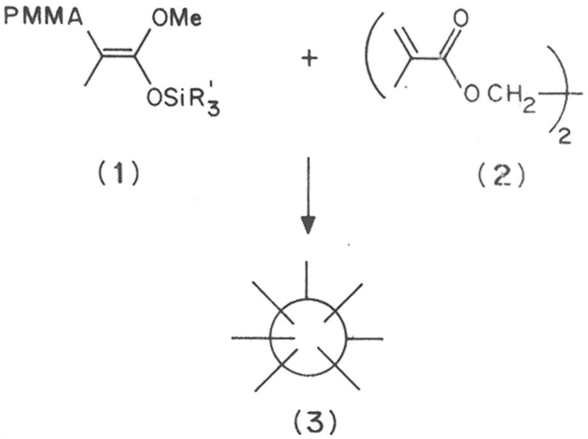
In addition to these, two additional factors also increase the yields of the star polymers (d) an alkyl vinyl ether with a less bulky substituent and (e) a divinyl ether with a long and rigid spacer.

1.7.3 : GTP Polymerization Techniques.

Star branched polymers containing polar, functional groups are difficult to make in the styrene/butadiene/isoprene/divinyl benzene technology because of the lack of proper monomers. Functional-group containing stars might be better made using methacrylate or acrylate monomers because of the availability of monomers.

Until very recently, polymerization techniques which allowed easy preparation of living methacrylate polymer arms, the first step in star formation, were unknown. Anionic polymerization of methacrylate monomers is impractical because preparative reactions must be done below about -50°C to prevent chain termination by internal reaction (back biting). Discovery of group transfer polymerization (GTP) of methacrylates by Sogah et al[169] permited practical living polymerization of methacrylates at or above room temperature.

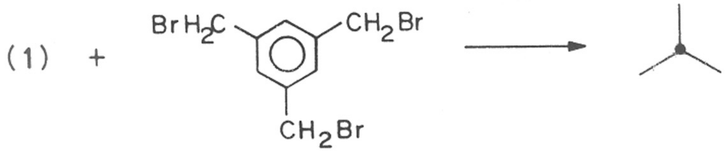
First report on the synthesis of star polymer of methacrylate by GTP was by Spinelli[170,171]. The linear part of the polymer was first prepared and the living arms were reacted with ethylene glycol dimethacrylate (EGDMA). Stars can be produced at temperatures as high as 85°C[172] (Scheme 1.13).



Scheme 1.13 : formation of star PMMA by GTP techneque.

Star polymers (3) with hydroxy ends blended with enamels improve the hardness/flexibility ratio.

Star polymers results when living GTP polymers can be coupled with a polyfunctional alkylating agent. For example, treatment of (1) with (4) gives the three arm star (5)[173].



(4)

1.8: Synthesis of star shaped polymer by initiation method.

1.8.1: Living anionic polymerization technique.

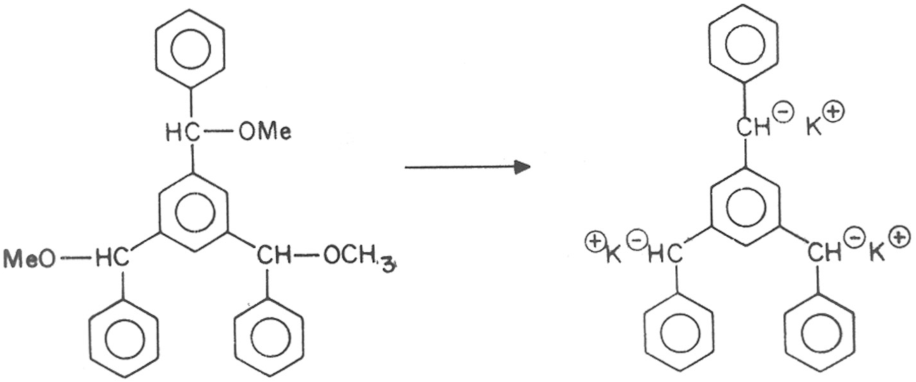
One of the major drawbacks of the synthesis of star branched polymer by termination reaction is the need to ensure stoichiometric balance to ensure precise branching. Moreover, the branching is not uniform owing to diffusion limitation of the accessability of living chain end to the branch site. Therefore, one has to go through highly complicated polymer fractionation procedures to isolate the star polymer with desired functionality/purity. Furthermore, the end functionalization of star polymer is not possible when this approach to branching is used.

Star polymer synthesis by initiation method thus provides an useful alternative.

Nagaswa and Fujimoto[174] and Popar et al.[175] tried to prepare a number of tri- and tetrafunctional initiators for anionic polymerization. These authors, however, failed to obtain star-shaped poly (α -methyl styrene) with "living" chain ends having a well defined number of side arms.

This reaction is not diffusion controlled since there is no steric hindrance for the monomer during reaction with the living chain end of the polymer.

Difficulties arise, however, in the preparation of the well-defined active polyfunctional initiators. Very low solubility of these multifunctional, anionic initiators in organic solvent is the main problem associated with its preparation. This is the only reason for scenty reports available on the synthesis of star polymer by initiation method. The most successful multifunctional anionic initiator **(47)** was reported by Nagawa and workers[176] in 1978.



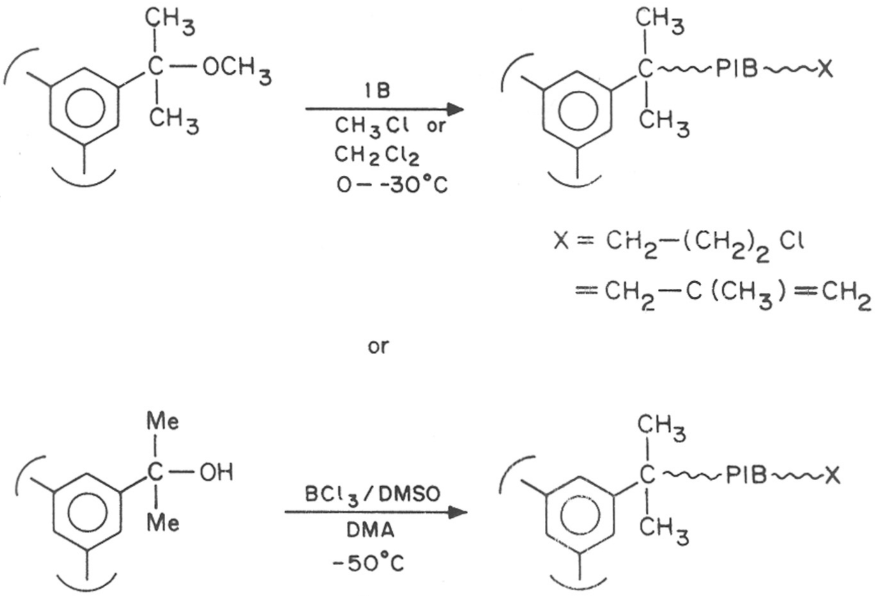
(46) **(47)**

However, the initiator appeared to be unstable even at low temperatrues. The colour disappeared and a fairly large amount of precipitant appeared in ampules in a week at -25°C. α- Methyl styrene was polymerized in THF at -78°C. The polymerization products contained one and two branched (linear) polymers in addition to the star shaped polymer. It was confirmed that those three components have molecular weights in the ratio of 1:2:3.

The solubility problem associated with polyfunctional anionic initiator was overcome by Burchard and coworkers[179] by preparing a polyfunctional living microgel which was used as initiator. DVB was first polymerized anionically by butyl lithium in dilute benzene solution. Soluble microgels of high molecular weight are obtained, and these microgels bear a large number of anionic end groups which can initiate the polymerization of any monomer susceptible to anionic polymerization. Polydisperse (both in arm molecular weight and overall molecular weight) polystyrene stars containing upto about 1.7 x 10^4 arms were obtained. This system indicated a slow and incomplete reaction between both styrene and diene monomers and the poly (divinyl benzyl lithium) anions in the poly (divinyl benzene) nodule.

1.8.2 : Living Cationic Polymerization techniques.

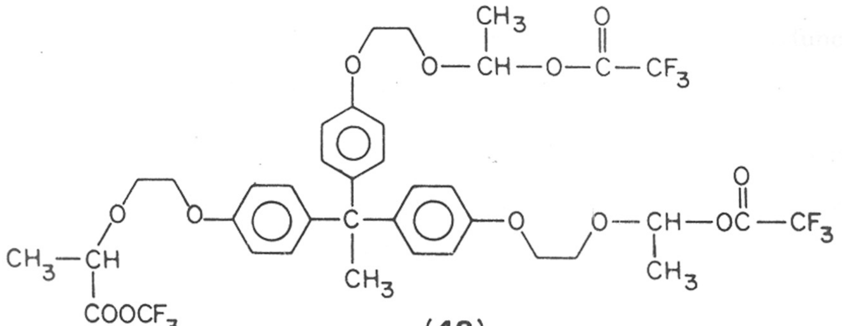
Some trifunctional initiators have been developed by Kennedy et al., who obtained three armed star isobutylenes via the inifer method[180] and living cationic polymerization[181-185]. They used the following trifunctional initiators (scheme 1.14).



Scheme 1.14 : Synthesis of three armed star poly (isobutylene).

However, these methods have been limitted to nonpolar hydrocarbon monomers (isobutylene, etc.). In addition, direct proof for the attachment of exactly three arms to a single core entity, as well as, for their uniformity in length has been given only one study[186].

Trifunctional initiators **(48)**, **(49)** for living polymerization of isobutyl vinyl ether was reported by Higashimura, et al., in 1991[187] (scheme 1.15).



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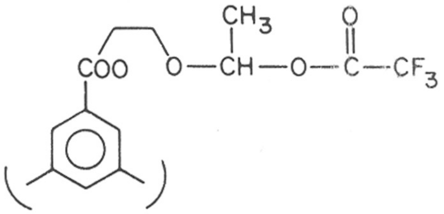


(49)

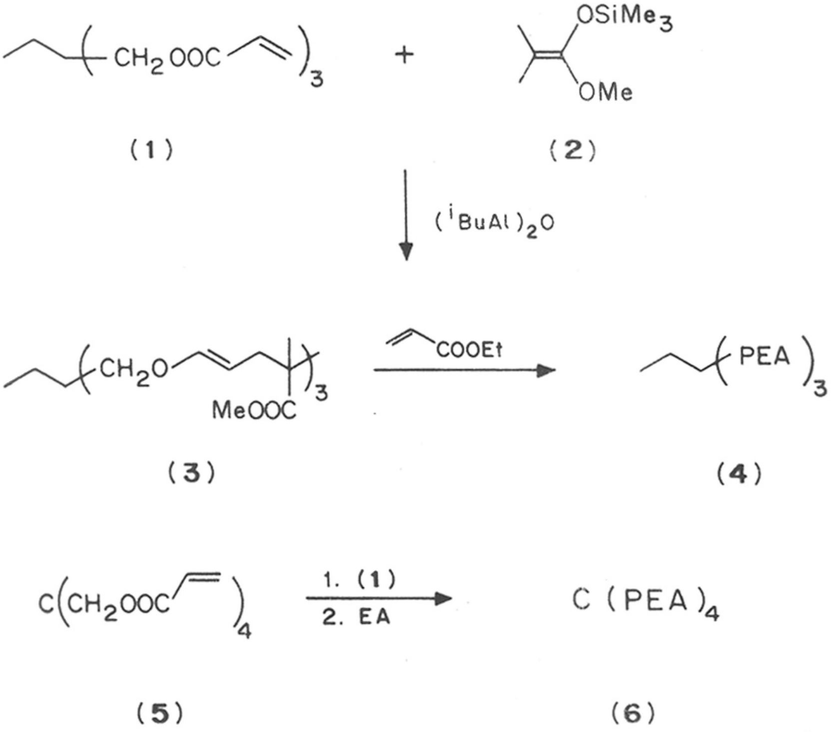
Scheme 1.15 : Initiator for the synthesis of star poly (isobutylene)

Recently trifunctional initiators[188,189] were used to yield star-shaped polyoxazoline having three living chain ends. Latter on, a tetrafunctional initiator, tetrakis (bromomethyl) ethylene[190] and a hexafunctional initiator, hexakis [p-(bromomethyl) phenoxy] cyclotriphosphazene[191] were employed in polymerization of 2-methyl-2-oxazoline to produced four arm and six arm star branched polymers respectively.

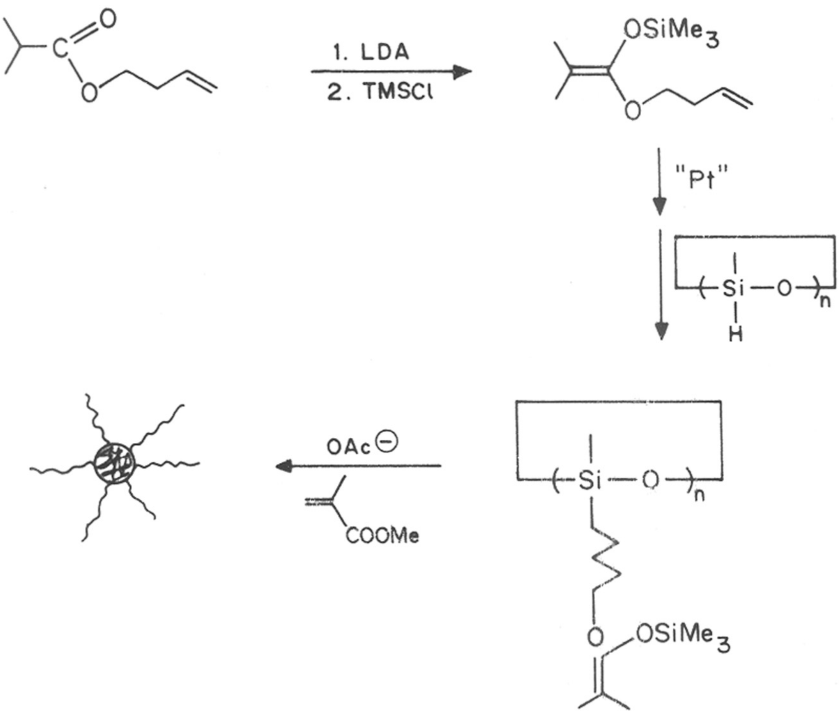
1.8.3 : GTP techniques.

Initiation of GTP with polyfunctional initiators to produce star polymers presents the problem of synthesis of large, reactive, polyfunctional ketene silyl acetals. An alternative approach, which is described by Sogah et al.,[192] is to generate polyfucntional initiators insitu by the michael addition reaction of polyfunctional monomers with silicon reagents as schown in scheme 1.16.

Another approach recently reported by Zhu et al.,[193] to synthesis polyfunctional GTP initiator is that hydrosilylation of a silyl ketene acetal bearing a terminal olefin such as 1-[(but-3-en-1-yl)]-1- (trimethyl silyl)-2-methyl-1-1propene, as outlined in scheme 1.17.



Scheme 1.16 : Synthesis of insitu polyfunctional GTP initiators.



Scheme 1.17: Synthesis of polyfunctional GTP initiator

SECTION C

Living cationic polymerization of vinyl ethers.

1.9: Introduction .

In 1956, Szwarc and coworkers discovered the anionic polymerization of styrene without chain transfer and termination[194] and this reaction was called "living" polymerization. Subsequently, number of reports appeared in the literature about living anionic polymerization systems.[195] In the field of cationic polymerization, two research groups reported in 1965 that the propagating species in ring opening polymerization of tetrahydrofuran have an unusually extended lifetime.[196,197]

These two examples of living polymerization (anionic and ring opening) involve rather stable propagating species, carbanion and oxonium ions, respectively, and hence their lifetime can be prolonged under carefully selected conditions using meticulously purified reagents.

In cationic polymerization of vinyl compounds on the other hand, the propagating species is an inherently unstable carbocation that is extremely susceptible to deactivation (termination and chain transfer), even in the absence of interfering impurities. It has, therefore, been considered that living cationic polymerization of vinyl monomers would be almost impossible to achieve.

Inherent criteria for the living polymerization are as follows.

(A) Increase in polymer molecular weight (Mn) with increasing amount of consumed monomers.

B) Increase in polymer molecular weight on addition of a fresh monomer feed to a completely polymerized solution of the same monomer.

C) Formation of block polymers on addition of a second monomer to a completely polymerized solution of the first monomer.

A survey of literature based on these criteria reveals the presence of long lived propagating species even in cationic polymerization. Examples of these are found in the pioneering work by Schildknecht[198] who observed an increase in molecular weight (by viscometry) with conversion in the polymerization of allyl vinyl ether by BF_3OEt_2 in aliphatic hydrocarbon solvents at low temperature.

More than a decade latter, Asami and Tokura suggested the formation of living polymers in the styrene polymerization in liquid sulfurdioxide, a solvent of strong solventing power, initiated with stannic chloride[199] and BF_3OEt_2[200]. They observed that the molecular weight of the polymer was in direct proportion to the ratio of monomer to initiator concentration. Unfortunately, no further studies was pursued concerning living cationic polymerization.

Beginning 1975, the second generation of investigations on this subject started to appear in the literature. Table 1.5 lists typical systems for which the formation of living polymers has been claimed. Pepper, who obtained polystyrene with a bimodal MWD with perchloric acid as an initiator at low temperature noted that the lower molecular weight fraction of this polymer increased in molecular weight as the polymerization proceeded.[201] Johnson and Young polymerized 2-butyl vinyl ether with iodine by repeatedly adding a monomer feed to a completely polymerized solution (sequential polymerization) and found an increase in polymer molecular weight with increasing numbers of monomer addition.[202]

Similarly, sequential polymerizations also led to synthesis of block polymers[203-205]. Despite such a long history of research which provided many interesting findings, vinyl ether polymerization attracted limited interest among polymer scientists primarily because vinyl ether polymers had failed to find extensive industrial use.[206-208]

However, more recent developments in this field have revitalized this area of research which are directed particularly towards the synthesis of novel functional

Table 1.5 : Evidence for the formation of living/long-lived propagating species in cationic polymerization.

A. Homopolymerization

Monomer	Initiator	Solvent	Temperature, in °C
Styrene	$HClO_4$	CH_2Cl_2	-45
p-Methoxy styrene	I_2	CCl_4	0, -15
Methyl-p-methoxy styrene	I_2	CH_2Cl_2	0, -15
Isobutyl vinyl ether	I_2	Toluene	-15
n.Butyl vinyl ether	I_2	CH_2Cl_2	-60
Isobutyl vinyl ether	I_2/HI	n.C_6H_{14}	-15
Isobutyl propenyl ether	I_2	Toluene	-40
Isobutyl vinyl ether	p.DCC/$AgSbF_6$	CH_2Cl_2	-70, 90
Methyl vinyl ether	p.DCC/$AgSbF_6$	CH_2Cl_2	-70

Continued......

B. Block Polymerization

First monomer	2nd monomer	Initiator	Solvent	Temperature
Isobutyl vinyl ether	N-vinyl carbozole	$Ph_3C^+SbCl_6^-$	CH_2Cl_2	0
Ethyl vinyl ether	N-vinyl carbazole	$Ph_3C^+SbCl_6^-$	CH_2Cl_2	0
Isobutyl vinyl ether	2-Methyl-2-oxazoline	I_2	n.C_6H_4	0
p-Methoxystyrene	Isobutylvinyl ether	I_2	CCl_4	-15
Isobutyl vinyl ether	α -Methyl Styrene	p.DCC/$AgSbF_6$	CH_2Cl_2	-90
Isobutyl vinyl ether	Methyl vinyl ether	p.DCC/$AgSbF_6$	CH_2Cl_2	-70

polymers based on the living cationic polymerization of vinyl ethers. This approarch has allowed hitherto unattainable control of both molecular weight and structure of poly(vinyl ethers).[209]

1.10: Monomers and initiators.

Monomer : The vinyl ethers studied so far are classified as follows :

i) alkyl vinyl ethers ($CH_2 = CH\ OR$), R = alkyl (linear, branched or cyclic), ii) aryl vinyl ethers ($CH_2 = CHO\ Ar$), Ar = phenyl, substituted phenyl, naphthyl, iii) functionally substituted vinyl ethers ($CH_2 = CHOX$), X = alkyl group with a hetero atom (halogen, silicon, etc.), ether, ester, amine or their derivatives, iv) divinylethers ($CH_2 = CHOCH = CH_2$ and $CH_2 = CHOXOCH = CH_2$), X = $(CH_2)_n$, $(CH_2CH_2\text{-}O)_n$, CH_2CH_2, $\text{-}CH_2CH_2OCMe_2C_6H_4CMe_2OCH_2CH_2$, etc., v) α -substituted vinyl ethers ($CH_2 = CHROR$), R = alkyl, R' = methyl, alkoxy, chlorine, vi) β -substituted vinyl ethers $R^1CH{=}CHOR$, R = alkyl, R^1 = alkyl, alkoxy, chlorine.

Initiators :

Because of their high reactivity, vinyl ethers can be polymerized by a variety of acidic compounds including those which are too weakly acidic to initiate cationic polymerization of styrene, isobutene and other less reactive vinyl monomers.

Typical examples are : i) protic acids (e.g. CF_3COOH, CF_3SO_3H), ii) metal halides (e.g. $SnCl_4$, $FeCl_3$, BF_3, BF_3OEt_2), iii) halogenated metal alkyls (e.g. $RAlCl_2$, R_2AlCl, RMgX; R = alkyl, X = halogen, iv) cation forming salts (e.g. $Ph_3C^+\ SnCl_5^-$, $C_7H_7^+SbCl_6^-$, $MeCO^+\ ClO_4^-$), v) halogens (e.g. I_2, IBr), vi) modified Ziegler-Natta Catalysts (e.g. $Et_3\ Al\text{-}VCl_4\text{-}Bu_3Al\text{-}THF$), vii) solid acids (e.g. Cr_2O_3, $Al_2(SO_4)_3\text{-}H_2SO_4$) viii) high energy radiation (e.g. γ -ray).

1.11: Kinetics of the polymerization.

The systematic study of the kinetics of vinyl ether polymerization was started in 1947 by Eley and coworkers[210] who polymerized n-butyl vinyl ether with $SnCl_4$[211], iodine[212], $AgClO_4$[213] and Ph_3CCl[213]. This research group eventually established the cationic chain polymerization mechanism for vinyl ethers, consisting of initiation, propagation, chain transfer and termination.

1.11.1: Protic acids.

Polymerization of vinyl ethers by a protic acid hardly ever produces high polymers because of accompanying side reactions and little study has been devoted to this field. Only recently, the polymerization of isobutyl vinyl ether with CF_3CO_2H was kinetically investigated in detail.[214] High polymers[215] may form at lower temperatures for instant, at -78°C the CF_3SO_3H initiated polymerization of 2-chloroethyl vinyl ether in CH_2Cl_2 gives polymers of molecular weight $>10^5$.

1.12: Initiation.

The initiation step in the cationic polymerization of vinyl ethers in an electrophilic addition of a cation , derived from an initiator ($A^+ B^-$), across a vinyl ether double bond, to form a monomeric carbocation (equation 1.10).

$$A^+ B^- + CH_2{=}\underset{\displaystyle OR}{\underset{|}{CH}} \longrightarrow A\ CH_2\ \underset{\displaystyle OR}{\underset{|}{\overset{+}{CH}}}\ B^- \quad \ldots\ldots\ldots\ 1{\cdot}10$$

1.12.1: Metal halides and halogenated metal alkyls.

In general, metal halides need a catiogen or protogen (AB) called cocatalyst in order to initiate cationic polymerization (equation 1.11, 1.12).

$$Mx_n + AB \longrightarrow \overset{+}{A}\ (MX_nB)^{-}$$

.... 1·11

$$\overset{+}{A}\ (MXB)^{-} \quad CH_2 = \underset{OR}{\underset{|}{CH}} \longrightarrow ACH_2\ \underset{OR}{\underset{|}{\overset{+}{CH}}}\ (MX_nB)^{-}$$

.... 1·12

Among metal halides, BF_3OEt_2 is most frequently employed for alkyl vinyl ether polymerization because it readily produces high polymers at low temperature. Metal alkyls also polymerize vinyl ethers either by themselves or in conjuction with an appropriate catiogen (protogen)[216].

1.12.2: Cation forming salts.

Organic salts of suitably reactive carbocations or acyl cations initiate vinyl ether polymerization.[217] Some onium salts decompose upon irradiation in uv and visible light to form a cation or cation radical that in turn polymerizes vinyl ethers.[218] Among these, iodonium (1) and sulphonium (2) salts are useful as thermally stable photoinitators.

$Ar_2I^+X^-$

(1) Ar = Ph, C_6H_4OMe etc.

X^- = SbF_6^-, AsF_6^-, PF_6^-, BF_4^- etc.

$Ar_3S^+X^-$

(2) Ar = Ph, C_6H_4OMe, etc.

X^- = SbF_6^-, AsF_6^-, PF_6^-, BF_4^-, etc.

1.12.3: Halogens.

Historically, iodine was the first initiator employed for vinyl ether polymerization, for which kinetices studies were carried out by Eley and Richards.[211]

Other halogens and interhalogen compounds also induce polymerization of vinyl ethers. The rate of polymerization of n-butyl vinyl ether with these initiators decreases in the order : I_2>ICl>1Br>Br_2.[219]

1.12.4: Heterogeneous initiators[220].

Metal oxide and related solid acids have been extensively studied as initiators for the synthesis of stereoregular or high molecular weight poly (vinyl ethers) at room temperature.

1.12.5: High energy radiation.

See Section 1.13.2

1.13: Propagation.

The propagation reaction in vinyl ether polymerization proceeds via a carbocation (**50**) as the growing species (equation 1.13). The kinetics and mechanism of the propagation process for vinyl ethers have been investigated in detail.[211,221]

$$\sim\!\sim CH_2\underset{\underset{OR}{|}}{\overset{+}{CH}}\ \overset{-}{B} + CH_2=\underset{\underset{OR}{|}}{CH} \longrightarrow \sim\!\sim CH_2-\underset{\underset{OR}{|}}{CH}-CH_2\underset{\underset{OR}{|}}{\overset{+}{CH}}\ \overset{-}{B}$$

(50)

............1·13

1.13.1: Propagation rate constant.

In an organic solvent, the carbocationic growing species either exists as free ion or an ion pair or an equilibrium mixture of both. The free ion propagation rate constant K_p may be obtained in the polymerization by high energy radiation[222,223] or cation forming salts[217,224] under suitable conditions. The ion pair propagation rate constant K_p has not yet been determined separately.

Table 1.6 lists the representative K_p^+ value for series of alkyl vinyl ethers.

1.13.2: Radiation - induced polymerization in solution.

Because of the difficulty in purifying and drying solvents, radiation-induced polymerization is usually performed in bulk monomer[225,223]. For comparison with these bulk processes, Stannett and coworkers studied γ-ray-induced polymerizations of ethyl and isopropyl vinyl ethers in various solvents under the so called super-dry conditions.[226-231] With the monomers, the polymerization rate and k_p sharply decrease on going from bulk to solution : bulk > C_6H_6 > Et_2O >> CH_2Cl_2 >> $MeNO_2$. Stannett concluded that the decrease in k_p is due to the solvation (or stabilization) of the free ionic propagating carbocation, either by solvent or by a pendant ether oxygen[231].

1.13.3: Polymerization initiated by iodide.

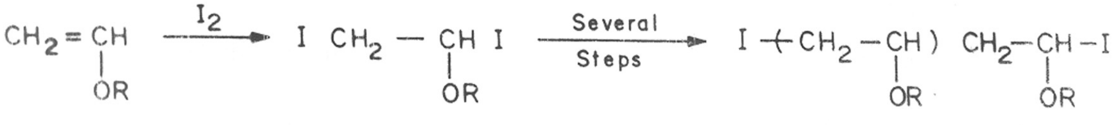
Ledwith and Sherrington reported the rapid formation of the iodine-vinyl ether adduct **(51)** in methylene chlorde at -40°C and proposed an initiation mechanism in which the CH-I bond of **(51)** undergoes electrophilic addition of vinyl ether monomer with the help of free iodine (Scheme 1.17).

