SYNTHESIS POLYMERIZATION AND CHARACTERIZATION OF PROTECTED ACRYLAMIDES

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BY

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DEDICATED TO MY PARENTS

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(ARNAB DASGUPTA)

DECLARATION

Certified that the work incorporated in this thesis **"Synthesis Polymerization and Characterization of Protected Acrylamides"** submitted by Mr. Arnab Dasgupta was carried out by the candidate under my supervision. Such materials as has been obtained from other sources has been duly acknowledged.

S. Sivaram
(S.Sivaram)
Research Supervisor

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ABSTRACT

This thesis presents the results of the studies on the effect of silyl substitution of the amide hydrogen(s) on the polymerization of acrylamide. Silylation brings about a major change in the polarity of acrylamide resulting in its solublity in non-polar organic solvents. The synthesis and characterization of four silylated acrylamide monomers have been reported. These monomers are N-trimethylsilylacrylamide (TMSAm), N,O-bis(trimethylsilyl)acrylamide (BTSAm), N-tert-butyldimethylsilylacrylamide (TBDMSAm), and N-methyl,N-tert-butyldimethylsilyl acrylamide (MTBDMSAm). The tautomeric structure of the monomers were established by NMR spectroscopy.

Solution polymerization of TMSAm and BTSAm were studied. Homopolymers derived from TMSAm and BTSAm were isolated and characterized by NMR. The silylated polymer could be easily hydrolyzed to poly(acrylamide). The kinetics of solution homopolymerization of silylated acrylmides were studied.

The reactivity of TMSAm, BTSAm and TBDMSAm towards copolymerization with styrene in benzene under free radical polymerization technique were examined. Based on compositional analysis of copolymers (^{1}H NMR and elemental analysis) reactivity ratios were computed. The silylated acrylmides exhibit a different reactivity pattern as compared to acrylamide. The reactivity ratio values are tabulated below:

Monomer (M_1)	Solvent	Temperature	r_1	r_2
TMSAm	benzene	50°C	0.13	0.57
TMSAm	benzene	80°C	0.18	0.89
BTSAm	benzene	50°C	0.28	0.47
BTSAm	benzene	80°C	0.20	0.68
TBDMSAm	benzene	80°C	0.04	0.68

The monomer sequence distribution of copolymers was established using ^{13}C NMR spectroscopy. The thermal behavior of the copolymers were studied using TGA and DSC. Attempts to anionically polymerize the monomers BTSAm and MTBDMSAm were unsuccessful.

GLOSSARY

TMS	trimethylsilyl
TBDMS	tert-butyldimethylsilyl
TMSAm	N-trimethylsilyl acrylamide
BTSAm	N,O-Bis(trimethylsilyl) acrylamide
TBDMSAm	N-tert-butyldimethylsilyl acrylamide
MTBDMSAm	N-methyl,-N-tert-butyldimethylsilyla acrylamide
BdTMS	butadienyloxy silane
GTP	group transfer polymerization
AIBN	2,2'-azobisisobutyronitrile
BPO	benzoyl peroxide
THF	tetrahydrofuran
DMF	N,N-dimethylformamide
DMSO	Dimethyl sulfoxide
k_d	Rate contstat for initiator decomposition
k_p	Rate constant for chain propagation
k_t	Rate constant for chain termination
R_p	Rate of polymerization
S/A	Styrene/acrylamide
r_1	reactivity ratio of this monomer 1 (M_1)
$[\eta]$	intrinsic viscosity
η_S	number average sequence length of styrene in the copolymer

η_A	number average sequence length of acrylamide in the copolymer
R	run number: average number of segments of either type of monomers per every 100 monomer units
T_g	Glass transition temperature
MW	molecular weight
M_w	Weight average molecular weight
M_n	Number average molecular weight
MWD	molecular weitht distribution.

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CHAPTER - I

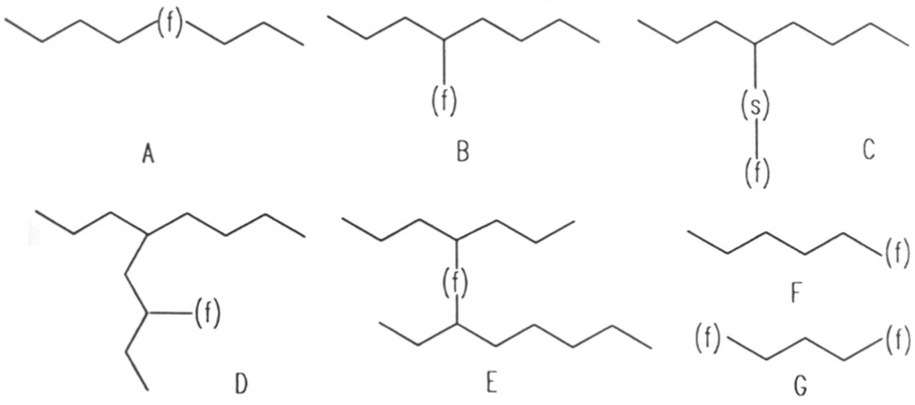
CHAPTER I:

PROTECTION AND POLYMERIZATION OF FUNCTIONAL MONOMERS:

1.1. Introduction:

By definition, a functional group is a moiety attached to a molecule which performs a function in terms of the reactivity and/or the physical properties of the molecule bearing it. Monomers which contain such functional groups are known as functional monomers. Thus $CH_2=CHX$ is a functional monomer where X is the functional group.

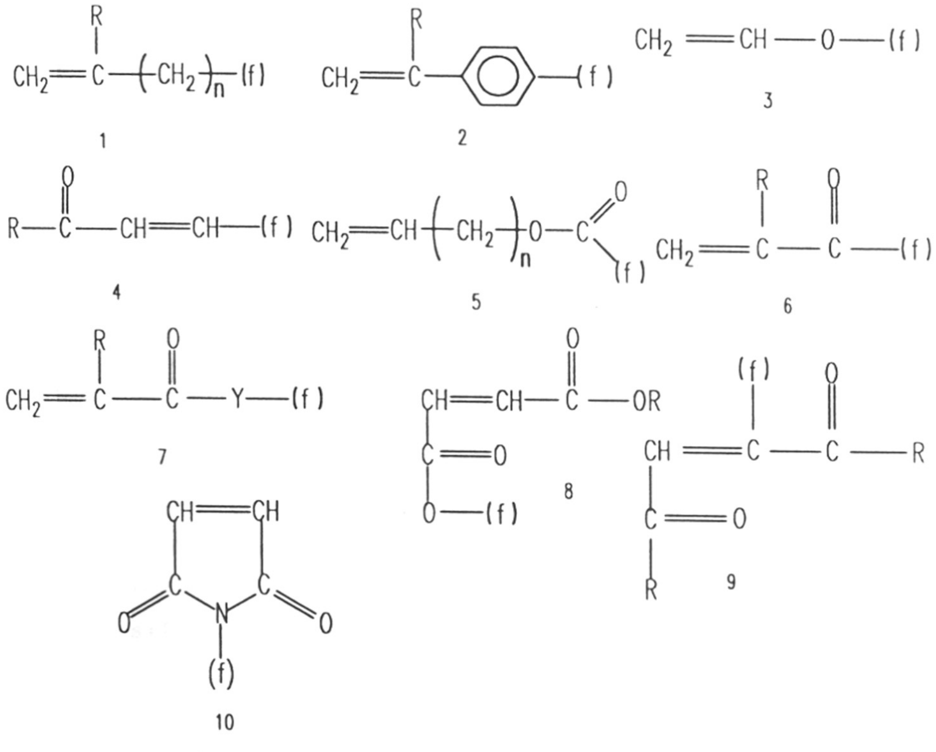
A functional group can be introduced onto a polymeric chain by (a) incorporation during the synthesis of the chain itself through polymerization and copolymerization of monomers containing the desired functional group (b) chemical modification of a suitably non-functionalized polymer chain, and (c) by a combination of (a) and (b). The functional polymers thus synthesized are a useful class of materials where the physical and mechanical properties of the polymer is combined with the property of the functional group. Scheme-1.1 shows the various ways a functional groups (f) may be distributed in a macromolecule.



Scheme-1.1

The functional group (f) can be a part of the repeat unit and built into the polymer backbone (Type A); it may be attached directly (Type B) to the polymer backbone or by means of a spacer (Type C). In a homopolymer of a functional monomer the functional group (f) is attached to every unit and in polycondensates or copolymers it may have an alternate or random distribution. Types D and E respectively represent attachment of (f) to side chains in grafted copolymers and in crosslinks respectively. Types F and G are models of polymers endcapped with functional endcapping agents.

All typical functional polymers are prepared by polymerizing a polymerizable function (p) characterized by the presence of a double bond C=C. The functional groups (f) are bound with (p) either directly (f)-(p), or by means of a spacer(f)-(s)-(p). Using this kind of a monomer, one can make linear homopolymers and statistical copolymers of the type B and C or graft copolymers of type D (scheme 1). More than one functionality may also be present in the same monomer. Monomers containing two or more polymerizable functions (p) can be exploited either for the synthesis of functional polymers of the type B or C or for crosslinked polymer bearing a functional moiety (type E). The most common types of polymerizable functions bearing a functional group (f) are shown in Scheme-1.2 (spacers are not given)



Scheme-1.2

Monomers bearing vinyl (1, R=H, n=0), isopropenyl (1, R=Me, n=1) or allyl (1, R=H, n=1) groups, styrene type functions (2, R=H,Me), vinyloxy groups (3), α,β-unsaturated ketone moiety (4, R=alkyl), vinyl or allyl esters of carboxylic acids (5, n=0,1), acryloyl or methacryloyl (6, R=H,Me), acryloyloxy or methacryloyloxy (7, R=H,Me Y=O) and acryloylamino or methacryloylamino groups (7, R=H,Me, Y=NH), moieties of cinnamic (4, R=OR', NHR') or maleic acids (8,9; similarly moieties of itaconic and mesaconic acid may be included) or maleic imide (10) are characteristic monomers. Other functional monomers may be synthesized by alkenylation of functionalized moieties with linear dienes, cyclic dienes or isoprenoid alcohols[1]

Among the different approaches to functional polymer synthesis, polymerization of protected functional monomers has attracted considerable attention in recent years. There are two major reasons for this increased attention. Firstly, the polymerization technique may not be compatible with the unprotected monomer since the functional group may be reactive towards the initiator and/or the propagating end; and secondly, it may be possible to chemically modify the polymer obtained by polymerizing the protected monomer, which might not be feasible with the polymer formed from the unprotected one. However there are certain other reasons for using a monomeric precursor and not the monomer as such for the synthesis of some particular polymers. For example, a derivatized functionality may allow one to achieve a desired tacticity and/or an improved copolymerizability under certain circumstances which the monomer as such is not capable of. In the following sections the protection and vinyl polymerization of functional monomers by various polymerization techniques will be reviewed. Emphasis will be more on the use of silyl protection. The specific characteristics of silicon (electropositivity higher than that of carbon, strong affinity for oxygen and fluorine , accessible 3d-orbitals, β-effect) have made organosilicon derivatives extremely useful in synthetic organic and polymer chemistry; particularly in the fields of selective activation of reagents and substrates by replacing specific hydrogens with an appropriate silyl group and functional group protection[2].

1.2. Free Radical Polymerization:

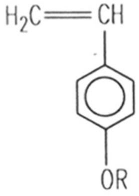
Free Radical Polymerization is the most extensively utilized technique for vinyl polymerization. In free radical polymerization reactions protection of functional group(s) is not always a prerequisite. However, for many functional monomers it is generally practised. A classic example is the synthesis of poly(vinylalcohol) by polymerization of vinyl acetate. The various functional monomers which have been protected or derivatized for the purpose of conveniently polymerizing them using free radical initiators will be discussed in the following section.

1.2.1. Synthesis of polymers containing hydroxyl (-OH) functionality:

1.2.1.1. Poly(vinyl alcohol): Among the aliphatic monomers the protection of vinyl alcohol is the most prominent example. The very non-existence of the vinyl alcohol monomer (the tautomer, acetaldehyde, is the stable form; however, traces of vinyl alcohol have been detected[3]) makes it necessary to synthesize vinyl acetate, the acetyl protected vinyl alcohol, its polymerization and deprotection to poly(vinylalcohol). Poly(vinylalcohol) (PVA), a polyhydroxy polymer, is the largest volume synthetic water soluble resin produced in the world. The discovery of PVA dates back to 1924 when Herrman and Haehnel added alkali to a clear alcoholic solution of poly(vinylacetate) and obtained the ivory coloured poly(vinylalcohol). Staudinger studied the reversible transformation between alcohol and poly(vinylacetate) via esterification and saponification. The first scientific reports on poly(vinylalcohol) were published in 1927[4]. There are also reports on the synthesis of syndiotactic poly(vinylalcohol) by hydrolysis of poly(vinyl trifluoroacetate)[5], formate[6], and acetate[6].

The other class of monomers which could give poly(vinylalcohol) on polymerization followed by deprotection are the vinyltrialkylsilylethers. Free radical polymerization of these monomers does not seem to have been studied. Numerous vinylalcohol copolymers have also been prepared. Copolymers with ethylene and methylmethacrylates have found commercial utility[7-11].

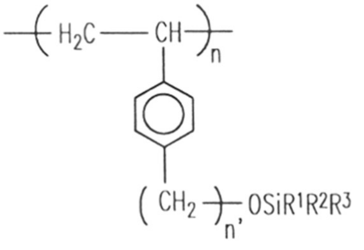
1.2.1.2. Poly(4-vinylphenol): Poly(4-vinylphenol)(1.1a) and other polyhydroxystyrenes are useful as curing agents for epoxy resins, as polymeric adsorbents for the removal of organic material from aqueous waste and as matrix resin for a photoresist system[12]. These monomers are known to be inhibitors or retarders for radical chain polymerization, and therefore their radical polymerization is expected to proceed with difficulty. Although poly(4-vinylphenol) polymers with molecular weight in the range of 10^3 - 10^4 are reported[13-17], it is difficult to obtain poly(1.1a) of high MW (greater than 10^5) by radical polymerization. Furthermore, the resulting poly(1.1a) seems to be branched. These difficulties have been partially overcome by a protection of the phenol functionality during the polymerization, followed by removal of the protecting group. Polymerization of acetoxy-(1.1b) and benzoyloxy-(1.1c) protected 4-vinylphenols have previously been reported. 1.1(b) and 1.1(c) could be readily polymerized with radical initiators to give high molecular weight polymers. However, it has been observed that the resulting polymers could not be completely deprotected under reasonably mild conditions[18-20]. Frechet and coworkers have reported the potential utility of the t-butoxycarbonyl group as a phenol protecting group in polymerization[21]. Soluble poly(1.1a)s with M_n values of 3-6 x 10^4 have thus been prepared by the cationic or radical polymerization of t-butyl p-vinylphenyl carbonate (1.1d) followed by the thermolysis. The t-butoxycarbonyl group could be removed cleanly and quantitatively from the resulting polymer by thermolysis at 200°C. Although the radical and cationic polymerization of p-(benzyloxy)-styrene(1.1e) and p-(trimethylsilyloxy)styrene(1.1f)have been briefly described, the data given were not sufficient to show the usefulness of these protecting groups[22].



a. $R = H$
b. $R = COCH_3$
c. $R = COC_6H_5$
d. $R = OCOOBu^t$
e. $R = OCH_2C_6H_5$
f. $R = OSiMe_3$

1.1 (a-f)

Some alkoxysilyl substituted styrene derivatives were synthesized by Manami and Nishizaki[23] and polymerized with free radical initiators by Jenkins and his coworkers[24]. The latter group also examined the hydrolytic behavior of the resulting polymers. These results indicate facile radical initiated polymerization of the monomers with Si-OR bonds. In a later report, Madit et.al. have described the synthesis of homo and copolymers of a series of siloxystyrenes[25]. Poly(p-trialkylsiloxystyrene), poly(p-trialkylsiloxyα-methylstyrene) and poly{p-[2-siloxyethyl]styrene} polymers (1.2a-e) were prepared where the silyl groups are trimethylsilyl and tert-butyldimethylsilyl.

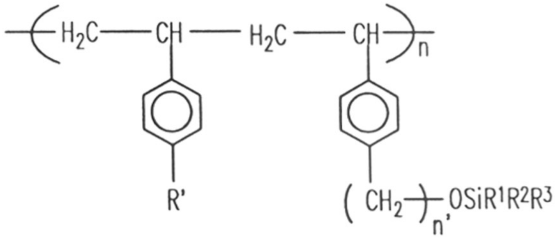


1.2 (a-e)

a. $R=H$, $n'=0$, $R^1=R^2=R^3=CH_3$
b. $R=H$, $n'=0$, $R^1=R^2=CH_3$, $R^3=SiMe_3$
c. $R=CH_3$, $n'=0$, $R^1=R^2=R^3=CH_3$
d. $R=CH_3$, $n'=0$, $R^1=R^2=CH_3$, $R^3=C(CH_3)_3$
e. $R= H$, $n'=2$, $R^1=R^2=CH_3$, $R^3=C(CH_3)_3$

This series or monomers were polymerized by the free radical or cationic polymerization of the corresponding monomers.

Poly{[p-2(trimethylsiloxy)ethyl]styrene]}-- co --[p-(2-hydroxyethyl)styrene]} (1.3a) was synthesized by anionic polymerization of the corresponding trimethylsilylated monomer, followed by hydrolysis of the resulting polymer. Poly{[p-[2-trimethylsiloxy)ethyl]styrene]-co-[p-(tert-butoxycarbonyloxy)- styrene]} (1.3b) were prepared by free radical polymerization of the corresponding monomers.



1.3 a: $R' = CH_2CH_2OH$, $n' = 2$, $R^1 = R^2 = R^3 = CH_3$

1.3 b: $R' = OCO_2Bu^t$, $n' = 0$, $R^1 = R^2 = R^3 = CH_3$

Recently Uhrich et.al. have reported successful homo- and copolymerization of 4-((trimethylsilyl)oxy)styrene (1.1f) and the deprotection of the polymer to generate poly(4-vinylphenol) and its copolymers[26]. The poly(hydroxystyrene)s, could be easily synthesized following the silyl protection and deprotection methodology and establishes the silyl group as superior to other protecting groups. For example, incorporation of silicon into the polymers gives increased thermal stability and reduced weight loss after post exposure bake as compared to resists formulated with poly([(tert-bytoxycarbonyl)oxy]styrene sulfone)[27].

1.2.2. Synthesis of polymers containing thiol (-SH) functionality:

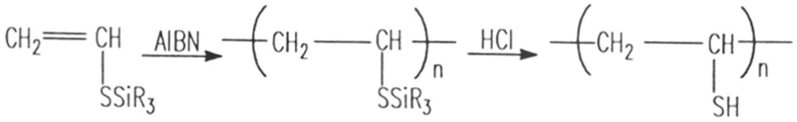
Free radical polymerization of monomers containing the thiol functionality is not possible because of the reactivity of the monomers as chain transfer agents. The mercaptan moiety needs to be protected by a blocking group, which can subsequently be removed quantitatively under mild conditions. A number of vinyl mercaptan derivatives have been evaluated, including vinyl thioacetate[28,29], vinyl thiobenzoate[30], vinylmercaptals[31,32] methacryloyloxy alkyl isothiuronium salts[33], S-vinyl-O-alkylthiocarbonates[34], and S-vinyl-N,N-dialkyldithiocarbonates[35]. Most of these protective groups are removed by alkaline hydrolysis. Since autoxidation of mercaptans is extremely rapid in basic media[36], this technique usually yields crosslinked insoluble polymers. Convenient synthesis of soluble poly(vinylmercaptan)s could be achieved by using S-vinyl-O-tert-butylthiocarbonate as the precursor. The tert-butyloxycarbonyl blocking group could be removed by either acid hydrolysis or thermolysis under conditions which minimize the oxidation of the liberated mercaptan to disulfide. The monomer S-vinyl-O-tert-butylthiocarbonate (M_2) could be conveniently copolymerized with styrene ($r_1 = 3.0$, $r_2 = 0.3$), methylmethacrylate ($r_1 = 1.4$, $r_2 = 0.17$) and vinylacetate ($r_1 = 0.04$, $r_2 = 11.0$). Copolymerization with N-vinylpyrrolidone ($r_1 = 0.12$ and $r_2 = 3.94$) or N-isopropylacrylamide ($r_1 = 1.16$, $r_2 = 0.3$) resulted in polymers which are water soluble in the protected stage.

The sulphur analog of 4-vinylphenol, i.e. 4-vinylthiophenol is also difficult to polymerize by radical vinyl polymerization[36,37]. Radical polymerization of this monomer has not been reported. However there are reports on the protection of aliphatic and benzylic thiol groups and their polymerization by free radical method. A series of methyl vinyl thiosilanes, $(CH_3)_{4-n}Si(SCH{=}CH_2)_n$ ($n = 1$-3), were synthesized by the reaction of the corresponding methylchlorosilanes and vinylthiomagnesiumbromide. Free radical polymerization of these monomers have been studied.[38]

$$(CH_3)_{4-n}SiCl_n + n\,CH_2{=}CH{-}SMgBr \longrightarrow (CH_3)_{4-n}Si(SCH{=}CH_2)_n + n\,MgBrCl$$

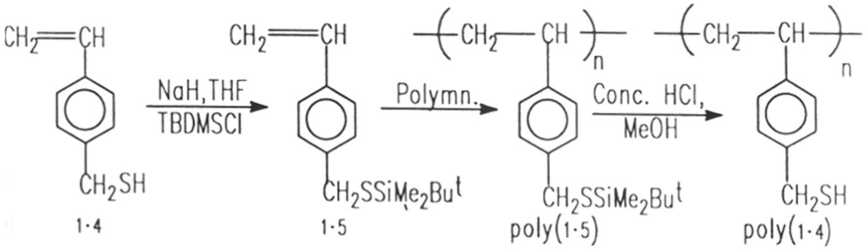
Scheme-1.3

The radical polymerization of di- and trivinylthiosilanes seemed to involve cyclopolymerization. Homopolymer of trimethylvinylthiosilane was hydrolyzed to poly(vinylmercaptan) by acidic hydrolysis.