The formation of the diiodide **(51)** or its higher homologs **(52)** was also observed in the polymerization of n-butyl vinyl ether with iodine in n-hexane.[232] It was proposed that propagation might proceed via polymer **(51)** with terminal C-I bond (Scheme 1.18).[232-234]

Table 1.6 : Free ion propagation rate constants (kp) for alkyl vinyl ethers (CH2 = CH OR) at O°C.

Monomer (R)	Radiation (γ ray, bulk) k_p	Initiator	Carbocation salts (CH_2Cl_2) k_p
Methyl	a	$C_7H_7^+SbCl_6^-$	1.4×10^2
Ethyl	7.2×10^3	$C_7H_7^+SbCl_6^-$	1.5×10^3
Isopropyl	9.0×10^5	$Ph_3C^+SbCl_6^-$	1.6×10^3
Isobutyl	3.8×10^4	$Ph_3C^+SbCl_6^-$	$4.0 \times 10_3$
Butyl	5.0×10^4	$C_7H_7^+SbCl_6^-$	3.5×10^3
Cyclohexyl	a	-do-	3.3×10^3
2-Chloroethyl	a	-do-	2.0×10^3

a) No polymerization due to radiolysis of methyl vinyl ether.



(51)

(52)

Scheme 1.18 : Polymerization of vinyl ether by iodine.

1.14: Chain Transfer and Termination.

Cationic polymerization of vinyl ethers hardly ever produce high polymers unless carried out at low temperature. The low molecular weight of the product is due to the chain transfer that frequently occurs, particularly, at or above room temperature.

1.14.1: Termination.

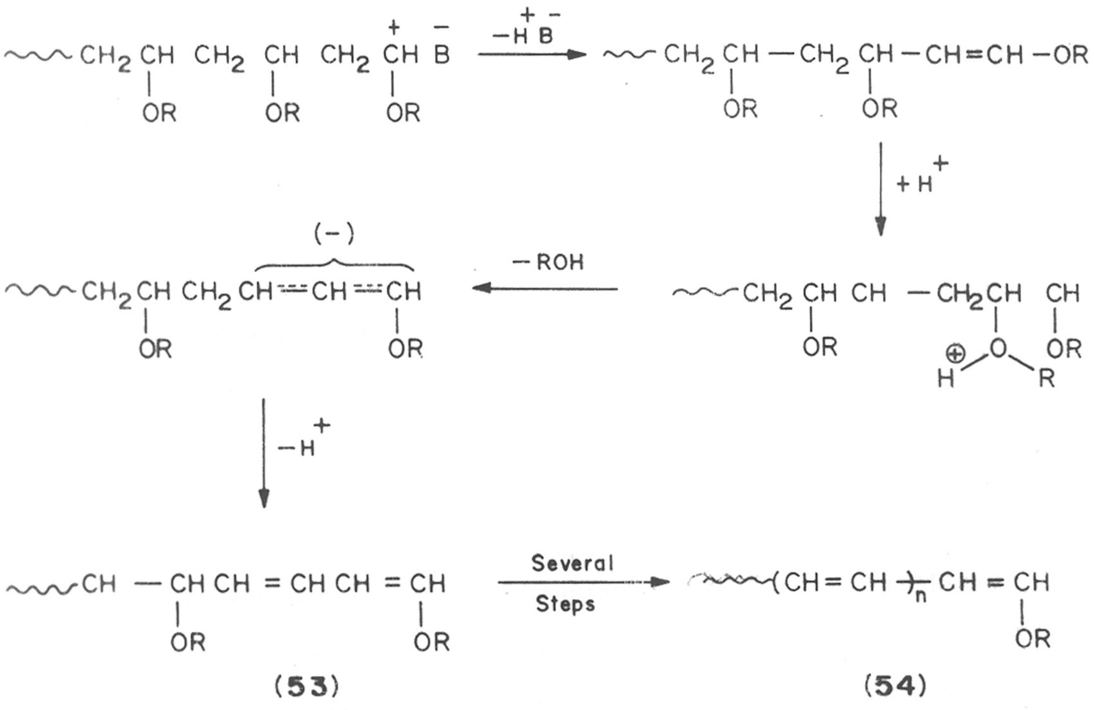
Compared with chain transfer, termination is much less important as a chian breaking reaction in vinyl ether polymerization, except when a basic compound (e.g. pyridine[235]) is present in the reaction mixture.

1.14.2: Chain Transfer.

Chain transfer to bases (or transfer agents) in vinyl ether polymerization was first recognised by Eley and coworkers.[211-212]

Even in the absence of a transfer agent, it is usually difficult to obtain high polymers from vinyl ethers at room temperature. This difficulty is attributed to the instability of the propagating carbocation, which tends to transfer its -proton either to the counter anion or to the incoming monomer. In most cases,[212,213,223,236,237] the more frequently chain transfer occurs, the higher are the amounts of terminal double bond ($CH = CHOR$) and acetal end group ($CH_2\,CH(OR)_2$ in the polymers.

The polymerization mixture of vinyl ethers in polar media or at high temperatures often exhibit an intense colour that changes from yellow through blue-green to dark violet with the progress of the reaction. This coloration long eluded a consistent explanation, but has recently been established to result from delocalized polymeric carbocations that form via protonation of conjugated polymer terminals such as **(53)** and **(54)**.[238] Scheme 1.19 illustrates the manner of formation of **(53)** and **(54)**



Scheme 1.19 : Chain transfer to bases.

1.15: Living cationic polymerization of vinyl ethers.

1.15.1: Hydrogen iodide/iodine initiating system.

In 1984, Higashimura and coworkers demonstrated, for the first time that an initiating system consisting of hydrogen iodide and molecular iodine (HI/I_2) induces truly living polymerization of 1BVE in nonpolar media[239]. When hydrogen iodide is added to excess 1BVE in a non polar solvent at low temperature (below -15°C) no polymerization occurs, but instead an adduct **(55)** is formed between the acid and IBVE.

$$CH_2{=}\underset{\displaystyle OR}{\underset{|}{CH}} + HI \longrightarrow CH_3-\underset{\displaystyle OR}{\underset{|}{CH}}-I$$

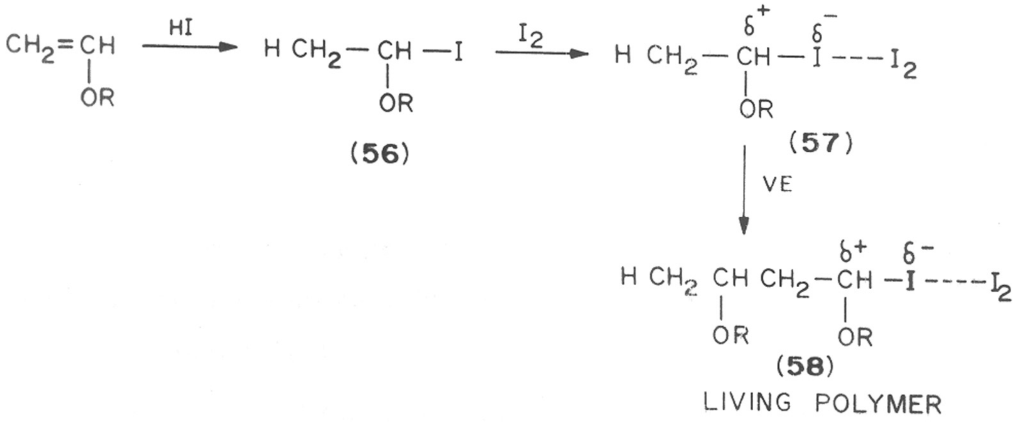
(55)

However, addition of a small amount of iodide to this quiescent mixture leads to a rapid polymerization, which is faster than that by iodine alone under similar conditions. Detailed studies demonstrated the perfectly living nature of the HI/I_2 initiated polymerization of 1BVE[239,240]. For examples, the number average molecular weight (Mn) of the polymer increases linearly with monomer conversion is inversely proportional to the initial concentration of HI. The obtained Mn is in good agreement with the calculated value assuming one polymer chain per unit HI. The molecular weight distribution (MWD) of the polymers stays very narrow ($Mw/Mn<1.1$) at all levels of conversion.

1.15.2: Mechanism of living polymerization.

Higashimura et al.[241] analyzed the living polymerization system initiated by HI/I_2 in situ by low temperature ^1HNMR and uv spectroscopy. On the basis of these and other studies, the initiation/propagation mechanism shown in scheme 1.20 was proposed.

The C-I bond of **(56)** and its higher homologs **(58)** are activated (dissociated or polarized) by added iodine as in **(57)**, and the incoming monomer reacts with this activated bond. According to this mechanism, a stable C-I bond is formed at the growing end in each propagation step. The formation of this bond is attributed to the strong interaction of iodide anion with the propagating carbocation.[242] The stability of the propagating species, in turn, suppresses chain transfer, termination and other side reactions. It is concluded that a suitable combination of the stability of the growing carbocation and the nucleophilicity of its counteranion is the key to living cationic polymerization.[242,243]



Scheme 1.20 : Polymerization of VE by HI/I_2 initiating system.

1.15.3: Hydrogen iodide/Zinc iodide initiating system.

In the living polymerization by HI/I_2 system, iodine acts as a weak acid that activates electrophilically the terminal C-I bond of the propagating species. This mechanism implies that weak lewis acids other than iodine may serve to activate the terminal C-I linkage for living propagation.

Sawamoto et al.[244] found that zinc iodide (ZnI_2) in conjuction with hydrogen iodide induces living polymerizations of 1BVE and 2-acetoxy ethyl vinyl ether in methylene chlorde or toluene in a wide range of temperature from -40 to +25°C. The HI/ZnI_2 initiating system is superior to HI/I_2 on account of higher rate of polymerization. Like, iodine, ZnI_2 apparently interacts with the C-I bond for its activation. Table 1.7 summarises the effects of Lewis acids (MXn) on the nature of livingness.[245]

1.15.4: $EtAlCl_2$/ester and EtAlCl2/ether initiating systems.

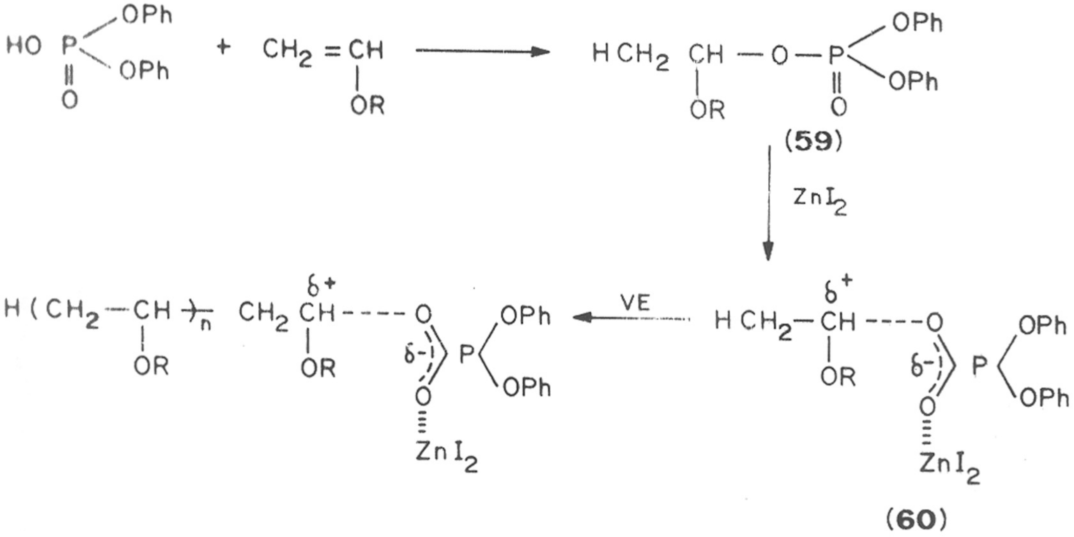
$EtAlCl_2$ by itself efficiently induces cationic polymerization of vinyl ethers, but the polymerization is not living. However, combination of $EtAlCl_2$ with a large excess of inert esters (e.g. $MeCO_2Et$)[245] or ethers (e.g. dioxane)[246] as initiating systems lead to living polymerization of 1BVE. It is notable that living polymers with a high molecular weight (Mn> 10^5) and a narrow MWD (Mw/Mn = 1.1 - 1.2) are prepared in a wide temperature range from 40 to even +70°C. For ester containing vinyl ethers, the presence of an ester additive is unnecessary. The polymerization of such monomers with $EtAlCl_2$ alone are living.

The discovery of the HI/ZnI_2, $EtAlCl_2$/ester and $EtAlCl_2$/ether initiating system particularly significant in that for the first time, living cationic polymerization of vinyl monomers, has been realised at or above room temperature.

Table 1.8 summarizes the effects of reactions conditions on the living polymerization initiated by the HI/ZnI_2 and HI/I_2 systems.[245]

1.15.5: $R_2P(O)OH/ZnX_2$ Initiating systems.

A series of monoacidic phosphate esters have been shown to initiate living cationic polymerization of vinyl ether in the presence of zinc halide as an activator.[246] For examples, a mixture of diphenyl phosphate [$(PhO)_2P(O)OH$] and ZnI_2 efficiently polymerizes isobutyl vinyl ether in toluene below 0°C to form nearly monodisperse polymers whose number average molecular weights (Mn) are controlled by conversion and the feed ratio of phosphate and 1BVE monomer. The Mn of the polymers is in direct proportion of monomer conversions, and further increases upon addition of a fresh feed of 1BVE to a completely polymerized reaction mixture (scheme 1.21).



Scheme 1.21 : Polymerization of vinyl ether by $R_2P(O)OH/ZnX_2$ initiating system.

Scheme 1.21 depicts the proposed pathway of the phosphate mediated living cationic polymerization of vinyl ethers. In accordance with generalized pathway in Section 1.15.1 the phosphate initiator acts as a protic acid and forms an adduct **(59)** with

Table 1.7 : Living cationic polymerization of 1BVE by HI/Lewis acid initiating systems : Effects of Lewis acids (MXn)a

Mx_n	Toluene		CH_2Cl_2	
	-40°C	+25°C	-40°C	+25°C
ZnI_2	0	0	0	X
$ZnBr_2$	0	-	0	X
$ZnCl_2$	0	-	0	X
$SnCl_2$	0	-	0	X

a) 0 : Living ; X : Not living

Table 1.8 : Living cationic polymerization of IBVE by HI / lewis acid initiating system : HI/ZnI$_2$ vs HI/I$_2$^{a}

Solvent	Tolune				CH$_2$Cl$_2$			
Temp. °C	-40°C	0	+25	+40	-40	0	+25	+40
HI/ZnI$_2$	0	0	0	0	0	0	X	X
HI/I$_2$	0	0	X	X	0	0	X	X

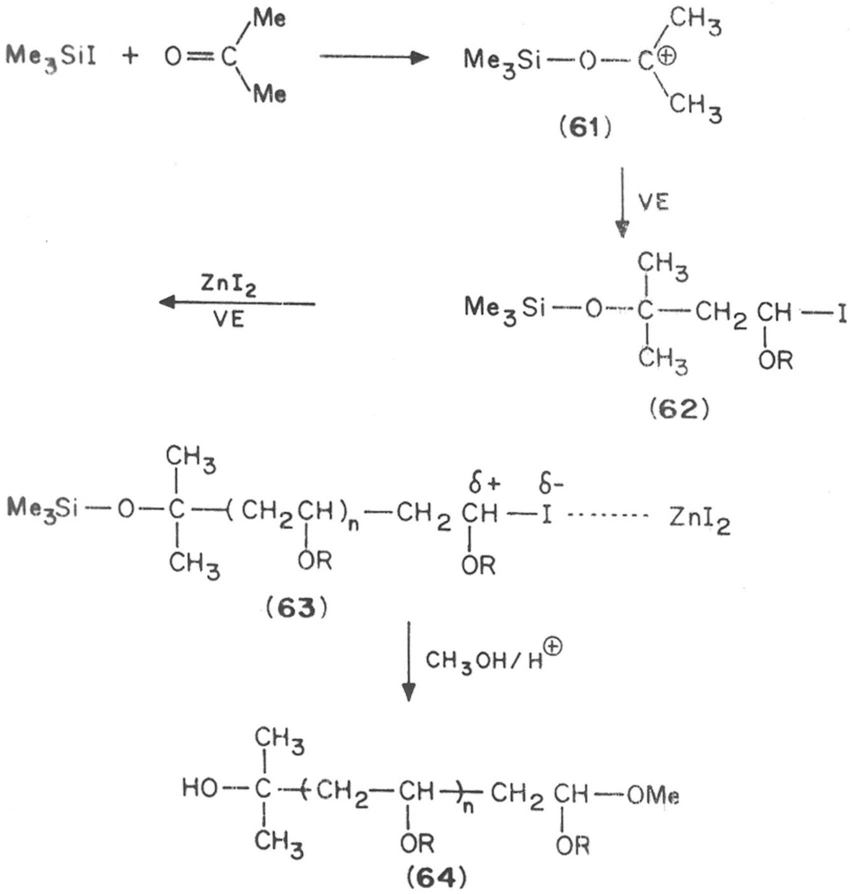
a) O : :Living; X : Not living

vinyl ether. The subsequent process involves activation of the carbon-phosphate linkage by zinc halides as in **(60)** and living propagation starts. Other derivatives for examples $R_2P(O)OH$; R^1 = n.Bu, Ph, etc. also induce similar living process in the presence of zinc halides. Importantly, those findigs have shown the phosphate anions to be as effective as the iodide anion in nucleophilic stabilization of the growing carbocations.

1.15.6: $Me_3SiI/ZnI2$ Initiating system.

This system replaces the proton in HI/ZnI_2 with the trimethyl silyl group, while utilizing the iodide anion for carbocation stabilization.[247] Despite the apparent similarity to the HI/ZnI_2 system, however, it turned out that the Me_3Si I/ZnI_2 mixture alone cannot induce perfectly living polymerization of vinyl ethers but needs a carbonyl compound ($O = CR^1R^2$; aldehyde or ketone).

Thus, the trimethyl silyl initiator reacts with a carbonyl compound to give a silyl oxycarbocation **(61)** which in turn forms an iodide type adduct **(62)** (scheme 1.22). The carbon iodide bond in **(62)** is then activated by ZnI_2, generating intermediated **(63)** and the subsequent living polymerization follows the same pathway as in the corresponding HI/ZnI_2 mediated process.



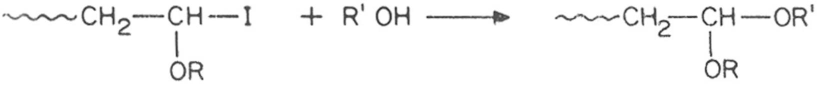
Scheme 1.22 : Polymerization of vinyl ether by Me$_3$SiI/ZnI$_2$ initiating system.

The carbonyl compounds for the Me$_3$SiI/ZnI$_2$ system include acetone, benzaldehyde and their derivatives. With these 1BVE can be polymerized into well defined living polymers in toluene even at room temperature.

One of the merits of the Me_3SiI/ZnI_2 system is that on treatment with a dilute acid, living polymer **(63)** gives an alcohol capped poly (1BVE) (**64**, either secondary or tertiary). The acetal terminal that arises from quenching the living end of **(62)** with methanol remains intact in this transformation.[248]

1.15.7: Acetals/Me_3SiI initiating system.

Acetal can also play an important role in the vinyl ether polymerization. The usual termination of the polymerization by an alcohol leads to an acetal end group **(65)** for example.

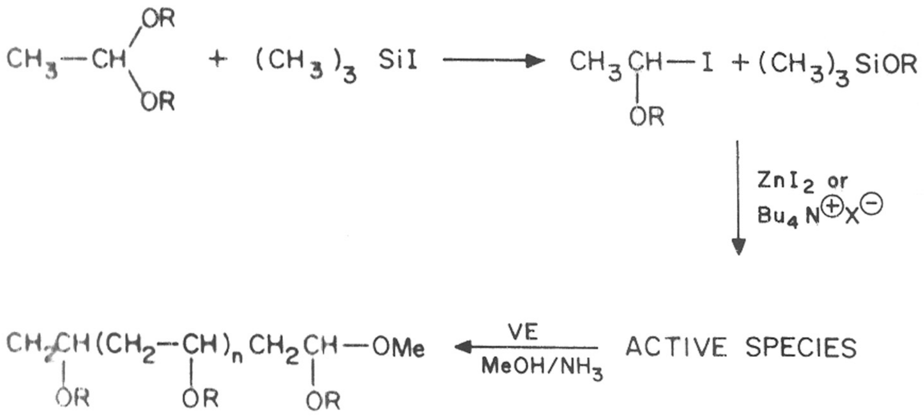


$$\sim\sim CH_2-\underset{OR}{\underset{|}{CH}}-I \;+\; R'OH \longrightarrow \sim\sim CH_2-\underset{OR}{\underset{|}{CH}}-OR'$$

(65)

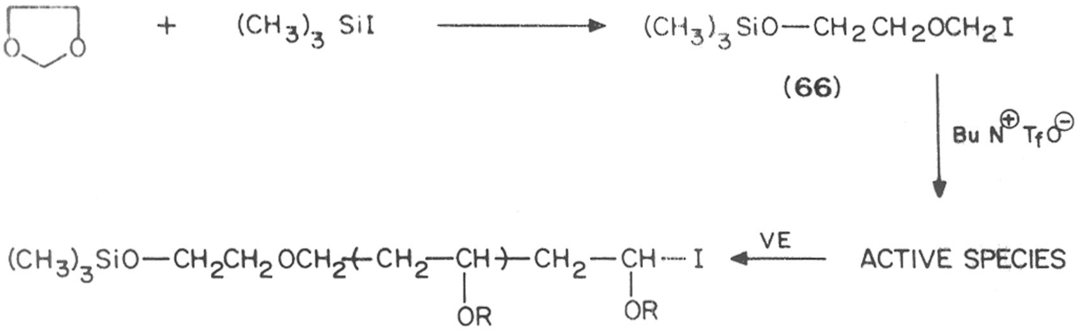
This acetal can be used as a precursor for the preparation of the active species. In the presence of the suitable nucleophile, species similar to the active species in the vinyl polymerization can be obtained (scheme 1.23).

This principle was first used with a cyclic acetal, 1,3 dioxolane (DXL), and trimethyl silyl iodide as electrophile, leading to the corresponding 1-trimethylsiloxy-4-iodo-3-oxabutane **(66)** which in conjuction with a tetrabutyl ammonium salt of a non nucleophilic counter ion, acts as an initiator for the vinyl ether polymerization.[249] The head group produced by this initiating system is a trimethyl silyl ether that hydrolyses to the corresponding alcohol.



Scheme 1.23 : Polymerization of vinyl ether by acetals/Me$_3$SiI initiating system.

Since other polymer chain end can be endcapped in the usual way, this initiating system provides an opportunity to synthesise PVE with two hydroxyl end groups or with one hydroxyl and another end group, the structure of which is determined by the nature of the end capping agent as shown in scheme 1.24.



Scheme 1.24 : Polymerization of vinyl ether by acetals/Me$_3$SiI initiating system.

Table 1.9 summerizes some results of PVE's obtained with the acetal/TMSI combination for different acetal precursor[250].

1.16: Kinetics and Mechanism of Living Cationic Polymerization.

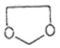
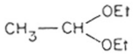
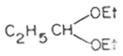
1.16.1: Lifetime of Living Polymerization.

As defined, living polymers have life times long enough to continue an undisturbed growth during the time span of polymerization, but they are not completely immune to chain breaking reactions.[251] Thus, the life time of living polymers is an important factor that should be considered in designing living polymerization.

1.16.2: End-Capping Analysis.

Higashimura and coworkers[252] developed a convenient method to measure the concentration of the propagating species [(P*) **(67)** Scheme 1.24] in living cationic polymerization. As shown in scheme 1.25 , the method employes an end-capping reaction of **(67)** with sodiomalonic ester **(68)** which has been confirmed to be

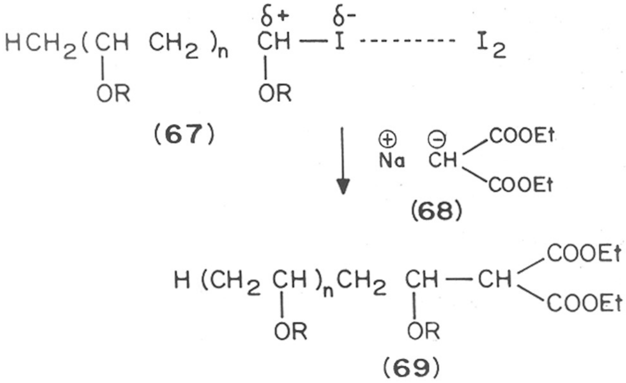
Table 1.9 : Polymerization of VEs by acetals/TMSI initiating system.

Monomer	Acetal	Mw	Mw	Mw/Mn
CEVE		3270	3380	1.1
IBVE	 $CH_3-CH(OEt)_2$	5120	4350	1.1
BVE	 $C_2H_5CH(OEt)_2$	4000	3900	1.2

Polymerization condition : temperature, -40 °C ; Solvent : CH_2Cl_2, [TMSI]/[acetal] = 1.1; Polymerization time : 1h, (yield = 100%)

instantaneous, quantitative and specific to the active growth species. The resulting polymer **(69)** carries a terminal malonate function from which [P*] can be determined by ^{1}H-NMR analysis. Following changes in [P*] as a function of time then allows one to evaluate the life time of the living species **(67)**.

End-Capping method has been shown applicable to the living polymerization of vinyl ethers initiated by such initiating systems as HI/I$_2$, HI/ZnX$_2$, and adduct of 1BVE and acetic acid/EtAlCl$_2$ (with 1,4-dioxane as added base).



Scheme 1.25 : End capping reaction of living VE polymer with sodiomalonic ester.

1.16.3: Life time.

As shown in Scheme 1.24, the living cationic polymerization of 1BVE by HI/I$_2$ was terminated by the carbanion salt **(61).** During the polymerization, [P*] remains constant and nearly equal to the initial concentration of [HI] which is consistent with the livingness of **(60)**.

The living species, however, started decaying immediately after complete consumption of the monomer. The decay process is first order with respect to the living end, and thus its half life (f) is obtained from first order plots (table 1.10). The life time is fairly long, ranging from 10 to 1000 min in toluene and CH_2Cl_2. As expected, the living end survives longer at lower temperature, and this fact allows storage of living polymer solutions at -78°C for atleast 24 h without deteriorating their reactivity. The decay process is most likely a proton elimination from the active site.

1.16.4: Kinetics of Living Cationic Polymerization.

Two research groups[253,254] studied the kinetics of the HI/ZnI_2 initiated living polymerization of alkyl vinyl ethers in non polar media.

For n-butyl and 2-chloroethyl vinyl ethers, both of them observed that the polymerizations are zeroth order in monomer and then proposed a polymerization mechanism that differs from Higashimura proposals involving the activation of the HI-derived carbon-iodine terminal by iodine [as in (57)].

Higashimura and coworkers,[255] however, found that the dependance of the living vinyl ether polymerization on monomer concentration is affected by solvents and the structure of the monomers. The reactions in n-hexane are indeed of zeroth order in monomer, but those in toluene show a first order dependance on monomer, giving linear first order plots (In(M) vs. time]. More comprehensive data are summarized in table 1.11 for three vinyl ethers and three solvents.

It is obvious that even for a particular monomer, the kinetics of the HI/I_2 mediated living processes change from zeroth to first order in monomer with increasing polarity of the polymerization solvents.[253]

Table 1.10 : Life time ($T_{1/2}$) of living polymers in the 1BVE polymerization by HI/I_2

Temperature, °C	-40	-15	0
$t_{1/2}$(min) in tolune	950	120	40
in CH_2Cl_2	1030	65	44

Table 1.11 : Reaction order in monomer for living polymerizations of vinyl ethers by HI/I_2 at -40°C.