Scheme-1.4

Apart from vinylmercaptans, 1-(4-mercaptomethylphenyl)ethylene(1.4) has also been polymerized[39]. The -SH functionality in the monomer was protected by tert-butyldimethylsilyl group. The tert-butyldimethylsilyl thiomethylstyrene (1.5) so formed was then polymerized by AIBN at 80°C (Scheme-1.5).

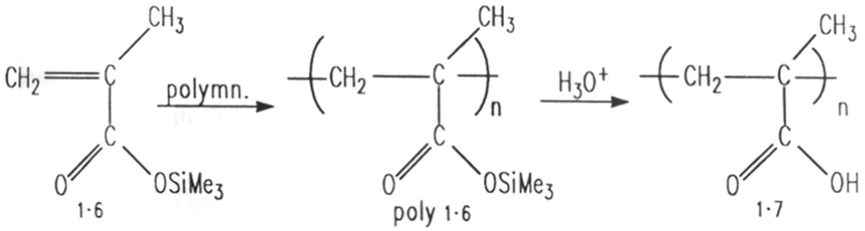


Scheme-1.5

Solution of the polymer was treated with conc. HCl at room temperature for 2 h and the mixture was poured into methanol to get the poly{1-[4-(mercaptomethyl)phenyl]ethylene} in 75% yield.

1.2.3. Protection and polymerization of acrylic acid monomers:

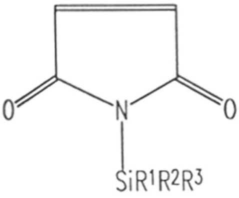
Although acrylic acid can be conveniently polymerized as such by free radical initiators, there are reports where trimethylsilyl or tert-butyldimethylsilyl groups have been used to protect the carboxylic acid functionality prior to radical polymerization, primarily for the purpose of getting some control on the tacticity of the resulting polymer.



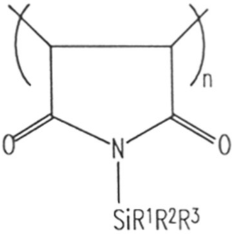
Scheme-1.6

1.2.4. Poly(N-trialkylsilylmaleimide)s:

Organic soluble homopolymers of (N-trialkylsilyl) maleimides (RSiMI, 1.11, where R= Me_3Si, Bu^tMe_2Si, and $C_6H_{13}{}^tMe_2Si$) have been synthesized and polymerized using free radical initiators by Matsumoto et. al[44]. High molecular weight polymers were obtained which were soluble in organic solvents such as benzene and have excellent thermal stability. The hydrolysis of poly(RSiMI)s leads to quantitative formation of polymaleimide (1.12). Hydrolysis required mild conditions for the trimethylsilyl derivative and slightly harsher conditions for deprotection of the bulkier silyl groups.



1.11



1.12

1. $R_1 = R_2 = R_3 = SiMe_3$
2. $R_1 = R_2 = SiMe_3$;
   $R_3 = SiMe_2Bu^t$
3. $R_1 = R_2 = SiMe_3$;
   $R_3 = SiMe_2C_6H_{13}{}^t$

An ESR spectroscopic study of the kinetics of polymerization reveals that an increase in the size of the silyl or alkyl N-substituent induces reduced polymerization reactivity i.e. decrease in the yield and molecular weight of the polymers[45].

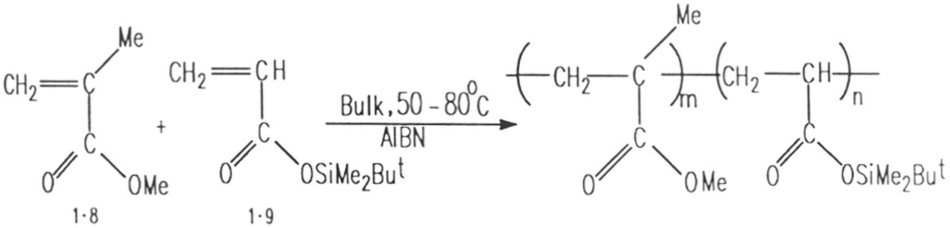
1.2.5. Protection and polymerization of monomers containing aldehyde and ketone functionality:

The silyl enol ethers of aldehydes and ketones have been often employed as useful intermediates in various organic syntheses[46-49]. Therefore polymers of such silyl enol ethers which will have a pendent silyloxy group, a reactive functionality for various synthetic purpose, are also likely to be useful in macromolecule syntheses.

The free radical homo and copolymerizabilities of silyl enol ethers of acetophenone[50,51] and of methyl vinyl ketone[52] have been well studied by Nagai and his coworkers. The homopolymerization of silyl enol ether of acetophenone, namely, α-trimethylsilyloxystyrene (TMSST,1.13) was unsuccessful with both radical and cationic initiators under various conditions. The lack of homopolymerizability of TMSST has been ascribed to a steric effect owing to two bulky substituents at the same carbon atom of the vinyl group.

In an attempt to make poly(methacrylic acid) supports for rhodium catalysts, Chapman and Billingham studied the radical copolymerization of trimethylsilylmethacrylate (1.6)[40]. The monomer was prepared by reacting methacrylic acid with hexamethyldisilazane[41]. Polymerizations was done at 60°C using AIBN initiator in toluene. ^{13}C NMR spectra were recorded in DMSO-d_6. Bernoullian propagation was observed in which heterotactic triads are slightly favoured whereas some polymers synthesized in aqueous solutions (10% solution, AIBN 80°C) were more syndiotactic.

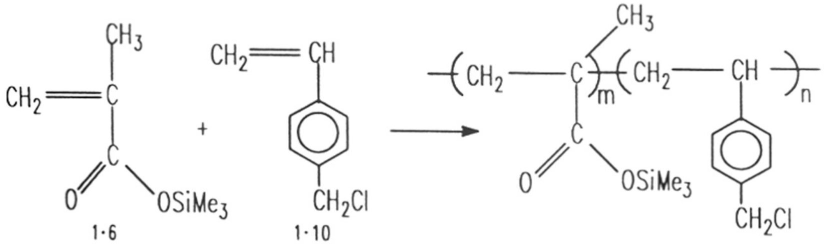
The silyl protected acrylic acid namely tert-butyldimethylsilylacrylate (1.8) was copolymerized with methylmethacrylate (1.9) in bulk at 50°C, 60°C and 80°C using AIBN initiator (Scheme-1.7).



Scheme-1.7

The reactivity ratios for tert-butyldimethylsilylacrylate (M_1) and methylmethacrylate (M_2) were $r_1 = 0.44, 0.64, 1.27$ and $r_2 = 0.83, 0.89$ and 0.93 at 50, 60 and 80°C respectively[42].

The copolymers of silylprotected acrylic acids are useful in the protected form also. Thus the copolymer of trimethylsilylmethacrylate (1.6) with chloromethylstyrene (1.10) is a negative electron-beam and deep-UV resist which can withstand erosion in O_2-containing plasma environments.



Scheme-1.8

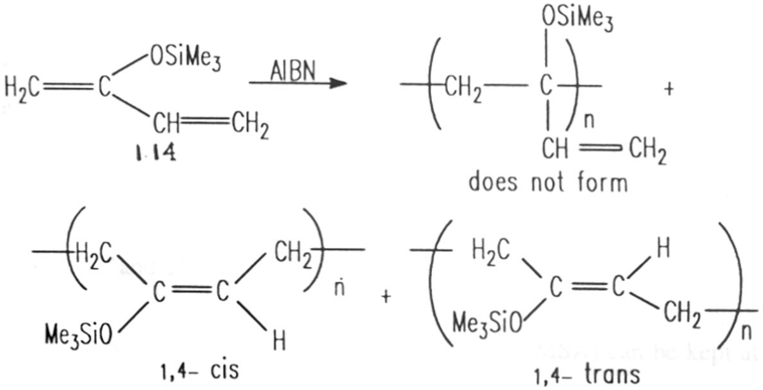
Manipulations of the copolymer composition and molecular weight allows one to have control on the etch resistance and radiation sensitivity properties. Such properties of the copolymers may be tailored depending on the specific lithographic demands[43].

1.13

The copolymerization has been studied with styrene(ST), maleic anhydride(MA), acrylonitrile(AN), fumaronitrile(FN), and diethylfumarate(DEF). Copolymerization were done in bulk at 60°C using AIBN as the initiator. Failure of TMSST to homopolymerize is manifested in its tendency towards alternation in copolymerization with all these monomers excepting DEF, with which copolymerization did not occur. For copolymerization of acrylonitrile (M_1) and styrene (M_1) with TMSST (M_2), the reactivity ratios are reported to be $r_{1(AN)} = 0.05$ and $r_{1(ST)} = 1.48$, whereas $r_2 = 0.0$ in both cases. With MA, AN and FN the attainable molecular weights of the copolymers were of the order 10^6, 10^4 and 10^4 respectively.

2-Trimethylsilyloxy-1,3-butadiene (TMSBD,1.14), the silyl enol ether of methylvinylketone is a conjugated diene having the silyl ether group at the 2-position. Polymers containing TMSBD units, on desilylation were expected to give analogous polymers having carbonyl groups. Besides, a possible synthetic utility of the pendant silyloxy functionality was their use as initiator for polymerization of acrylonitrile in a similar manner as group transfer polymerization, which resulted in the grafting of polyacrylonitrile onto those copolymers[53].

Homo and copolymerization of TMSBD were carried out in dioxane at 60°C using AIBN as the initiator. In homopolymerization, polymers having a M_w,of the order 10^4 were obtained The resulting polymer was soluble in most organic solvents barring MeOH. Like TMSST, with TMSBD also 1,2-polymerization did not occur.



Scheme-1.9

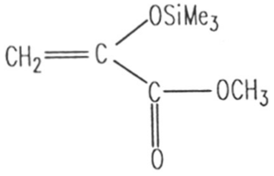
However 3,4-polymerization was found to occur since only one bulky substitution was present. As determined from the ^{1}H NMR, the ratio was 18.6% of 3,4- and 81.4% of 1,4-structures. Copolymerization of TMSBD was studied with styrene and acrylonitrile. The reactivity ratios as determined by Kelen Tudos method were as follows: for styrene(M_1) and TMSBD (M_2), $r_1 = 0.64$ and $r_2 = 1.20$; for acrylonitrile (M_1) and TMSBD (M_2), $r_1 = 0.036$ and $r_2 = 0.065$. Rate of copolymerization and the molecular weight were found to decrease with increasing amounts of TMSBD in the feed. This was similar to the observation for TMSST although decrease in the rate was less steep for TMSBD.

Desilylation of these copolymers were done by treating them with conc.HCl at elevated temperatures. Considerable desilylation was found to occure in a small span of time, but complete desilylation requied prolonged heating. Desilylation was confirmed from the i.r. spectra of the acid treated copolymers. I.r. spectra reveal lactone ring formation during the process of desilylation of copolymers of TMSST; this has been proposed as a method for introducing lactone rings in the polymer chain. On desilylation, copolymers of TMSST and ST gives polystyrene partially substituted with hydroxyl groups. For the TMSBD copolymers, a comparison of the i.r. spectrum with that of a heated (dehydration) sample of poly(vinylmethylketone) indicated that desilylation was accompanied with cyclization. However, if the desilylation is carried out using acetic acid, cyclization did not occur.

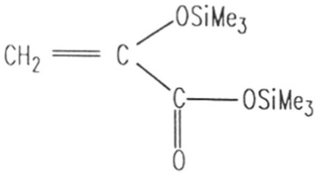
Asada et.al.[52] did not report the ratio of cis-1,4 to trans-1,4 structures of poly(TMSBD). In a recent report Penelle et. al. have investigated the microstructure of poly(TMSBD) made at varying experimental conditions in some more detail using a 500 MHz NMR instrument[54]. According to this report also, 1,2-structure is not observed, and the ratio between 1,4 and 3,4 structure is always close to 82:18. Penelle et. al. have determined that the cis/trans ratio for the two 1,4-structures range from 0.5 to 0.9. That the extent of 3,4-polymerization is much less compared to the 1,4-polymerization has been ascribed to the steric crowding by two bulky groups on the same carbon[55].

1.2.6. Polymerization of functional captodative monomers: poly(methyl α-trimethylsilyloxyacrylate):

Methyl α-trimethylsilyloxyacrylate [$CH_2{=}C(OSiMe_3)COOMe$] (MSA,1.15) is the silyl protected α-hydroxy acrylate, the later being the tautomer of methylpyruvate. The monomer can be conveniently prepared by a one step procedure starting from methylpyruvate and trimethylsilylchloride[55]. Penelle and Verraver have studied the free radical polymerization of MSA.[56]. Unlike TMSST and TMSBD, MSA has a very good free radical homopolymerizability despite its 1,1-disubstitution; polymers with high molecular weight of the order of upto 10^5 could be obtained under standard conditions (AIBN, 50-95°C). Poly(MSA) can be kept at ambient temperature for a long time without any visible change but starts to depolymerize at about 150°C. Tendency to depolymerize has been ascribed to the captodative stabilization of radicals substituted by ester and ether groups[57,58]. Copolymerizability of the monomer however, has not been reported.



1.15

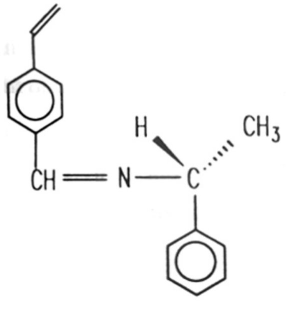


1.16

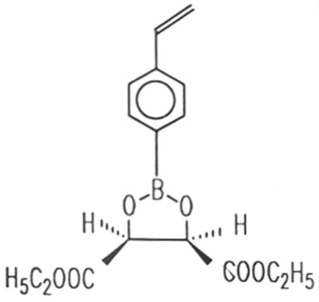
A similar monomer, trimethylsilyl α-trimethylsilyloxyacrylate [$CH_2=C(OSiMe_3)COOSiMe_3$] (SSA,1.16) fails to undergo radical or thermal homopolymerization in solution or in bulk. However it shows some copolymerizability with styrene[59]. This observation is similar to that observed with TMSST and TMSBD (1,2 polymerization does not occur) and is somewhat contradictory to the results with MSA. Probably, the larger size of the silylester group of SSA makes the difference.

1.2.7. Protective group methodology for synthesis of chiral polymers:

De et.al. have explored the protective group methodology for the synthesis of chiral polymer materials[60]. They established the asymetric induction in the backbone of copolymers based on 1,2-disubstituted olefins and 1-substituted olefins. It has been reported that polymer bound functional groups protected in the form of boronic esters[61], acetals (or ketals)[62], and azomethines[63], can be quantitatively deprotected under mild experimental conditions without adversely affecting the polymer structues. De et. al.[60] synthesized two protected chiral monomers namely, N-[(4-vinylphenyl)methylene]R(+)-1-phenylethylamine (1.17) and Diethyl-L-tartrate-O-[(4-vinylphenyl)boronate] (1.18).



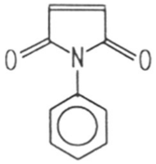
1.17

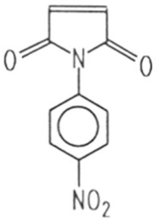


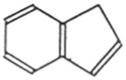
1.18

The monomer 1.17 was synthesized by reacting 4-vinylbenzaldehyde with R(+)-1-phenylethylamine in dry benzene, whereas 1.18 was synthesized by reacting 4-vinylaboronic acid and diethyl-L-tartrate.

The chiral monomers 1.17 or 1.18 were copolymerized with three 1,2-disubstituted vinyl monomers namely, N-phenylmaleimide (1.19), N-(4-nitrophenyl)maleimide (1.20) and indene (1.21).


1.19


1.20


1.21

The chiral template models were then removed quantitatively. Deprotection was done under mild conditions to prevent any racemization/epimerization of the main chain chiral centers during hydrolysis. Complete removal of the template residues were confirmed from ^{1}H NMR and FTIR spectra of the hydrolyzed copolymers. The copolymers obtained (before hydrolysis) showed appreciable optical rotations. The sign of the optical rotations of these copolymers were the same as those of the respective starting monomers. Magnitudes of the specific rotations were found to be dependent on the copolymer compositions and the nature of the 1,2-disubstituted vinyl monomers. The specific rotations were reported to be higher than the chiral monomers alone on their homopolymers. The results suggested asymmetric inductions by the chiral groups on the copolymer chains. However, the existence in solution of a short polymer segment having a helical conformation of a prevailing screw sense that could be responsible for the observed enhancement of the optical rotation was not ruled out.

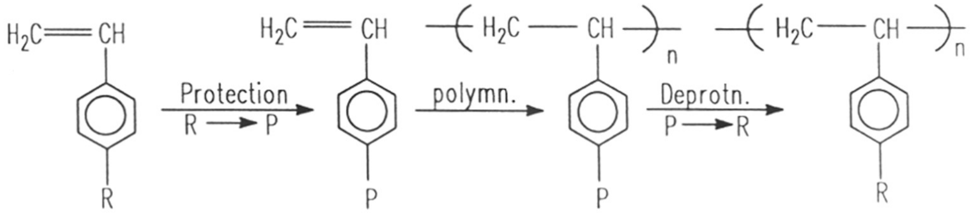
The specific optical rotation values of the hydrolyzed copolymers were found to be lower compared to their template bearing precursors. Copolymers containing 1.19 and 1.20 exhibited negative specific rotations contrary to their precursors which were positively rotating. On the otherhand, 1.20-based copolymers showed positive specific rotations and their magnitudes were higher than those based on 1.19 and 1.20. The specific rotation values were found to be independent of the copolymer compositions.

In contrary to the azomethine based copolymers, 1.18-based copolymers involving diethyltartrate template showed zero or negligible optical activity after removal of the optical residues. Therefore, it was concluded that although the structural requirement for main chain chirality are met, the choice of the chiral auxiliary can be critical in inducing enantioselectivity on the macromolecular chain.

1.3 Anionic Polymerization:

Among the limited number of vinyl monomers amenable to anionic polymerization are conjugated hydrocarbon monomers such as styrenes and 1,3-dienes. Under certain very specific conditions, vinyl pyridines and some alkyl methacrylates can undergo anionic living polymeization without side reactions[64,65,66]. However, monomers with potentially useful functional groups such as hydroxyl, amino, and carbonyl functions are not amenable to polymerization by anionic techniques. This is because these functional groups are incompatible with both anionic initiators as well as the active propagating chain ends.

This difficulty is usually overcome by protecting the functional group and thus preventing it from interfering during the polymerization as shown in scheme-1.10.



R = Functional group ; P = Protected functional group
Scheme-1.10

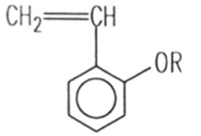
The area anionic polymerization of protected functional monomers has been extensively investigated by Nakahama et.al. who has reviewed the literature available till 1990[67]. Therefore only the more recent literature in this area will be described in the following sections.

1.3.1. Protection and polymerization of monomers containing hydroxyl (-OH) functionality:

The monomers having hydroxyl functionality, which have been so far protected and polymerized by anionic method can be classified into four groups namely, (i) vinyl phenols, (ii) vinylphenylmethanols, (iii) vinylphenylethanols and (iv) hydroxyethyl methacrylates.

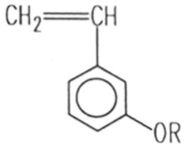
1.3.1.1. Vinylphenols: Only the tert-butyldimethylsilyl group has been found to be useful for protecting the hydroxyl group of vinylphenols which is connected directly to an aromatic nucleus. 2,3,and 4-vinylphenols (1.22-1.24) have been converted into the corresponding tert-butyldimethylsilyl ethers (1.25-1.27) by reacting with tert-butyldimethylsilylchloride (TBDMS chloride) in presence of imidazole in anhydrous DMF.

Successful polymerizations could be achieved for 3 and 4-substitutions with initiators like



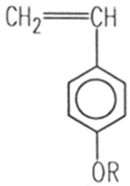
1·22 : R = H

1·25 : R = $SiMe_2Bu^t$



1·23 : R = H

1·26 : R = $SiMe_2Bu^t$

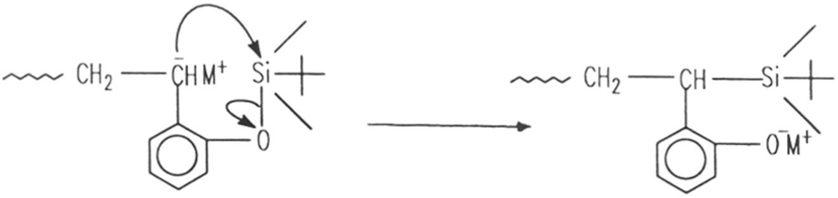


1·24 : R = H

1·27 : R = $SiMe_2Bu^t$

alkyllithium; Li, Na, and K naphthalenides, oligo(α-methylstyryl)dilithium, disodium, and dipotassium, and cumyl potassium. (THF, -78°C)[68,69]

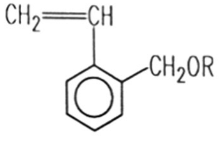
For poly(4-vinylphenol) $\overline{M}_n$s were in the range of 10000 to 100000; and MWD (molecular weight distribution) values were between 1.04 and 1.10; for poly (3-vinylphenol) $\overline{M}_n$s were in the range of 8000 to 54000 and MWDs were between 1.04 and 1.08. The 2-tert-bytyldimethylsilylether of 2-vinylphenol did not undergo anionic polymerization. This has been ascribed to a silyl exchange reaction[70,71]. (Scheme-1.11)



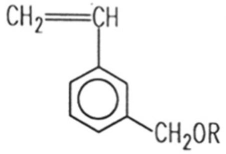
Scheme-1.11

The deprotection of tert-butyldimethylsilyl groups from the polymers was accomplished by treatment of the polymers with 2N HCl in aqueous 1,4-dioxane or with Bu_4NF in THF at 30°C[72,73]. Complete removal of the protecting groups could be confirmed from the IR and ^1H NMR spectra. The SEC analyses of the deprotected polymer indicated that it still retained a narrow MWD.