Solvent	$n.C_6H_{14}$	Toluene	CH_2Cl_2
CH_2=CH=$OCH_2C_3H_7$	Zeroth	First	First
CH_2=CH-OCH_2CH_3	Zeroth	First	First
CH_2=C-OCH_2CH_2Cl	a	Zeroth	First

a) Polymerization precipitated.

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CHAPTER 2

CHAPTER 2

Objective and scope of the investigation.

2.1 : Introduction.

Synthesis of multiarm star shaped polymers has been an area of contemporary research interest[1-6], both from a theoretical and practical point of view. Star polymers are generally prepared by two general methods, namely, (a) core first and (b) arm first.

(a) In the core first method, core will form first from which polyemrization propagates radially. Generally, polyfunctional initiators function as a core.

(b) In the arm first method, linear arm will form first by a living polymerization technique and then terminate by a multifunctional terminator.

In spite of considerable efforts, synthetic routes to star shaped branched polymers are still beset with many problems such as, precise control of stoichiometric balance to ensure precise number of branches. Moreover, the branching is not uniform owing to limitation of the accessibility of the living chain end to the branch site. Furthermore, the end functionalization of star polymer is not possible when arm first approach to branching is used. Also, difficulties aries in the preparation of the well-defined active polyfunctional initiator (core first).

The objective of this research was to explore the synthetic utility of a novel tribromo compound, namely, 2-perbromomethyl-2-oxazoline, **(TBO)** in living ring opening, anionic and cationic polymerization. It was believed that the unique structure of this compound as well as the highly electrophilic nature of the C-Br bond may find applications in synthetic polymer chemistry, either as initiators or terminators of living polymerizations. Accordingly the following investigations were undertaken.

a) Since any alkyl halide which is strongly electrophilic in nature, can act as an initiator for the ring opening polymerization of 2-alkyl-2-oxazoline. It was reasoned that TBO can also function as an initiator. Furthermore, since this initiator contains three reactive electrophilic sites (C-Br bond) for initiation , it was of interest to explore the synthesis of three arm star polymers by ring opening polymerization of 2-oxazoline.

b) Previous studies have established the utility of multifunctional alkyl halides as a linking agent for living anionic polymeric chain ends for the synthesis of star polymers. TBO can be considered as a multifunctional alkyl halide. The most interesting feature of this linking agent is that it produces a star polymer with a reactive oxazoline functionality at the core. This may facilitate further synthetic manipulation of star polymer.

c) TBO may initiate cationic polymerization of vinyl ethers in presence of a suitable cocatalyst. If it shows the characteristic of living cationic polymerization and acts as a multifunctional initiator , it will produce a star polymer with oxazoline functionality.

Thus, should TBO act as a multifunctional initiator or as a linking agent, it will always produce a star polymer with a polymerizable functional group at the core. This will be a novel macromonomer with a star shape architecture. Furthermore, the branching reaction would lead to a tertiary carbon with the three polymeric chains.

2.2 : Approaches.

2.2.1 : Synthesis of initiator.

It is proposed to examine the exhaustive bromination reaction of 2-methyl-2-oxazoline by N-bromosuccinimide as a potential route to synthesis TBO. Since TBO may not be stable at high temperatures (> 60°C in solution), it is proposed to perform the synthesis at 25-27°C. The product will be characterized by a combination of spectroscopic techniques.

2.2.2 : Polymerization of 2-methyl-2-oxazoline using TBO as an initiator.

Cationic ring opening polymerization of 2-methyl-2-oxazoline will be studied using TBO as an initiator in solution. It is of interest to examine the livingness of the polymerization. Since TBO contains three electrophilic C-Br bonds, it can produce either a linear polymer or a star shaped polymer. Therefore, detailed characterization of the polymer will be undertaken to establish the structure of the polymer.

2.2.3 : Synthesis of star shaped polymer by termination of living anionic polymer using TBO as a linking agent.

Living anionic polymerization of styrene, isoprene, and butadiene in both polar as well as nonpolar solvents will be performed and terminated by TBO as a linking agent at room temperature (25-27°C) as well as at higher temperatures (50°C). Polymerization and linking reactions will be carried out under nitrogen as well as high vacuum (10^{-6} torr). Polymer thus formed will be characterized by size exclusion chromatography using multiple detectors.

2.2.4 : Cationic polymerization of isobutyl vinyl ether using TBO as initiator.

Cationic polymerization of isobutyl vinyl ether using TBO as an initiator and ZnI_2 as coinitiator will be examined. Polymerization will be carried out at different temperatures and solvents to establish the livingness of the polymerization.

CHAPTER 3

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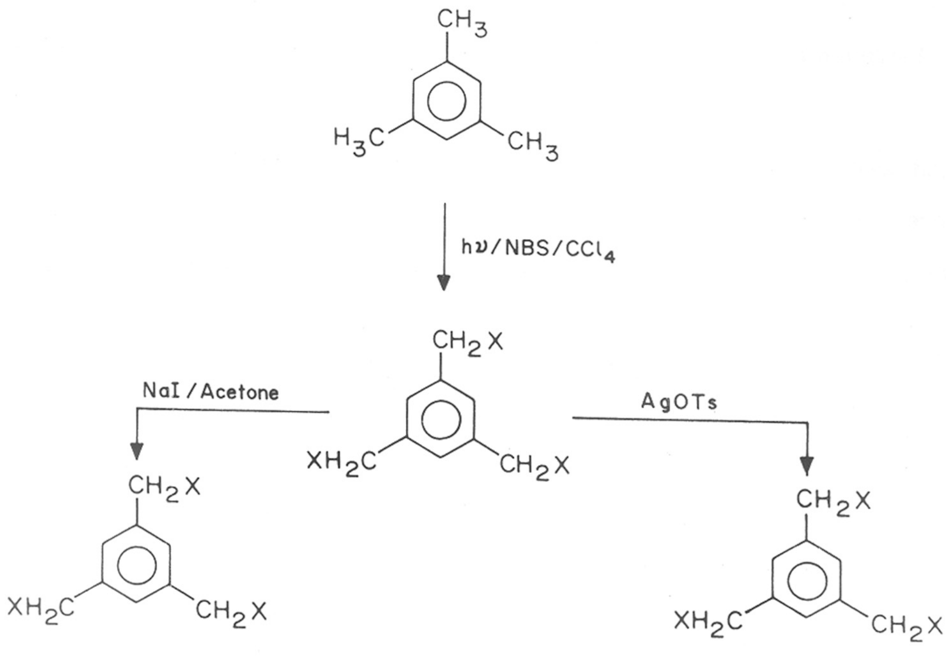
CHAPTER 3

2-(Perbromomethyl)-2-oxazoline: A novel trifunctional initiator for the ring opening polymerization of 2-methyl-2-oxazoline.

3.1 : Introduction.

Cationic ring opening polymerization of cyclic imino ethers produces linear poly(N-acylalkylenimines)[1]. Various kinds of initiators have been examined for the polymerization of 2-oxazolines. Examples are, metal chlorides and their stable salts[2,3], strong protic acids and their oxazolinium salts[2,4], ester of sulfuric acids and sulfonic acids[2,5] and alkyl halides[6]. n.Butyl chloride was inactive for the 2-oxazoline polymerization[6]. The reaction shows the characteristics of living polymerization using methyl iodide, methyl-p-toluenesulfonate and benzyl bromide as monofunctional initiators. Several bifunctional initiators such as α,ω-dodecamethylene-bis (p-toluenesulfonate)[7], bis(oxazolinium tosylate) from 1,4-tetramethylene-2,2-bisoxazoline[8], allylic dihalides such as 1,4-dibromo-2-butene and 3-iodomethyl-1-propene[9] have been examined as bifunctional initiators for the living polymerization of 2-methyl-2-oxazolines to prepare telechelic or block copolymers.

On the contrary, there are only few reports in the literature on the synthesis of star-shaped polymers of 2-methyl-2-oxazoline. Recently, a trifunctional initiator, namely, 1,3,5-(trisbromomethyl)benzene[10] has been reported for 2-methyl-2-oxazoline. However, no details were mentioned concerning the star-shaped polymers. Later , similar type of trifunctional initiators, namely 1,3,5-tris(p-toluenesulfonyloxymethyl)-benzene (2) and 1,3,5-tris(iodomethyl)-benzene (3) were used to yield star-shaped polyoxazoline having three living ends as shown in scheme 3.1[11].



(3) X = I

(2) X = OTs

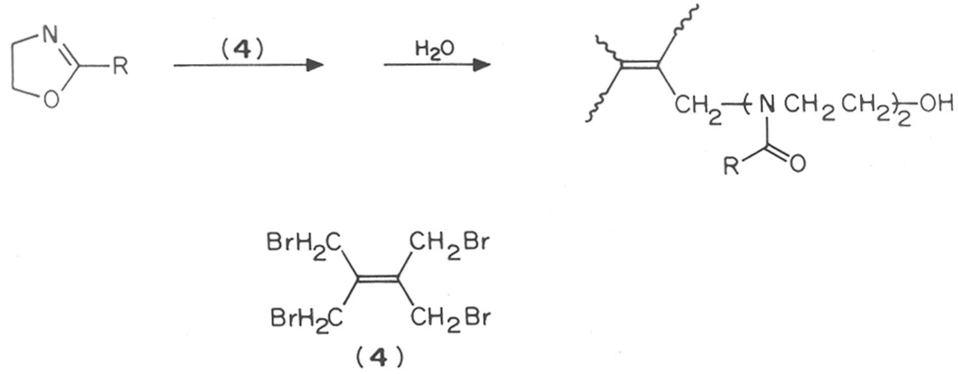
Scheme 3.1: Preparation of initiators

The polymerization was monitored by ^{1}H NMR. From results of ^{1}H NMR, the initiation was shown to take place stepwise. That is, one of three electrophiles in (2 or 3) initiated the polymerization faster than other two functional group. This reaction was then followed by the initiation with the second electrophilic group. The last initiating functional group had very low reactivity.

These observations indicate that the lengths of three arms of the resulting star-shaped polymers should be different. The star-shaped polyoxazoline having three oxazolinium propagating chain ends was subjected to the reaction with benzylamine. The functionality of the terminal benzylamino group was estimated by titration using perchloric acid in acetic acid. These results are summarized in table 3.1.

The functionality of the star-shaped polymer, however, was found to be less than unity. As described before, three electrophilic substituents in the trifunctional initiator initiate the polymerization quantitatively under the present reaction condition from ^{1}H NMR study. Low functionality determined by titration might be due to termination (or chain transfer) of the propagating end during polymerization or low capping efficiency of the reaction of the oxazolinium ion with benzylamine, or due to low efficiency of the conversion from the terminal salts to the free bases by the treatment with anion exchange resin. The specific factor causing low functionality was not identified experimentally. However, since yield is very low (table 3.1), termination or chain transfer appears to be a probable cause for low functionality.

An allylic tetrahalide, tetrakis (bromomethyl) ethylene **(4)** was employed as a tetra functional initiator to give four-armed star polymer of polyoxazoline as shown in scheme 3.2[9].



(4)

Scheme 3.2 : Polymerization of ROZO initiated by (4).

Table 3.1 : Synthesis of star shaped polyoxazoline.

Run	feed ratio	yield, %	f[a]	Mn[b]
1	15.0	45	0.56	1280
2	17.7	39	0.66	1140
3	59.8	63	0.82	---

(a) Functionality (f) was estimated by titration; (b) determined by GPC (polystyrene standards).

The Mw/Mn values obtained by GPC were fairly small. In order to confirm that the polymerization proceeds from four sites of (4), the average number of polymer chains per molecules of star polymer was determined under various monomers/initiator feed ratios by ^{1}H NMR spectroscopy (Figure 3.1).

The average number increased with increasing feed ratio. When the feed ratio was more than 10, the number was beyond three, indicating that the polymer was of star shape.

Hexakis [p-(bromomethyl)phenoxy] cyclotriphosphazene was employed in initiating polymerization of 2-methyl-2-oxazoline to produce six armed star branched polymer[12]. Although authors claimed that this initiator produces six arm star polymer, no characterization data was given to substantiate their claim. Thus reports available so far reveal scope for synthesis and unambiguous characterization of star shaped poly (N-acylethylenimines). In this context, it was decided to synthesize 2-perbromomethyl-2-oxazoline by exhaustive bromination of 2-methyl-2-oxazoline and study the initiating ability of this compound for the cationic ring opening polymerization of 2-methyl-2-oxazoline.[13].

3.2 : Experimental.

All experiments were carried out under nitrogen atmosphere using standard bench top inert atmosphere techniques .

3.2.1 : Materials.

Acetonitrile (Loba Chemie Industries, Bombay) was distilled over phosphorous pentoxide and then refluxed over calcium hydride followed by distillation under argon prior to use. 2-Methyl-2-oxazoline (MeOXZ) was synthesized according to a procedure reported in the literature[4]. The monomer was stirred over calcium hydride followed by distillation under argon prior to use. N-bromosuccinimide (NBS) (Loba Chemie Industry, Bombay) was recrystallised from hot water and dried

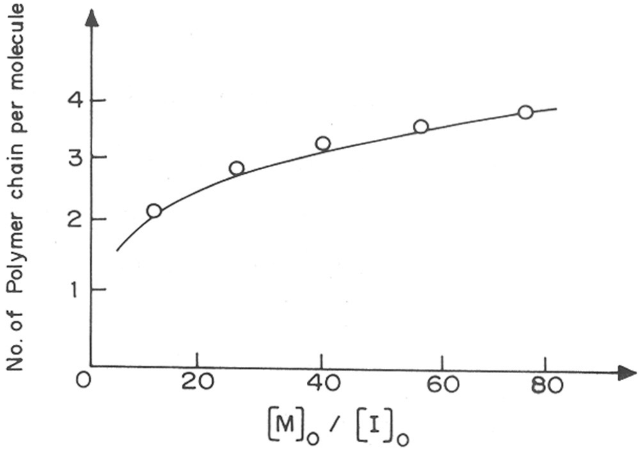


Figure 3.1 Relationship between the feed ratio ($[M]_0/[I]_0$) and the number of polymer chain per molecules

in a dessicator, m.p.181 ^{0}C (lit. value 181 ^{0}C)[14]. Benzoyl peroxide was precipitated in methanol from chloroform solution and dried, decomposition temperature 105 ^{0}C (lit. Value 105 ^{0}C)[14]. Methyl tosylate (Aldrich) was distilled at 145 ^{0}C / 5 mm of Hg prior to use. DMF (S.D. Fine Chemical Ltd. Bombay.) was stirred over calcium hydride for 24 h under argon atmosphere and distilled at 40 ^{0}C /0.1 mm of Hg. Potassium iodide was dried at 150 ^{0}C for 24 h prior to use .

3.2.2 : Synthesis of 2-perbromomethyl-2-oxazoline (TBO).

3.2.2.1 : In Carbon terachloride as solvent.

In a 100 mL round bottom flask, carbon tetrachloride (50 mL), MeOXZ, 1.O g (0.0117 mol) NBS, 6.24 g (0.035 mol) and benzoyl peroxide, 100 mg, were placed. The temperature was allowed to rise to 80 ^{0}C during the reaction. The reaction mixture was irradiated using an I.R lamp under the reflux of solvent. After 1 h, the succinimide began to float. The reaction mixture was cooled to room temperature, filtered and the product isolated after removing the solvent under reduced pressure (0.075 mm of Hg.) at 25-27°C. The product was recrystallised from n.hexane, m.p. 105-106^{0}C, yield, 0.93 g (26.2%).

3.2.2.2 : In DMF as solvent.

Nitrogen was passed through previously dried DMF for 6 h with constant stirring prior to use. In a 100 mL round bottom flask, DMF (50 mL), MeOXZ, 1.O g (0.0117 mol) NBS, 6.24 g (0.035 mol) and benzoyl peroxide, 100 mg, were placed at 0 ^{0}C with constant stirring. The temperature was allowed to rise to 25-27 ^{0}C during the reaction. After 4 h, the reaction mixture was poured into 200 mL ice cold water and the product separated in the form of white crystals. The product was recrystallised from n.hexane, m.p. 105-106^{0}C, yield, 3.3 g (88%).

I.R (in cm^{-1}). 750 (CBr$_3$),900 (CH$_2$-O), 950 (C-O), 1000 (C-N). 1230 (C-H), 1400(C-O), 1490 (C-N), 1650 (C=N). **^{1}H NMR** (in CDCl$_3$,). 4.1,t (N-CH$_2$), 4.6 t (O-CH$_2$). **^{13}C NMR** (in CDCl$_3$,ppm).19.75 (CBr$_3$),55.11 (CH$_2$-N), 71.59 (O-CH$_2$),163.59 (C=N). **Mass** (m/e) 242 (base peak) [C$_4$H$_4$Br$_2$NO].

Elemental analysis	C	H	N	Br
(calc.)	14.93	1.25	4.35	74.50
(found)	15.10	1.51	4.32	74.51

3.2.3 : Typical procedure for polymerization.

Into a two neck round bottom flask equipped with a nitrogen inlet, reflux condenser and a nitrogen outlet fitted to the top of the condenser connected to a mercury bubbler was placed CH$_3$CN (10 mL) and initiator TBO, 0.214g (0.7 mmol). The monomer, MeOXZ, 2 g (23.5 mmol) was transferred into the flask through a cannula. The mixture was heated to 80 ^{0}C with stirring under an atmosphere of nitrogen. The reaction was terminated by pouring the reaction mixture into excess of dry diethyl ether. The precipitated polymer was dried under vacuum at 40 ^{0}C / 1.0 mm of Hg.

3.2.4 : Synthesis of oxazolinium ion complex from TBO and MeOXZ.

In a 50 mL round bottom flask, 10 mL of CH$_3$CN, 0.5 g (0.0015 mol.) of TBO and 0.39 g (0.0045 mol.) of MeOXZ were place under nitrogen. It was stirred for 6 h. 50 mL of dry diethyl ether was added to it . No precipitation was observed. After removing CH$_3$CN and diethyl ether, TBO was recovered quantitatively.

3.2.5 : Analyses.

^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AC200 MHz NMR operating at 50.37 MHz or Bruker 300 MSL NMR spectrometer. The number average molecular weights (Mn) were determined using a Knauer Vapor Phase Osmometer in chloroform at 32 ^{0}C. Microanalyses were performed on Carlo-Erba

CHNS elemental analyser model M08. End group bromide ions of polymers were determined with a bromide ion selective electrode, using an Orion Research Inc., instrument in water at 25 ^{0}C. Anhydrous KBr was used for calibration.

3.2.5.1 : Br^- Estimation.

Aqueous solution of anhydrous KBr in concentrations of 1, 10, 100, 1000 ppm containing a drop of 0.1 N $NaNO_3$ solution were prepared and corresponding voltages were measured using a bromide ion selective electrode connected to a pH meter. Using these data a calibration curve was drawn. Aqueous solutions of polymer (0.5% by weight) containing a drop of 0.1 N $NaNO_3$ solution were prepared and voltages measured using the same electrode. Ionized bromide ion concentration was calculated using the calibration curve.

3.2.5.2 : End group titration of free oxazoline group[15,16].

Aqueous solution of polymer (0.5% by weight) was titrated against 0.005 N p-toluenesulfonic acid using a pH meter. A plot of pH vs titer volume of acid was made. The end point was determined from the curve. Equivalent functionality was determined from the following equation: Equivalent Functionality = volume of acid X strength of acid / wt of polymer X 10. Mn was determined using the expression: Mn = Functionality (theoretical)/equivalent functionality X 100. Observed functionality = Mn (determined from titration)/ Mn (determined by VPO).

3.2.5.3 : NMR Measurement.

TBO was dissolved in CD_3CN and was added to a stirred solution of MeOXZ in CD_3CN containing small amount of benzene as an internal standard. The composition of the solution was as follows : TBO, 0.062 mmol, MeOXZ, 2.78 mmol, CD_3CN, 1.0 mL, benzene, 0.07 mL. A small portion of this mixture was placed in a nmr tube sealed under nitrogen and heated to 80 ^{0}C in the nmr probe. The instantaneous concentrations of monomer and propagating oxazolinium species were determined from nmr spectra taken at several intervals of time using a Bruker 300 MSL NMR spectrometer.

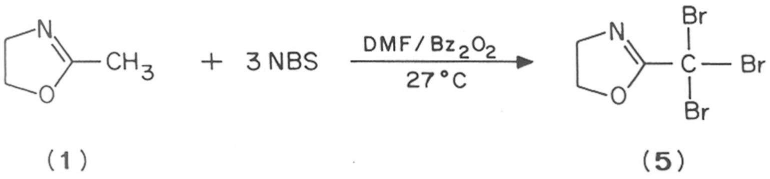
3.2.5.4 : GPC.

GPC measurements were carried out using a Waters GPC unit equipped with a TSK Gel PW columns of porosities 6000, 5000, 4000, 3000 and a 401 RI detector and 0.02 M KH_2PO_4 as mobile phase at ambient temperature. Polyethylene oxide standarts were used to calibrate the columns. All the chromatographic data were processed using Waters 730 data module.

3.3 : Results and Discussion.

3.3.1 : Synthesis of initiator.

The preparation of 2-perbromomethyl-2-oxazoline (**TBO**) has been earlier reported in a solitary patent by a reaction of N-(2-bromoethyl) amide of 2-perbromocarboxylic acid with KOH in benzene[17]. It was used as insect eradicators, soil disinfectant, and combustion retardants for plastics. We therfore, attempted the synthesis of 2-perbromomethyl-2-oxazoline (TBO) starting from 2-methyl-2-oxazoline (MeOXZ) as the starting material. During first attempt, MeOXZ was bromonated by NBS in carbon tetrachloride at 80°C. Since TBO apparently decomposed at this temperature, synthesis of this compound at room temperature was attempted. Therefore, bromination by NBS was done at room temperature (25-27°C) in DMF. 2-methyl-2-oxazoline (MeOXZ) was found to be exhaustively brominated by NBS to give 2-(perbromo methyl)-2-oxazoline **(TBO,5)** (equation 1)[17].



The structure of TBO was confirmed by spectral and elemental analysis. The IR, ^{1}H-NMR, ^{13}C-NMR and mass spectra of the TBO are given in figures 3.2-3.5.

3.3.2 : Polymerization of MeOXZ initiated by TBO.