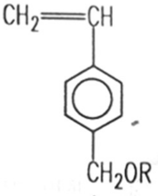
1.3.1.2. Vinylphenylmethanols: Hirao et.al. have investigated the anionic polymerization of tert-butyldimethylsilyl ethers of 2-, 3-, and 4-vinylphenylmethanols[69] (1.28a-1.30a).



1·28 (a,b)



1·29 (a,b)



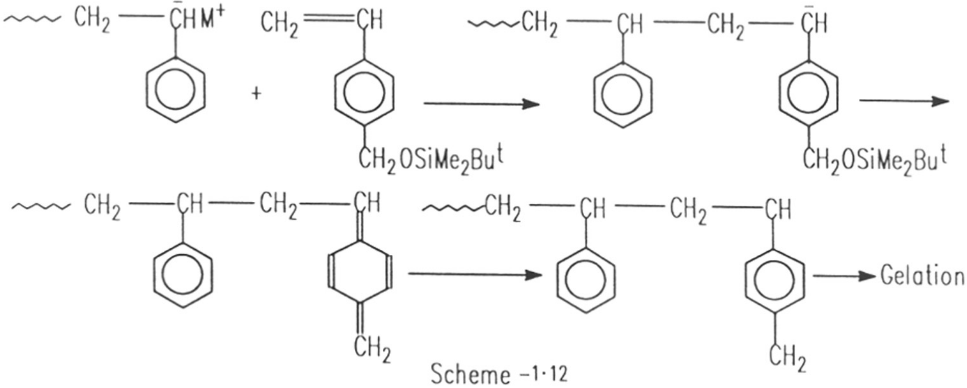
1·30 (a,b)

a: R = H

b: R = $SiMe_2Bu^t$

The monomers were synthesized by the reduction of the corresponding benzaldehyde with $NaBH_4$. Because of the high polymerizability of these monomers, immediately after isolation in a moderately pure form they were reacted with tert-butyldimethylsilyl chloride in presence of imidazole (anhydrous DMF, 0-25°C). The ethers so formed could be distilled under reduced pressure (1.28b-1.30b).

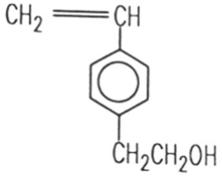
The ortho and para isomers did not undergo appreciable polymerization. The non-polymerizability of these o- and p- isomers and the formation of some crosslinked material has been attributed to the decomposition of the growing anion. (Scheme-1.12)



Scheme -1·12

Thus the carbanion at the polymer chain end may induce 1,6-elimination for the para isomers or 1,4-elimination for the ortho isomer. The intermediate of such an elimination is a very reactive p-xylylene (or o-xylylene), which might react readily with each other resulting in crosslinkings. Unlike the ortho and para isomers the meta isomer (1.29b) could be polymerized by oligo(α-methylstyryl)dipotassium in THF at -78°C. The $\overline{M}_n$s were between 10000 and 54000. MWD was less than 1.20. The polymers were deprotected to regenerate the hydroxyl (-OH) functionality by treatment with $(C_4H_9)_4NF$ or a dilute HCl solution.

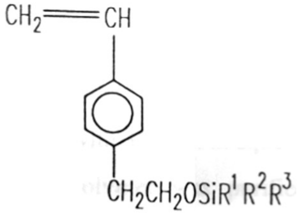
1.3.1.3. Poly[2-(4-vinylphenyl)ethanol]: In 2-(4-vinylphenylethanol) (1.31), the hydroxyl group is separated from aromatic ring by two methylene groups and interacts little with the phenyl ring. Thus (1.31) is an example of a styrene containing alcoholic hydroxyl group.



1·31

Hirao et.al. studied the anionic polymerizability of a series of silyl protected (1.31) monomers[74,75].

2-(4-Vinylphenyl)ethyl]trimethylsilyl ether (1.31a) was obtained quantitatively by the reaction of (1.31) with hexamethyldisilazane. Triethylsilyl(1.31b), dimethyl(i-propyl)silyl (1.31c), dimethyl(t-bytyl)silyl (1.31d) and dimethyl(t-butoxy)silyl (1.31c) ethers of (1.31) were prepared in good yields by treating (1.31) with the corresponding silylchlorides in the presence of imidazole in DMF.



1.31(a-e)

a. $R^1 = R^2 = R^3 = CH_3$

b. $R^1 = R^2 = R^3 = C_2H_5$

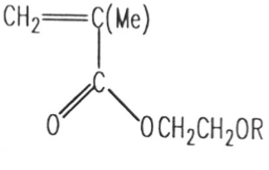
c. $R^1 = R^2 = CH_3$, $R^3 = C_3H_7^i$

d. $R^1 = R^2 = CH_3$, $R^3 = C_4H_9^t$

e. $R^1 = R^2 = CH_3$,
$R^3 = OC_4H_9^t$

The anionic polymerization of all these monomers proceeded well in THF at -78°C with typical initiators such as alkali metal naphthalenes, oligo(α-methylstyryl)alkali metal derivatives and butyllithium. $\overline{M}_n$ values were in the range of 20000 and 69000 and the polymers possessed narrow molecular distributions with values of $\overline{M}_w/\overline{M}_n$ in the range of 1.06-1.16. Thus all silyl groups are suitable for protecting an alcoholic hydroxyl group for anionic polymerization; this is in sharp contrast to the case of protection of hydroxystyrenes with silyl groups, where only the tert-butyldimethylsilyl group is useful. Among the silyl protecting groups used, the trimethylsilyl group is the most labile towards hydrolysis. It is removed completely by aqueous dioxane containing few drops of acetic acid at 25°C. The bulkier groups required little harsher conditions like heating and/or using concentrated HCl or by using Bu_4NF.

1.3.1.4. Protection and polymerization of hydroxyethylmethacrylate: Hydroxyethylmethacrylate (1.32a) was converted to 2-(trimethylsilyloxy)ethylmethacrylte (1.32b).



1.32 (a-d)

a. $R = H$

b. $R = Si(CH_3)_3$

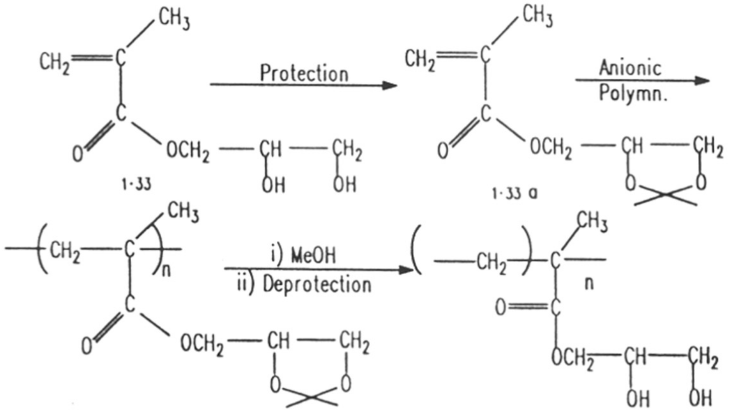
c. $R = SiMe_2Bu^t$

d. $R = CH_2\text{-}O\text{-}CH_3$

below 1.1. In absence of LiCl for poly(1.32c) and poly(1.32d) they were 1.52 and 1.24 respectively. For (1.32c) and (1.32d) $\overline{M}_n$ were in the range of 9000-19000 and 8000-24000 respectively.

The trimethylsilyl group of poly(1.32b) was partially cleaved during treatment with MeOH and was removed quantitatively to regenerate a hydroxy group under very mild condition. On the otherhand the tert-butyldimethylsilyl group of poly(1.32c) and the methoxymethyl group of poly(1.32d) stayed intact during the polymer purification step. The Si-O bond in poly(1.32c) and the acetal linkage in poly(1.32d) were readily cleaved to generate the hydroxyl functionity by treating the polymers with 3N HCl in aqueous 1,4-dioxane solution at room temperature for 24h. The deprotected polymer was purified by reprecipitation from THF-methanol in hexane-EtOH (1:1).

1.3.1.5. Protection and polymerization of 2,3-dihydroxypropylmethacrylate: Mori, et.al. have recently reported the synthesis of poly(2,3-dihydroxypropylmethacrylate) (1.33) having two hydroxyl groups in the repeating unit through anionic polymeization of the protected monomer viz. 2,2-dimethyl-1,3-dioxolan-4-yl methylmethacrylate (1.33a) followed by deprotection[80] (Scheme-1.13).

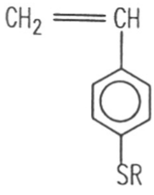


Scheme -1·13

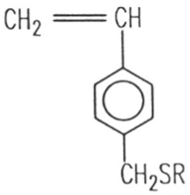
The protected monomer was prepared from isopropylidene glycerol and methacryloyl chloride in benzene in presence of triethylamine, according to a reported method[81]. It was polymerized by 1,1-diphenylhexyllithium in THF at -78°C both in presence and absence of LiCl. The presence of LiCl reduced the rate of polymerization and resulted in the formation of polymers with very narrow molecular weight distribution (1.05). $\overline{M}_n$ values were between 4000 and 26000.

1.3.2. Protection and polymerization of monomers containing thiol (-SH) group:

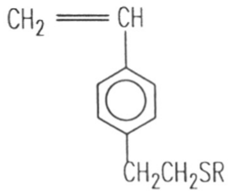
The monomers which contain a thiol group and have been protected and polymerized by anionic method are 4-vinylthiophenol(1.34), (4-vinylphenyl)methyl mercaptan(1.35) and (4-vinylphenyl)ethyl mercaptan(1.36). Thiol groups of these monomers are protected by a tert-butyldimethylsilyl group to form the corresponding TBDMS thioethers.



1.34(a,b)



1.35(a,b)



1.36(a,b)

a: $R = H$

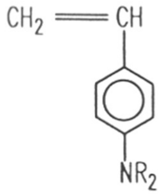
b: $R = SiMe_2Bu^t$

4-Vinylphenyl tert-butyldimethylsilyl sulfide (1.34b) was made by reacting the Grignard reagent from Mg and 4-bromophenyl tert-butyldimethylsilyl sulfide and vinyl bromide in dry ether and in presence of $NiCl_2(Ph_2PCH_2CH_2PPh_2)$. (4-Vinylphenyl)methyl tert-butyldimethylsilyl sulfide (1.35b) and 2-(4-vinylphenyl)ethyl tert-butyldimethylsilyl sulphide (1.36b) could be conveniently polymerized using metal alkyls and naphthalenides at -78°C in THF. But under similar conditions anionic polymerization of 4-vinylphenylmethyl tert-butyldimethylsilyl sulfide did not occur. This observation was similar to the pattern observed with tert-butyldimethylsilyl ether of 4-vinylphenylmethanol and has been explained to occur via similar mechanism[82] (Scheme-1.12).

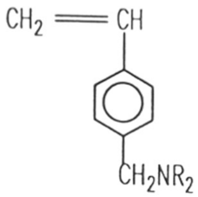
Using highly purified monomers of 4-vinylphenyl tert-butyldimethylsilyl sulfide, polymers having MWD values between 1.11 and 1.13 were obtained. $\overline{M}_n$ values were between 1.3 and 1.7. For poly-(4-vinylphenyl ethyl tert-butyldimethylsilyl sulfide) the observed $\overline{M}_n$ values were in the range of 8000-67000 and MWD values were mostly below 1.1 (excepting for cumyl potassium and potassium naphthalenide initiators when the values were around 1.2). Between poly 4-vinylphenylethyl tert-butyldimethylsilyl sulfide and poly 4-vinylphenylethyl tert-butyldimethylsilyl sulfide the former undergoes crosslinking if exposed to air, while the latter is quite stable.

1.3.3. Protection and polymerization of monomers containing amino group[83-85]:

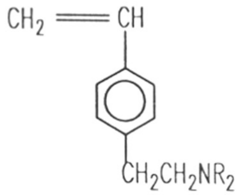
4-vinylaniline (1.37), (4-vinylphenyl)methylamine (1.38) and 2-(4-vinylphenyl)ethylamine (1.39) are the three monomers containing amino groups which have been polymerized using anionic initiators. In order to protect the amine functionality, both the hydrogens were replaced by trimethylsilyl group. Mono-silylation of p-aminostyrene could be done by reacting with hexamethyldisilazane and the monosilylated product could be further silylated by treating with EtMgBr followed by Me_3SiCl. Bis-silylated compounds from (4-vinylphenyl)methylamine and (4-vinylphenyl)ethylamine were prepared by the reactions of Grignard reagents derived from p-chloromethylstryene and p-(2-bromoethyl)styrene with N,N-bis(trimethylsilyl)methoxymethylamine.



1.37(a,b)



1.38(a,b)



1.39(a,b)

a: R = H

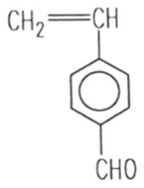
b: $R = SiMe_3$

For all these monomers anionic polymerization using alkali metal alkyls and naphthalenides were good initiators giving polymers having $\overline{M}_n$ in the range of 15000 to 95000 and MWD values between 1.04 and 1.51. MWD values were found to be dependent on the choice of initiators. The silyl substitutions were quite stable during polymerization and isolation of the polymers. They could be easily deprotected by acid hydrolysis.

1.3.4. Protection and polymerization of monomers containing aldehyde (-CHO) group:

4-Vinylbenzaldehydes (1.40) are the representative monomers in this class which has been protected in several forms and polymerized by anionic initiators. Polymerization followed by deprotection of three protected monomers have been studied for the synthesis of poly(4-vinylbenzaldehyde). These are 2-(vinylphenyl)-1,3-dioxolanes, 1,3-dimethyl-2-(vinylphenyl)imidazolidine and N-[(vinylphenyl)methylene] cyclohexamine.

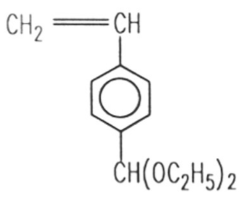
1.3.4.1. Poly(4-vinylbenzaldehyde): 4-Vinylbenzaldehyde (1.40) was prepared in 40-50% yields by the decarboxylation of p-formylcinnamic acid[86] or by a modified Sommelet reaction, starting from p-chloromethylstyrene[87-89]. (1.40) was also synthesized in reasonable yield by the reaction of 4-vinylphenylmagnesium chloride with DMF in THF[87].



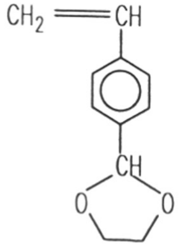
1.40

Some studies have been published on the radical polymerization of the ortho isomer of (1.40) with $BF_3.Et_2O$[91]. Nakahama and his co-workers have studied the possibility of anionic living polymerization of monomers in which the aldehyde group of (1.40) is protected as its acetal-, 1,3-N,N'-dimethylimidazolidine-, or N-cyclohexylimine form[67]. This will be discussed below.

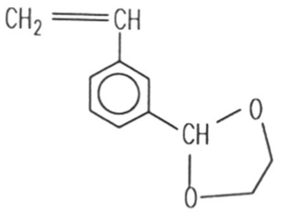
1.3.4.1.1. Anionic Polymerization of 2-(3-vinylphenyl)- and 2-(4-vinylphenyl)-1,3-dioxolane[67]: Acetals are known to be stable to basic and nucleophilic reagents and are cleaved under mild acidic conditions. Diethylacetal (1.40a) and 1,3-dioxolane (1.40b) derivatives of (1.40) were prepared and tested for polymerizability with anionic initiators.



1·40 a

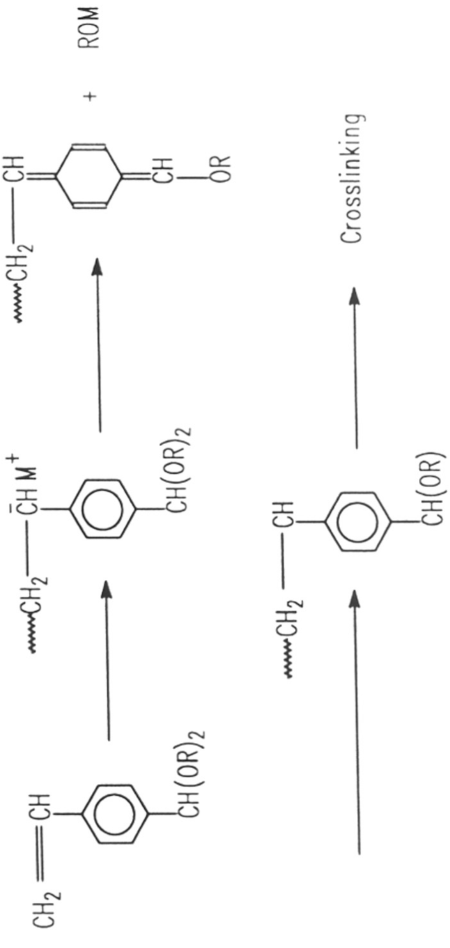


1·40 b



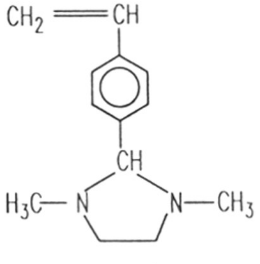
1·40 C

The polymerization of (1.40a) and (1.40b) was carried out in THF at -78°C with lithium-, sodium- and potassium- naphthalenes. The red colour of the reaction mixture disappeared slowly in about 10 min. most likely due to the generation of the reactive p-xylylene intermediate by 1,6-elimination of alkoxide as it happens with silylated 4-vinylphenyl methanol (Scheme-1.14). However, the meta isomer (1.40c) undergoes anionic living polymerization[92]. Poly(1.40c) could be readily and completely converted into poly(3-vinylbenzaldehyde) by treating with 2N aqueous 1,4-dioxane at 30°C. The polymer thus obtained was observed by SEC and VPO to have the predicted MW as well as a narrow MWD[92].


CH2=CH
CH(OR)2
CH2–C̄H M+
CH(OR)2
CH2–CH
CH(OR)
CH2–CH
CH
OR
+ ROM
Crosslinking

Scheme -1·14

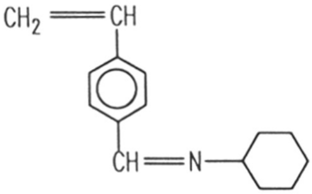
1.3.4.1.2. Anionic Polymerization of 1,3-dimethyl-2-(4-vinylphenyl)imidazolidine[67]: 4-Vinylbenzaldehyde (1.40) was easily converted to the imidazolidine protected monomer (1.40d) in good yield by treatment with N,N'-dimethylethylenediamine.



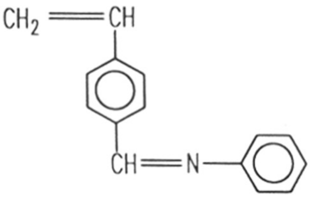
1·40 d

(1.40d) was easily polymerized with lithium-, sodium-, and potassium- naphthalenes in THF at -78°C[93]. Yields of polymers were quantitative in all cases. The imidazolidine group was readily and completely removed at 25°C in an aqueous THF solution under slightly acidic conditions (pH 3 - 5). Agreement of the calculated and observed values of $\overline{M}_n$ (15000 - 100000) and narrowness of MWD (1.04 - 1.19) indicate the living nature of the anionic polymerization of (1.40d). The effectiveness of the N,N'-imidazolidinyl group is thus evident for the protection of the aldehyde group.

1.3.4.1.3. Anionic Polymerization of N-[(4-vinylphenyl)methylene]cyclohexamine: Ziegler and his coworkers demonstrated the interesting result that the N-cyclohexylimine of piperonal was stable to lithiation with butyllithium at -78°C[94,95]. Addition of butyllithium to a C=N bond can be suppressed by careful choice of reaction temperature and probably by the N-substituent of the imine. Hirao and Nakahama carried out the anionic polymerization of the N-cyclohexylimine of 1.40, namely, N-[(4-vinylphenyl)methylene] cyclohexamine (1.40e)[96].



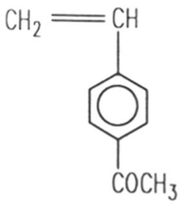
1.40e



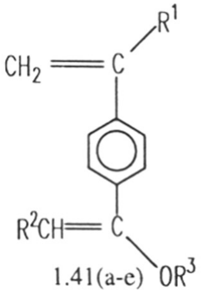
1.40f

The anionic polymerization of (1.40e) readily proceeded in THF at -78°C with potassium naphthalene, cumylpotassium or oligo(α-methylstyryl)dilithium, disodium or dipotassium as initiators. The reaction mixtures were always orange to dark red in colour. Yields of polymers were quantitative in all cases. There was fair agreement between the calculated $\overline{M}_n$s and the values measured by VPO (63000 - 110000). SEC revealed narrow MWDs around 1.06. Deprotection was successfully achieved treatment of the poly(1.40e) at 25°C for 5-20h. with aqueous 1,4-dioxane containing a few drops of concentrated HCl. Choice of the N-substituent in the imine derivative is important since Hirao and Nakahama found that the N-[(4-vinylphenyl)methylene]benzenamine (1.40f), in which the phenyl group is the N-substituent does not undergo anionic polymerization[67].

1.3.5. Protection of the carbonyl functionality: The carbonyl group of 4-vinylacetophenone (1.41) could be protected as silyl enol ether functionalities. Several protected monomers namely, trimethylsilyl enol ether of 4-vinylacetophenone (1.41a), tert-butyldimethylsilyl enol ethers of 4-, 3- and 2-vinylacetophenones (1.41b-d), of 4-vinylpropiophenone (1.42), of 4-(2-propenyl)acetophenone (1.43), and of 4-(2-propenyl)propiophenone (1.44) were synthesized and anionclly polymerized by Hirao et.al.[97].



1.41



1.41(a-e)

a: R_1:H,R_2:Me,R_3:$SiMe_3$

b: R_1:H,R_2:H,R_3:$SiMe_2Bu^t$

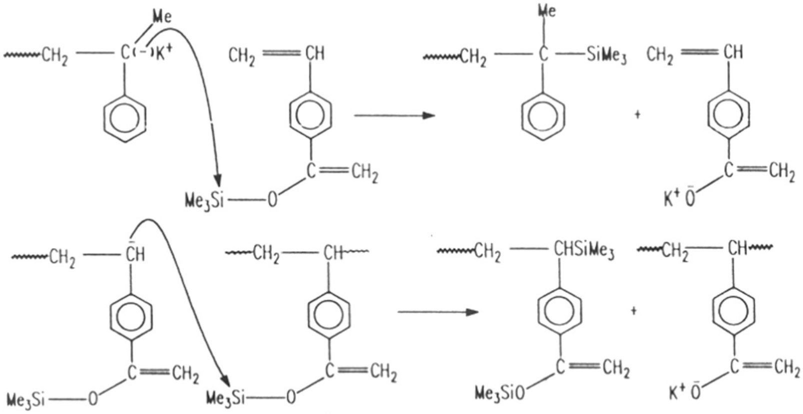
c: R_1:H,R_2:Me,R_3:$SiMe_2Bu^t$

d: R_1:Me,R_2:H,R_3:$SiMe_2Bu^t$

e: R_1=R_2=Me; R_3:$SiMe_2Bu^t$

Among the monomers, 1.41b, 1.41c, 1.41d, 1.41e, and 1.42 underwent anionic living polymerization to afford quantitatively polymers of predictable molecular weights. Novel, well defined triblock copolymers of both ABA and BAB types were also synthesized by sequential polymerization of 2a and 2b and styrene vice versa. On the contrary, attempts to anionically polymerize (1.41) and (1.43) failed under the same conditions. Complete deprotection of the tert-butyldimethylsilyl groups of poly(1.41b) and poly(1.42) to poly(vinylacetophenone)s could be achieved by treatment with either 0.5N HCl or n-Bu_4NF. The resulting poly(vinylacetophenone)s were found to possess narrow molecular weight distributions, almost identical to those of the parent poly(1.41b) and poly(1.42).

The polymerization of trimethylsilyl enol ether of 4-vinylacetophenone (1.41a) was carried out in THF at -78°C with oligo(α-methylstyryl)dipotassium. However, no polymerization occured. An instantaneous disappearence of the characteristic dark red colour of oligo(α-methylstyryl)dipotassium was indicative of rapid termination. This has been ascribed to a possible side reaction of the initiator, or the propagating chain end at the early stage of polymerization with the trimethylsilyl enol ether (Scheme-1.15).



Scheme-1.15

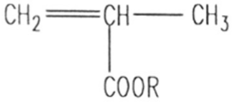
This could be overcome by using TBDMS group in place of trimethylsilyl. Tert-butyldimethylsilyl enol ether namely 1.41b could be conveniently polymerized using oligo(α-methylstyryl)dipotassium. Characteristic red colour of the solution indicated the living nature of polymerization. The yield of the polymer was quantitative. Molecular weights were in the range of 10000-40000 and MWDs less than 1.1.

Similarly Hirao et.al.[97] have reported effective polymerization of (1.42), the meta-isomer using oligo(α-methylstyryl)lithium and cumylpotassium to result polymers having observed $\overline{M}_n$ values in the range of 11000 to 54000 which were close to the calculated values. The MWDs were between 1.04 and 1.06. However, attempts to anionically polymerize the ortho isomer (1.43) was not successful. This observation is similar to the anionic polymerization of o-tert-butyldimethylsilyloxy styrene (Scheme-1.11).

1.3.6. Protection and polymerization of monomers containing carboxylic acid (-COOH) group:

Methacrylic acid and 4-vinylbenzoic acid are the two monomers which have been protected and polymerized by anionic polymerization method.

Well-defined poly(methacrylic acid) can be prepared by the anionic living polymerization of methacrylic esters, followed by hydrolysis of the ester groups. The methacrylic esters reported are trimethylsilyl (1.44a), methyl (1.44b), diphenylmethyl (1.44c), triphenylmethyl (1.44d), and t-butyl (1.44e) methacrylates.



$CH_2{=}CH(COOR){-}CH_3$

1.44(a-e)

a: R = $SiMe_3$
b: R = Me
c: R = $(C_6H_5)_2CH$
d: R = $(C_6H_5)_3C$
e: R = $C_4H_9^t$

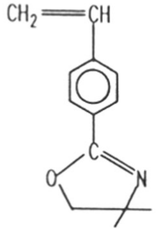
(1.44a) was reported to undergo anionic polymerization. A variety of block copolymers were synthesized by sequential anionic polymerization of styrene, vinylpyridines, and 9-vinyl-phenanthrene with (a)[98-100]. Unfortunately, the analysis of the polymers indicates that some side reactions occur during the polymerization of (1.44a).

On the otherhand, the anionic polymerization of 1.44(b-e) proceed without side reactions. The hydrolysis of these polymers to poly(methacrylic acid) is frequently inefficient, especially under basic conditions. The polymers of 1.44c, 1.44d and 1.44e are considered to be inherently more reactive than poly(b) to acid hydrolysis. Doherty and Hogen-Esch reported that poly((c)-b-(d)) was hydrolyzed completely to well-defined poly(methacrylic acid) by 5% HCl/MeOH. The disadvantage is that its hydrolysis requires elevated temperature for a long reaction time of 7 days[101]. The tert-bytyl ester of poly(e) was readily and completely cleaved with Me_3SiI at room temperature for 4h. Block copolymers of poly[(b)-b-(methacrylic acid)] were successfully prepared by Bugner[102].

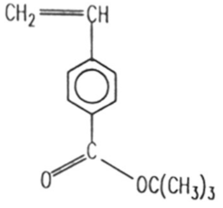
4-vinylbenzoic acid (1.45) could be protected as the ester, 2-oxazoline and tertiary amides and polymerized anionically. Poly (4-vinylbenzoic acid) with well controlled molecular weights and narrow molecular weight distributions have been made by anionic living polymerization of any of the three monomers viz. 2-(4-vinylphenyl)-4,4-dimethyl-2-oxazoline (1.46), tert-butyl 4-vinylbenzoate (1.47) or N-(4-vinylbenzoyl)-N'-methylpiperazine (1.48) followed by deprotection.[103]

1.3.6.1. Anionic Polymerization of 2-(4-vinylphenyl)-4-4-dimethyl-2-oxazoline[104,105]: Meyers et.al. have demonstrated the utility of the 1,3-oxazoline moiety as a protecting group for various carboxylic acids[106,107]. The 2-substituted 1,3-oxazoline ring can mask both the carbonyl and hydroxyl groups of a COOH moiety at the same time and is remarkably stable toward highly reactive nucleophiles such as organolithium compounds. Thus, the protected monomer 2-(4-vinylphenyl)-4,4-dimethyl-2-oxazoline could be anionically polymerized quantitatively in THF at -78°C with oligo(α-methylstyryl)dialkali metal salts (Li,Na,K) and cumyl potassium. The resulting poly(1.45)s possessed predictable molecular weights (35000 - 80000) and narrow MWDs (1.06).

1.3.6.2. Anionic polymerization of tert-butyl 4-vinylbenzoate: Parham and coworkers reported that tert-butyl-o-lithiobenzoate could be formed and was stable for a certain time at -100°C[108]. It has also been suggested 2,4,6-trialkylbenzoates are resistant to carbonyl attack by alkyllithium reagents[109,110]. Thus, aryl carboxylic acids can be protected even toward highly reactive nucleophiles in the form of esters with bulky groups under carefully controlled conditions. Nakahama and coworkers have studied the anionic polymerization of tert-butyl 4-vinylbenzoate[111]. The monomer was readily obtained in 70-90% yields by the reaction of 4-vinylbenzoylchloride with lithium tert-butoxide.



1.46



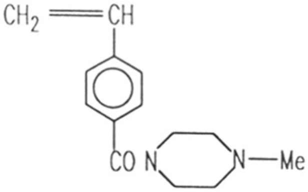
1.47

Anionic polymerization of (1.47) at -78°C was always accompanied by some side reactions such as carbonyl attack by carbanions from the initiator and active propagating chain ends during the polymerization. This was eliminated by lowering the polymerization temperature to -95°C. The polymerization of (1.46) then proceeded smoothly with oligo(α-methylstyryl)dipotassium or cumylpotassium in THF. The reaction mixtures were always dark red in colour, which remained unchanged at -95°C for 5h. The IR, ^1H and ^{13}C NMR data of the resulting polymers indicated the structure of poly 19. Molecular weights were in the range 50000-60000 and MWDs around 1.16.

Complete removal of the tert-butylester function from the poly 1.45 was achieved by treatment with $(CH_3)_3SiCl$ and NaI in acetonitrile. The reaction was complete within 10 min. at room temperature. IR and ^1H NMR analysis of the resulting polymer indicate the structure of poly(4-vinylbenzoic acid). SEC of the methylated poly(1.45) showed a single peak with a narrow MWD eluting in the predicted MW region, indicating that no side reactions occur in the deprotection step.

1.3.6.3. Anionic polymerization of N-(4-vinylbenzoyl)-N'-methylpiperazine:

Anionic polymerizations of N-(4-vinylbenzoyl)-N'-methylpiperazine (1.48) was carried out in tetrahydrofuran at -78°C with oligo(α-methylstyryl)dilithium, disodium and dipotassium.

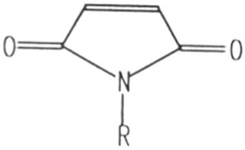


1·48

The polymerization of (1.48) proceeded quantitatively to give stable living polymers having predicted molecular weights and narrow MWD. For (1.48) M_n was in the range between 4200 and 21000 and MWD between 1.05-1.13. Under acidic condition (6N HCl in 1,4-dioxane) quantitative hydrolysis of the amide linkage of poly(1.48) was achieved to give a well defined poly(4-vinyl-benzoic acid). Some other N,N-dialkyl benzamides were also successfully polymerized using anionic initiators. However, deprotection of the tertiary amide group into carbonyl group by hydrolysis was not possible[112].

1.3.7. Protection and polymerization of functional monomers containing imide (-CO-NH-CO-) group:

The only report of protection and polymerization of a monomer containing imide functionality is that of the polymerization of silyl protected maleimides[113]. These N-trialkylsilylmaleimides (1.49), e.g. N-(trimethylsilyl)maleimides (1.49a), N-(tert-bytyldimethylsilyl)maleimide (1.49b) and N-(dimehylthexylsilyl)maleimide (1.49c), were prepared by the reaction of maleimide or silver maleimide with the corresponding trialkylsilyl chlorides.



1.49(a-c)

a: $R = SiMe_3$

b: $R = SiMe_2Bu^t$

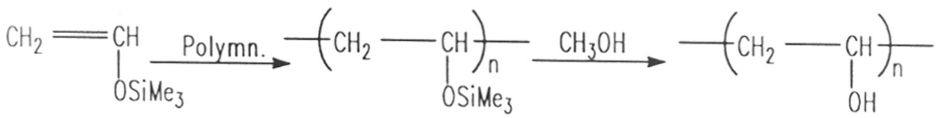
c: $R = SiMe_2CMe_2CHMe_2$

Anionic polymerization of these monomers were carried out with s-BuLi as the initiator in THF at -78°C. 1.49b was found to give a high molecular weight polymer {$[\eta] = 0.35$ dL/g}] whereas 1.49a did not give any polymer. Apparently the trimethylsilyl group gets deblocked by an attack of the anion onto the N-Si bond. Tert-butyldimethylsilyl group is more stable to this side reaction. Yield obtained for 1.49b is reported to be 34.7%.

1.4. Cationic Polymerization:

The only reported synthesis of functional polymer by cationic polymerization of a protected monomer is that of poly(vinyl alcohol) (PVA). Syndiotactic PVA was obtained by cationically polymerizing poly(vinyl t-butyl ether) by treatment with hydrogen bromide[114]. Isotactic PVA was derived either from isotactic poly(vinyl benzyl ether)[115,116] or poly(vinyl t-butyl ether)[117], by the cleavage of the ether linkages. Murahashi et. al. have reported a route to both syndiotactic and isotactic PVA by the use of cationic polymerization of vinyl trimethylsilyl ether[118].

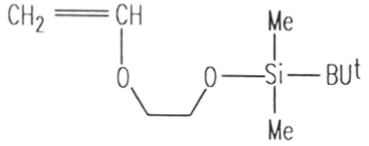
Cationic polymerization of silyl protected monomers for the synthesis of both syndiotactic and isotactic PVA was first documented in the literature by Murahashi et. al.[118]. Vinyl trimethylsilyl ethers were polymerized using initiator systems which include Et_2AlCl, $EtAlCl_2$ and $SnCl_4$. Each catalyst was used in the three solvents viz. toluene, n-hexane and CH_2Cl_2. The polymerizations were carried out at -78°C and immediately after polymerization the silylated polymers were hydrolyzed to poly(vinyl alcohol) by treating with excess methanol(Scheme-1.16).



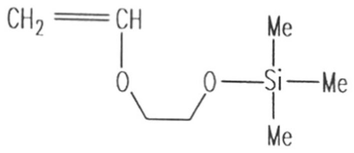
Scheme-1.16

Using $BF_3.Et_2O$ appreciable amount of polymer was not obtained. Interestingly, vinyl t-butylether, which is the carbon analog of vinyl trimethylsilyl ether, is reported to give a good yield of polymer with $BF_3.Et_2O$[4]. Conversions were mostly in the range of 86-100%. The intrinsic viscosity [η] (30°C in water) values were between 0.1 and 0.6 dL/g. The stereoregularity of the polymer samples were evaluated according to Fujii method, by measuring the ratio of optical densities of infrared absorption[119,120]. Murahashi et.al. showed that stereoregularity of PVA obtained by the cationic polymerization of trimethylsilyl vinyl ethers can be regulated by a suitable choice of solvent and catalyst[118].

Subsequently Higashimura et. al. reported the living cationic polymerization of 2-(t-butyldimethylsilyloxy)ethyl vinyl ether (1.50) and 2-(trimethylsilyloxy) ethyl vinyl ether (1.51)[121]. Polymerizations were carried out using the HI/I_2 initiating system in toluene solvent at -40°C. Smooth polymerizations occured without an induction phase and was completed within an hour to give soluble polymers in quantitative yield. The bulkier TBDMS group resulted in a slower rate of polymerization of (1.50) as compared to the rate for (1.51). For both the monomers the MWDs were below 1.1.



1.50

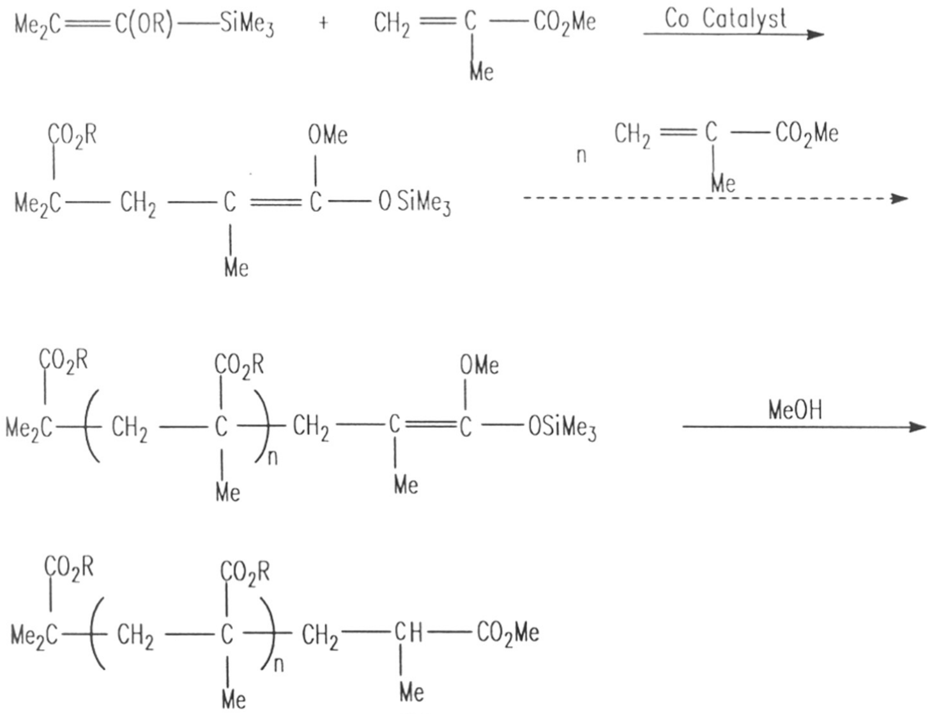


1.51

Desilylation was performed by stirring about 0.2 gm of poly(1.51) with methanolic HCl (1 mol% conc. HCl aq., 10 mL) at room temp. The mixture was neutralized, filtered and evaporated to dryness to afford the polymeric alcohol in quantitative yield. Complete desilylation was confirmed from ^{1}H NMR. Poly(1.50) was desilylated by treatment with nBu_4NF in THF. The HI/I_2-mediated living polymerization of (1.50) and (1.51) were applied to the synthesis of silicon-containing AB block copolymers and macromonomers.

1.5. Group Transfer Polymerization:

Since the discovery of group transfer polymerization (GTP) by the researchers at Du Pont in 1983[122], there has been considerable interest in this method for the living polymerization of acrylic monomers[123,124]. GTP involves the repeated addition of monomer to a growing polymer chain end bearing a reactive silicon group. During the addition, the silyl group transfers to incoming monomer. Scheme-1 illustrates the method for polymerization of methyl methacrylate in which the reactive end group is a silyl ketene acetal.



Scheme-1.17

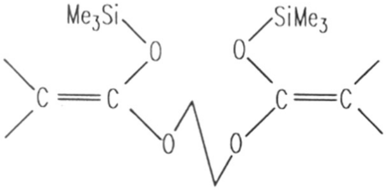
The major advantage of GTP is that the reactions can be conveniently carried out at room temperature unlike anionic initiators which need low temperatures.

Webster and Sogah have reviewed the GTP process in terms of the catalysts, initiators, reaction conditions, molecular weight control, stereochemistry, mechanism and the relative reactivity of monomers[125]. Functional groups sensitive to free radicals, such as 4-vinyl benzyl[126], allyl and sorbyl can be present on the ester groups of the monomer and are unaffected. Glycidyl methacrylate can be polymerized wihout interference from the epoxy groups provided the temperature is held below 0°C.

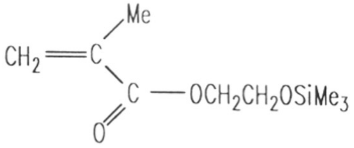
Active hydrogen compounds interfere with GTP and stop chain growth if present in amounts greater than the initiator concentration. Therefore functional monomers containing active hydrogens need to be protected prior to group transfer polymerization. In the following sections the literature on the group transfer polymerization of the protected functional monomers will be briefly reviewed. Silyl protected hydroxyethylmethacrylate and silyl vinyl ethers are the monomers which have been polymerized to give polymers containing hydroxyl functionality and silyl and benzyl methacrylates have been polymerized to produce polymers containing carboxylic acid functionality.

1.5.1. Synthesis of polymers containing pendent hydroxyl functionality:

1.5.1.1. Synthesis of copolymers containing 2-hydroxyethylmethacrylate by group transfer polymerization: An ABA block copolymer with A blocks consisting of a random copolymer of MMA and 2-hydroxyethylmethacrylate and a B block of lauryl methacrylate was successfully synthesized by GTP[127]. With the use of a difunctional initiator (1.52) the B block (lauryl methacrylate) was constructed first as a homopolymer with two living ends followed by addition of the random copolymer A blocks.



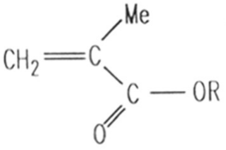
1.52



1.53

The trimethylsilyl-protected monomer, (1.53), was used in forming the A blocks. The resulting polymer had $M_n = 9340$, $M_w = 11200$, and MWD = 1.20 (theoretical $M_n = 13600$). Deprotection of the hydroxyl groups was done by methanolic tetrabutylammonium fluoride. This polymerization technique works best with methacrylates, to which most of the published data refer[122,125-127].

1.5.2. Synthesis of poly(methacrylic acid) by protection and group transfer polymerization of benzylmethacrylate: Mykytiuk et.al. have reported the synthesis of near-monodisperse poly(methacrylic acid)s by group transfer polymerization of benzyl methacrylate (1.54a) followed by removal of the benzyl group[128]. Rannard et.al. have also reported the group transfer polymerization of trimethylsilyl methacrylate (1.54b), the trimethylsilyl protected methacrylic acid[129]. However, this monomer is difficult to handle because of its extreme moisture sensitivity. Therefore, protection of the acid group of methacrylic acid in the form of its benzylic ester is preferred for GTP. The benzylmethacrylate monomer has been polymerized using methyl-3-trimethylsiloxy-2-butenoate as the initiator and tetrabutylammonium fluoride (TBAF) as the catalyst at around 20°C.