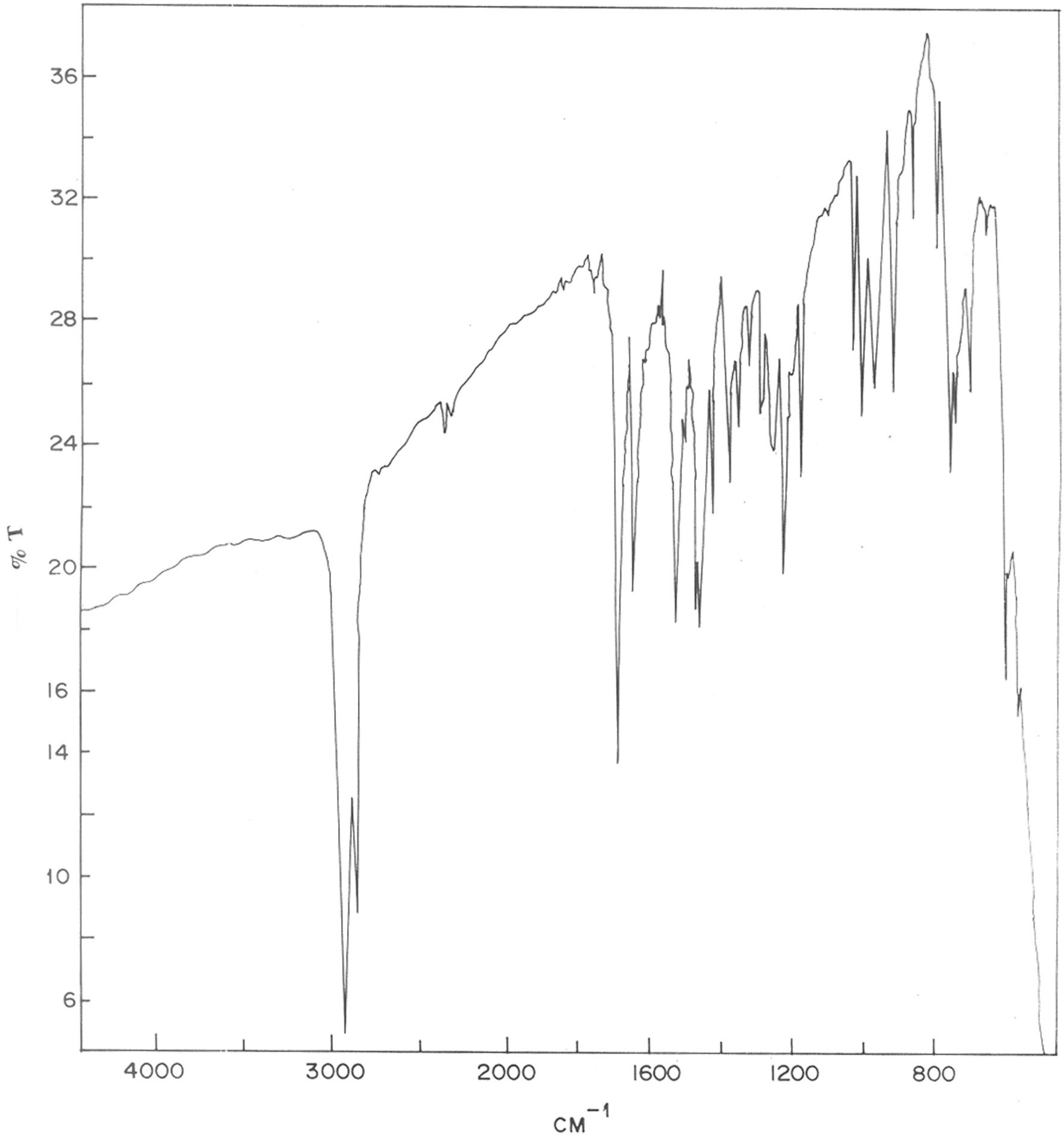


Figure 3.2 FTIR of TBO

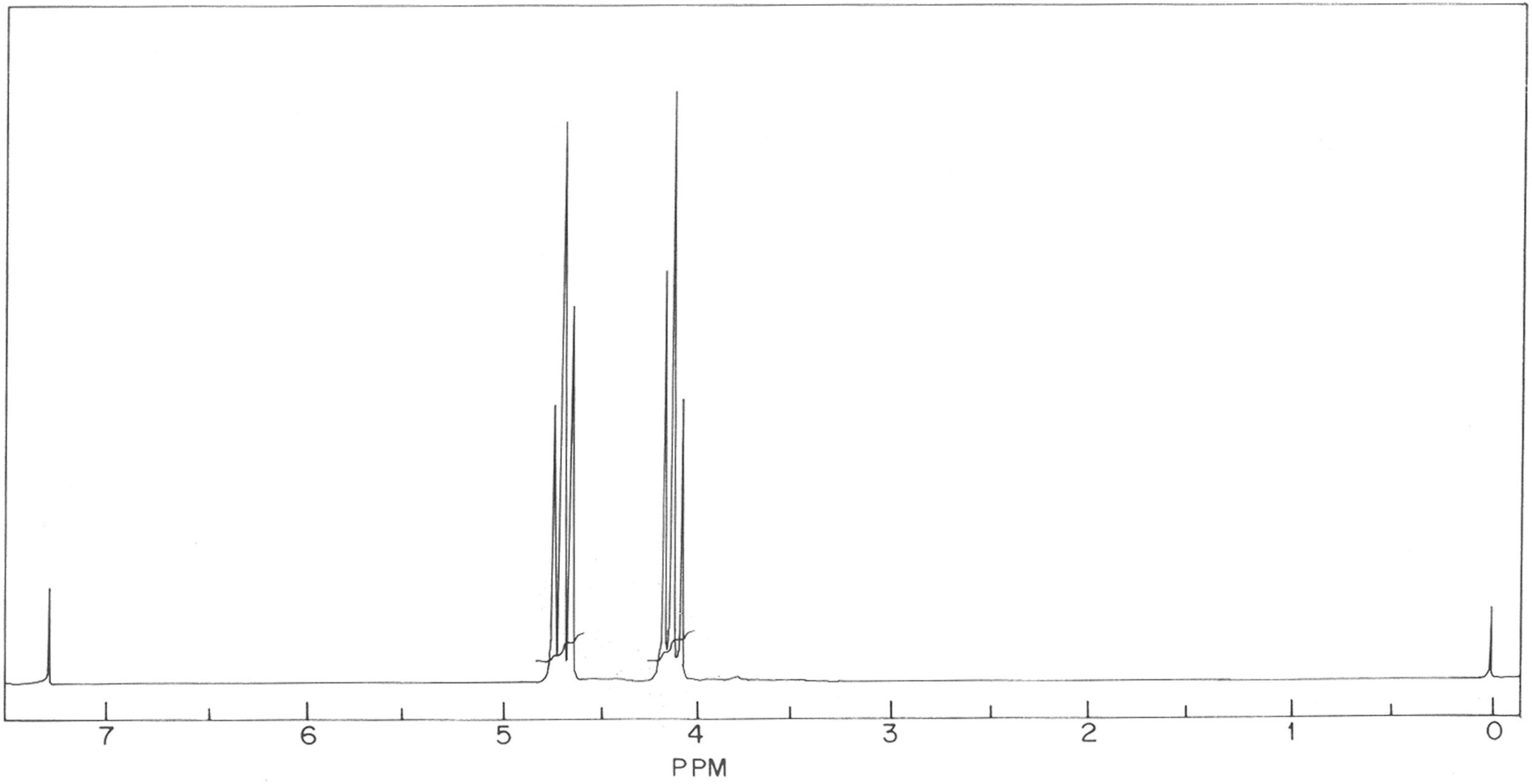


Figure 3.3 ^{1}H-NMR of TBO

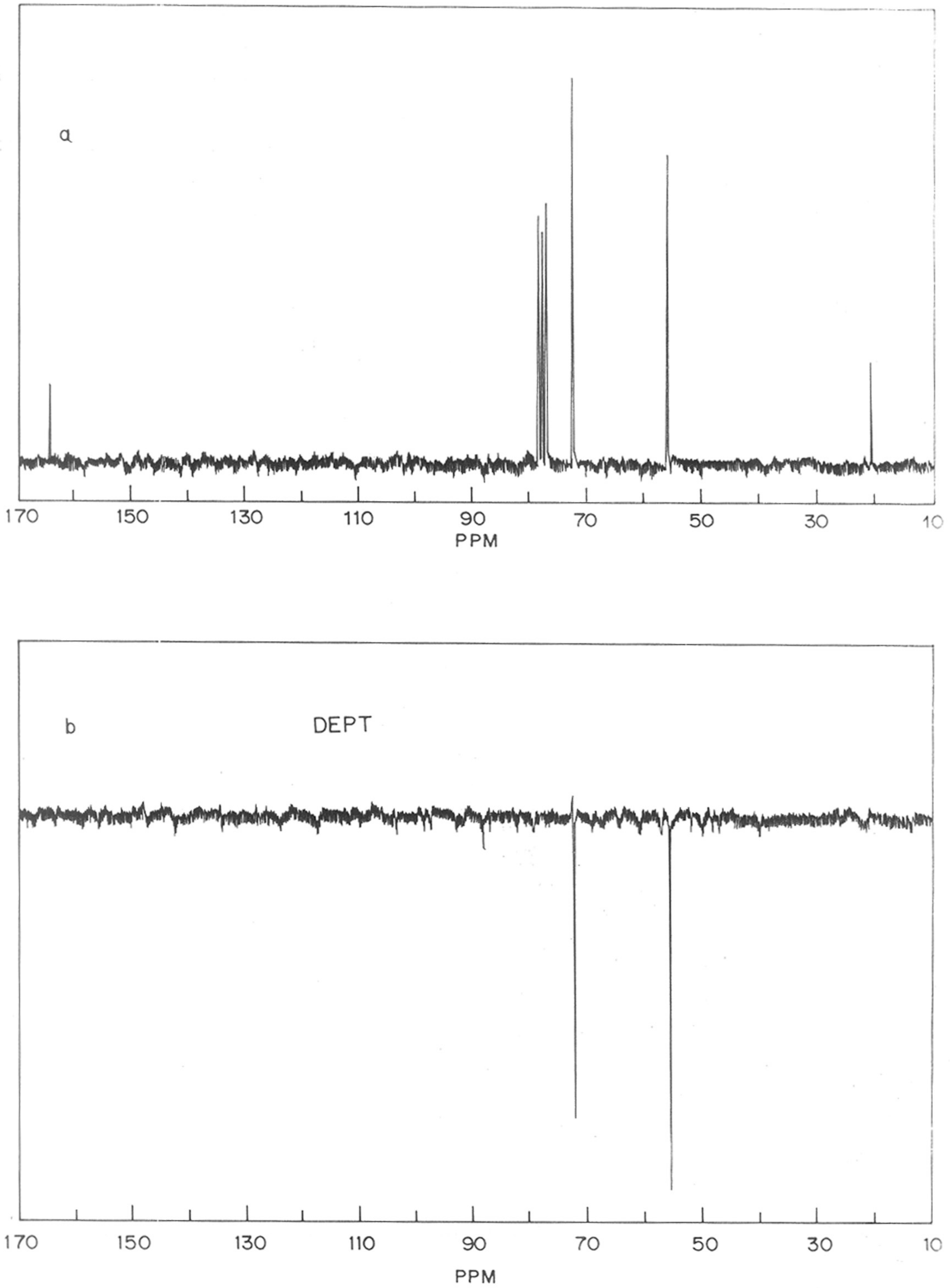


Figure 3.4 ^{13}C-NMR of TBO

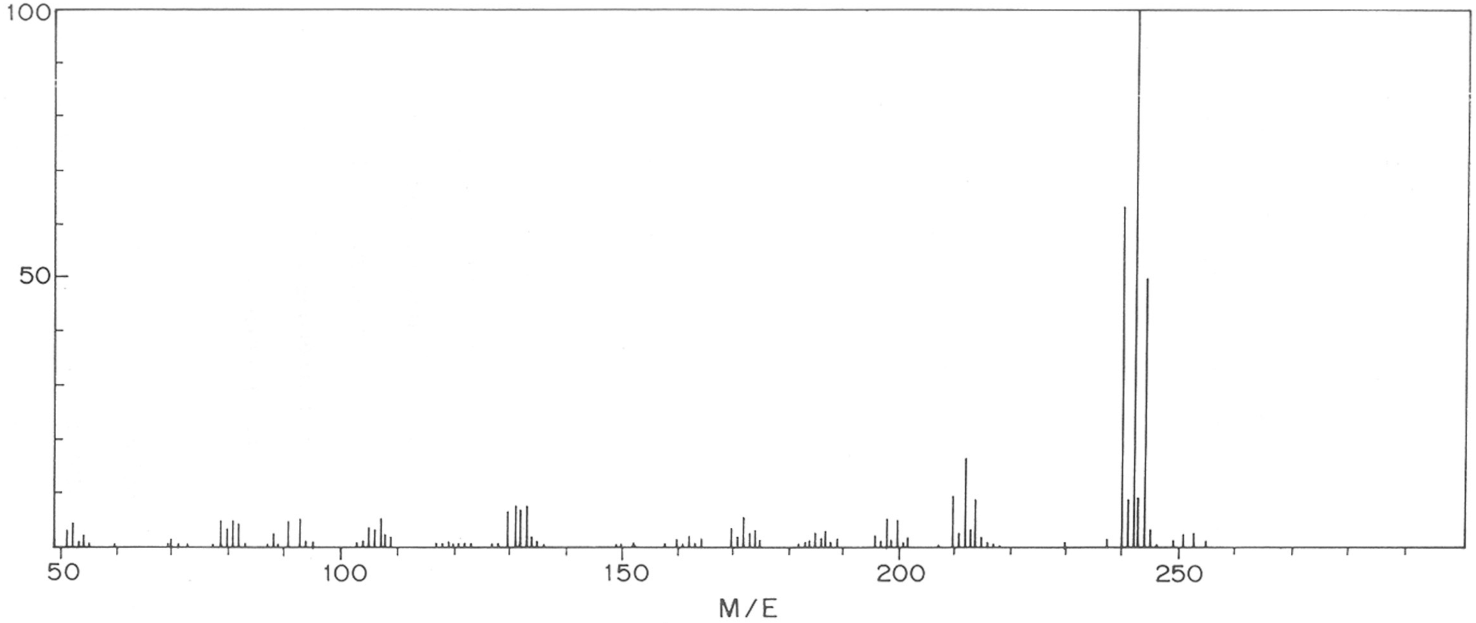
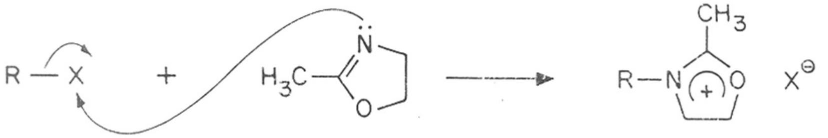


Figure 3.5 Mass spectra of TBO

TBO initiated smoothly the ring opening polymerization of MeOXZ in refluxing acetonitrile. Quantitative conversion to polymers were obtained. Polymers with Mn in the range 1000-12000 were obtained with excellent agreement between calculated and experimentally found molecular weights (table 3.2). Unlike methyl-p-toluenesulfonate, TBO showed an appreciable induction period (figure 3.6). However, addition of 10 mol% of KI to TBO caused the induction period to disappear. It is well documented that initiation process involves nucleophilic addition of monomer to the electrophilic initiator as shown in scheme 3.3[18].



Scheme 3.3 : Initiation of 2-methyl-2-oxazoline by alkyl halide.

Therefore, efficiency of initiation depends not only on the nucleophilicity of monomer but also on the electrophilicity of the initiator. Propagation starts with an oxazolinium cation. The electrophilicity of C-Br bond of initiator is not sufficient enough to start rapid initiation. Therefore, induction period was observed. However, upon addition of KI, due to halogen exchange reaction, C-I bond was formed whose electrophilicity is sufficient enough to start a fast initiation causing induction period to disappear.

To further confirm the living nature of the polymerization initiated by TBO, fresh monomer, was added to the reaction mixture after 8 h and thereafter in three equal instalments. Each time the reaction was allowed to proceed for 2 h. Mn increased

Table 3.2: Polymerization of 2-methyl-2-oxazoline (1) using TBO (5) as initiator[a]

Entry	1 g	5 mole x 10^{-4}	time h	conv. %	Mn[b] (calc.)	Mn[c] (found)
1[d]	2	6.6	8.0	100	3026	2989
2	2	6.6	6.0	75	2269	2120
3	2	6.6	5.0	46	1392	1190
4[e]	4	6.6	10.5	100	6354	6500
5	6	6.6	13.0	100	9380	9700
6	4	3.3	15.5	100	12,104	12,600
7	2[f]	6.6	3.0	100	3026	2979
8	2[f]	6.6	1.0	71	2118	2515

[a] in CH_3CN at 80°C; [b] Mn calculated from grams of monomer/moles of initiator x % yield; [c] by VPO in chloroform at 32°C; [d] polydispersity: 1.3; [e] polydispersity: 1.2; [f] 2+KI [10 moles % of 2].

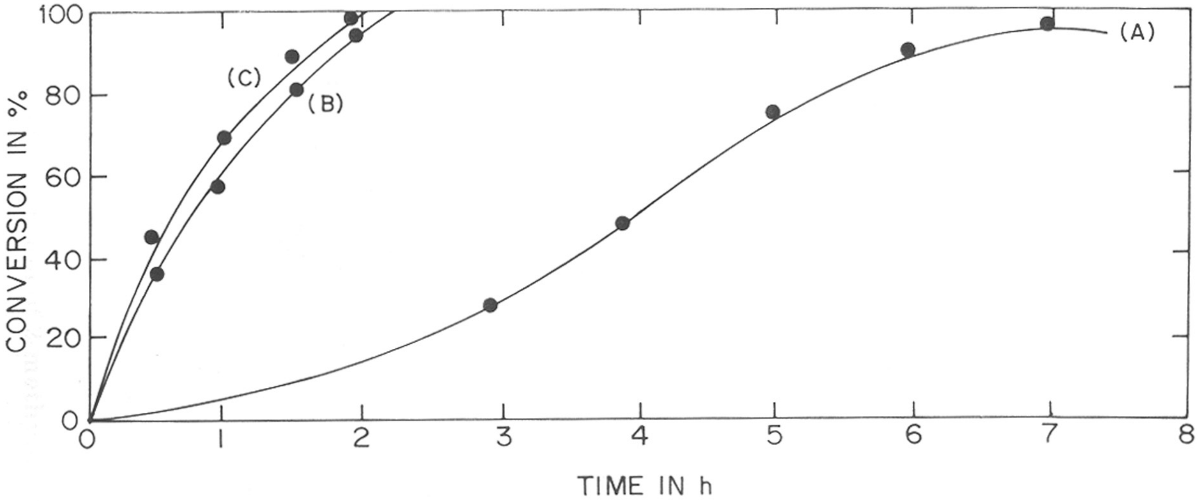
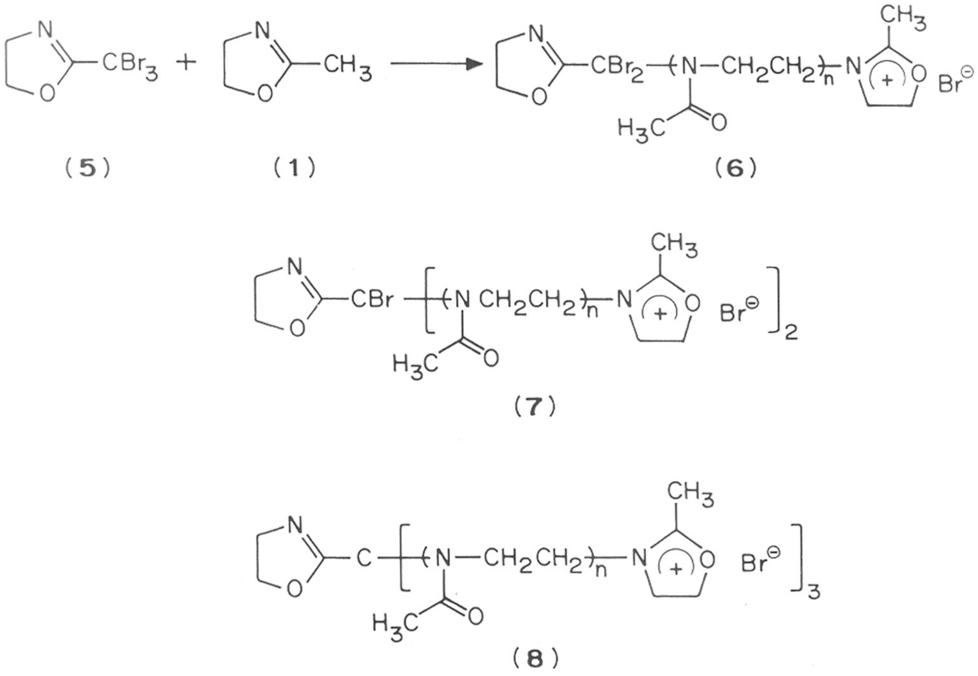


Figure 3.6 Plot of % conversion against time for the polymerization of (1) initiated by (A) initiator 5(TBO), (B) methyl tosylate (MeOTS), (C) 5 + 10 mol % KI

linearly with conversion indicating the living nature of the propagating chain ends. The plot of [M]/[I] against Mn was linear (figure 3.7). In addition the polydispersity of polymers were found to be in the range of 1.2-1.3 (figure 3.8).

Having cofirmed the livingness of this system, the next objective was to investigate the mode of polymerization and establish the structure of the polymer.

Initiation can occur through one, two, or three electrophilic sites on the initiator TBO (5) as shown in scheme 3.4.



Scheme 3.4 : Polymerization of 2-methyl-2-oxazoline by TBO(5).

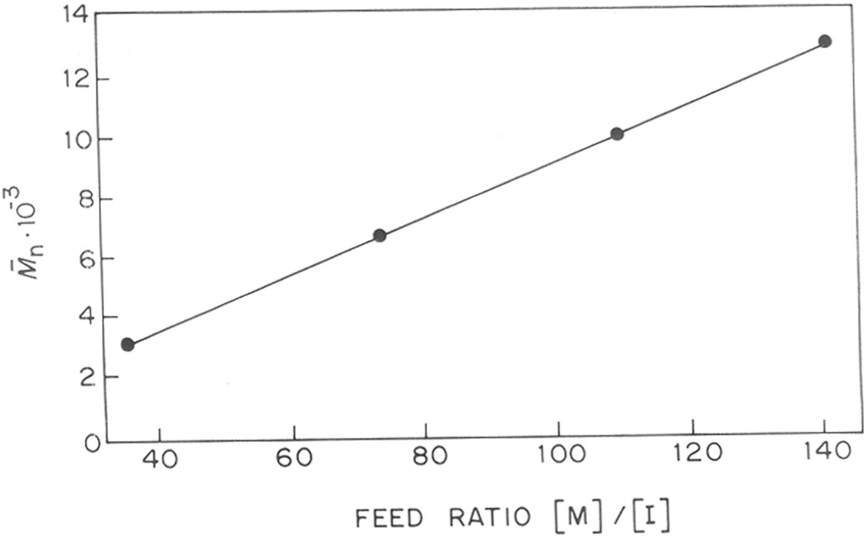


Figure 3.7 Plot of [M] / [I] against Mn for the polymerization of 1 initiated by 5. [5] = 0.0664 mol / lit; Solvent : CH_3CN, Temp. : 80°C

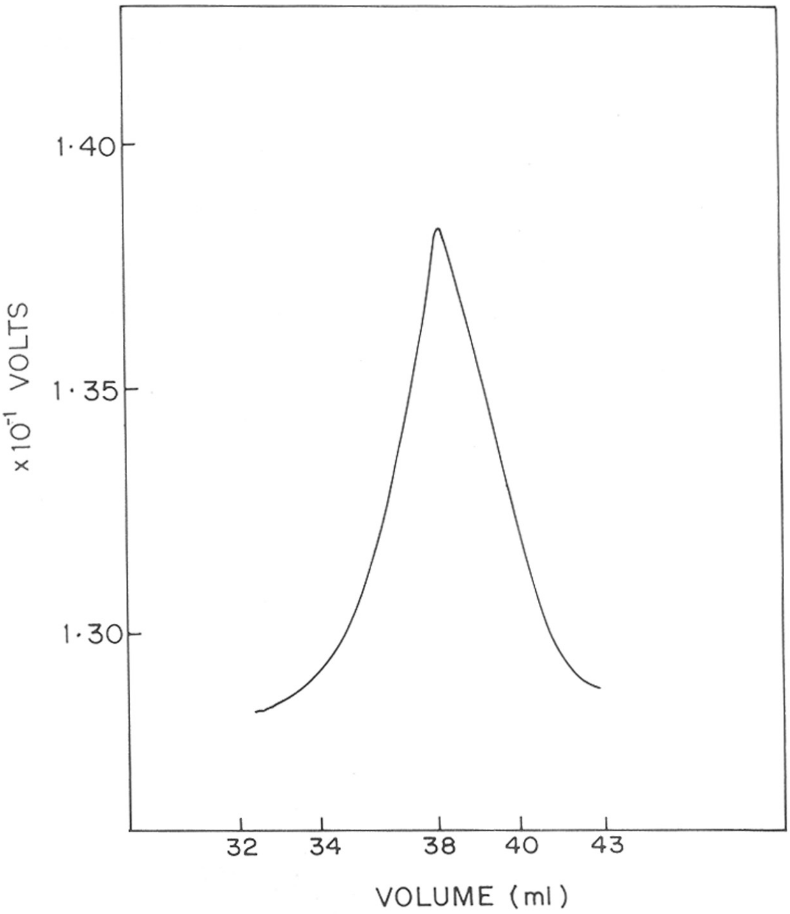
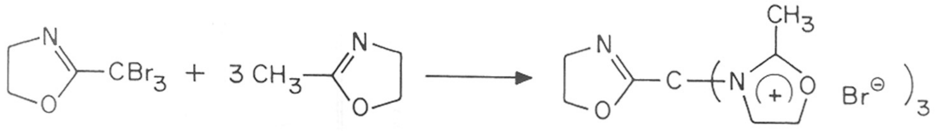


Figure 3.8 GPC Chromatogram of three arm star branched poly (N-acylethylenimine)

Thus, either a linear (**6** or **7**) or branched (3 arm star) polymer (**8**) could be formed. Upon initiation, the covalent C-Br bond present in the initiator will ionize and bromide anion thus formed remains as a counter anion of the propagating oxazolinium cation. The terminal ionized chain- end bromide ions concentration was estimated using a selective ion electrode titration. The results are shown in table 3.3. The concentration of ionized chain end bromide ions determined experimentally was in agreement with the value expected of a three arm star polymer formed by trifunctional initiation (scheme 3.4). Control experiments showed that under identical conditions, TBO bearing only covalent C-Br bonds shows no response to the bromide ion selective electrode. This confirms that all the three covalent C-Br bonds of TBO have participated in the initiation of polymerization, giving rise to three polymer chains bearing the oxazolinium cation-bromide anion pair as the terminal groups.

The next objective was to investigate the mode of initiation. If all the three covalent C-Br bonds of TBO (5) have participated in the initiation of polymerization, then the following oxazolinium ion complex should form first (scheme 3.5).



(5) (1) (9)

Scheme 3.5 : Formation of oxazolinium ion complex from TBO(5) and 2-methyl-2-oxazoline.

Table 3.3 : Chain -end bromide ion analysis.

		Bromide content in wt %.	
Entry no.	Mn	found	expected[a]
1	3000	7.9	8.0
2	6500	4.2	3.7
3	9700	2.9	2.5
4	12600	2.2	1.9

a) Assuming three bromide ions per molecule of polymer.

Several attempts to isolate the complex, **(9)**, failed. For example, synthesis of **(9)** was attempted at room temperature (25-27°C) in CH_3CN. Reaction did not take place. Synthesis of **(9)** at higher temperature (60°C) resulted in formation of polymer consisting of N-acyl ethylenimine group as indicated by ^{1}H-NMR spectroscopy. The inability to form a trioxazolinium cation is presumably due to excessive steric crowding around the tertiary carbon.

The increase in the living chain end concentration during polymerization of MeOXZ was monitored by ^{1}H NMR spectroscopy (figure 3.9). The resonance characteristic of the methyl protons of oxazolinium living end, methyl protons of the monomer and methyl protons of the N-acyl polymer backbone appeared at 2.15-2.25,1.7 and 1.8 - 2.0 ppm, respectively. To confirm that polymerization proceeds from three sites of the initiator , the average number of polymer chain per molecule of initiator was determined under various monomer / initiator feed ratios from ^{1}H NMR spectroscopy (figure 3.10). From the intensity of methyl protons of oxazolinium cation (2.15 ppm), the total moles of polymer chain was determined since, each polymer chain carries one oxazolinium cation at the propagating chain end. The ratio of total number of moles of polymer chains to the moles of initiator gives the average number of polymer chain per molecule of initiator . When the feed ratio was greater than 28, the average number of polymer chains per molecule of initiator reached an asymptotic value of 2.6-2.7. This indicates that the polymer has a star shaped molecular architecture. It is also evident from ^{1}H NMR spectroscopy that initiation takes place stepwise. The initiation of the first polymer arm is faster than the second polymer arm. The third initiation step is apparently slow. Thus the relative length of the three arms of the resulting star-shaped polymer are unequal.

The ratio of oxazolinium ion concentration to initiator concentration was determined at various conversion from ^{1}H NMR spectroscopy (figure 3.11). At less than 7% conversion, ratio reaches more than one. At 34% conversion , ratio exceeds two. These observations are very significant and following conclusion can be drawn.