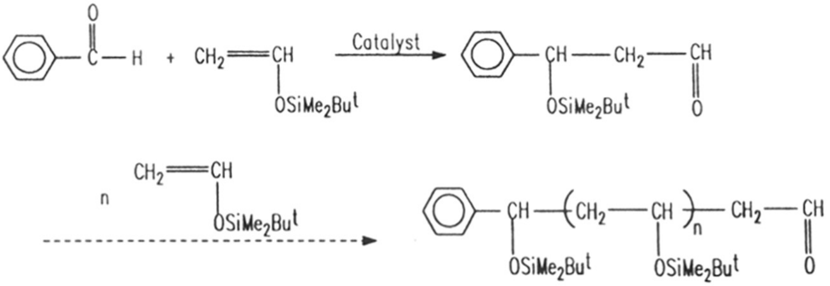
1.54(a,b)

a: Benzyl methacrylate; R: $-CH_2C_6H_5$

b: Trimethylsilylmethacrylate; R: $-SiMe_3$

Caron et.al. have shown that Pd/Charcoal catalysed hydrogenation is a convenient way to cleave the benzyl ester protecting groups in polymers[130]. Billingham et.al. have used the same methodology to deprotect the poly(1.54a). Hydrogenation of poly(1.54a) was performed by adding catalytic amount of palladium/charcoal into a solution of the polymer in a solvent mixture (ethylacetate and methanol, 10:1) and stirring under an atmosphere of hydrogen at room temperature. Methylation of the polyacrylic acids thus obtained followed by GPC shows that the polymethacrylic acids have the desired molecular weight and low polydispersity.

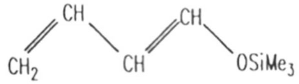
1.5.3. Polymerization of protected monomers by aldol-GTP: Besides the group transfer polymerization of acrylic monomers, there is another type of group transfer polymerization which proceeds via an aldol type reaction[131]. The polymerization of silyl vinyl ethers initiated by aldehydes is an example of the Aldol-GTP(scheme-1.18).



Scheme-1.18

This method gives monodisperse poly(silylvinyl ether) whose molecular weight ($\overline{M}_n$ 1000-160000) is controlled by the aldehyde initiator. As shown in scheme-1.18, this process involves a silyl group transfer from monomer to the carbonyl oxygen of either the initiator or the living polymer leading to generation of a new terminal aldehyde functionality. The reaction is generally catalyzed by Lewis acids. The living polymers are stable, neutral materials, whose hydrolytic stability depends on the bulkiness of the silyl group. In general, aromatic aldehydes tend to react more cleanly as initiators than do aliphatic aldehydes. Some of the advantages of aldol-GTP over existing methods such as cationic polymerization include operability over a broad temperature range, complete monomer conversion, living polymer formation, very good molecular weight control and facile block copolymer synthesis. It permits control of hydrophilicity of block copolymers. The recent reports on the aldol-GTP includes the polymerization of some butadienyloxytrimethylsilanes[132] and 2-phenyl-1,3,2-dioxaborole[133]

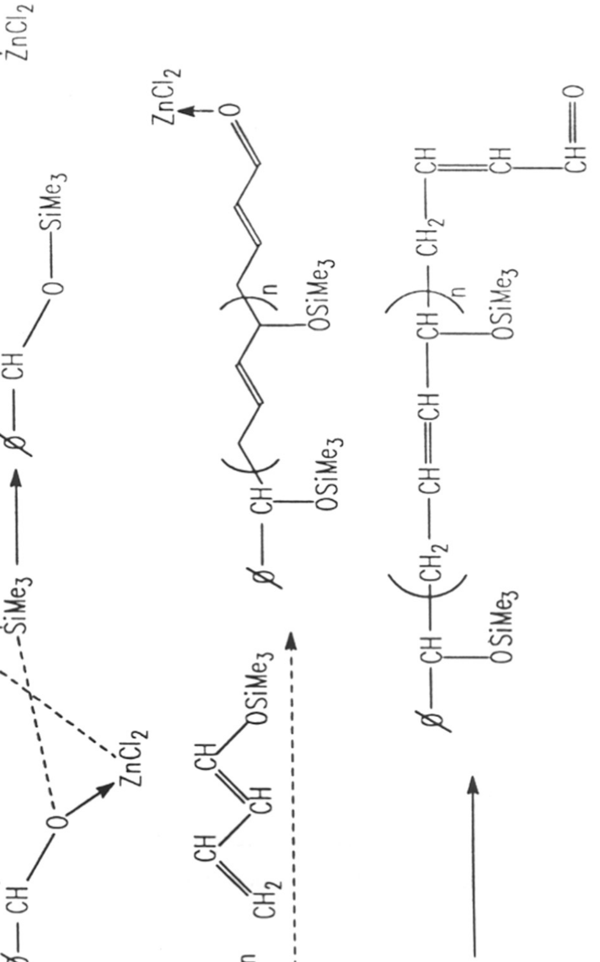
1.5.3.1. Aldol-GTP of butadienyloxysilanes: Hirabayashi et.al. published their results on the group transfer and cationic polymerization of 1-butadienyloxytrimethylsilane (BdTMS, 1.55)[132]. Equimolar quantities of benzaldehyde (BAld)-$ZnCl_2$ catalysts in benzene at 20°C are effective to give a soluble polymer in organic solvents.



1.55

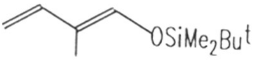
Polymerization of BdTMS was examined by various catalysts (initiators). Lewis acid catalysts were effective, while no polymer could be obtained with typical radical and cationic initiators (-78°C). By using $SnCl_4$ and ethylaluminium sesquichloride, BdTMS could be polymerized rapidly even at (-78°C), but was accompanied by serious gelation resulting in almost insoluble polymer in conventional organic solvents. The preferable catalyst was $ZnCl_2$, which gave soluble polymer under mild conditions (20-60°C). The addition of equimolar benzaldehyde to $ZnCl_2$ also gave a soluble polymer and made the molecular weight distribution of the polymer narrower than that from $ZnCl_2$ alone. The proposed polymerization mechanism catalyzed by BAld-$ZnCl_2$ is shown in the scheme-1.19.

Hirabayashi and co workers reported results using different aldehydes and inferred that the MWDs were dependent on the choice of initiating aldehyde[134]. Among the para substituted derivatives of benzaldehyde, electron-donating substituents ($-OCH_3$, $-CH_3$) caused a narrowing of the MWD (1.28 for $-OCH_3$ and 1.40 for $-CH_3$), while electron-accepting groups resulted in a broadening of the MWD (1.86 for NO_2). This shows that the electron density on carbonyl group in aldehyde may play an important role in determining the molecular weight distribution of the resulting polymers. An NMR monitoring of the initiation indicated a slow reaction (long induction period) of the polymerization reaction by the initiators with less electron density on the carbonyl group (due to more electron withdrawing para-substitution) which might be responsible for the molecular weight distribution broadening. Similarly a higher electron density on the carbonyl oxygen might result in narrowing of molecular weight distribution by virtue of a stronger interaction of the formyl group with both $ZnCl_2$ and with $SiMe_3$ (Scheme-1.19).

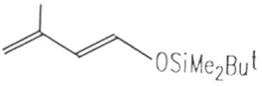


Scheme – 1·19

Shen and Sogah have synthesized and polymerized the substituted silyl dienolates ((2-methylbutadienyl)oxy)tert-butyldimethylsilane (1.56) and ((3-methylbutadienyl)oxy)tert-butyldimethylsilane (1.57) by aldol-GTP^{135}.



1.56



1.57

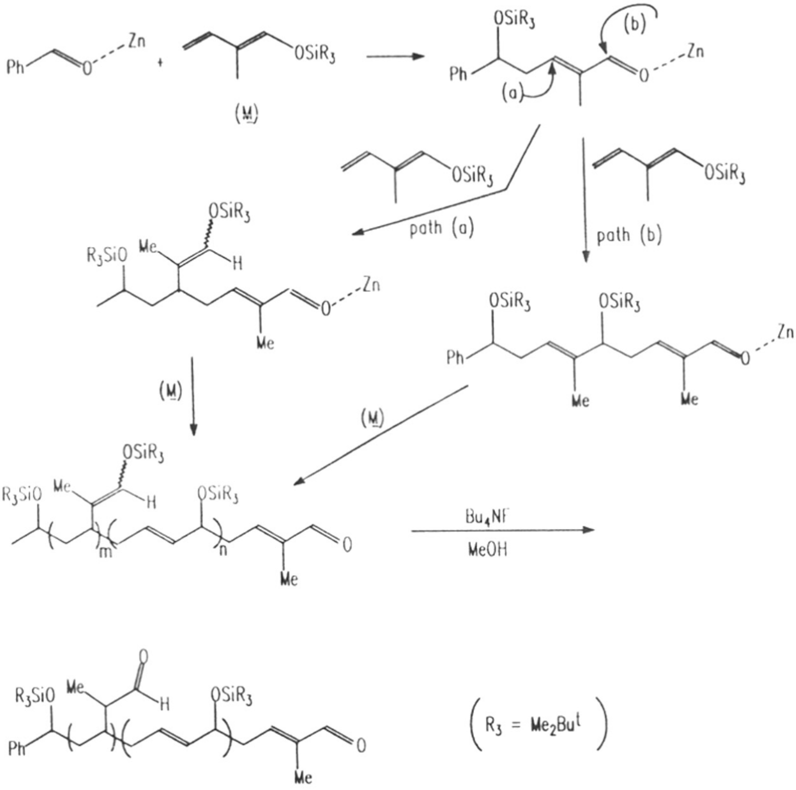
The polymers obtained from (1.56) and (1.57) were reduced and desilylated to produce propylene-vinylalcohol copolymer with head-head, tail-tail linkages and head-tail linkages respectively. Based on this work on substituted butadienyloxysilanes it was established that there are two possible pathways for the polymerization of the substituted butadienyloxysilanes as shown in scheme-1.20.

There are two possible reaction pathways available to the 1:1 adduct 1.58. Conjugate addition of 1.56, (nucleophile) to the 3 position of the adduct 1.58 to give 1.59 (path a) or 1,2-nucleophile carbonyl addition (path b) to give 1.60. Spectroscopic studies confirmed that both occur, and the relative peak areas showed that 1.61, (final pdt.) contained only 17% of pendant silyl enolate. Thus, nucleophilic 1,2-carbonyl addition is the predominant pathway.

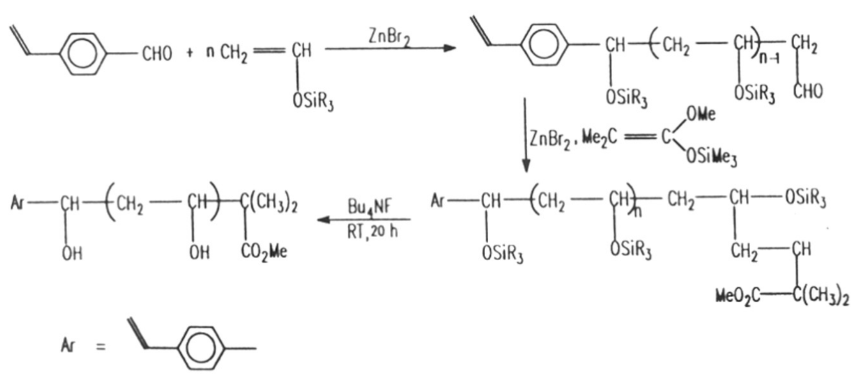
Charleux and Pichot have reported the synthesis of styrene-terminated poly(vinylalcohol) macromonomers by aldol-GTP^{136}. Polymerization of tert-butyldimethylsilyl vinyl ether initiated by an unsaturated compound, p-formylstyrene, and catalyzed by zinc-bromide allowed synthesis of styryl-silylated poly(vinylalcohol) macromonomers bearing an aldehyde end-function. Macromonomers with average degrees of polymerization up to 28 were prepared and characterized. In order to improve the stability of the end-group, the aldehyde function was reacted with a silyl ketene acetal compound, 1-methoxy-2-methyl-1-trimethylsiloxy-propene, which resulted in the formation of a β-hydroxy ester end group, much more stable towards side reactions. Later, the silyl ether side groups were hydrolyzed with tetrabutylammonium fluoride in order to obtain hydrophilic styryl-poly(vinylalcohol) macromonomer. The reaction is reported to be quite efficient; however, purification was found to be difficult and often incomplete (Scheme-1.21).

1.5.3.2. Polymerization of 2-phenyl-1,3,2-dioxaborole:

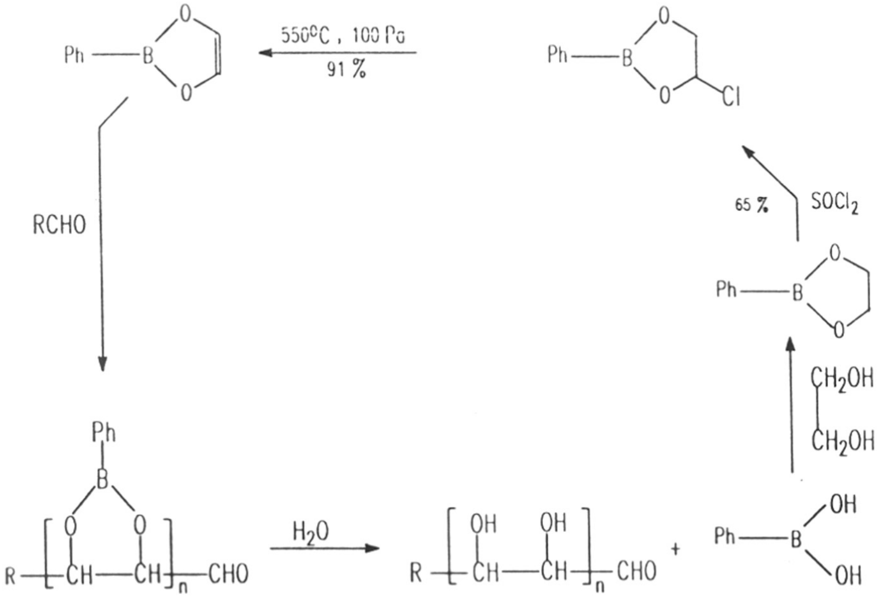
2-Phenyl-1,3,2-dioxaborole (1.63) was originally prepared via an anthracene adduct by a retro-Diels-Alder reaction^{137,138}. It can be obtained more readily from 2-phenyl-1,3,2-dioxaborolane (prepared from phenyl boronic acid and ethylene glycol) by photochlorination with sulfuryl chloride to give the monocholoro derivative 1.62 and subsequent thermal elimination of HCl to give 1.63 in 91% yield. Trace impurity of HCl in the dioxaborole prepared in this manner helps in catalyzing the aldol-GTP reaction (Scheme-1.22).



Scheme-1.20

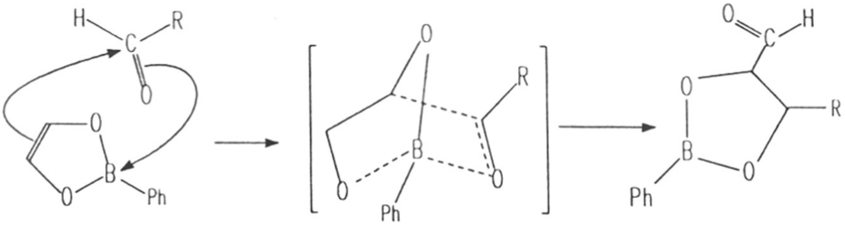


Scheme-1.21


Ph
B
O
O
550°C, 100 Pa
91 %
Cl
RCHO
65 %
$SOCl_2$
CH_2OH
CH_2OH
H_2O
R
CH
CHO
OH
n
+

Scheme-1.22

The enediolate 1.63, undergoes an aldol reaction with aldehydes to give, initially, the mono and diaddition products, both of which can be isolated. During the aldol reaction of the heterocycle 1.63, a new aldehyde is generated in each step. As a result, in the presence of excess 1.63, the reaction leads to oligomeric or polymeric products 1.64, depending on the monomer/initiator ratio. During this polymerization, the phenylborane diyl groups transferred from one oxygen of the incoming monomer to the oxygen of the aldehyde group. This parallels the silyl-group transfer in aldol-GTP as described by Sogah et.al.[135] and is an example of aldol-GTP of a 1,2-disubstituted olefin[133]. In contrast to the polymerization of silyl vinyl ether derivatives (Scheme-1.17), the polymerization of 1.63 does not need Lewis acid initiation and the reaction is much faster. The acceleration of the reaction rate compared to silylvinylethers may be attributed to the participation of the boron atom acting as Lewis acid in the transition state of the reaction as shown in scheme-1.23.



Scheme-1.23

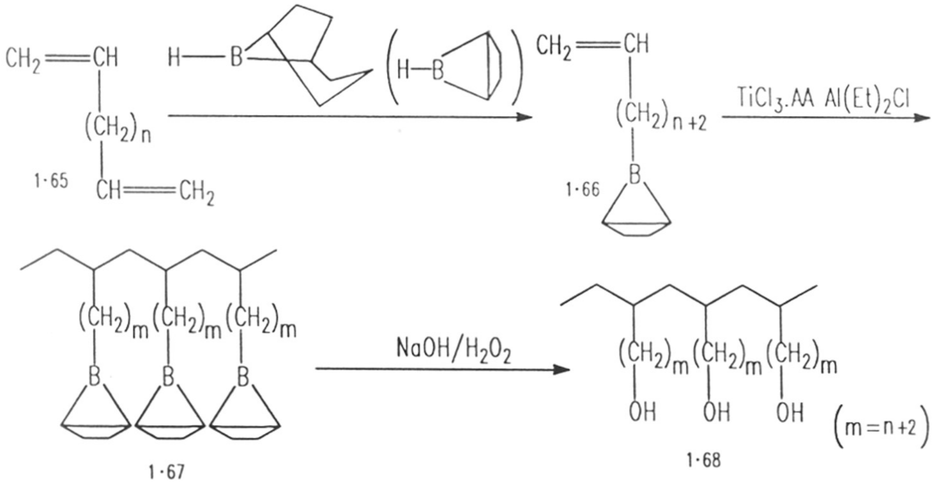
Polymers with molecular weights between 700-130000 have been obtained and molecular weight of the oligomers or polymers could be controlled to some extent which indicates a transfer-free polymerization. MWDs were mostly around 1.5.

Group transfer polymerization offers a good opportunity to prepare macromonomers with a polymerizable double bond[139-141]. In aldol-GTP, the introduction of a double bond is possible using 4-vinylbenzaldehyde as the initiator[141]. The same procedure has been used by Wulff and co-worker to prepare a number of macromonomers where the hydroxyl groups are protected in the form of a dioxaborole[142].

1.6. Ziegler-Natta and Ring Opening Metathesis Polymerization:

1.6.1. Ziegler Natta Polymerization:

The synthesis of functional polymers using Ziegler-Natta and ring opening metathesis polymerization processes received significant attention in recent years. The borane(1.66) derived from monohydroboration of appropriate dienes (1.65) with dialkylborane have been found to be stable to titanium-based Ziegler-Natta catalysts and could be conveniently polymerized[143]. The polymers (1.67) were converted into polyalcohols (1.68) under mild reaction conditions (Scheme-1.24).



Scheme -1·24

The nonconjugated terminal dienes such as 1,7-octadiene, 1,5-hexadiene, and 1,4-pentadiene were monohydroborated by treating a large excess of the diene with borabicyclo [3-3-1] nonane (9-BBN) in THF solution. A typical monomer B-7-octenyl-9BBN was polymerized in toluene using $TiCl_3$.AA-$Al(Et)_2Cl$ catalyst. Stability of the borane moiety during and after the polymerization was confirmed from ^{11}B NMR spectra.

Copolymerization of borane monomers with other α-olefins are also reported by Ramakrishnan et.al[144]. Differences in reactivity of the comonomers and the variation of composition with conversion have been studied from ^1H NMR spectra. Conditions were optimized for developing a homogeneity in the copolymer composition. DSCs of the copolymers exhibited a single glass transition temperatures (T_g) which lies between those of the two homopolymers. Presence of only one T_g implies that copolymer samples were fairly homogeneous.

Copolymerization of hexenyl-9-BBN (1.70) with propylene (1.69) resulted in the formation of a molecular structure which has a blocky microstructure of isotactic polypropylene and a functional polymer. The borane groups in polypropylene copolymer (1.71) could be oxidized ($NaOH/H_2O_2$, 40°C, 5 h, THF) completely to the corresponding hydroxy group containing polypropylene(1.72) (Scheme-1.25).

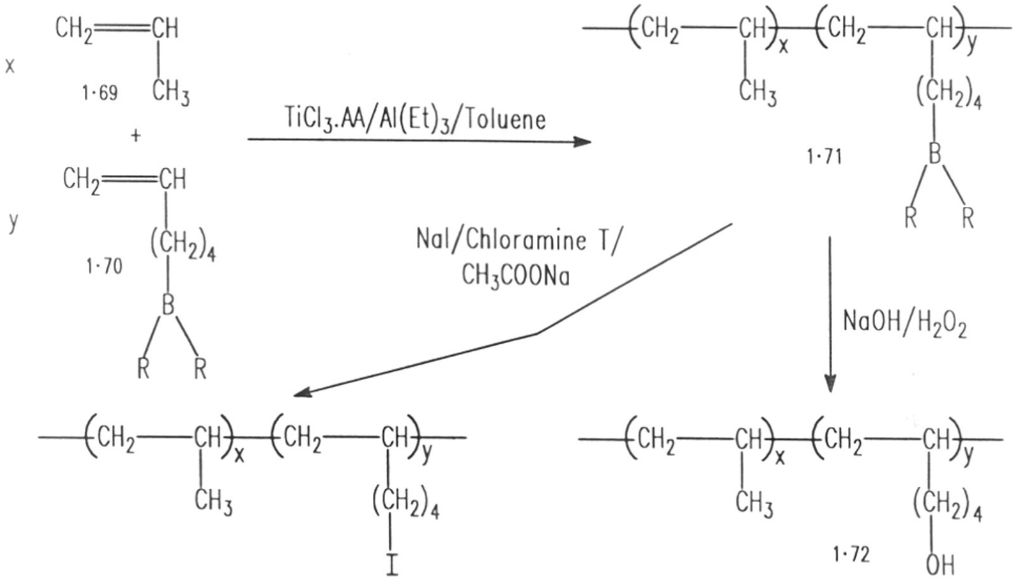
Conversion to corresponding Iodine-containing polymer was achieved by treating the borane-containing polymer by NaI/chloramine-T hydrate in basic condition at room temperature[145] (Scheme-1.25).