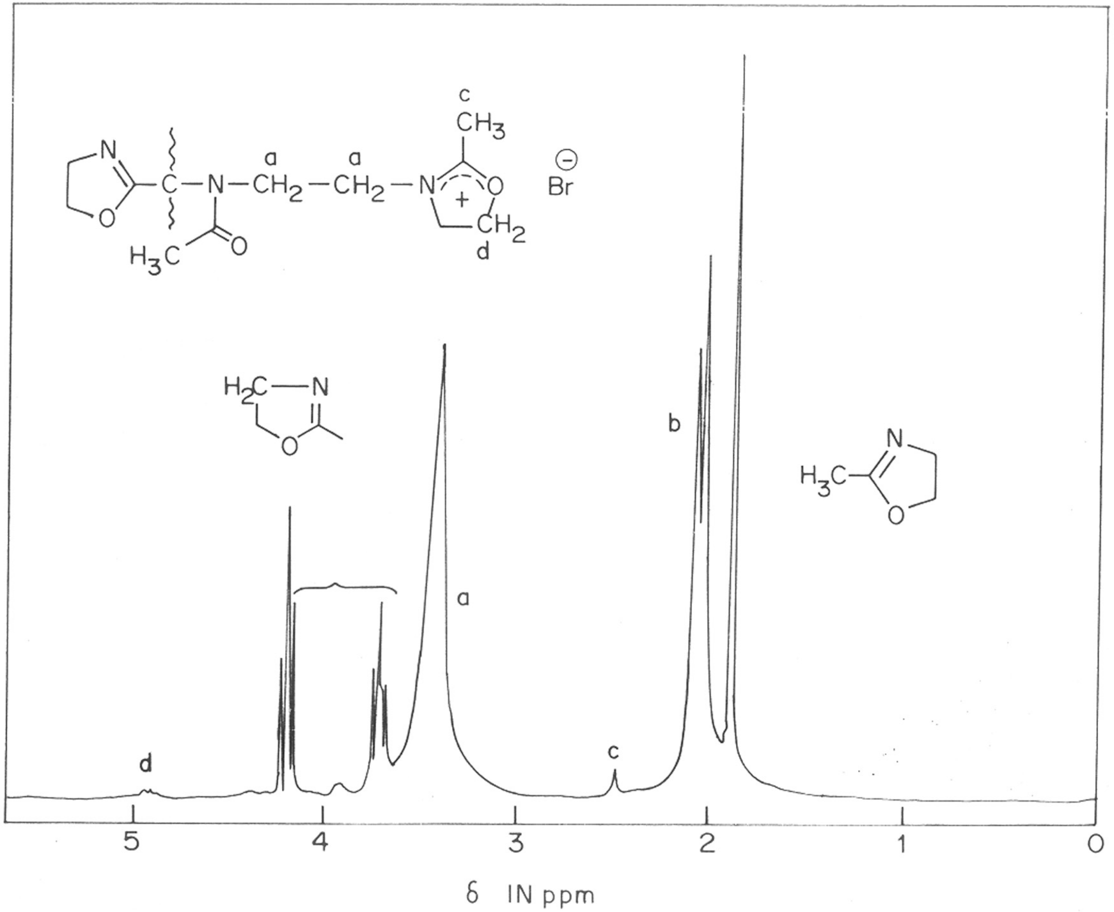


Figure 3.9 ^{1}H-NMR spectra of the (1) polymerization system initiated by (5) in CD_3CN (after 5 h at 80°C)

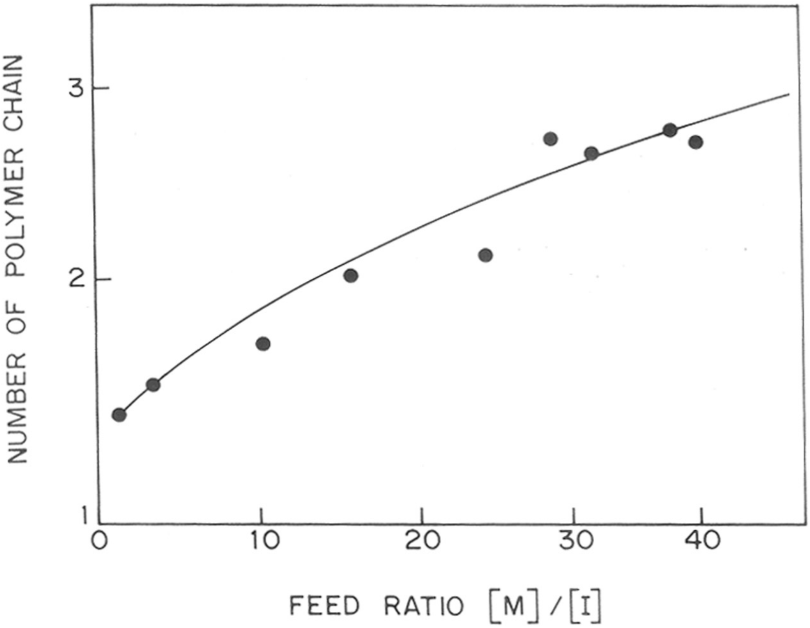


Figure 3.10 Relationship between the feed ratio and the average number of polymer chains per initiator 5. The polymerization of 1 was carried out in CD_3CN at 80°C in a sealed NMR tube

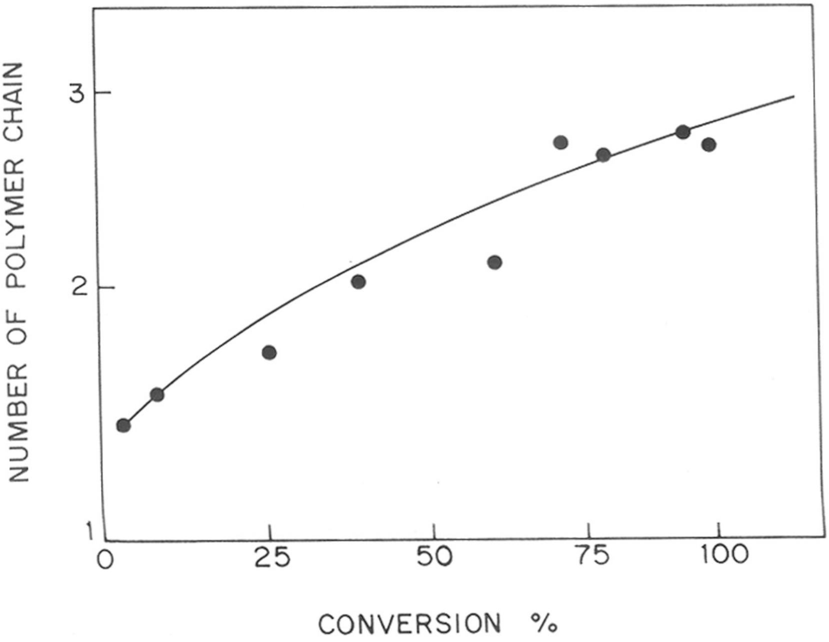


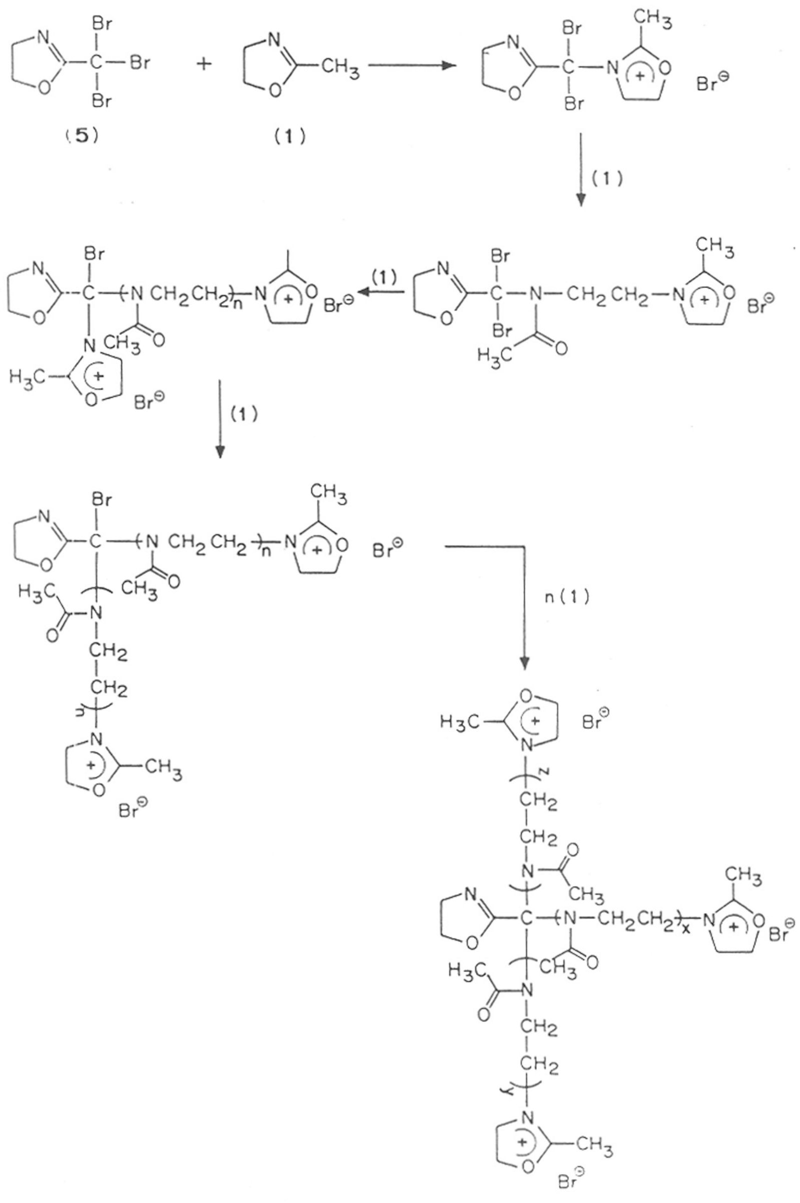
Figure 3.11 Relationship between the % conversion and the average number of polymer chains per initiator 5. The polymerization of 1 was carried out in CD_3CN at 80°C in a sealed NMR tube

First, one of the three C-Br bonds of TBO participates in initiation and forms an oxazolinium ion. Second C-Br bond of TBO can not participate in initiation unless the first oxazolinium ion opens up i.e. propagation starts and thus release steric crowding. At this stage propagation of first C-Br bond and initiation of second C-Br bond are simultaneously going on. Third initiation occurs only when second oxazolinium ion opens up and starts propagation. Therefore, all three C-Br bonds of TBO do not participate in initiation simultaneously because of steric crowding. Based on these observation, the mode of initiation, propagation and final structure of polymer is shown in scheme 3.6.

The presence of oxazoline group from initiator in the polymer chain was established by estimating its concentration of the end group using a pH titration method [15,16] (table 3.4). Based on Mn estimated by end group titrations, the functionality was found to be close to 1.0. This indicates that every polymer chain has, on an average, one oxazoline group. Thus, under the present experimental conditions, the oxazoline group of the initiator does not undergo any ring opening reactions. This can be understood based on the reported nucleophilicity of various 2-substituted oxazoline[19]. The nucleophilicity of TBO is lower than MeOXZ. Hence, ring opening polymerization occurs preferentially with the more nucleophilic MeOXZ.

3.4 : Conclusion.

The results of this study establish that TBO is an effective trifunctional initiator for the ring opening polymerization of 2-methyl-2-oxazoline, leading to a branched three arm star polymer bearing unequal arm length. It is evident from ^{1}H NMR spectroscopy that initiation takes place stepwise. The initiation of first polymer arm is faster than second polymer arm. The third initiation is apparently slow. Thus, the relative length of the three arms of the resulting star-shaped polymer are unequal. Evidence is also presented to show that under conditions explored, the oxazoline group of the initiator remains intact and does not undergo any ring opening reactions.



Scheme 3.6 : Polymerization of MeOXZ (1) by TBO (5)

Table 3.4 : Potentiometric titration of oxazoline group present in polymer.

Sl.No	Mn(Calculated)	Mn Found (VPO)	Mn Found(Titration)	Functionality[a]
1	2269	2120	2467	1.16
2	3000	2989	3030	1.01
3	6000	6500	5882	0.90

[a] Functionality = Mn(titration)/Mn(VPO)

The interesting feature of this polymer is that it has one reactive oxazoline functionality at the core and three oxazolinium ions at the chain end. The former could be used for chain extension or coupling whereas the latter can be functionalized by nucleophiles such as meth(acrylate)[20,7], methacrylamide[21], glycol[22], hydroxyl and amine[23,24]. This opens up new possibilities for synthesis of graft copolymers and star shaped block copolymers.

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CHAPTER 4

CHAPTER 4

2-Perbromomethyl-2-oxazoline : A novel trifunctional linking agent for living anionic chain end for the synthesis of 3-arm star polymer.

4.1 : Indroduction.

Multiarmed polymers (star polymers) have been synthesized by using the following methods.

i) Living polymerization using a multifunctional initiator.

ii) The coupling reaction of linear living polymers with a multifunctional coupling agent (terminator).

iii) The linking reaction of linear living polymers with a difunctional vinyl compound through microgel formation.

Although a number of reports are available in the literature on the polyfunctional cationic initiators [1-11] which produce star polymers by a living polymerization processes, synthesis of anionic polyfunctional initiators [12-14] have met with very limited success because of their difficult solubility even in very polar solvents and their very low stability even at -25^{0}C [14].

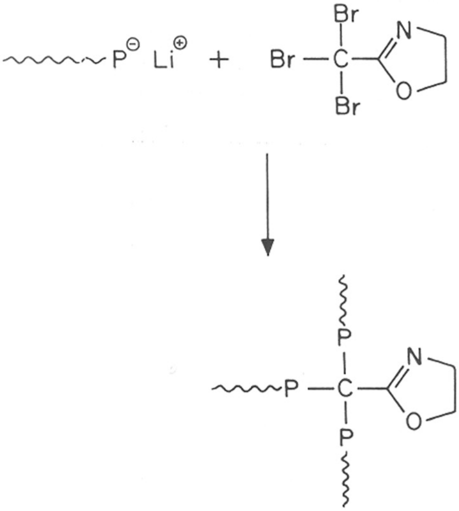
This solubility problem associated with polyfunctional anionic initiators was overcome by Burchard and coworkers[15,16,17] by preparing a polyfunctional living microgel which was used as initiator. DVB was first polymerized anionically by butyllithium in dilute benzene solution. Soluble microgels of high molecular weight are obtained and these microgels bear a large number of anionic end groups which can initiate polymerization of any monomers susceptible to anionic polymerization. Polydisperse (both in arm molecular weight and overall molecular weight) polystyrene stars containing upto about 1.7 x 10^4 arms were obtained. This system indicated a slow and incomplete reaction between both styrene and diene monomers and the poly (divinyl benzyl lithium) anions in the poly (divinyl benzyl) nodule. This slow initiation reaction appears to be mainly due to steric factor.

An alternative method of star branched polymers formation involves the sequential polymerization of the monomers used for arm, followed by the addition of divinyl benzene through microgel formation.[18-20].

The preparation of star branched polymers by termination method i.e by the use of polyfunctional terminator in conjunction with anionic polymerization was first shown to be a feasible concept by Morton, Helminiak, Gadkary and Bueche[21] in 1962. Using methyltrichlorosilane and tetrachlorosilane in conjunction with polystyryl lithium in benzene, they were able to prepare both three- and four arm polystyrene stars. As a consequence of the termination free nature[22] of this anionic polymerization system, these star branched polystyrenes contained relatively narrow molecular weight distributions.

Since then, several reports have appeared on the synthesis of star polymers by terminating anionic chain end by a polyfunctional compound. The method provides good control of molecular weight of arms as well as number of arms (functionality) with relatively narrow molecular weight distribution. Because of this reason, this is the most preferred method for the synthesis of star polymer. With the availability of higher functionality chlorosilane coupling compound (terminator), synthesis of star polymer with number of arms as high as 64-, 128[23] and 200, 270[24] has become possible.

2-perbromomethyl-2-oxazoline has been shown to be a useful trifunctional initiator for the living cationic ring opening polymerization of 2-methyl-2-oxazoline. It produces a three arm star polymer[25]. 2-perbromomethyl-2-oxazoline has been shown to initiate vinyl ether polymerization[26]. All these findings confirm that C-Br bond of 2-perbromomethyl-2-oxazoline is strongly electrophilic in nature. Therefore, 2-perbromomethyl-2-oxazoline could be used as a linking agent for living anionic polymer chain ends which could lead to the formation of three arm star polymer of predetermined molecular weight of arm and with narrow molecular weight distributions (scheme 4.1).



Scheme 4.1 : Synthesis of three arm star polymer using TBO as linking agent.

The most interesting feature of this coupling agent is that it will produce a star polymer with an oxazoline functionality at the core. This allows further synthetic manipulations, for examples, a) synthesis of fourth arm of hydrophilic polyoxazoline b) synthesis of graft copolymers. In this chapter, exploration of 2-perbromomethyl-2-oxazoline as a linking agent for living anionic chain ends to form star shaped polymers is described.

4.2 : Experimental.

All manipulations were done under a positive pressure of high purity Argon or nitrogen using standard bench top inert atmosphere techniques or under high vacuum using break-seal techniques[27,28].

4.2.1 : Materials.

n.BuLi (Chemetall GMBH, Germany a 15% solution in n.Hexane) was further diluted to a 0.46 M solution in dry toluene. Toluene and tetrahydrofuran were procured from S. D. Fine Chemical, Bombay. Butadiene and styrene were procured from Aldrich, USA. Isoprene was procured from Fluka, Switzerland.

4.2.2 : Purification of solvents and monomers.

Solvents :

Toluene : Trace amount of thiophene was freed by washing with conc. H_2SO_4. It was then washed with distilled water , 10% $NaHCO_3$ solution and finally with distilled water twice. It was initially dried over fused $CaCl_2$ over night. Final drying was done by refluxing over CaH_2 under nitrogen. Dry toluene was added to styryl lithium oligomer solution in toluene until the orange red colour persisted and subsequently distilled under reduced pressure (0.075 mm of Hg) just prior to use.

Tetrahydrofuran (THF) : Initial drying was done by refluxing over Na-benzophenone under nitrogen. Dry THF was then added to styryl lithium oligomer solution in toluene until the orange red colour persisted and subsequently distilled under reduced pressure (0.075 mm of Hg) just prior to use.

Monomers :

Styrene : Styrene was washed with 10% NaOH aqueous solution and washed with distilled water repeatedly until the wash water was neutral to litmus paper. Initial drying was done by keeping the monomer over fused anhyydrous $CaCl_2$ over night. It was filtered and stirred over CaH_2 over night at 0°C temperature under nitrogen, distilled under vacuum and stored at -10^0C temperature. It was then finally distilled over fluorenyl lithium solution in toluene under reduced pressure (0.075 mm of Hg) just prior to use.

Butadiene : Butadiene was collected in a round bottom flask at liquid nitrogen temperature after passing through CaH_2 and NaOH pellet towers consecutively.

Frozen butadiene was liquified at -40^{0}C temperature. n.BuLi solution in toluene was then added to it until light yellow colour persisted and distilled under reduced pressure (0.075 mm of Hg) just prior to use.

Isoprene : Isoprene was stirred over CaH_2 over night at 0^{0}C temperature. It was then distilled under reduced pressure and stored at -10^{0}C . Finally, n.BuLi solution in toluene was added to isoprene until light yellow colour persisted and distilled under reduced pressure (0.075 mm of Hg) just prior to use.

4.2.3 : Analyses.

Molecular weight measurements were performed on a 150C Waters GPC using μ-ultrastyragel columns (100, 500, 10^4, 10^5 A°) in tetrahydrofuran solvent at 30^{0}C (0.2% w/v polymer, flow rate 1mL/min). Both MALLS and as well as RI detector were used. For MALLS (Wyatt Tech. Corp., Model : DAWN F), He-Ne lasser (633 nm) source was used with SF 10 flow cell. Measurements were done at various fixed angles varying from 42-135°. For polyisoprene, dn/dc = 0.118 was used for molecular weight determination. Monodisperse polystyrene standards were used for molecular weight calibrations when RI detector was used.

4.2.4 : Reaction Assembly.

4.2.4.1 : Reaction under positive pressure of nitrogen.

Nitrogen Purification : Nitrogen received from commercial suppliers was not sufficiently pure for anionic polymerization. It contains moisture and oxygen as the main impurity which has to be removed from nitrogen. Purifications were performed by passing nitrogen through several purification columns. A sketch of the assembly is provided in figure 4.1. Column A contain copper powder. At elevated temperature (> 200^{0}C) copper reacts with O_2 and forms black CuO and thus removes O_2 from nitrogen.

$$2\,Cu + O_2 \text{ -------> } 2\,CuO$$

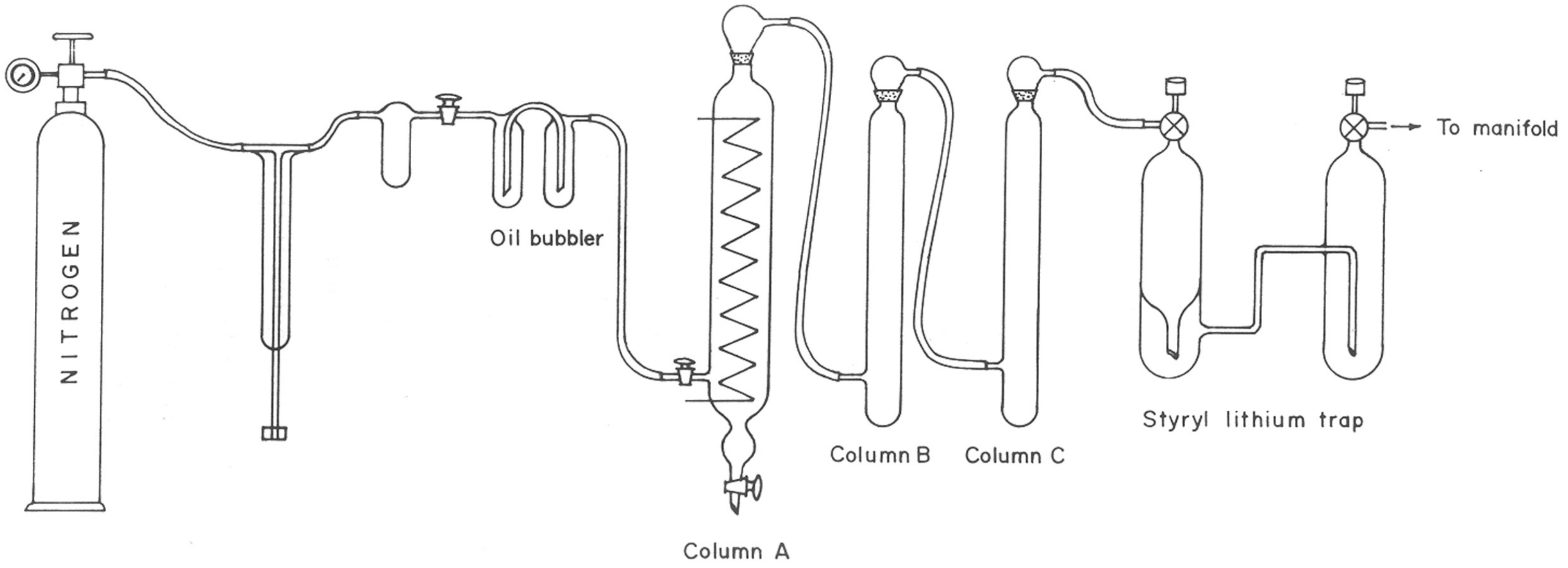


Figure 4.1 Nitrogen purification assembly

After certain period, regeneration of CuO to Cu was done by reacting CuO with H_2 gas at 200^0C.

$$CuO + H_2 \text{------>} H_2O + Cu.$$

Columns B and C contain molecular sieves 4 A^0 which removes moisture from nitrogen. After every fortnight, molecular sieves were activated at 200^0C under reduced pressure.

After passing through columns (A, B and C) nitrogen was passed through a trap which contained styryl lithium oligomer solution in toluene. This solution has a characteristic orange red colour. As long as colour persists , nitrogen coming out through this solution is free of oxygen or protic impurities which affect living polymer systems. This purified nitrogen was then used for polymerization with the help of a manifold shown in figure 4.2.

4.2.4.1.1: Distillation under reduced pressure.

All distillations (monomers and solvents) under reduced pressure were carried out in a flash distillation unit shown in figure.4.3 by freeze thaw technique.

In a flame dried (under reduced pressure) flash distillation unit, solvents or monomers were introduced through septum inlet adapter by the use of double needle head cannula or syringe under a positive pressure of nitrogen. Purifying agents were then introduced through septum inlet adaptor the same way as solvents were introduced. The contents of the flask was stirred for 5 to 10 minutes and frozen in liquid nitrogen temperature. When half frozen, vacuum was applied through the septum inlet adaptor for about 30 minutes. This process removed all dissolved gases. The distillation unit was closed by turning the three way stopcock of the inlet septum adapter to keep the distillation unit under static vacuum. Proper care was taken to ensure that vacuum did not leak. The frozen materials were melted and distilled

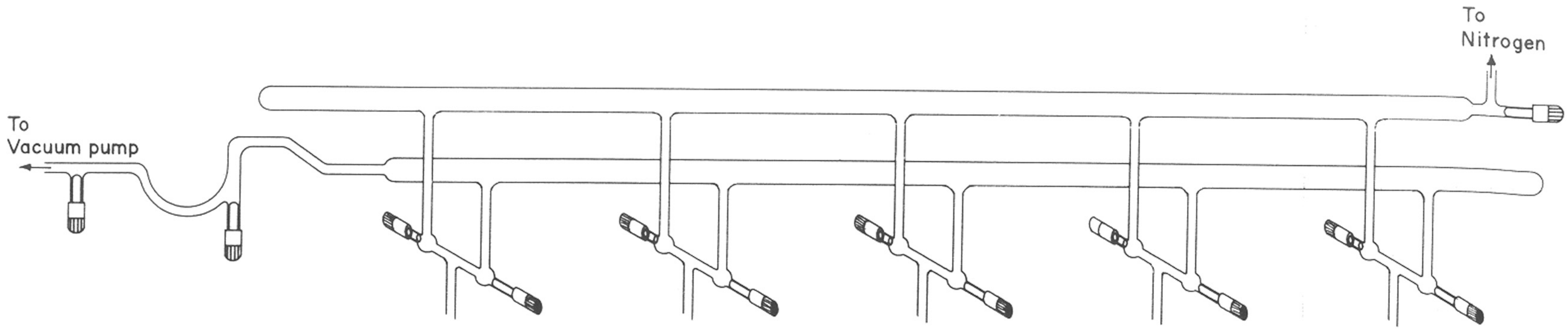


Figure 4.2 Manifold

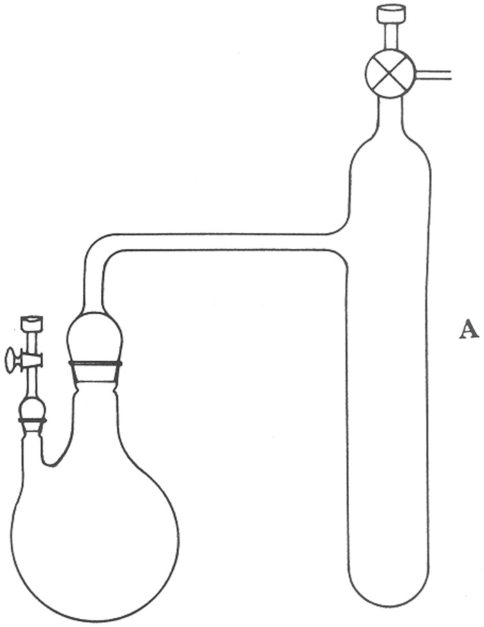


Figure 4.3 Flash distillation unit

at room temperature and collected in the side arm (A) of the flash distillation unit under liquid nitrogen temperature. After melting of distilled material, vacuum was released by admitting purified nitrogen.

4.2.4.1.2 : Reaction of TBO with n.BuLi at room temperature (25-27°C).

To a flame dried 50 mL round bottom flask, 20 mL of dry toluene, 0.5 g (0.0015 mol.) of TBO was placed. To this solution, 4 mL of 1.2M n.BuLi (0.0048 mol.) was added slowly with continuous stirring. After 1 h stirring at room temperature (25-27°C) , chilled methanol (-40°C) was added. The reaction mixture was washed with water and dried over sodium sulfate. Product was isolated after removing solvent and analyzed by ^{1}H-NMR.

4.2.4.1.3 Polymerization and coupling reaction : Glass reactor used for polymerization and coupling reactions is a one necked round bottom flask fitted with a inlet septum adaptor. In a flame dried (under reduced pressure) glass reactor, containing a magnetic bar for vigorous stirring, required amount of solvent was transferred from flash distillation unit with the help of double head needle cannula under a positive pressure of nitrogen. Monomers were transferred into the polymerization flask directly from flash distillation unit the same way as solvents were introduced. To this, initiator was introduced by syringe with vigorous stirring under positive pressure of nitrogen. Polymerization was continued till its completion. A known amount of pick out was taken from the polymerization mixture through cannula under positive pressure of nitrogen and pickout was terminated by methanol. It was analysed by SEC for molecular weight and molecular weight distribution. Based on SEC results required amount of coupling agent, 2-perbromomethyl-2-oxazoline (one third of total remaining living polymeric anionic chain ends) was added in solution of dried toluene. Coupling reaction was continued for 48 h at room temperature with constant stirring. The reaction was then terminated by methanol and the product was isolated by precipitating in methanol .

4.2.4.2 : Reaction under vacuum (10^3 torr) using break-seal techniques.

Polymerization under high vacuum requires distilliation of solvent and monomer directly into the polymerization flask under vacuum without using cannula or syringe after purifications. For this the apparatus as shown in figure 4.4 was used.

It consists of a polymerization flask A with an inlet septum adapter L, monomer purification flask C with a inlet septum adapter F, solvent purification flask B with a inlet septum adapter G. Monomer purification flask C and solvent purification flask B are separated from polymerization flask A by break-seal I and J respectively. Polymerization flask A is attached with a pickout chamber H with a constriction . On the top of the polymerization flask A, linking agent chamber D is attached which is separated from the polymerization flask A by a break-seal K. An inlet septum adapter E is attached with chamber D with a constriction .