1.6.2. Ring Opening Metathesis Polymerization:

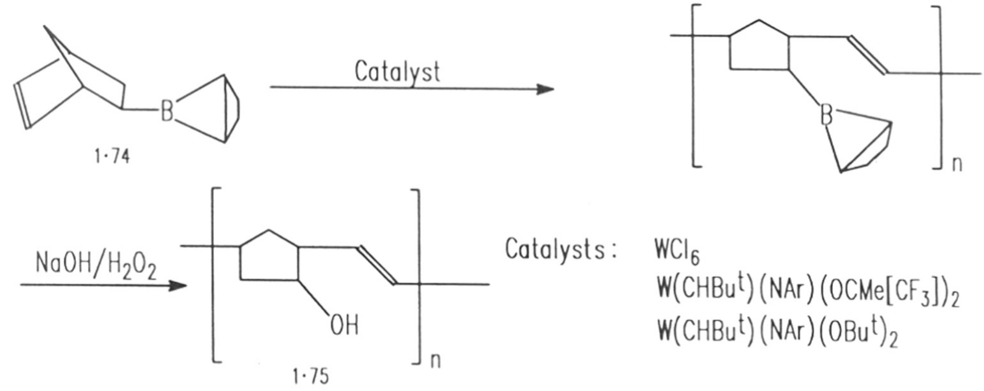
Chung et.al.[146,147] have shown that both ring-opening metathesis polymerization and metathesis degration on borane-containing olefins are very useful for functionalization of hydrocarbon polymers. Synthesis of polymer structures like poly(exo-5-hydroxynorbornene) and alternating ethylene-vinylalcohol copolymers will be briefly discussed. These are the two major accomplishments in the area of functionalization chemistry involving metathesis catalysts and borane monomers.

Poly(exo-5-hydroxynorbornene)[146,147]: The monomer exo-5-hydroxynorborn-2-enyl-9-BBN (1.74) was synthesized by selective hydroboration of 2,5-norbornadiene with 9-BBN, using an excess of the diene to minimize formation of the bis-hydroboration product. The polymerization of 1.74 was carried out at room temperature in the presence of several catalysts using a 2M solution of the monomer in toluene (Scheme-1.26).

Polymerization reactions catalyzed by the tungsten-based catalysts were rapid and were terminated after 2 h with isopropanol. Polymers were oxidized ($NaOH/H_2O_2/THF$, 25°C.) resulting in the complete transformation of borane-substituted polymer to poly(exo-5-hydroxynorbornene) (1.75). From ^1H NMR spectra of polymer (1.75), prepared with various tungsten based catalysts, the cis and trans contents were calculated from the integrated intensities of the allylic hydrogens. The isomer ratio was found to be strongly dependent on the nature of the catalyst. The effects of the various catalysts on the microstructure have been rationalized in terms of stereospecificity of cycloaddition during the propagation process.


x
1·69
y
1·70
TiCl$_3$.AA/Al(Et)$_3$/Toluene
1·71
NaI/Chloramine T/
CH$_3$COONa
NaOH/H$_2$O$_2$
1·72

Scheme -1·25

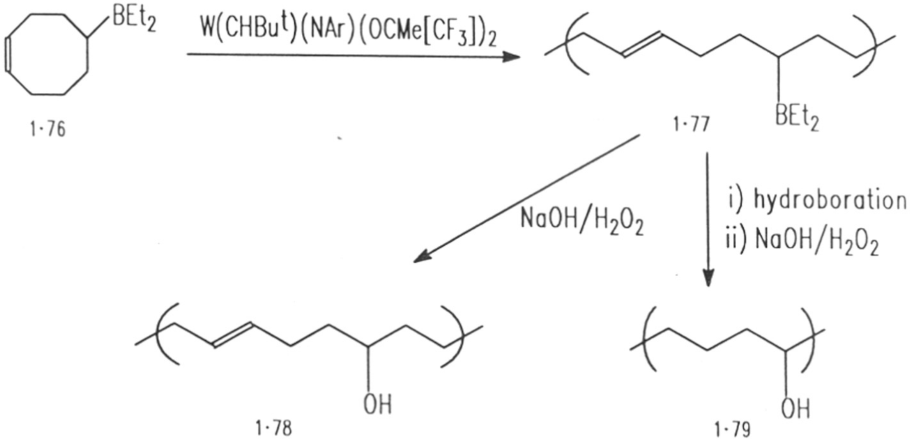


1·74

1·75

Catalysts: WCl_6
$W(CHBu^t)(NAr)(OCMe[CF_3])_2$
$W(CHBu^t)(NAr)(OBu^t)_2$

Scheme –1·26



1·76

1·77

1·78

1·79

Scheme –1·27

The glass transition temperature of poly(exo-5-hydroxyl-norbornene) (T_g>110°C) is much higher than that of polynorbornene (T_g = 37°C). Obviously, hydrogen-bonding plays an important role in increasing intermolecular interactions. The glass transition temperature of polymers depend on the cis-trans ratio of the double bond. Both high-cis and high-trans structures were found to have higher glass transition temperature than the mixture. This implies a better molecular interaction in both high-cis and high-trans polymers.

1.6.2.1. Synthesis of alternating ethylene-vinylalcohol copolymer:

Synthesis of alternating ethylene-vinylalcohol copolymers were carried out by the ROMP of cyclooct-5-enyldiethylborane (1.76). The monomer (1.76) was prepared by reacting neat 1,5-cyclooctadiene with catecholborane at 100°C using a four-to-five fold excess of the diene. The excess of the diene was distilled off and the residue was treated with Et_2AlCl in hexane. The dialkoxyaluminium chloride that precipitated was filtered, the solvent removed by evacuation and the residual oil was subjected to vacuum distillation to yield the required monomer. The Lewis acid free tungsten carbene $[W(CHBu^t)(NAr)(OCMe(CF_3)_2)_2]$, was used for polymerization (Scheme-1.27).

The polymerization was very rapid, causing an instantaneous gelation of the solution. The polymer (1.77) was precipitated and oxidized to give polymer (1.78). Prior to oxidation reaction, further hydroboration of (1.77) followed by oxidation resulted in the formation of a molecular structure (1.79) which is the same as that of an alternating copolymer of ethylene and vinyl alcohol. GPC of acetylated polymer (1.79) in THF showed that the molecular weight was 122,000 and the polydispersity 2.8. Thus, by the successful synthesis of polymer (1.79), it was established that the synthetic method based on borane-substituted monomers has several advantages, namely, (a) tungsted-based transition metal compounds talerate the borane functionality; (b) the 0
borane-containing polymer formed during the polymerization is soluble in common hydrocarbon solvents and (c) interconversion of the borane group to yield the desired functionality occurs under mild reaction conditions. Ethylene-vinyl alcohol copolymers were characterized by DSC and TGA. They were found to be thermally much more stable than poly(vinyl alcohol) inspite of their similarity in molecular structure. Weight loss of the copolymer begins at 400°C whereas for poly(vinyl alcohol) onset of decomposition occurs at 250°C.

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CHAPTER - II

CHAPTER-II:

OBJECTIVES AND SCOPE OF THE PRESENT INVESTIGATION:

Functional polymers are a useful class of materials wherein the properties conferred by virtue of the high molecular weight of the polymers are combined with those derived from the presence of specific functional groups. Among the different methods of synthesizing functional polymers, protection, polymerization and deprotection of functional monomers have attracted considerable attention in recent years. Protecting a functionality of a monomer by an easily deprotectable functional group prior to polymerization is important because of two reasons. Firstly, many polymerization techniques are not compatible with the unprotected monomer since the functional group may be reactive towards the initiator and/or the propagating end; and secondly, it may be possible to chemically modify the polymer obtained by polymerizing the protected monomer, which might not be feasible with the polymer formed from the unprotected one.

Among the various protecting groups used in synthetic organic and polymer chemistry, trimethylsilyl and tert-butyldimethylsilyl groups have been used most extensively. For the synthesis of functional polymers by free radical polymerization, monomers containing several functionalities such as, thiol (-SH)[1], hydroxyl (-OH)[2], keto (>C=O)[3], acid (-COOH)[4], imide (-CO-NH-CO-)[5] etc. have been protected using a silyl group. Silylation has been extensively used as a general method for the protection and polymerization of functional monomers in anionic polymerization[6].

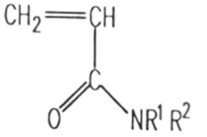
However, practically no attention has been paid to the study of protected acrylic amide monomers. Suitably protected acrylamides on account of reduced hydrogen bonding should improve its solubility in organic solvents. Thus it could show interesting changes in its reactivity pattern during copolymerization. Literature reveals that copolymerization of acrylamide with hydrophobic monomers produce copolymers which are blocky i.e. compositionally inhomogeneous in nature. It is believed that the properties of copolymers, in particular, of those containing polar and non-polar monomers can be improved by decreasing their compositional inhomogeneity[7]. Furthermore, protected acrylamides could also be polymerized in the "vinyl polymerization" mode using anionic initiators. Unprotected acrylamide are known to undergo "hydrogen transfer polymerization" under such conditions[8].

The present investigation was undertaken with a view to understand the effects of silylation of the amide functionality in acrylamide on its polymerization and copolymerization behavior.

Approaches:

Monomer synthesis:

Anionic polymerization would require protection of both the hydrogens of the amide functionality of acrylamide and free radical solution homo and copolymerization in organic medium would require substitution of at least one of the two hydrogens. Therefore the synthesis of the following monomers was undertaken:



2.1(a-d)

a. $R^1 = H, R^2 = SiMe_3$
b. $R^1 = R^2 = SiMe_3$
c. $R^1 = H, R^2 = SiMe_2Bu^t$
d. $R^1 = CH_3, R^2 = SiMe_2Bu^t$

Polymerization of the silylated acrylamide monomers:

Free radical solution polymerization of 1a and 1b would be studied to establish the homopolymerization behavior of the silylated monomers in solution. It would also be of interest to examine the stability of the polymers in view of the known hydrolytic instability of the silyl groups attached to the amide functionality.

In view of the anticipated solubility of 1(a-c) in organic solvents it would be of interest to study the solution copolymerization of 1(a-c) with styrene. It was expected that copolymerization in a homogeneous medium will improve the reactivity of the protected acrylamide towards styrene. Upon hydrolysis, the amide functionality of the copolymers would be regenerated. This could provide a new approach towards synthesis of copolymers containing randomly distributed hydrophilic and hydrophobic monomers.

Kinetics of solution homo and copolymerization would be investigated to understand the effect of monomer concentration, initiator concentration and temperature on the rate of polymerization. The relative reactivity ratios of 1(a-c) with respect to styrene would confirm the copolymerization behavior. Further the dyad and triad sequence distribution of comonomers would be examined by ^{13}C NMR spectroscopy.

The silylated monomers 1b and 1d possess no active hydrogen and hence could undergo anionic polymerization. Subsequent deprotection could lead to poly(acrylamide)s with controlled molecular properties.

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CHAPTER - III

CHAPTER III:

SYNTHESIS OF SILYLATED ACRYLAMIDE MONOMERS:

3.1 Introduction:

Organic compounds containing silylated amide functionality have been well studied in terms of their usefulness as silyl transfer agents[1]. Silyl transfer has been investigated using a number of trimethylsilyl derivatives of amide compounds e.g. bis(trimethylsilyl)formamide, bis(trimethylsilyl)propionamide, bis(trimethylsilyl)dimethylacetamide, bis(trimethylsilyl)trimethylacetamide, and bis(trimethylsilyl)trifluoroacetamide[2]. In spite of this there has been scant reports in the literature on the synthesis of silylated acrylamide monomers and their polymerization. There are only two reports on N,O-Bis(trimethylsilylacrylamide), but without any evidence for the isolation or unequivocal characterization of this monomer[3,4]. N-trimethylsilylacrylamide has also been reported in the literature, but it does not seem to have been adequately characterized[5]. The other monomers namely, N-tert-butyldimethylsilylacrylamide and N-methyl,N-tert-butyldimethylsilyl acrylamide has not been reported in the literature so far. In this chapter the syntheses and characterization of various silyl derivatives of acrylamide will be discussed.

3.2. Experimental:

3.2.1. Instruments: The ^{13}C and ^{1}H NMR spectra were recorded using a Bruker AC-200 MHz spectrometer at 50.3 and 200 MHz respectively. Gas chromatographic analyses were done using a Blue-Star gas chromatogrph model 421 and 10% SE 30 column on chromosorb W (6′x 1/8″) and nitrogen as the carrier gas (30 mL/min) at a column temperature of 175°C using flame ionization detector. The column was conditioned by repeated injection of hexamethyldisilazane prior to use. Elemental analyses were performed on a Carlo-Erba model CHNS-O EA 1008 elemental analyzer. Analysis for C, H and N were done using helium as the carrier gas.

3.2.2. Materials: Acrylamide (BDH, India) was recrystallized from chloroform. Triethylamine (SD fine chemicals, Bombay) was refluxed over KOH for 6 h., distilled under argon and collected over KOH pellets. Chlorotrimethylsilane (Spectrochem India Ltd.) was distilled after stirring overnight over calcium hydride. Methylamine (40% aqueous solution, SD fine chemicals), acryloyl chloride (Aldrich) and tert-butyldimethylsilyl chloride (Aldrich) were used as supplied. Benzene and hexane were dried and distilled over blue sodium-benzophenone ketyl radical.

3.2.3. Synthesis and characterization of monosubstituted Acrylamides:

3.2.3.1. Synthesis and characterization of N-trimethylsilylacrylamide (TMSAm):

Acrylamide (5g., 0.07 mol), triethylamine (12 mL, 0.086 mol) and 80 mL of dry benzene were placed into a 500 mL three neck round bottom flask under a positive argon flow. The flask, equipped with a mechanical stirrer, was cooled in an ice bath. Chlorotrimethylsilane (11 mL, 0.086 mol) was slowly added to the reaction mixture by means of a hypodermic syringe. The mixture was mechanically stirred for 6h. at room temperature and filtered under argon. The filtrate and solvent were distilled off, leaving a white mass stirred with a minimum volume of hexane (40°C) and filtered under argon. On cooling the filtrate in an ice bath, flakes of TMSAm separated out; yield 92%, m.p. 58°C.

^{1}H NMR ($CDCl_3$) (Fig.3.1): δ = 0.28 (s,-NH-Si(CH_3)$_3$, 5.3 (hump, D_2O exchangeable, -NH-), 5.65 (dd; 1H, =CH-), 6.2 (m, 2H, CH_2=).

^{13}C NMR ($CDCl_3$) (Fig.3.2): δ = -0.59 (-NH-Si(CH_3)$_3$), 126.5 (CH_2=), 132.8 (=CH-), 171.0 (>C=O).

$C_6H_{13}NOSi$ (143.23)	Calc.	C 50.30	H 9.15	N 9.76
	Found	C 50.91	H 9.09	N 9.81

Gas chromatography of a solution of TMSAm in dry benzene showed that the compound was more than 98% pure.

3.2.3.2. Synthesis and characterization of N-tert-butyldimethylsilylacrylamide (TBDMSAm):

Acrylamide (4 g, 0.06 mol), triethylamine (12 mL, 0.09 mol) and 100 mL of dry benzene were placed into a 500 mL three neck flask under a positive argon flow. The flask, equipped with a mechanical stirrer, was cooled in an ice bath. Tert-butyldimethylsilylchloride (10 g, 0.07 mol), was introduced under a positive flow of argon. The mixture was mechanically stirred for 8h. at room temperature and filtered under argon. The filtrate and solvent were distilled off, leaving a white mass which was stirred with a minimum volume of hexane (40°C) and filtered through a grade-3 sintered disc under argon. On cooling the filtrate in an ice bath, flakes of the TBDMSAm separated out; yield 90%, m.p. 76°C.

^{1}H NMR ($CDCl_3$) (Fig.3.3): δ = 0.30 (s, -Si(CH_3)$_2$-), 0.95 (s, -C(CH_3)$_3$), 5.0 (hump; D_2O exchangeable, -NH-), 5.65 (dd, 1H, =CH-), 6.2 (m, 2H, CH_2=)