Polymerization procedure and linking reaction :

Initiator was introduced into the polymerization flask A through a inlet septum adapter D with the help of a syringe. Immediately after addition of initiator, vacuum was applied through the inlet septum adapter D after freezing n.BuLi. Once the required vacuum was attained inlet septum adapter L was sealed off at the constriction from polymerization flask A. Monomer was then introduced into the monomer purification flask C with the help of a syringe through inlet septum adapter F. It was added with n.BuLi in toluene until a light yellow colour persisted. It was frozen and vacuum was applied into it through inlet adapter F. After attaining the required vacuum, inlet septum adapter F was sealed off at the constriction from monomer purification flask C. Distillation of monomer was started after breaking the break-seal I by a magnetic bar. After distillation of monomer was over, monomer purification flask C was sealed off at the constriction from polymerization flask A. Similarly solvent was purified by styryl lithium oligomer in toluene in solvent purification flask B. Distillation of solvent was started after breaking the break-seal J by a magnetic bar. Subsequently, solvent purification flask B was sealed off at

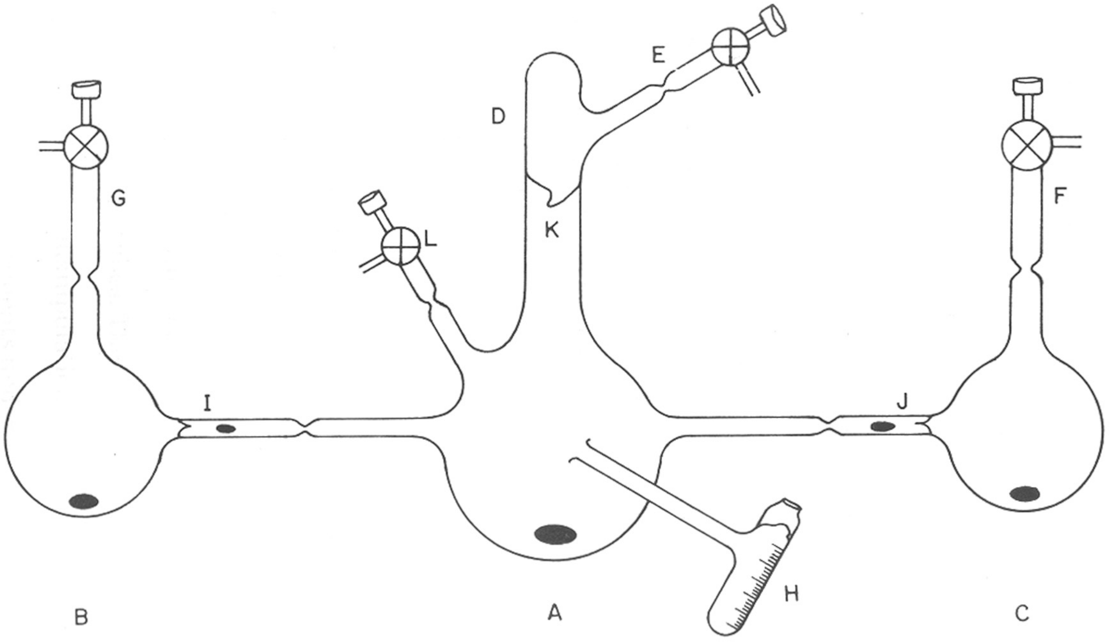


Figure 4.4 Apparatus used for the reaction under vacuum (10^{-3} torr) using breakseal techniques

the constriction from polymerization flask A. Polymerization mixture (solvent, monomer, initiator) was defreezed and polymerization was continued for 24 h at room temperature with continuous stirring. After the polymerization was over, a known amount of pick-out was taken into the side arm H and subsequently it was sealed off at the constriction from the polymerization flask A. Living polymer (homopolymer) in pick-out chamber H was terminated by methanol and analysed by SEC for molecular weight and molecular weight distribution. Based on SEC results, a known amount of linking agent (a one third of living polymer chain end) i,e., TBO in toluene solution was taken into the terminating chamber D through inlet septum adapter E with the help of a syringe. After removing toluene, inlet septum adapter E was sealed off at the constriction from the terminating chamber D. For linking reaction, polymerization flask A was turned up side down and shaken with the magnetic bar to smash the break-seal K. Immediately after smashing the break-seal, the linking agent started reacting with living polymeric chain end and a coco-cola type colour started developing from light to dark. Linking reaction was continued for 48 h at room temperature and was terminated by adding methanol.

4.2.4.3 : Reaction under high vacuum (10^6 torr) using break-seal techniques.

When experiments were carried out under 10^{-3} torr vacuum, rubber tubes were used in the manifold. Moreover, all glassware were connected to the manifold by rubber tubes. But when experiments were carried out under 10^{-6} torr vacuum, rubber tubes cannot be used because it can not withstand high vacuum and air diffusion will take place through rubber tubes. Therefore, manifold and all glassware had to designed such a way that, all manipulation could be done without using rubber tubes. A manifold used for experiments under 10^{-6} torr vacuum is shown in figure 4.5. All glasswares were attached with the manifold through interchangeable Pyrex

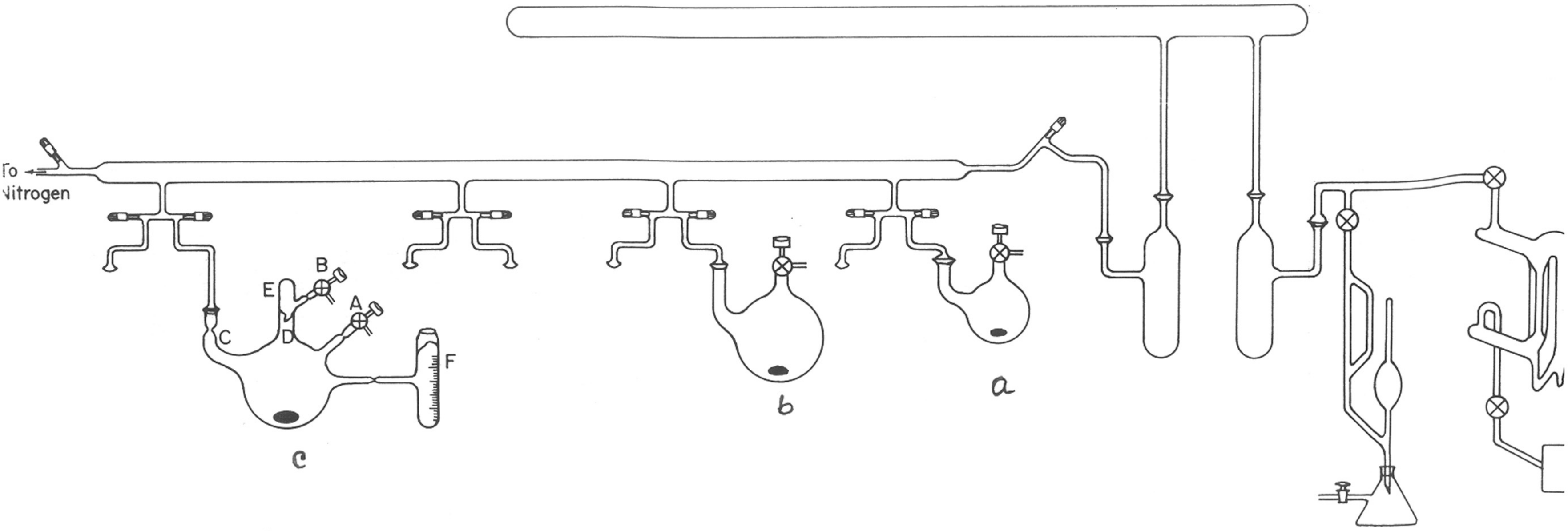


Figure 4.5 High vacuum manifold

glass joints. Monomer purification flask, solvent purification flask, and polymerization flask which were used for the experiments are shown in figure 4.5 a, 4.5 b, 4.5 c respectively.

4.2.4.3.1 : Polymerization.

Monomer purification flask 4.5 a, solvent purification flask 4.5 b, and a specially designed break-seal apparatus (polymerization flask 4.5 c) were connected to the all glassware manifold through Pyrex joints. The apparatus was flame dried under 10^{-6} torr vacuum. Initiator,(n.BuLi) in toluene solution was introduced into the break-seal apparatus under nitrogen pressure through inlet septum adapter A. Vacuum was applied through manifold and subsequently the inlet septum adapter A was sealed off from break-seal apparatus after freezing n.BuLi. Monomer was added into the monomer purification flask (4.5 a) through the inlet septum adapter under nitrogen pressure. To this was added n.BuLi in toluene solution until light yellow colour persisted with constant stirring. Vacuum was applied to the flask through the manifold after freezing monomer. The monomer was thawed and distilled directly into the break-seal apparatus. Similarly toluene was distilled from solvent purification flask (4.5 b) into the break-seal apparatus after drying over styryl lithium oligomer. The break-seal apparatus was disconnected from the manifold after attaining 10^{-6} torr vacuum inside the apparatus by sealing off the Pyrex joint at the constriction. The contents of the break-seal apparatus were brought to 27^{0}C and allowed to polymerize for 24 h. A known amount of pick-out was collected in a side arm F which was subsequently sealed off at the constriction. The pick-out was analysed by SEC and a one third mole of TBO was added as a toluene solution to the break-seal ampoule E through the inlet septum adapter B. Solvent was pumped off and inlet septum adapter B was sealed off at the constriction. Subsequently, the break-seal D separating the living chain ends and the linking agents was smashed with the agitating magnetic bar inside the apparatus and the linking reaction was allowed to proceed for 48 h. Finally, the reaction product was precipitated in methanol and dried in vacuo, at 35^0C for 24 h.

4.2.5 : Results and Discussion.

4.2.5.1 : Polymerization and linking reaction under positive pressure of nitrogen.

Model reaction of TBO with n.BuLi at room temperature (25-27°C) in toluene under nitrogen was attempted to check if all the three C-Br of TBO can be alkylated by a carbanion. It was observed that this reaction was failed to produce the desired compound, namely, 2-(1,1,1 tris butyl methyl)-2-oxazoline. Since n.BuLi is a strong carbanion, it reacts with acidic hydrogen of ring oxazoline group of TBO instead of reacting with C-Br bond. But since, chain end carbanion of a growing polymer is stabilized, it may not react with acidic hydrogen of oxazoline group and thus availlable to react with C-Br bond of TBO. With this view, linking reaction of living anionic chain end with TBO was examined.

Linking reaction of polystyrene initiated by n.BuLi in toluene solvent at -78^0C temperature by TBO was attempted. SEC results indicated that there is no increment of Mn after linking reaction compared to that of the homopolymer. Failure to form the branched polystyrene was attributed to the fact that, since, linking reaction has to take place at the tertiary carbon atom of TBO, polystyrene chains, perhaps create steric crowding owing to the presence of bulky phenyl groups adjacent to the linking point. To avoid this problem, isoprene was chosen as the monomer. Accordingly, linking reaction of TBO with polyisoprene initiated by n.BuLI in tetrahydrofuran at room temperature was attempted. Similar experiments were also carried out in toluene as solvent using both n.BuLi as well as , α-methylstyryl anion as initiator. The results are shown in table 4.1.

Table 4.1 : Linking reaction of cabanions with TBO under positive pressure of nitrogen^{a}.

Entry no.	polymer	[M] mol/lit	[I] mol/lit	solvent	initiator	Mn_{calcd}	Mn_{SEC} before linking^{b}	Mn_{SEC} after linking^{b}	Mw/Mn^{c}	degree of branc hing^{d}	linking efficiency^{e}, %
1.	PIP	1.47	0.032	THF	n.BuLi	3100	4440	13700	1.2/1.31	3.09	65
2.	PIP	1.47	0.032	THF	α-MeStLi	3100	2500	6930	1.10/1.20	2.77	60
3.	PIP	1.47	0.028	THF	α-MeStLi	3500	2800	7250	1.10/1.30	2.60	60
4.	PIP	1.47	0.033	THF	n.BuLi	3000	650	1100	1.09/1.18	1.69	45
5.	PIP	1.47	0.033	Toluene	n.BuLi	3000	5000	10,000	1.20/1.36	2.00	-
6.	PIP	1.47	0.035	Toluene	α-MeStLi	2800	3270	7100	1.09/1.17	2.17	-
7.	Pst^{f}	1.47	0.037	THF	α-MeStLi	2700	4930	9300	2.82/1.32	1.89	-

(a) Polymerization and linking reaction were carried out at 25-27°C (b) Mn's were determined using RI detector. Polystyrene standards were used for calibration. (c) MWD of before linking / MWD of after linking. (d) Branching functionality = Mn after linking / Mn before linking. (e) Linking efficiency = peak height of linked polymer / peak height of (free arm polymer + linked polymer). (f) The polystyrene living chain ends were end-capped with a few units of isoprene.

PIP = Polyisoprene; THF = tetrahydrofuran ; n.BuLi = n. butyl lithium ; α-MeStLi = α- Methylstyryllithium.

In every case, presence of homopolymer along with branched polymer was observed as shown by SEC (figure 4.6).

Branching functionality was determined from the ratio of Mn of homopolymer (before linking) to the Mn of branched polymer (after linking). When THF was used as solvent, branching functionality was found to be three (entry no 1-3, in table 4.1), whereas when toluene was used as solvent, branching functionality was found to be nearly two (entry no 5-6, in table 4.1) .

The presence of large amount of homopolymer in all cases indicates considerable termination of living chain ends. This is perhaps, due to the impurities present in the system. Futhermore, in THF all three C-Br bonds of TBO participated in the linking reaction whereas, in toluene only two C-Br bonds of TBO participated in the linking reaction. Termination of living chain ends by impurities present in the system is expected to be related to the exposure of living polymer to the environment. In toluene, the reaction being slower, longer exposer time was necessary. Also, linking reaction is displacement of an electrophile C-Br bond by a nucleophilic carbanion. This reaction is greatly influenced by the polarity of solvent. Higher the polarity of the solvent, faster is the displacement reaction . Since THF is more polar than toluene, linking reaction is relatively faster in THF than in toluene. Therefore, the living polymer chain exists in toluene for a longer duration increasing the probability of termination of the chain ends by adventitious impurities. This leads to incomplete linking. In THF, the linking reaction of chain ends with the C-Br bonds of TBO is sufficiently fast. Hence termination by adventitious impurities is less important.

5.2.5.2 : Polymerization and linking reaction under vacuum (10^{-3} torr).

Polymerization and linking reaction were carried out under 10^{-3} vacuum to obviate the problems faced due to adventitious termination due to impurities in the system.

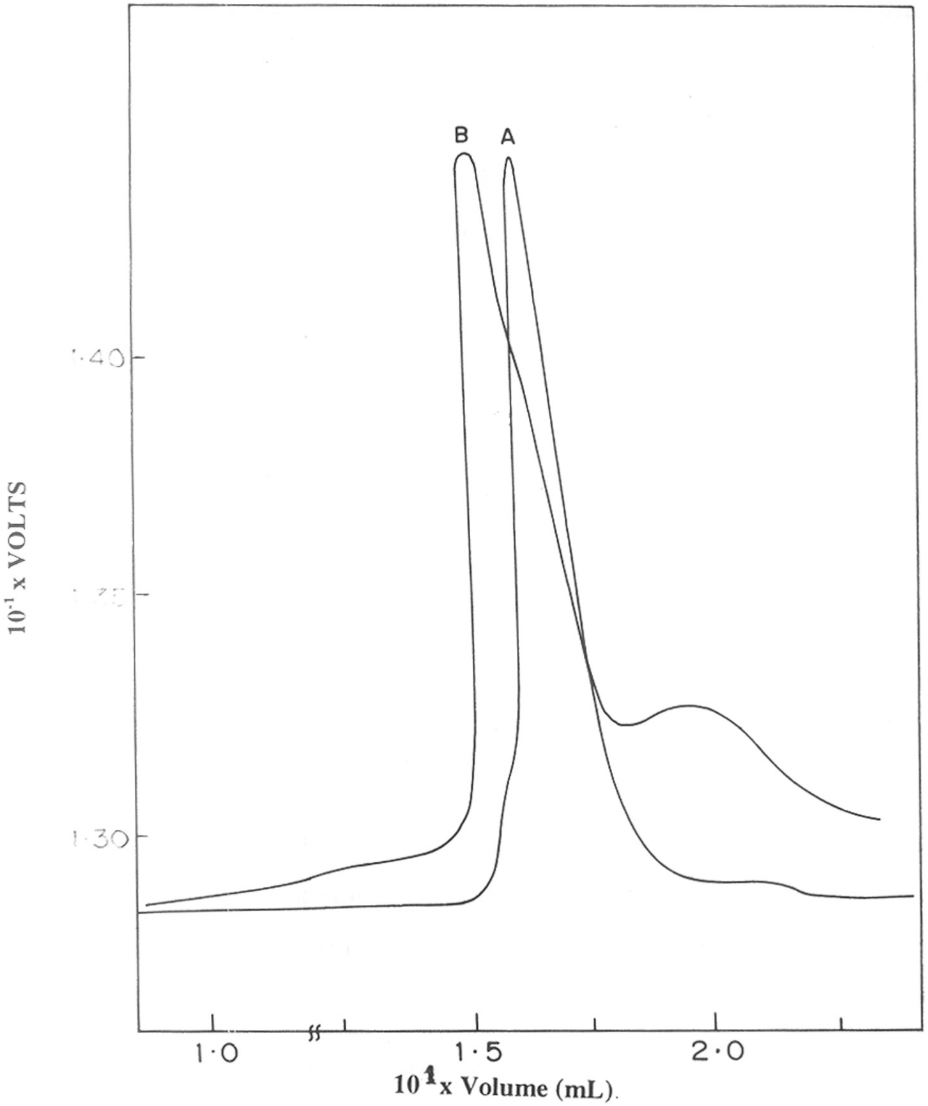


Figure 4.6 SEC of PIP prepared under nitrogen. A : Before linking; B : After linking

The results are shown in table 4.2. The molecular weight distribution is very broad and substantial amount of homopolymer is present. Molecular weight increased only by a factor of two. These results are still not very satisfactory (figure 4.7).

4.2.5.3 : Polymerization and linking reaction under high vacuum (10^6 torr).

The polymerization and linking experiments were performed under 10^{-6} torr vacuum. The results are shown in table 4.3. In all cases, absence of homopolymer was observed confirming 100% linking reaction (figure 4.8). However, molecular weight increased only by a factor of two in all cases. It was observed that SEC of homopolymer (fig 4.9) contain a distinct shoulder at the higher Mn side (C, fig 4.9) and that Mn of the shoulder was nearly double that of the actual Mn of the homopolymer. In view of the broad molecular weight distribution of homopolymer itself, determination of Mn of homopolymer from SEC would be difficult. Furthermore the actual Mn of homopolymer might be much less than what was determined from SEC. Moreover, the concentration of carbanion (anionic polymeric chain end) in moles after the completion of homopolymerization is calculated by using the following equation:

Concentration of carbanion in moles = wt of monomer taken in gram / Mn determined from SEC.

Depending on the concentration of carbanion in moles, one third mole of linking agent, TBO was taken for linking reaction. This stoichiometry is very important for star polymer formation. If Mn determined from SEC is erroneous, the stoichiometry (carbanion in moles : TBO in moles = 3 : 1) would also be erroneous.

Therefore, homopolymer of narrow molecular weight distribution and free of high molecular weight shoulder is needed in order to accurately determine the carbanion concentration prior to proceeding with the linking reaction.

Table 4.2 : Polymerization and linking reactions of linear polyisoprene with TBO by breakseal technique under vacuum (10^{-3} Torr) in toluene[a] .

Entry no.	[M] mol/lit	$[I]X10^{3}$ mol/lit	Mn_{calcd}	Mn_{SEC} before linking[b]	Mn_{SEC} after linking$_{b}$	Mw/Mn[c]	branching func[d].
1.	1.47	5.0	20,000	28,000	48,000	1.3/1.33	1.71
2.	1.47	2.5	40,000	49,000	85,000	1.29/1.34	1.73

(a) Polymerization and linking reaction were carried out at 25-27°C (b) Mn's were determined using RI detector. Polystyrene standards were used for calibration. (c) MWD of before linking / MWD of after linking. (d) Branching functionality = Mn after linking / Mn before linking.

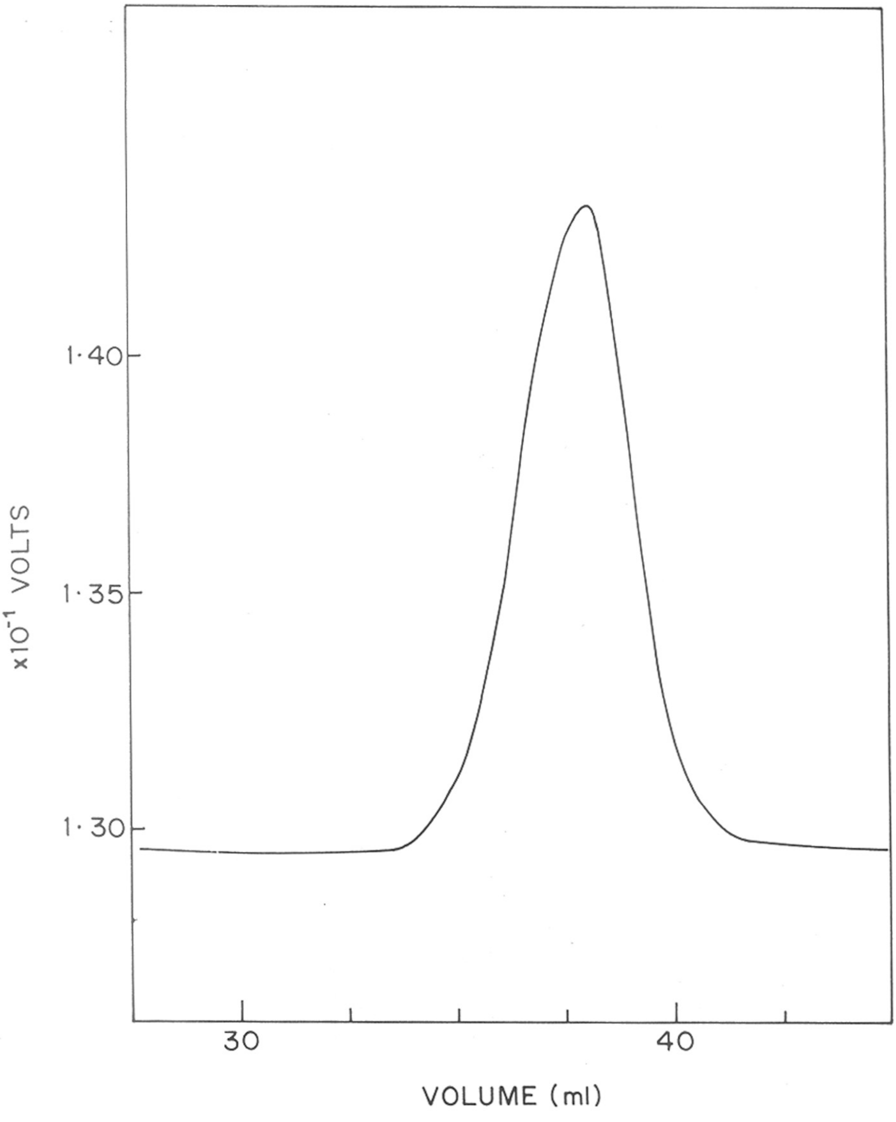


Figure 4.7 SEC of PIP prepared under vacuum (10^{-3} torr)

Table 4.3 : Linking reactions of linear polyisoprene with TBO by breakseal technique under high vacuum (10^{-6} torr) in toluene[a].

Entry no	[M] mol/lit	[I] X10^3 mol/lit	Mn_{calcd}	Mn_{SEC} before linking[b]	Mn_{SEC} after linking[b]	Mw/Mn[c]	branching funct.[d]
1.	1.47	6.70	15,000	21,731	38,560	1.18/1.2	1.77
2.	1.47	2.80	35,000	51,000	78,121	1.11/1.2	1.53
3.	1.47	6.70	15,000	22,000	40,000	1.1/1.18	1.80
4.	1.47	3.33	30,000	43,000	75,000	1.11/1.18	1.74
5.	1.20	1.60	50,000	62,000	126,000	1.1/1.18	2.03
6.	1.47	3.33	30,000	41,000	81,000	1.2/1.18	1.97

(a) Polymerization and linking reaction were carried out at 25-27°C (b) MALLS detector was used for molecular weight determination. (c) MWD of before linking / MWD of after linking. (d) Branching functionality = Mn after linking / Mn before linking.

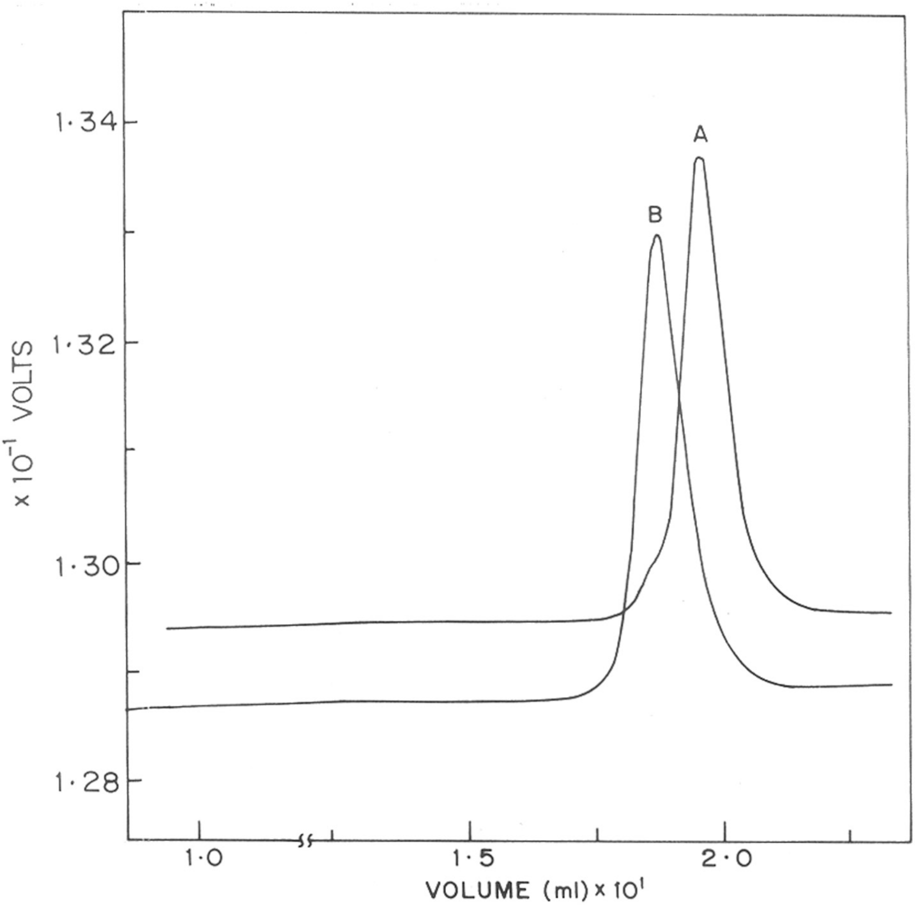
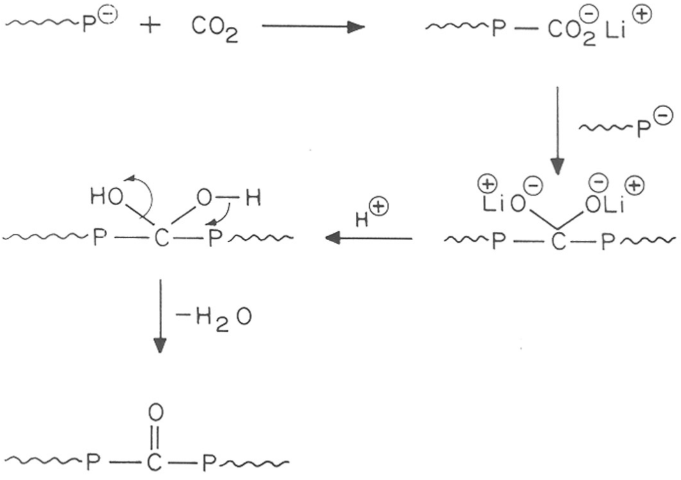


Figure 4.8 SEC of PIP prepared under vacuum (10^{-6} torr). A : Before linking; B : After linking

In view of previous reports[29,30], formation of the shoulder is attributed to the chain extension reaction of living polymer by CO_2 (scheme 4.2) during termination of the living chain end by methanol.



Scheme 4.2 : Chain extension reaction of living polymer by CO_2.

Dissolved CO_2 in methanol could act as a chain extension agent.

Therefore, to obviate this problem, degassed CO_2 free methanol (degassing was performed by bubbling nitrogen through methanol for an hour) was used for termination. The breakseal of the ampoule which contain homopolymer pickout was smashed inside the dry box and terminated by degassed methanol. SEC chromatogram confirmed the presence of coupled product (figure 4.10 a) but in lesser amounts. Therefore methanol was distilled by freeze thaw technique in a flash distillation unit. And the breakseal containing homopolymer pickout was broken inside the dry box. Here again, coupled product was observed in SEC but in lesser amounts (figure 4.10 b).