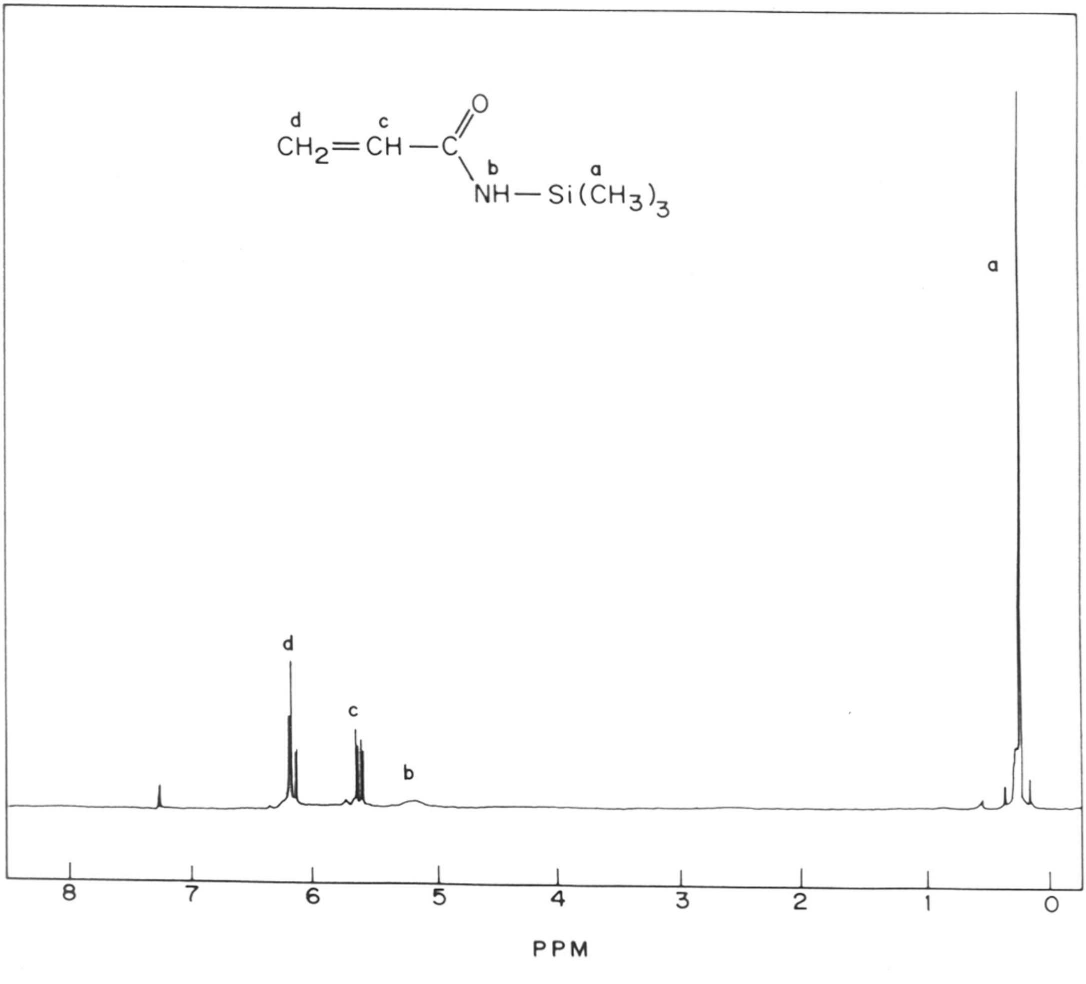


Fig. 3.1 ^{1}H NMR spectrum of N-trimethylsilyl acrylamide

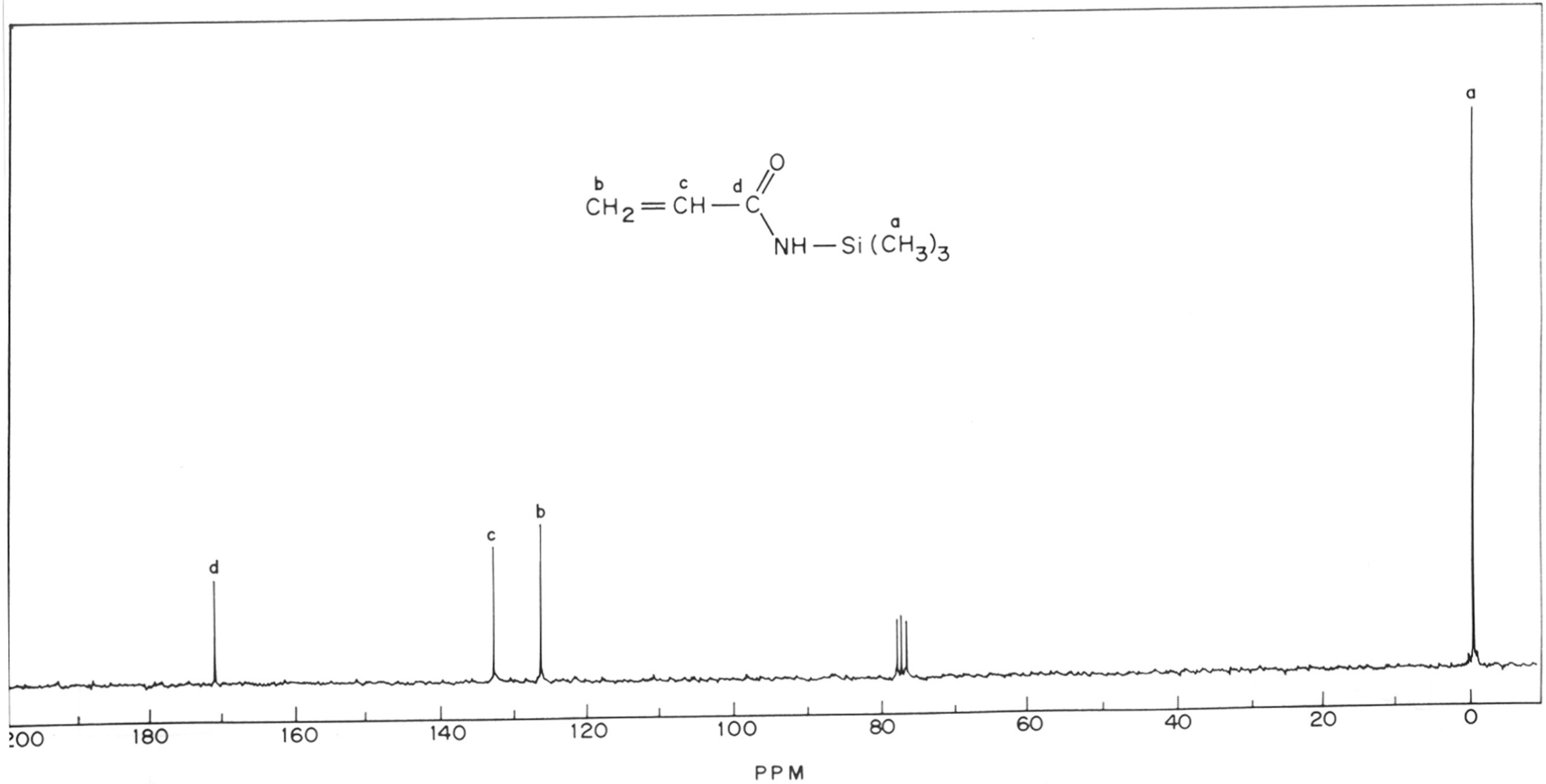


Fig. 3.2 ^{13}C NMR spectrum of N-trimethylsilyl acrylamide

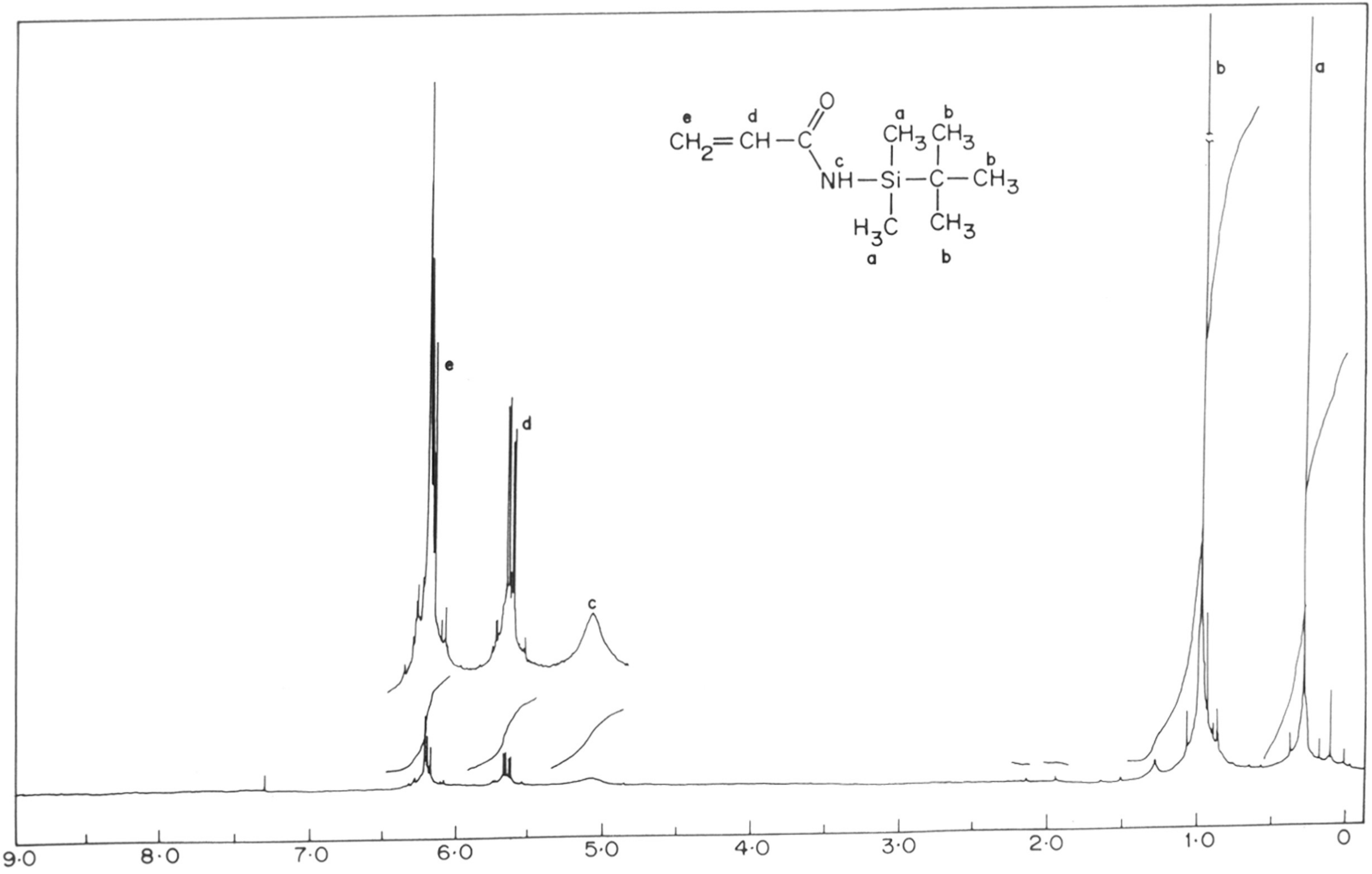


Fig. 3.3 ^{1}H NMR spectrum of N-tert-butyldimethylsilyl acrylamide

^{13}C NMR (CDCl$_3$) (Fig.3.4): δ = -5.05 (-Si(**C**H$_3$)$_2$-), 17.41 (-**C**(CH$_3$)$_3$), 26.26 (-C(**C**H$_3$)$_3$), 126.4 (**C**H$_2$=), 132.7 (=**C**H-), 170.9 (>**C**=O).

$C_9H_{19}NOSi$ (185.3)	Calc.	C 58.32 H 10.33 N 7.56
	Found	C 58.39 H 10.28 N 7.61

Gas chromatography of a solution of TBDSAm in dry benzene showed that the compound was 99% pure.

3.2.4. Synthesis of disubstituted acrylamides:

3.2.4.1. Synthesis and characterization of N,O-Bis(trimethylsilyl)acrylamide (BTSAm):

Acrylamide (4.2 g., 0.059 mol.), and about 50 mg. of copper wire pieces were placed in a 500mL four neck round bottom flask under a positive argon flow. Triethylamine (180 mL) was transferred into the same flask, and the flask was cooled in an ice bath. Chlorotrimethylsilane (18.5 g, 0.17 mol) was added to the flask by means of a hypodermic syringe. The mixture was mechanically stirred and gently refluxed (70°C) for 10 h. The contents of the flask was then filtered under argon and filtrate was distilled to remove unreacted triethylamine and chlorotrimethylsilane followed by vacuum distillation at 54°C (5.5 mbar) to give BTSAm in 65% yield. Trace impurities of the monosilylated compound could be separated from BTSAm by cooling the product to 0-10°C when the monosilylated derivative crystallized out. Attempts to obtain reproducible elemental analysis of BTSAm failed due to handling problems on account of its extreme sensitivity to atmospheric moisture. Gas chromatographic analysis was therefore employed for ascertaining the purity.

^{1}H NMR (CDCl$_3$) (Fig. 3.5): δ=0.20 and 0.35 (two singlets; =N-Si-(**C**H$_3$ and O-Si(**C**H$_3$)$_3$, respectively), 5.55 (t; 1H, =C**H**-), 6.02 (d, 2H, =C**H**$_2$).

^{13}C NMR (CDCl$_3$) (Fig. 3.6): δ = 0.58 and 1.36 (=N-Si(CH$_3$)$_3$) and O-Si(CH$_3$)$_3$); 124.48 (=CH$_2$), 131.58 (=CH-), 156.29 (-O-C=N-).

Gas chromatography of a solution of TMSAm in dry benzene showed that the compound was more than 98% pure.

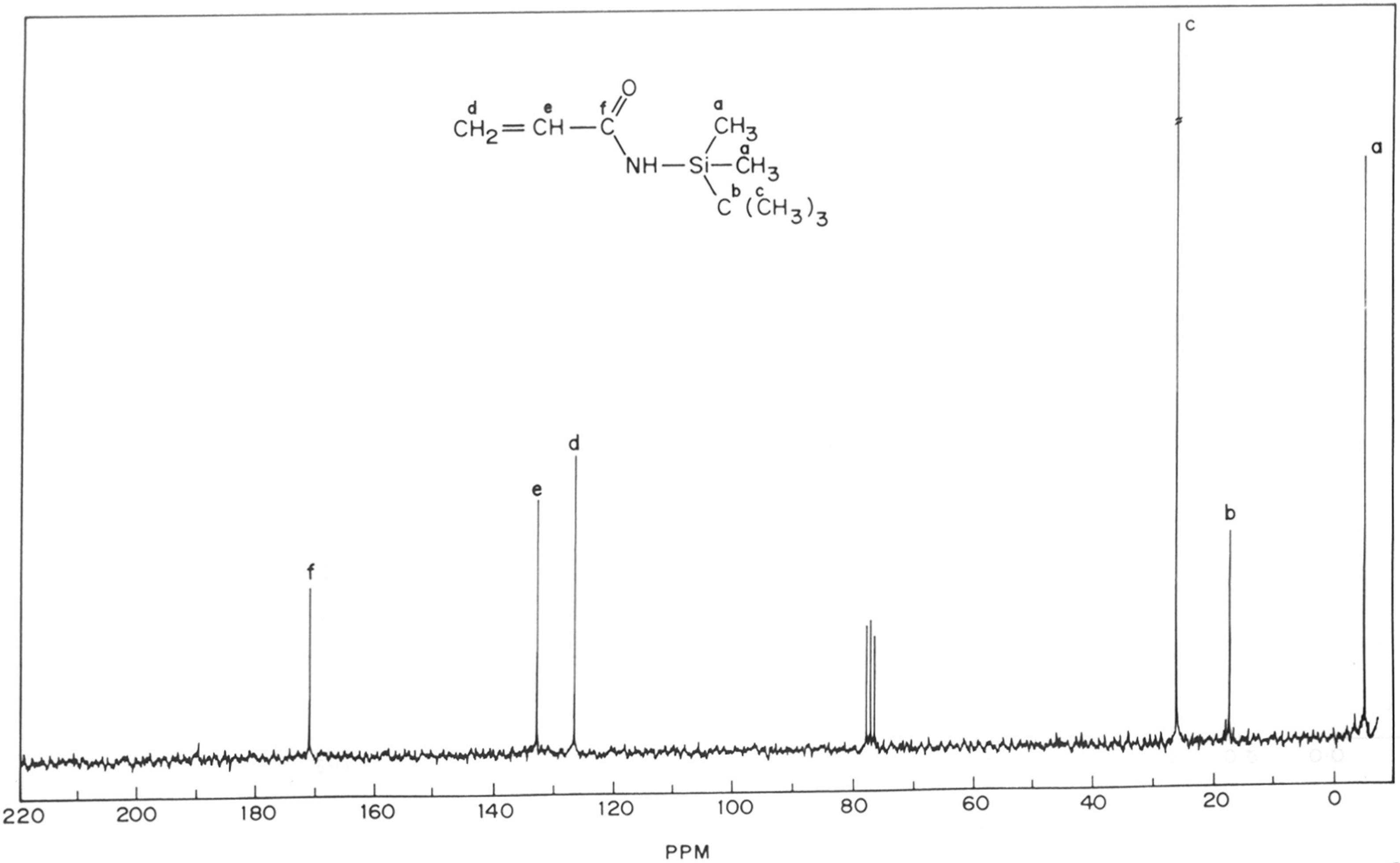


Fig. 3.4 ^{13}C NMR spectrum of N-tert-butyldimethylsilyl acrylamide

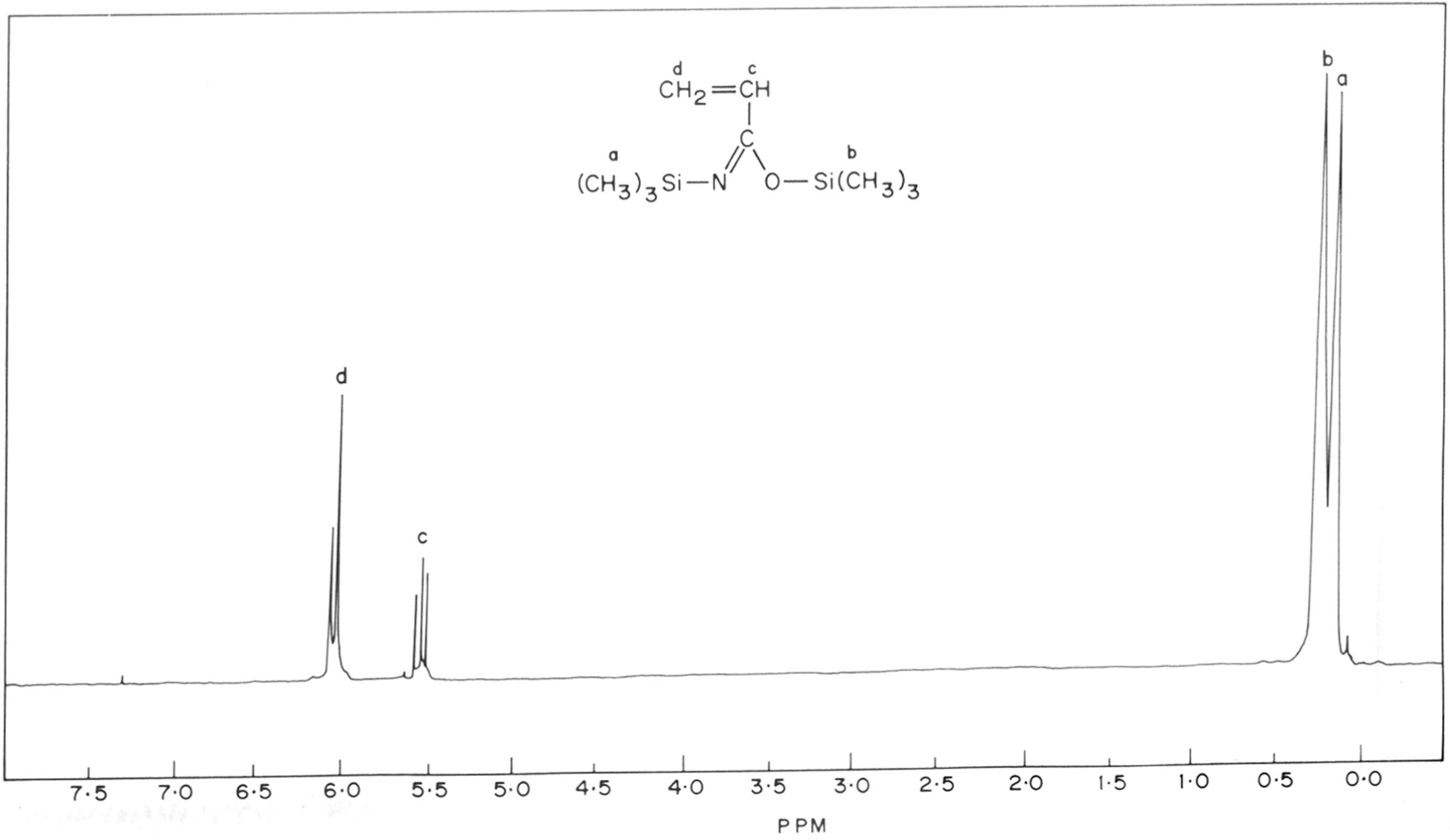


Fig. 3.5 ^{1}H NMR spectrum of N,O-bis(trimethylsilyl) acrylamide

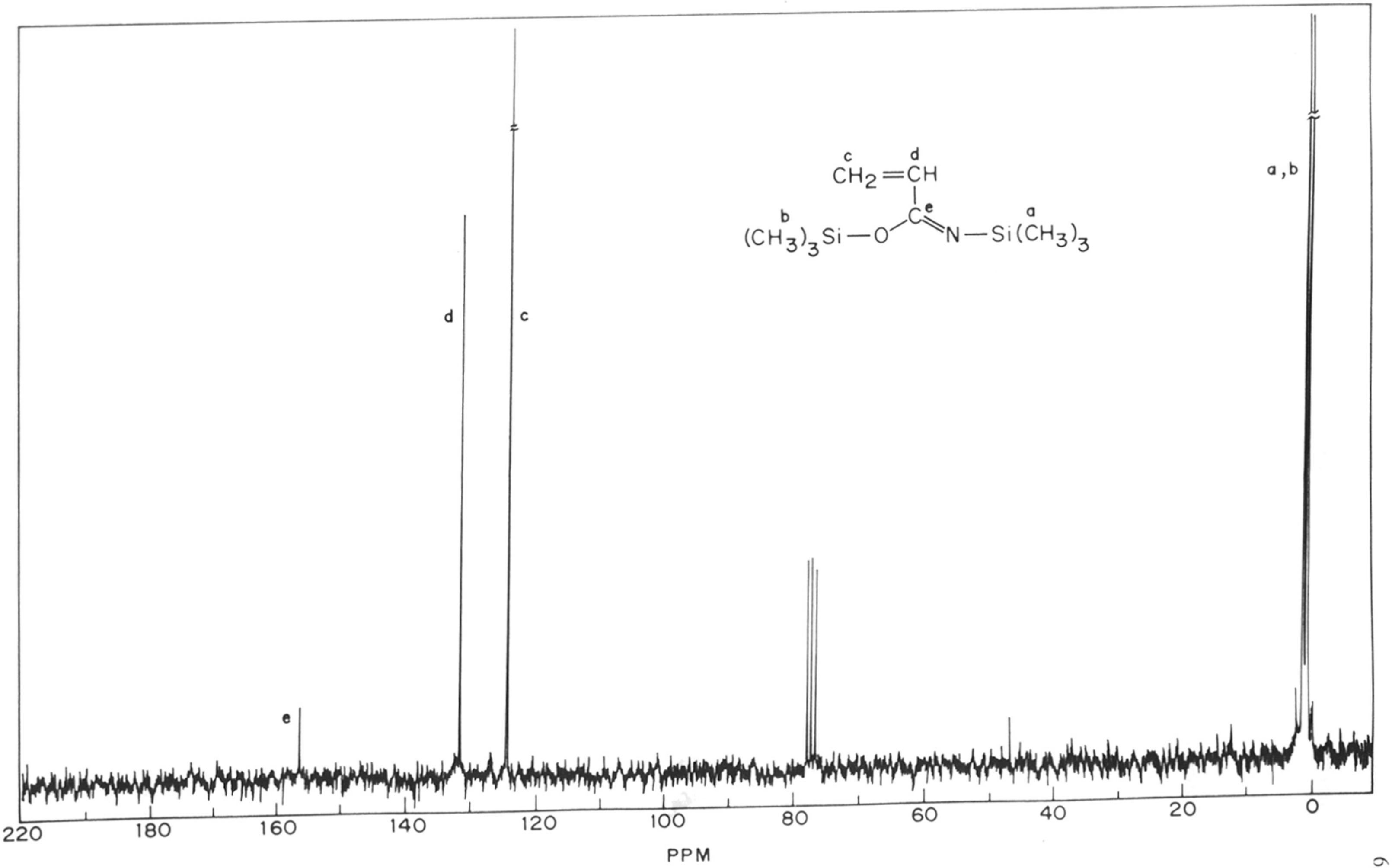


Fig. 3.6 ^{13}C NMR spectrum of N,O-bis(trimethylsilyl) acrylamide

3.2.4.2. Synthesis and characterization of N-methyl N-tert-butyldimethylsilylacrylamide (MTBDMSAm):

N-methyl acrylamide (NMA):

A 40% aqueous solution of methylamine (MeNH$_2$, 1.5 eqv.) was warmed and magnetically stirred with NaCl to generate MeNH$_2$ gas which was passed through a KOH column into dry benzene taken in a four neck flask. The flask, equipped with a mechanical stirrer and an addition funnel, was kept over an ice bath. Sufficient benzene was taken so that most of the liberated MeNH$_2$ gets dissolved in it. Later, 1 eqiv. of triethylamine was also added to the reaction mixture. Finally a solution of acryloyl chloride (1 eqiv.) in benzene was slowly added through an addition funnel with constant stirring of the reaction mixture. Care was taken to see that an yellowish to orange colour does not develop, which is the indication of some side reaction that occurs between triethylamine and acryloylchloride. After the addition was over, reaction mixture was stirred under a slow flow of argon for about 6 h. The product mixture was then filtered, the filtrate was concentrated and finally N-methylacrylamide was isolated in 87% yield by distillation under reduced pressure (75°C, 0.6 mbar). Figure 3.7 shows the schematic representation of the experimental set up for the synthesis of N-methylacrylamide.

^{1}H NMR (CDCl$_3$) (Fig.3.8):	δ = 2.8, d, >N-C**H**$_3$; 5.55, t, =C-**H**-; 6.17, d, C**H**$_2$=, 7.35, hump (D$_2$O exchangeable), -CON**H**-.	
^{13}C NMR (CDCl$_3$) (Fig.3.9)	δ = 25.79, -NHCH$_3$; 125.00, CH$_2$=; 130.86, =CH-; 166.69, >C=O	
C_4H_7NO (85.1)	Calc.	C 56.45 H 8.29 N 16.46
	Found	C 56.40 H 8.33 N 16.50

Gas chromatography of a solution of NMA in dry benzene showed that the compound was more than 99% pure.