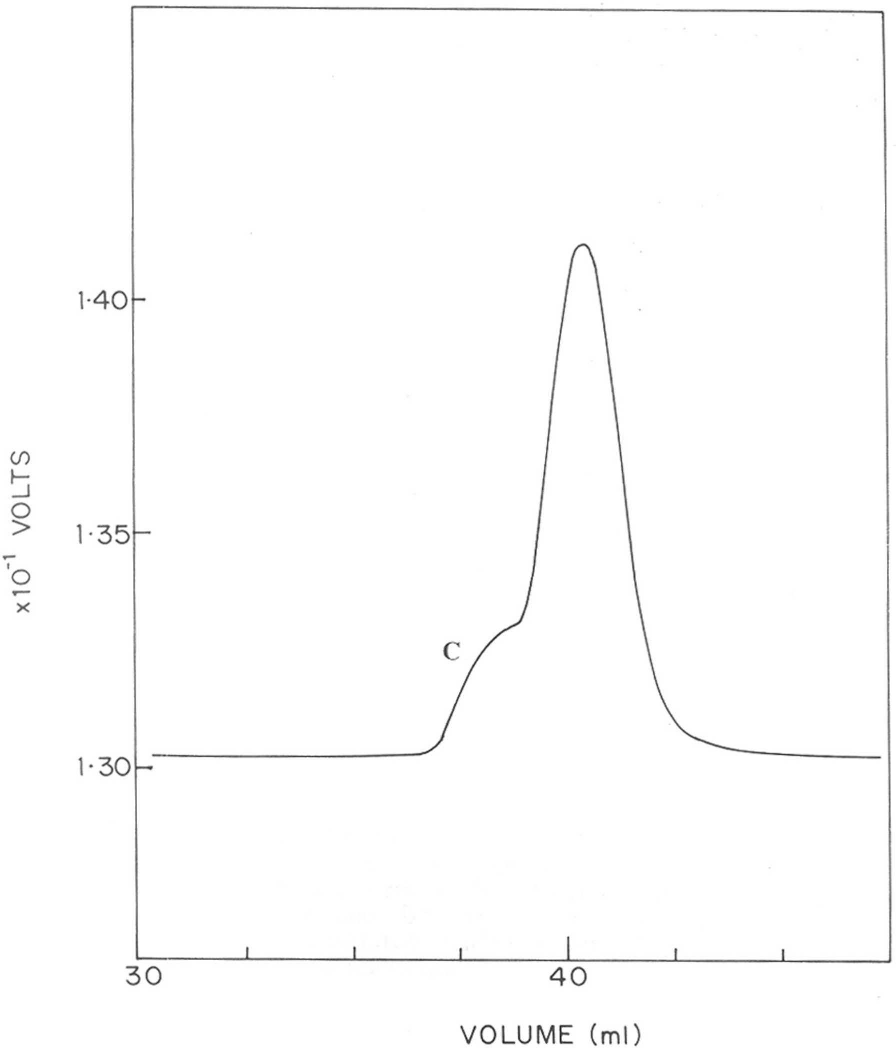


Figure 4.9 SEC of PIP terminated by degassed methanol

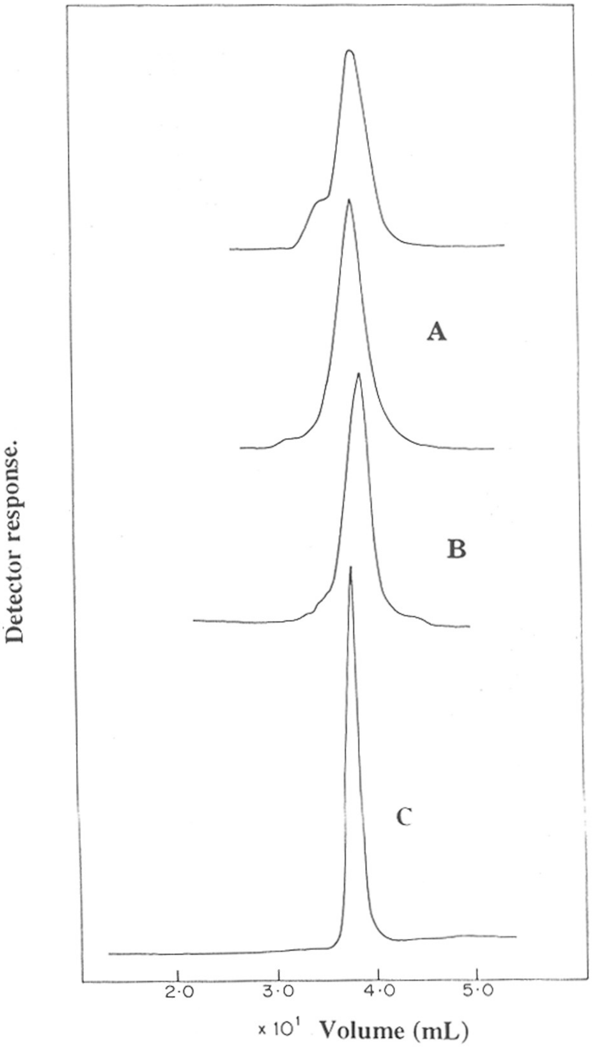


Figure 4.10 SEC of PIP prepared under high vacuum (10^{-6} torr). A : Terminated by degassed methanol inside drybox. B : Terminated by methanol distilled by freeze thaw technique. C : Terminated inside methanol distilled by freeze thaw technique

Table 4.4 : Linking reaction of linear polyisoprene with TBO by breakseal technique under high vacuum (10^{-6} torr) in toluene[a].

Entry no.	[M] mol/lit	[I] X 10^3 mol/lit	Mn_{calcd}	Mn_{SEC} before linking[b]	Mn_{SEC} after linking[b]	Mw/Mn[c]	branching funct.[d]
1.	1.47	3.33	30,000	36,446	85,774	1.08/1.1	2.30
2.	0.90	0.68	90,000	95,557	178,117	1.07/1.1	1.86
3.	0.70	0.31	150,000	179,476	360,105	1.06/1.2	2.00

(a) Polymerization and linking reaction were carried out at 25-27°C (b) MALLS detector was used for molecular weight determination. (c) MWD of before linking / MWD of after linking. (d) Branching functionality = Mn after linking / Mn before linking.

Finally, the breakseal was broken inside the methanol distilled by freeze-thaw technique. SEC of the homopolymer is shown in figure 4.10 c. Coupled product was completely absent. Adopting this process of termination of homopolymer pickout few experiments were carried out under 10^{-6} torr. The results are shown in table 4.4.

SEC of homopolymer was free of coupled product and molecular weight distribution was narrow in all cases. However, the Mn has increased only by a factor of two in all cases. This could possibly be due to steric factors. This could arise out of the methyl group present at the β proton in the poly(isoprene) chain end. In view of this, linking reaction was attempted using living 1,4 poly(butadiene) chain end in toluene. Poly(butadiene) is far less sterically hindered than poly(isoprene).

Accordingly, butadiene was polymerized using n.BuLi in toluene at room temperature for 12 h followed by linking reaction at room temperature for 48 h at 10^{-6} torr vacuum . The results are shown in table 4.5. Termination of homopolymer was done by smashing breakseal inside the methanol distilled by freeze thaw technique. In entry no 2 , linking reaction was done in presence of excess carbanion. In both the cases, Mn had increased only by a factor of two. These results indicate that steric factor may not be the only reason for the failure to achieve quantitative termination of the living chain end by TBO (figure 4.11).

Linking reaction is a nucleophilic substitution reaction. It is well known that this reaction is significantly affected by the polarity of solvent medium as well as on the temperature of the reaction.

Therefore, it was thought that increasing the solvent polarity or the temperature of the linking reaction may prove beneficial.

Accordingly, polymerization of isoprene as well as butadiene was done in toluene at room temperature to obtain a predominantly linear chain. After completion of polymerization , dry THF was added so that final mixed solvent composition was

Table 4.5 : Linking reaction of linear polybutadiene with TBO by breakseal technique under high vacuum (10^{-6} torr) in toluene[a].

Entry no.	[M] mol/lit	[I] X10^3 mol/lit	Mn_{calcd}	Mn_{SEC} before linking[b]	Mn_{SEC} after linking[b]	Mw/Mn[c]	branching funct.[d]
1.	1.47	4.00	25,000	29000	65000	1.03/1.08	2.24
2.	1.20	1.60	50,000	55000	108,000	1.06/1.1	1.96

(a) Polymerization and linking reaction were carried out at 25-27°C (b) MALLS detector was used for molecular weight determination. (c) MWD of before linking / MWD of after linking. (d) Branching functionality = Mn after linking / Mn before linking.

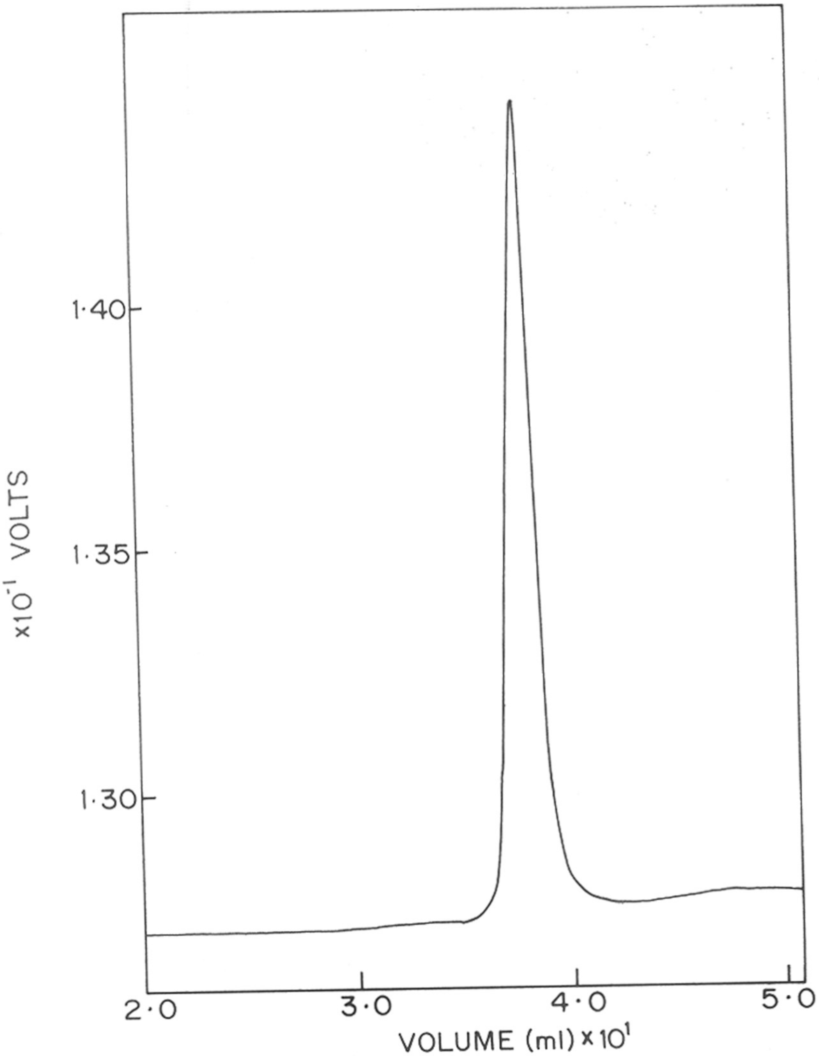


Figure 4.11 SEC of PBd prepared under vacuum (10^{-6} torr)

Table 4.6 : Linking reaction of carbanion with TBO by breakseal technique under high vacuum (10^{-6} torr) in toluene and THF solvent mixture[a].

Entry no.	[M] mol/lit	[I] X10^3 mol/lit	Mn_{calcd}	polymer	Mn_{SEC} before linking[b]	Mn_{SEC} after linking[b]	Mw/Mn[c]	branching funct[d].
1.	1.2	1.60	50,000	PBd	58951	115,166	1.02/1.09	1.95
2.	0.7	0.31	150,000	PIP	198,105	400,192	1.08/1.1	2.00

(a) Polymerization and linking reaction were carried out at 25-27°C (b) MALLS detector was used for molecular weight determination. (c) MWD of before linking / MWD of after linking. (d) Branching functionality = Mn after linking / Mn before linking. PIP : Polyisoprene; PBd : Polybutadiene

50:50 (v/v). To this reaction mixture TBO was added. Linking reaction was continued for 48 h. These reactions were done under a positive pressure of nitrogen. The results are shown in table 4.6. Results indicate incomplete linking.

Therefore, increasing the solvent polarity alone does not help. Linking reaction was then attempted at higher temperature. Accordingly, polymerization was carried out at room temperature using n.BuLi as initiator in toluene. After completion of polymerization, temperature of polymerization mixture was raised to 50°C. TBO solution in toluene was added dropwise to polymerization mixture. Pickout was taken at different intervals of time and analysed by SEC. The results are shown in table 4.7 and SEC chromatogram is shown in figure 4.12. Mn was found to increase by a factor of three. Therefore, at higher temperature, linking reaction is complete. However, substantial termination of living chain end occurred prior to linking resulting in a free arm content of approximately 20%.

Similar experiments were also carried out where TBO was added in THF solution at 50°C. The results are shown in table 4.8. SEC chromatogram is shown in figure 4.13. Mn increased by a factor of three.

In all experiments only a single product was isolated , either a linear or a three arm polymer. Also, it is known that if linking reaction takes place in steps, a mixture of product is likely to form. The results so far obtained indicates that linking reaction with TBO does not proceed in steps. After one of the three C-Br bonds of TBO was replaced by carbanion (R^-), the reactivity of C-Br bond of $-CBr_2-R$ will be higher than C-Br bond of $-CBr_3$. Therefore, second carbanion (R^-) would prefer to react with C-Br bond of-CBr_2-R and thus form $-CBrR^2$ (two arm polymer). Similarly third carbanion (R^-) would prefer to react with $-CBrR^2$ instead to react with either $-CBr_2-R$ or $-CBr_3$ and thus forms $-CR_3$ (three arm star polymer) only. Depending on the reaction conditions either two arm or three arm polymer forms

4.3 : Conclusion.

Formation of three arm star polymer has been demonstrated in THF at room temperature (25-27°C) (table 4.1) and in toluene at 50°C (table 4.7). However, even under the best conditions, free arm content could not be reduced below 20%.

Table 4.7 : Linking reaction of PBd with TBO solution in toluene under nitrogen in toluene[a].

Entry no.	time, h	[M] mol/lit	[I] X10^3 mol/lit	Mn_{calcd}	Mn_{SEC} before linking[b]	Mn_{SEC} after linking[b]	Mw/Mn[c]	% of free arm content[d]	branching func.[e]
1.	1	1.6	7.25	15,000	20,631	62,000	1.08/1.07	55	3.01
2.	2	1.6	7.25	15,000	20,631	62,221	1.06/1.09	20	3.01
3.	24	1.6	7.25	15,000	20,631	65,000	1.05/1.09	20	3.15

(a) Polymerization was carried out at 25-27°C and linking reaction was carried out at 50°C. (b) RI detector was used and polystyrene standards were used for molecular weight determination. (c) MWD before linking / MWD after linking. (d) Free arm content = peak height of free arm /peak height of (free arm + linked polymer). (e) Branching funtionality = Mn before linking / Mn after linking.

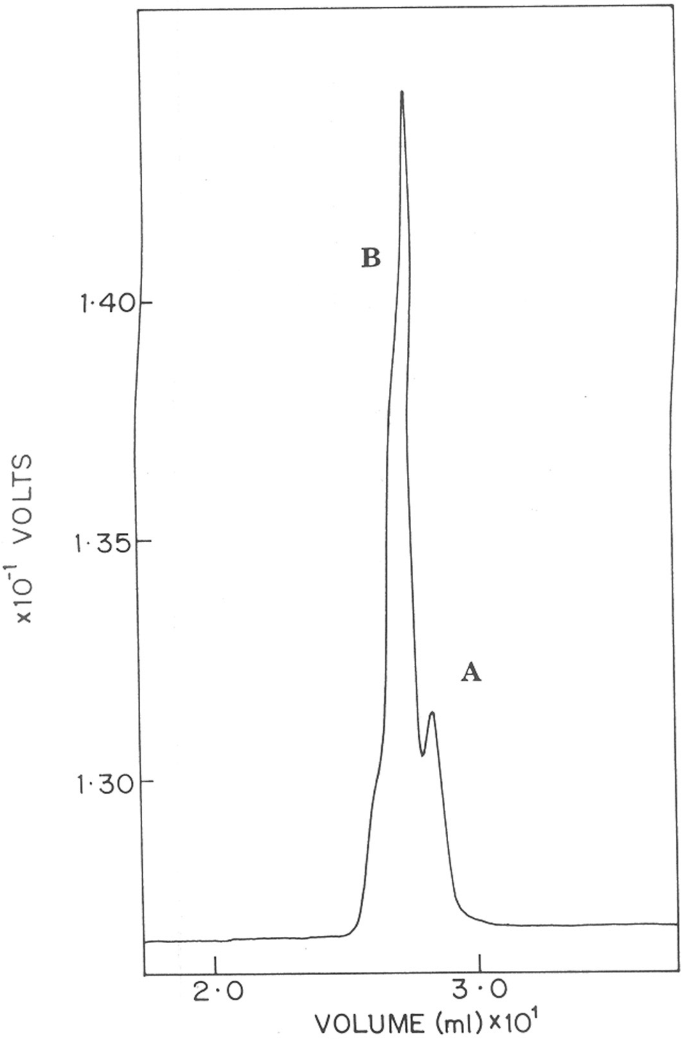


Figure 4.12 SEC of PBd terminated by TBO solution in toluene at 50°C. A : Free arm. B : 3-arm star polymer

Table 4.8 : Linking reaction of PBd with TBO solution in THF under nitrogen in toluene[a].

Entry no.	time, h	[M] mol/lit	[I] X10^2 mol/lit	Mn_{calcd}	Mn_{SEC} before linking[b]	Mn_{SEC} after linking[b]	MW/Mn[c]	% of free arm cotent[d]	branching func[e].
1.	1	1.6	1.08	10,000	14,579	42,712	1.06/1.09	46	2.90
2.	2	1.6	1.08	10,000	14,579	43,000	1.06/1.1	35	2.94
3.	3	1.6	1.08	10,000	14,579	45,000	1.05/1.1	34	3.0
4.	24	1.6	1.08	10,000	14,579	45,000	1.08/1.14	34	3.0

(a) Polymerization was carried out at 25-27°C and linking reaction was carried out at 50°C. (b) RI detector was used and polystyrene standards were used for molecular weight determination. (c) MWD before linking / MWD after linking. (d) Free arm content = peak height of free arm /peak height of (free arm + linked polymer). (e) Branching funtionality = Mn before linking / Mn after linking.

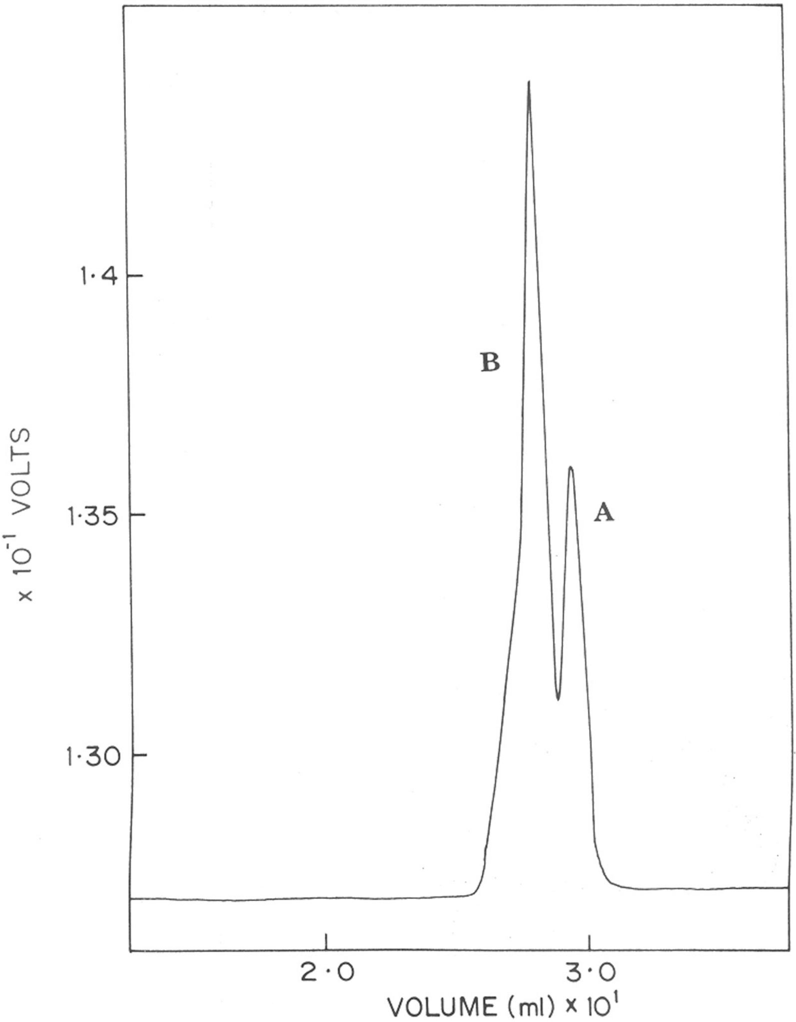


Figure 4.13 SEC of PBd terminated by TBO solution in THF at 50°C. A : Free arm. B : 3-arm star polymer

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CHAPTER 5

CHAPTER 5

Synthesis of poly (isobutyl vinyl ether) using 2-perbromomethyl-2-oxazoline as initiator.

5.1 : Introduction.

Despite a long history of research, which provided many interesting findings, vinyl ether polymerization has attracted limited interest amongst polymer scientists , presumably because vinyl ether polymers have so far failed to find extensive industrial use[1-3]. However, recent developments in this field have led to an intensive reexamination since the living cationic polymerization provides excellent control on molecular weights, molecular weight distribution and structure of poly (vinyl ether)s[4]. In 1984, Higashimura and coworkers demonstrated, that an initiating system consisting of hydrogen iodide and molecular iodine induces truly living polymerization of isobutyl vinyl ether (IBVE) in nonpolar media[5]. Since then several initiator systems have been discovered which truly show living polymerization of vinyl ethers. For examples, a) HI/ZnI_2[6], b) $EtAlCl_2$/ether and $EtAlCl_2$/ester[7], c) $R^2{}_1P(O)OH/ZnX_2$[8], d) Me_3SiI/ZnI_2[9], e) acetal/Me_3SiI[10].

The ability of 2-perbromomethyl-2-oxazoline (TBO) to initiate the ring opening polymerization of 2-methyl-2-oxazoline (MeOXZ) was demonstrated in chapter 3. Therefore, it can be inferred that TBO acts as an electrophile[11]. For cationic polymerization of vinyl ethers any strong or mild electrophile can act as an initiator. Examples are protic acids[12], cation forming salts[13], halogens[14], metal oxides and related solid acids[15]. However, these initiators do not provide any control on polymerization. On the contrary, mild electrophiles, such as HI, $EtAlCl_2$, $R^2{}_1P(O)OH$, Me_3SiI etc. promote the controlled living polymerization of IBVE in presence of a lewis acid cocatalyst.

Consequently, it was thought worthwhile to examine the ability of TBO to act as an initiator for the polymerization of IBVE in presence of a lewis acid cocatalyst. The results are described in this chapter.

5.2 : Experimental.

All experiments were carried out under nitrogen atmosphere using standard bench top inert atmosphere techniques.

5.2.1 : Materials.

Dichloromethane, diethylether and toluene were procured from Loba Chemie Industries, Bombay. Potassium iodide was procured from S. D. Fine Chemical Ltd., Bombay. Isobutyl vinyl ether and zinc iodide were procured from Aldrich, USA.

5.2.2 : Purification of solvents.

Dichloromethane was refluxed over CaH_2 for 24 h. It was again distilled over CaH_2 by freeze thaw technique just prior to use.

Toluene was washed with sulfuric acid repeatedly till sulfuric acid remained colourless after washing. It was then washed with 10% sodium bicarbonate aqueous solution and subsequently washed with distilled water repeatedly till washed water showed neutral to litmus paper. Initial drying was done by keeping it over fused $CaCl_2$ overnight. It was then refluxed over CaH_2 for two days. Finally, styryllithium solution in toluene was added till orange red colour persisted and distilled by freeze thaw technique prior to use.

Diethyl ether was dried by keeping over anhydrous $CaCl_2$ overnight. It was then refluxed over CaH_2 for 24 h. Finally, styryllithium solution in toluene was added to it till orange red colour persisted and distilled by freeze thaw technique prior to use.

Dioxane was dried over Na-benzophenone system and distilled prior to use .

5.2.3 : Monomer.

Isobutyl vinyl ether was washed with 10% aqueous sodium hydroxide solution and then water, dried overnight over potassium hydroxide, and distilled twice over calcium hydride by freeze thaw technique just prior to use.

5.2.4 : Reagents.

ZnI_2 : It was dried at 80^0C under reduced pressure (0.075 mm of Hg) for 24 h.

KI : It was dried at 130^0C under reduced pressure (0.075 mm of Hg) for 24 h.

5.2.5 : Polymerization of IBVE using TBO as initiator.

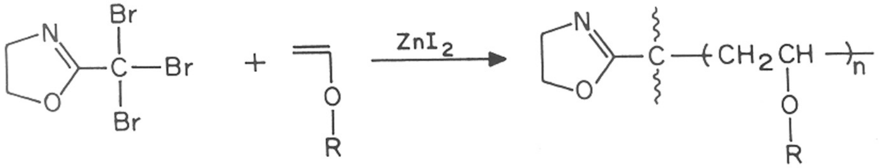
Polymerization were carried out under dry nitrogen in a round bottom flask equipped with a three way stop cock. TBO (0.225 g, 0.0007 mol.) was placed in the flask under a flow of nitrogen. To this, IBVE (2.0 g, 0.02 mol.) dissolved in 35 mL of dichloromethane or in toluene was added. After attaining the required temperature, ZnI_2 dissolved in either diethyl ether or in dioxane was added to commence polymerization. Polymerization was continued for 3 h. It was terminated with prechilled ammonical methanol. Polymer solution was washed with 10% aqueous sodium thiosulfate solution and then with distilled water twice and dried over sodium sulfate. Polymer was recovered by removing the solvent under vacuum and dried.

5.2.6 : Analyses.

Molecular weight measurement were performed on a 150C Waters GPC using μ-ultrastyragel columns (100, 500, 10^4, 10^5, A°) in tetrahydrofuran solvent at 30°C (0.2 % w/v polymer, flow rate 1 mL/min). RI detector was used. Monodisperse polystyrene standards were used for molecular weight calibrations.

5.3 : Results and Discussion .

TBO initiated smoothly the cationic polymerization of isobutyl vinyl ether at 0^0C or below 0^0C in dichloromethane as well as toluene (table 5.1). ZnI_2 was added as a solution in ether diethylether or dioxane. Polymerization was carried out for 3 h in all cases. With decreasing temperature , molecular weight distribution changed from 2.4 to 2.1 in dichloromethane. In toluene, at -40^{0}C polymerization did not take place. In every cases (table 5.1), molecular weight distribution remains approximately 2.0. Also, there was substantial discrepancy between the Mn$_{calc}$ and Mn$_{SEC}$. The results indicate the nonliving nature of the polymerization system. Moreover from size exclusion chromatography, it was observed that tailing of the peak occurs at lower Mn indicating slow initiation (figure 5.1 and 5.2). Since initiation reaction is the addition reaction of C-Br bond of TBO to the unsaturation (equation 5.2), efficiency of initiation is expected to depend on the polarization of C-Br bond.



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Since C-Br bond polarization was not sufficient enough to induce rapid initiation, interhalogen exchange with KI was attempted. It was thought that C-I bond, which is more polar than C-Br bond, might induce a rapid initiation. Accordingly two experiments in toluene at 0^{0}C and -20^{0}C were carried out for 3 h. The results are shown in table 5.2. Molecular weight distributions were still broad, although relatively narrower than what was observed without KI. Also tailing of the peak at lower Mn in SEC was still observed (figure 5.3). It was argued that since KI has limited solubility in toluene, interhalogen exchange was not very efficient. Therefore, the same reaction was attempted in dichloromethane. However, the result was unsatisfactory (table 5.2, entry 3).

Table 5.1 : Polymerization of isobutyl vinyl ether using 2-perbromomethyl-2-oxazoline as initiator.[a)]

Entry no.	targeted Mn.	solv.	temp. ^{0}C	conv. %	Mn (GPC)	Mw/Mn
1.	3000	CH_2Cl_2	0	100	7050	2.4
2.	3000	CH_2Cl_2	-20	90	7000	2.2
3.	3000	CH_2Cl_2	-40	75	6950	2.1
4.	3000	Toluene	0	100	7090	2.1
5.	3000	Toluene	-20	70	6900	2.0
6.	3000	Toluene	-40	-	-	-

a) [M] = 0.57 moles/lit. ; [I] = 0.018 moles/lit.

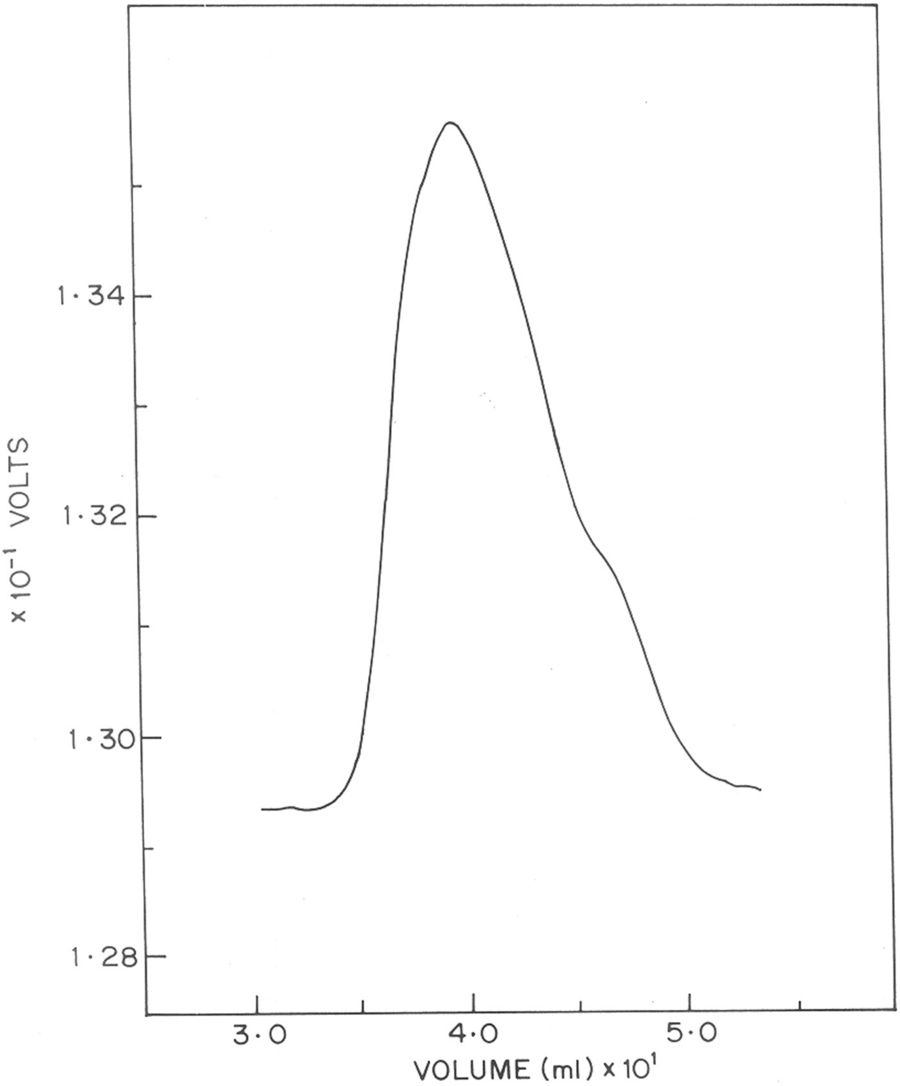

Figure 5.1 SEC of PIBVE prepared at room temperature (25-27°C) using TBO as initiator

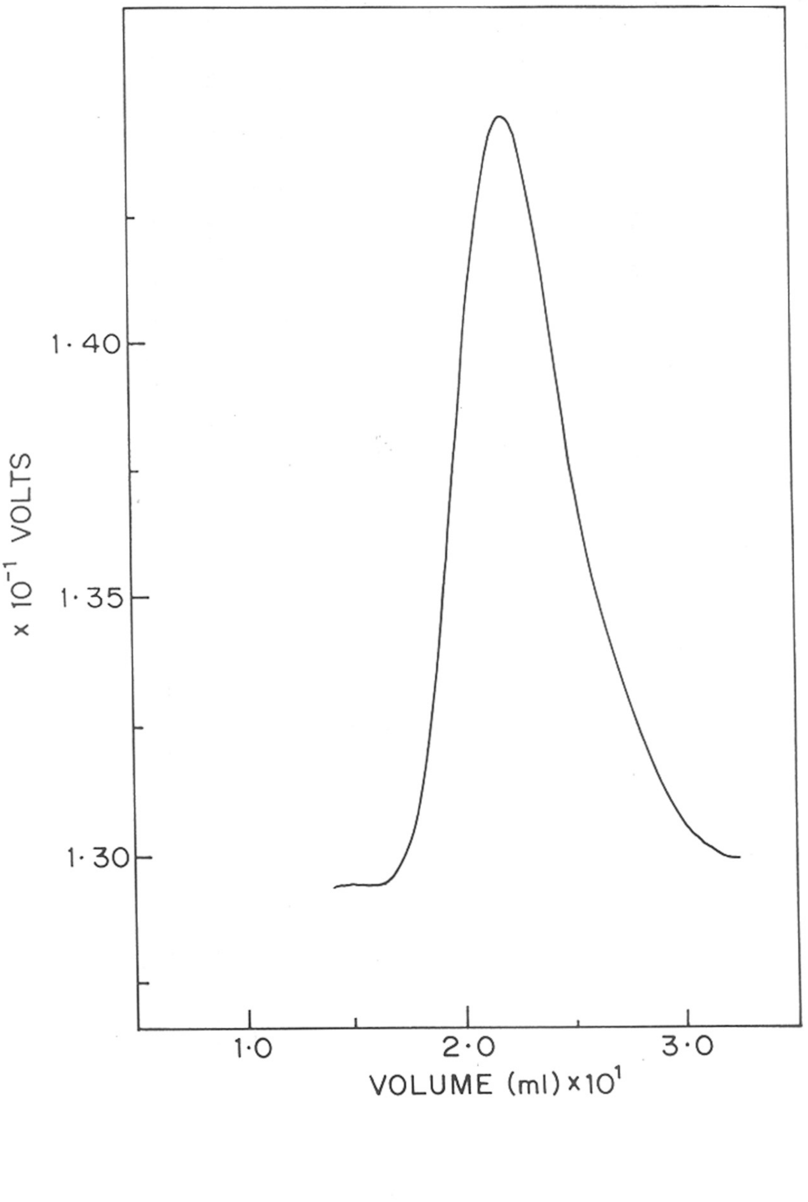

Figure 5.2 SEC of PIBVE prepared at -40°C using TBO as initiator.

Table 5.2 : Polymerization of isobutyl vinyl ether using 2-perbromomethyl-2-oxazoline as initiator in presence of KI[a)].

Entry no.	initiator, in g.	KI in g.	solvent.	temp. ^{0}C.	Mw/Mn
1.	0.225	1.0	toluene	0	1.8
2.	0.225	1.0	toluene	-20	1.5
3.	0.225	1.0	CH_2Cl_2	-40	1.52

a) [M] = 0.57 moles/lit. ; [I] = 0.018 moles/lit.

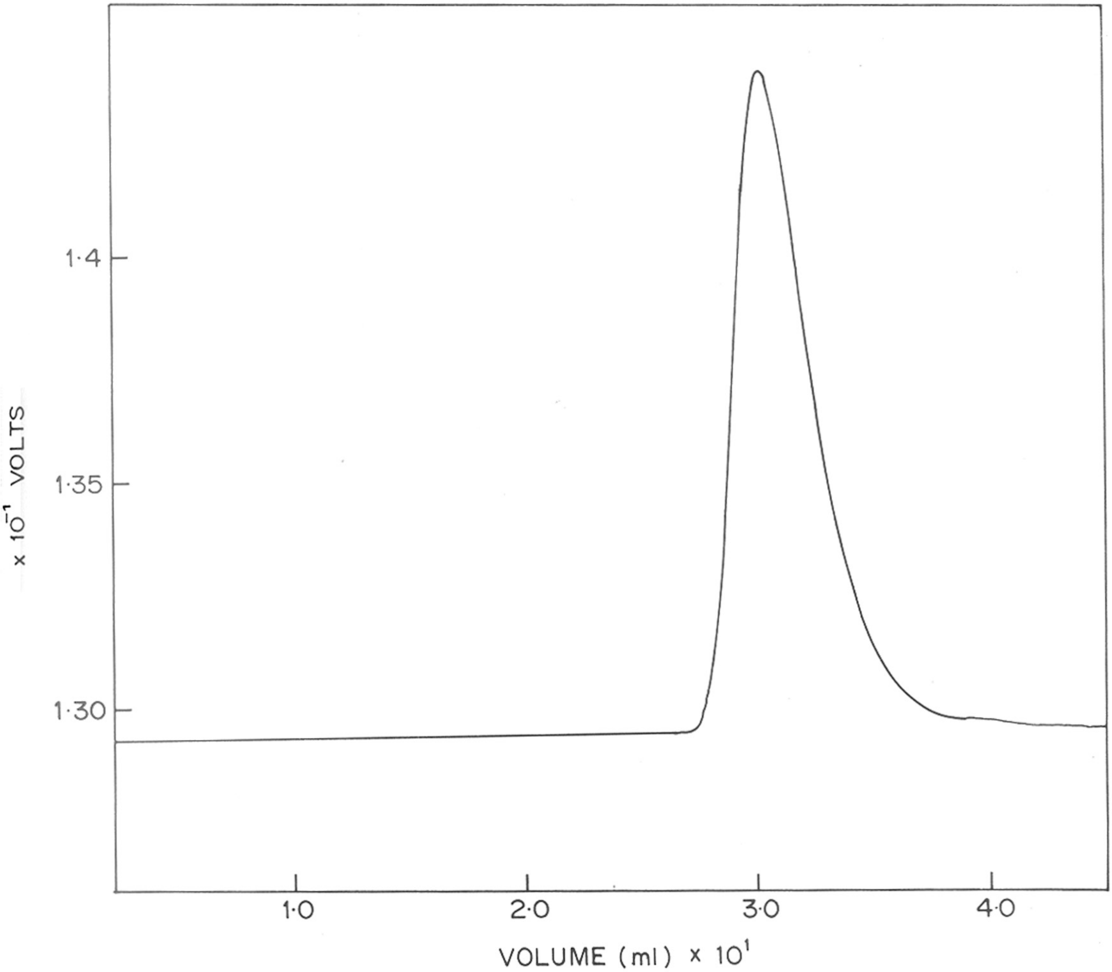

Figure 5.3 SEC of PIBVE prepared at -40°C using TBO as initiator in presence of KI

5.4 : Conclusions.

TBO in presence of ZnI_2 as coinitiator smoothly polymerized IBVE in dichloromethane as well as toluene between 25°C to -40°C. However, molecular weight distributions were broad in all cases. The tailing of the peak in SEC occurred at the lower Mn site. This is perhaps, due to the slow initiation. Interhalogen reaction with KI was attempted to improve the efficiency of the initiation. However, results were unsatisfactory. Therefore, TBO in presence of ZnI_2 as coinitiator does not induce living cationic polymerization of IBVE.

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CHAPTER 6

CHAPTER 6

Summary and conclusion.

6.1. 2-(Perbromomethyl)-2-oxazoline (TBO) : A novel trifunctional initiator for the ring opening polymerization of 2-methyl-2-oxazoline (MeOXZ).

Exhaustive bromination of MeOXZ was carried out by N-bromosuccinimide at room temperature as a potential route to synthesis TBO. The structure of TBO was confirmed by spectral and elemental analysis. Cationic ring opening polymerization of MeOXZ was studied using TBO as an initiator in acetonitrile solution. It was observed that TBO smoothly initiated the living cationic ring opening polymerization of MeOXZ in refluxing acetonitrile. All the C-Br bonds of TBO participated in the polymerization, leading to a branched three arm star polymer bearing unequal arm length. It is evident from ^{1}H-NMR spectroscopy that initiation takes place stepwise. The initiation of first polymer arm is faster than second polymer arm. The third initiation is apparently slow. Thus, the relative length of the three arms of the resulting star-shaped polymer are unequal. Evidence is also presented to show that under conditions explored, the oxazoline group of the initiator remains intact and does not undergo any ring opening reaction.

6.2. 2-(Perbromomethyl)-2-oxazoline : A novel trifunctional linking agent for living anionic chain end for the synthesis of 3-arm star polymer.

Living anionic polymerization of isoprene, butadiene in both polar as well as nonpolar solvents were performed using n.BuLi as an initiator and terminated by TBO as a linking agent at room temperature (25-27°C) and as well as higher temperature (50°C). Polymerization and linking reactions were carried out under nitrogen as well as high vacuum (10^{-6} torr). Formation of three arm star polymer has been demonstrated in THF at room temperature (25-27°C) and in toluene at 50°C. However, even under the best conditions, free arm content could not be reduced below 20%.

6.3. Synthesis of poly (isobutyl vinyl ether) (IBVE) using 2-(perbromomethyl)-2-oxazoline as an initiator.

TBO in presence of ZnI_2 as coinitiator smoothly polymerized IBVE in dichloromethane as well as toluene between 25°C to -40°C. However, molecular weight distributions were broad in all cases. The tailing of the peak in SEC occurred at the lower Mn side. This is perhaps, due to the slow initiation. Interhalogen reaction with KI was attempted to improve the efficiency of the initiation. However, results were unsatisfactory. Therefore, TBO in presence of ZnI_2 as an coinitiator does not initiate living cationic polymerization of IBVE.

In conclusion, TBO has been used successfully as an initiator for the living cationic ring opening polymerization of MeOXZ to synthesis three arm star polymer of poly (N-acylethylenimine) and as a terminator for living polymerization of isoprene and butadiene to synthesis three arm star polymer of polyisoprene and polybutadiene.

APPENDIX

APPENDIX

Polymerization of tetrahydrofuran (THF) in bulk using 2-perbromomethyl-2-oxazoline (TBO)/silver hexafluoride antimonate ($AgSbF_6$) as an initiator.

Introduction.

It is reported that any alkyl halide in presence of silver hexafluoride antimonate ($AgSbF_6$) as cocatalyst initiate the ring opening polymerization of THF between 0-25°C to form poly (tetrahydro furan). Acetyl chlorides[1] and diphenyl chloromethane[2], have been studied as initiator for the polymerization of THF in presence of $AgSbF_6$ as coinitiator. It was therefore, reasoned that TBO, in view of the high electrophilicity of the C-Br bond, could also function as an initiator for the polymerization of THF in presence of $AgSbF_6$ as coinitiator.

Results and discussion.

Polymerization of THF was performed at 0°C for 2 h in bulk. The concentration of coinitiator was 19.6 X 10^{-3} moles/lit which was three times higher than the concentration of initiator. Polymerization was terminated by addition of Na-phenoxide solution in THF followed by stirring overnight. The polymer was washed with conc. NaOH solution and extracted in boiling chloroform. The yield was 4% and Mn was only 700. From UV measurement it was found that there was no phenyl ether end group . The results are shown in Table 1. Even when polymerization was continued for 8 h at 0°C, there was no improvement in yield and Mn.

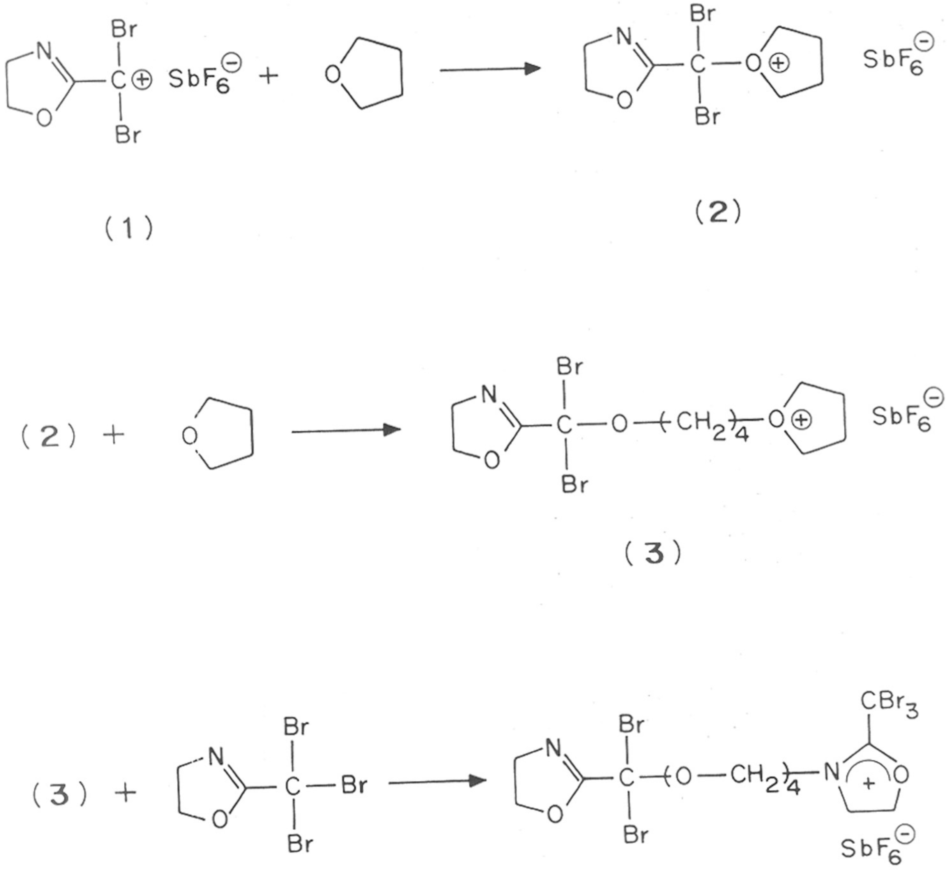
Generally, polymerization of THF yields a polymer of high Mn even when conversion is as low as 5%. However, the present initiating system (TBO/$AgSbF_6$) produced very low Mn. Polymerization of THF always propagates through oxonium ion which reacts with Na-phenoxide quantitatively to produce phenyl ether end groups [3]. However, in the present system the polymer does not contain phenyl ether end

Table : Polymerization of THF in bulk using TBO/$AgSbF_6$ as initiator

Entry no	TBO/$AgSbF_6$	temp.,°C	time, h	yield, %	Mn[a]	no.of phenyl link
1.	1/3	0	2	4	700	nil
2.	1/3	0/+25	2/24	4	850	nil
3.	1/3	0	8	6	900	nil

a) Determined by VPO

groups as indicated by UV measurement. This indicates that the growing polymer does not have a oxonium group as the chain end. This observation is understood based on the fact that the growing oxonium ion (scheme 1) undergoes a facile termination by the oxazoline group of the initiator which is nucleophilic in nature.



Scheme 1 : Polymerization of THF by TBO/AgSbF$_6$ initiating system.

Because of this self termination, phenyl ether linkage was absent in polymer and always low conversion was obtained even when polymerization was allowed to continue for 8 h. TBO, therefore, is not a useful initiator for the ring opening polymerization of THF.

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SYNOPSIS

SYNOPSIS

INTRODUCTION

Multiarmed polymers are interesting macromolecules with unique spatial shapes. They have been synthesized by addition polymerization using any one of the following methods.

(i) living polymerization using a multifunctional initiator

(ii) the coupling reaction of linear living polymers with a multifunctional coupling agent (terminator)

(iii) the linking reaction of linear living polymers with a difunctionalvinyl compound through microgel formation.

The occurrence of random branching in polymers is quite common. Chain transfer reactions cause short and long chain branching in polymerization. Branching can also be introduced intentionally by the use of polyfunctional monomers in end linking polymerizations. Similarly branching can be induced in addition polymerization by using a small amount of difunctional monomer, e.g., divinyl benzene. Branching can also be introduced by graft polymerization.

The properties of branched polymers are quite different from those of linear polymers of similar molecular weight. For example, bulk viscosities as well as concentrated and dilute solution viscosities are lower for branched polymers than for a linear polymers of equivalent molecular weight.

There is need to relate the type and degree of branching in a polymer with its physical properties in solution or melt. During the synthesis of branched polymers, frequently one obtains mixture of branched and unbranched polymers. The branched and unbranched polymers can have widely differing molecular weights and distributions. Also, the frequency of branches and the segment lengths between branch points can vary.

branched and unbranched polymers can have widely differing molecular weights and distributions. Also, the frequency of branches and the segment lengths between branch points can vary.

Hence, the physical properties of such materials represent an average of the properties of all the different species present. Such great diversity poses a problem with regard to the quantitative interpretation of the effects of branching. Thus, it is desirable to test a theory with the simple possible system. For branched polymers, this is a macromolecule with a single branch point with all the branches being of equal molecular weight, i.e., a star branched polymer in the simplest possible system.

The first successful attempt of model star-branched polymer synthesis was that of Schaefgen and Flory[1] in 1948. They were able to synthesize four and eight armed polyamide stars by condensation polymerization. The M_w/M_n ratio for these star branched materials was calculated to be between 1.2 and 1.37. For identical molecular weights, the model branched polymers exhibited lower viscosities, both in the melt and in dilute solution, than the equivalent linear materials.

The preparation of star branched polymers by the use of polyfunctional chlorosilanes in conjunction with anionic polymerization was first shown to be a feasible concept by Morton, Helminiak, Gadkary and Bueche[2] in 1962. Using methyltrichlorosilane and tetrachlorosilane in conjunction with polystyryl lithium in benzene, they were able to prepare both three - and four armed polystyrene stars. As a consequence of the termination free nature [3] of this anionic polymerization system, these star branched polystyrenes contained relatively narrow molecular weight distributions.

The polymerization involving the lithium counterion are suitable for star branched polymer formation since organolithium reagents readily undergo metathesis with the electronegatively substituted silanes, e.g.,

$SiX_4 + 4RLi \dashrightarrow SiR_4 + 4LiX$

Thus, if properly performed , this synthesis should allow the predetermined manipulation of molecular architecture with control over molecular weight and molecular weight distributions. This general reaction was subsequently extended following the work of Morton and coworkers[2], to polybutadienes[4,5,6]. Roovers and coworkers[7-12] have synthesized and studied a series of four- and six armed polystyrene and polyisoprene stars using 1,2-bis (dichlorosilyl)- and 1,2-bis (trichlorosilyl) ethane. Roovers work clearly constitutes the most thorough synthesis and characterization of a series of model star-branched polymers.

An alternative method of star branched polymers formation involves the sequential polymerization of the monomers used for arm, followed by the addition of divinyl benzene (termination method). The polymerization of this difunctional monomer produces a microgel nodule which serves as the branch point for the star-shaped polymer. The application of this procedure has led to the formation of star-branched polyisoprenes containing upto a 56 weight-average number of arm[13]. A later extension [13-15]of this procedure led to the synthesis of multiarmed star-branched polyisoprene homopolymers and polystyrene-polydiene block copolymers.

Burchard and coworkers[16,17] have synthesized star branched polystyrenes "the inside out" by building a polyfunctional initiator by reaction of divinylbenzene[18]. Polydisperse polystyrene stars containing upto about 1.7×10^4 arms were obtained. This system indicates a slow and incomplete reaction between both styrene and diene monomers and the poly(divinylbenzyllithium) anions in the poly(divinylbenzene) nodule. This slow initiation reaction appears to be mainly due to steric factors.

Objectives of the present investigation

The objectives of the present investigations are

(1) To explore the use of 2-perbromomethyl-2-oxazoline as a multifunctional initiator for the polymerization of 2-methyl-2-oxazoline to star branched polymers and there characterization.

(2) To explore the possibility of using 2-perbromomethyl-2-oxazoline as a coupling agent for polyisoprene initiated by n.BuLi. Isolation of branched polyisoprene and its characterization by GPC using multiple detectors was aimed.

(3) To explore the possibility of using 2-perbromomethyl-2-oxazoline as a multifunctional initiator for isobutyl vinyl ether via cationic polymerization.

Outline of the thesis

The present thesis titled 'Synthesis and characterization of branched polymers' is divided into six chapters.

Chapter 1

SECTION A

This introductory chapter briefly surveys the synthesis of poly(n-acylethylenemine) by living cationic ring opening polymerization. Extensive literature based on the diverse initiators used for the living polymerization of 2-alkyl-2-oxazoline are presented. A general background on kinetics and mechanism of polymerization are included. Finally literature on end functionalization, synthesis of macromonomers, random and block copolymerization are discussed very briefly.

SECTION B

This introductory chapter discusses the synthesis of star shaped polymers by living polymerization techniques. Extensive literature on the synthesis of star shaped polymers by initiation method as well as termination method using (a) living anionic polymerization technique (b) GTP technique (c) living cationic polymerization technique are presented. A general background on properties and applications of star shaped polymers are also discussed.

SECTION C

This introductory chapter briefly surveys the synthesis of poly(isobutylvinylether) by living cationic polymerization. Extensive literature based on the diverse initiators used for the living cationic polymerization of vinyl ethers has been presented. A general background on kinetics and mechanism of polymerization is included. Controlled polymer synthesis including synthesis of star polymer by living cationic polymerization is discussed .

Chapter 2

The objective and scope of the present investigation are described in this chapter.

Chapter 3

This chapter deals with the synthesis of branched poly(N-acylethyleneimine) using 2-perbromomethyl-2-oxazoline as initiator and their characterization. 2-methyl-2-oxazoline was exhaustively brominated by NBS to give 2-(perbromomethyl)-2-oxazoline[19](TBO).

The structure of TBO was confirmed by spectral and elemental analysis. TBO smoothly initiates the ring opening polymerization of 2-methyl-2-oxazoline in refluxing acetonitrile. It has been shown that the polymerization system is living in nature.

End group analysis by ion selective electrode titration and *in situ* proton nmr study showed that the polymer thus formed has a three arm star branch shaped structure. The presence of oxazoline groups from initiator in the polymer chain was established by potentiometric titration. This established that every polymer chain has, on an average, one oxazoline group. Thus under the present experimental conditions, the oxazoline group of the initiator does not undergo any ring opening reaction. The interesting feature of this polymer is that it has one reactive oxazoline functionality at the core and three oxazolinium ions at the chain end.

Chapter 4

This chapter deals with the synthesis of three arm star polymers of isoprene by termination of the living anionic chain ends using 2-perbromomethyl-2-oxazoline as the terminating agent. Polymerization of isoprene using n-BuLi as initiator under positive pressure of nitrogen as well as under reduced pressure (10^{-6} torr) are discussed. These polymeric isoprenyl anion were terminated by 2-perbromomethyl-2-oxazoline. A known amount of pick out was collected in a side arm which was subsequently sealed off from the break seal apparatus. The pick out was analyzed by SEC and a third of TBO was added as a toluene solution to the break seal ampule Star polymer was precipitated in methanol and analyzed by SEC .

Chapter 5

This chapter deals with the synthesis of poly isobutyl vinyl ether using 2-(perbromo methyl)-2-oxazoline (TBO) as initiator. Search for a suitable experimental condition, where TBO initiates polymerization of isobutyl vinyl ether via living cationic polymerization techniques is discussed. It was observed that TBO coupled with KI induce living polymerization in CH_2Cl_2 as solvent at -40°C in the presence of ZnI_2 cocatalyst. The kinetics of polymerization was described. The reaction showed all the characteristics of living polymerization using classical HI/ZnI_2 initiator system[20].

Chapter 6

This chapter summerizes the results and describes the silient conclusions of the investigations reported in the thesis.

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