N-methyl,N-tert-butyldimethylsilylacrylamide:

N-methylacrylamide (2 g., 0.024 mol.), and 35 mL of triethylamine were placed in a dry 100mL round bottom flask having a side arm and containing a magnetic needle. Under a positive flow of argon, about 5 g.(0.033 mol) of tert-butyldimethylsilylchloride was added into the flask. The contents of the flask was then subjected to hard stirring for about 30 min. at room temperature. The mixture was then transferred through a thick (16 gauge) cannula into an ampoule containing

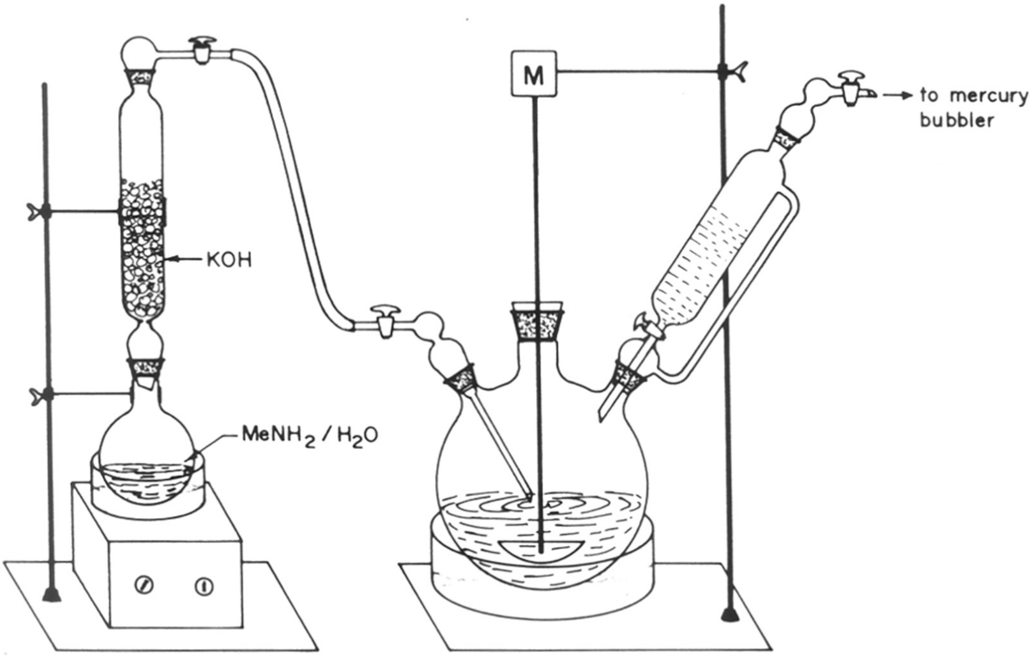


Fig. 3.7 Experimental set up for the synthesis of N-methylacrylamide

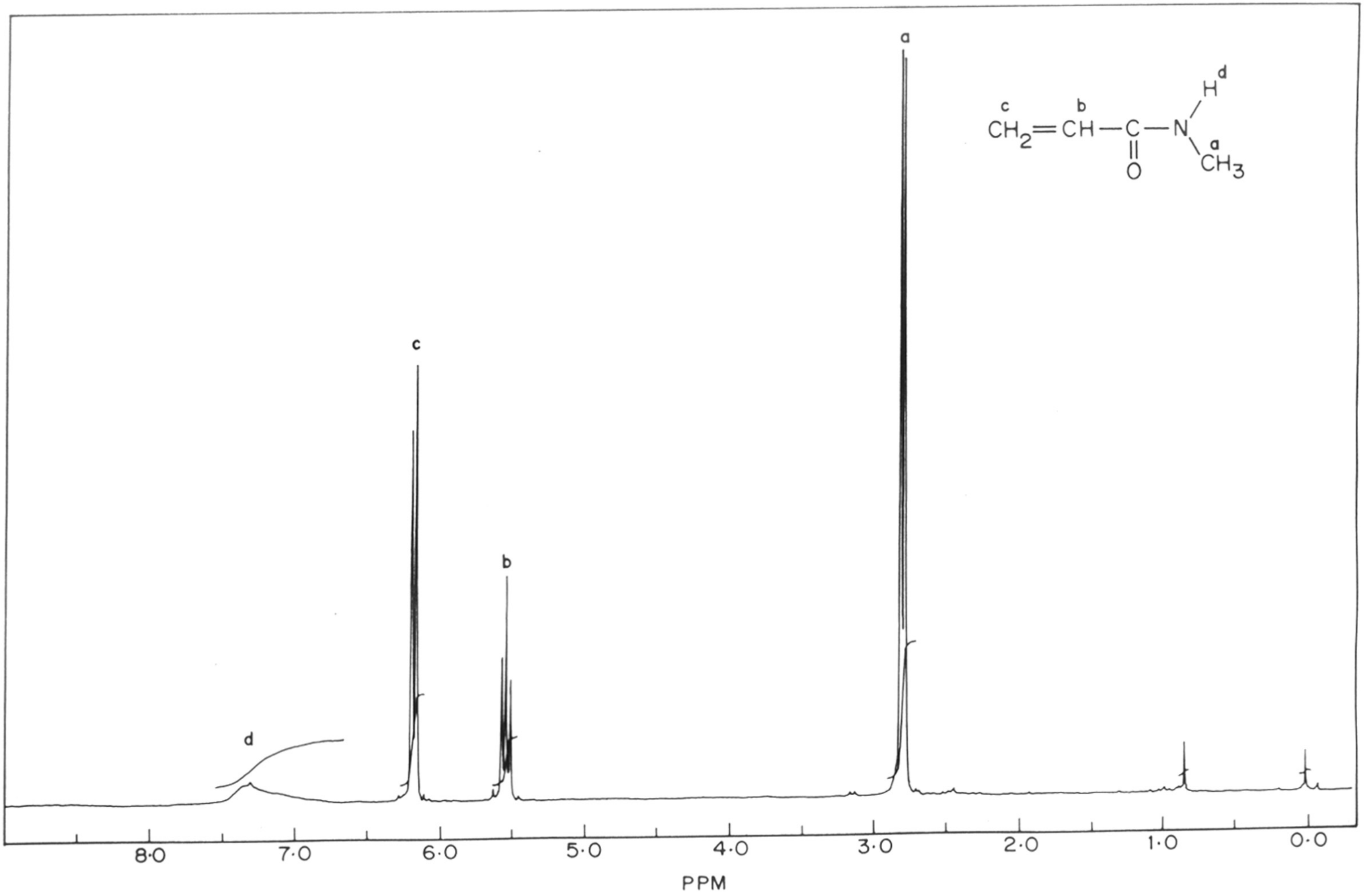


Fig. 3.8 ^{1}H NMR spectrum of N-methyl acrylamide

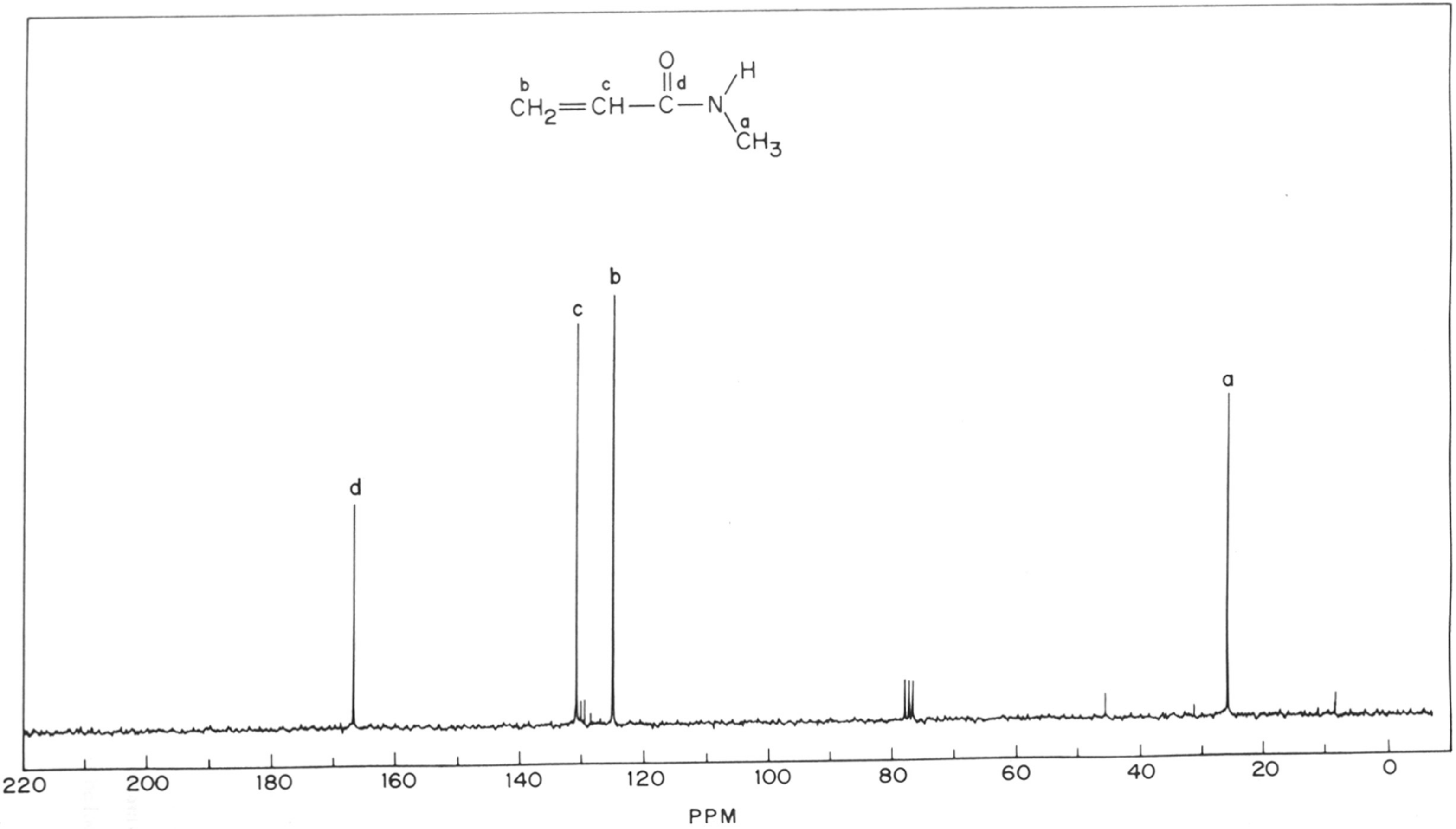


Fig. 3.9 ^{13}C NMR spectrum of N-methyl acrylamide

a magnetic needle under a positive pressure of argon. Remainings of the flask was washed with 10mL more of triethylamine and transferred into the ampoule. Subsequently the ampoule was sealed under vacuum. The ampoule was then kept in an oil bath adjusted to 55°C and the content of the ampoule was vigorously stirred for about 48 h. The seal was cut opened and the product mixture was filtered under argon. The filtrate was concentrated and the monomer MTBDMSAm was distilled at 75°C at 6.0 mbar. The monomer was obtained in about 72% yield based on N-methylacrylamide.

Imidate structure:

^{1}H NMR: (Fig. 3.10): δ = 0.25, s, -Si(CH_3)$_2$-; 0.90, s, -C(CH_3)$_3$; 2.84, s, >N-CH_3; 5.57, d, =CH-; 6.25, m, CH_2=.

^{13}C NMR: (Fig. 3.11): δ = -2.95, -Si(CH_3)$_2$-; 18.08, -C(CH_3)$_3$; 26.93, s, -C(CH_3)$_3$; 25.76, >N-CH_3, 122.10, CH_2=; 131.21, =CH-, 155.02, >C=N-.

Amide structure:

^{1}H NMR: (Fig. 3.10): δ = 0.25, s, -Si(CH_3)$_2$-; 0.90, s, -C(CH_3)$_3$; 2.84, s, >N-CH_3; 5.75, d, =CH-; 6.50, m, CH2=.

^{13}C NMR: (Fig. 3.11): δ = -3.31, -Si(CH_3)$_2$-; 18.08, -C(CH_3)$_3$; 26.93, s, -C(CH_3)$_3$; 25.80, >N-CH_3, 125.25, CH_2=; 133.76, =CH-, 166.45, >C=O.

3.3. Results and Discussion:

3.3.1. Monomer synthesis and characterization:

Substitution of the first amide hydrogen by a trimethlsilyl or tert-butyldimethylsilyl group could be performed easily by treating acrylamide with the corresponding silylchloride. Addition of chlorotrimethylsilane to a solution of triethylamine in benzene results in the formation of white fumes and a solid almost instantaneously. Greater than 90% yield are obtained in about 6-8h. time. The copious formation of solids (triethylamine hydrochloride) necessitated the use of a mechanical stirrer for a proper mixing of the reactants.

Introducing a methyl group in acrylamide cannot be done in a manner similar to silylation. The usual procedure for the synthesis of N-methylacrylamide is by reacting methylamine and acryloyl chloride. However, only two published procedures for this synthesis could be located[6,7].

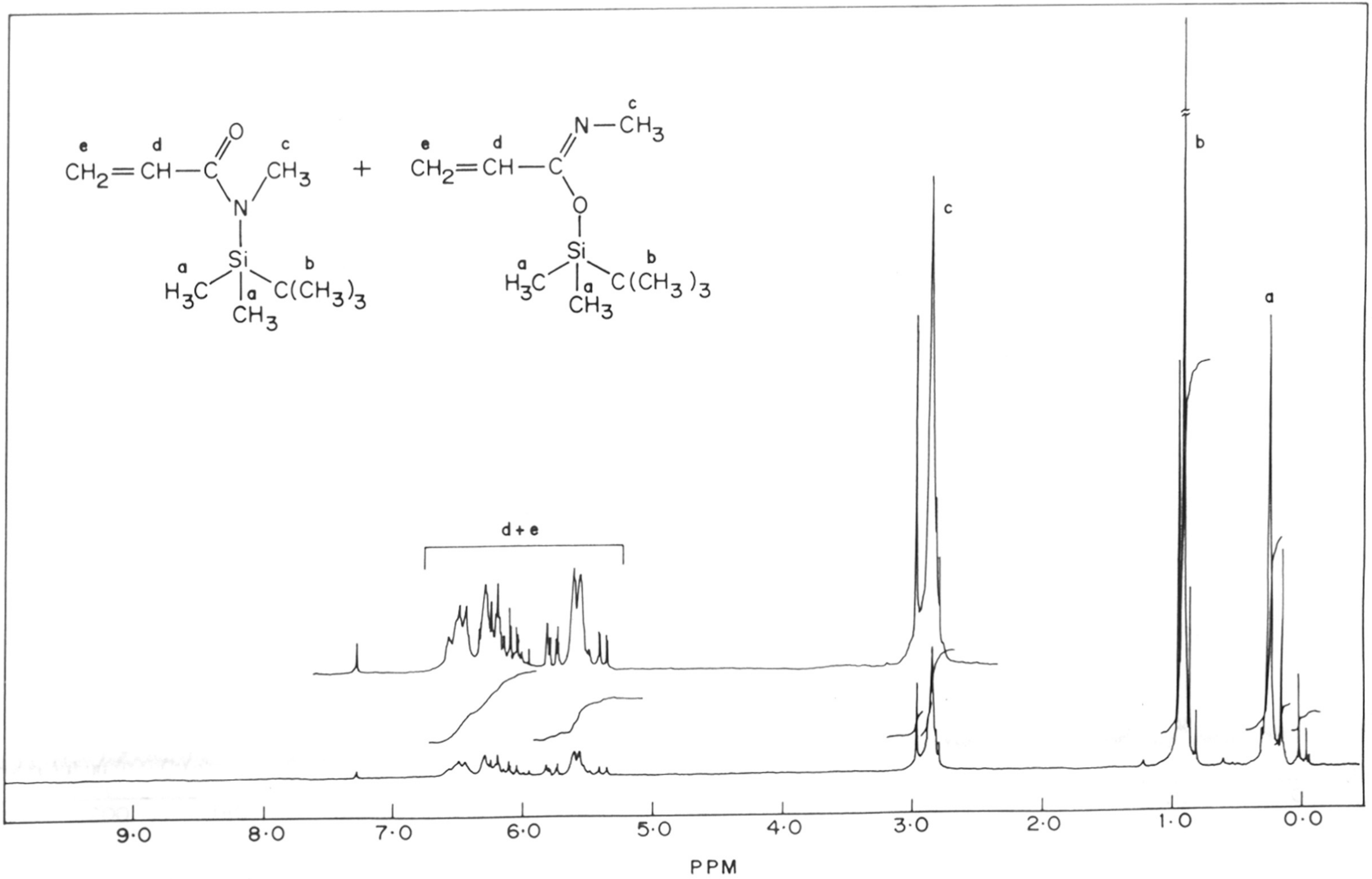


Fig. 3.10 ^{1}H NMR spectrum of N-methyl, N-tert-butyldimethylsilylacrylamide

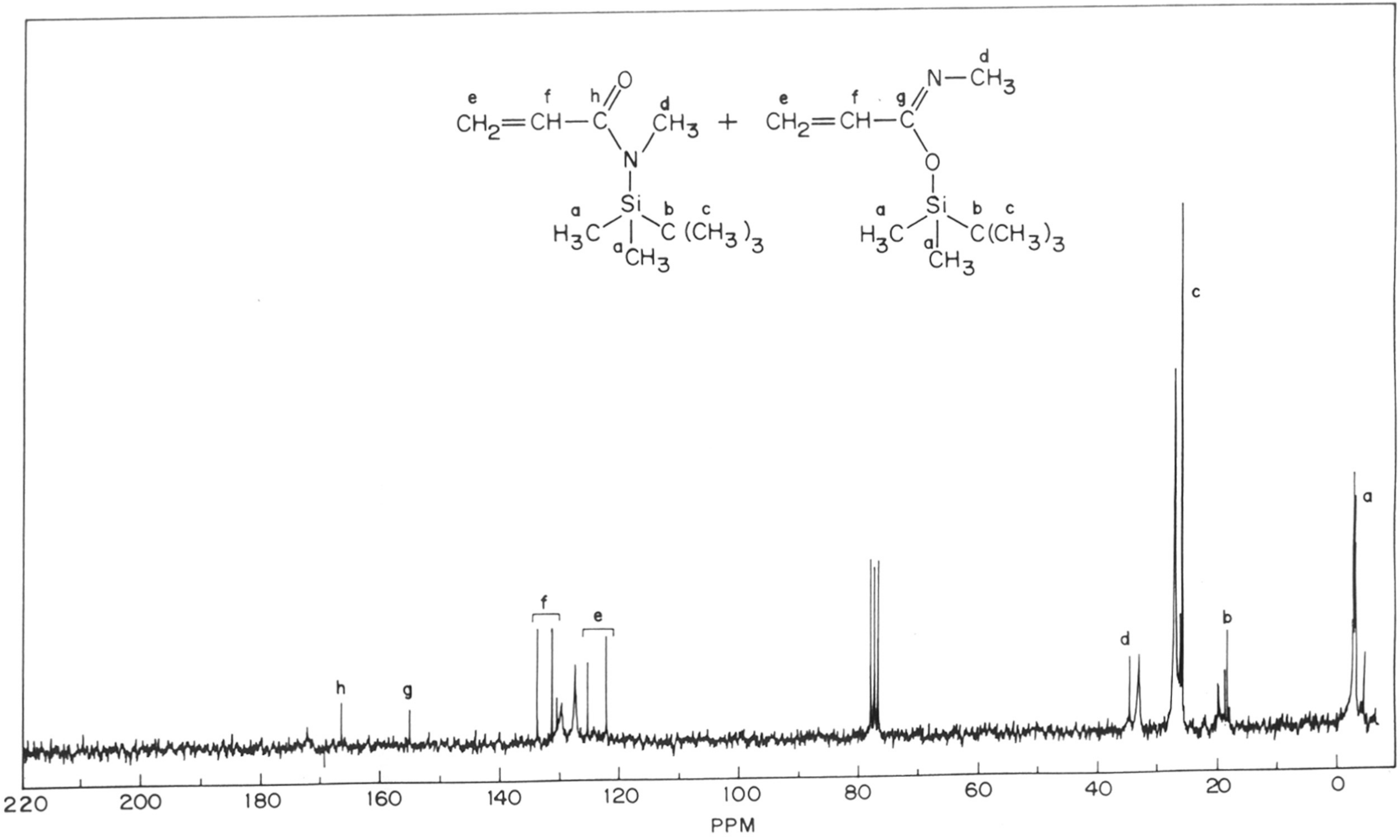


Fig. 3.11 ^{13}C NMR spectrum of N-methyl,N-tert-butyldimethylsilyl acrylamide

One of them[6] only mentions carrying out the reaction in benzene and does not describe the procedure whereas the other[7] prescribes the use of commercially available aqueous solution of methylamine. In the latter case the yields are expected to suffer on account of the ease of hydrolysis of acryloyl chloride. Therefore we used benzene solution of methylamine resulting in 87% yield of the N-methylacrylamide.

Monosilylation of acrylamide conveniently occured at room temperature. However, If one hydrogen of acrylamide is replaced by an alkyl or a silyl group, replacement of the second hydrogen by a silyl group always required much harsher conditions. Introduction of the second silyl group requires neat triethylamine as the solvent and prolonged refluxing of the reaction mixture (around 70°C). The use of a solvent such as benzene or toluene retards the bis silylation.

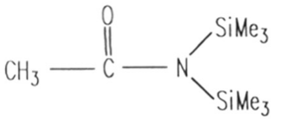
Triethylamine is generally believed to be a scavenger for the liberated hydrogen chloride. However, in silylation its role appears to be larger than this and effectively participates and facilitates the reaction.

Because of the larger size of the tert-butyldimethylsilyl group, introduction of this as a second substituent into a mono-N-substituted acrylamide was found to be a slower process.

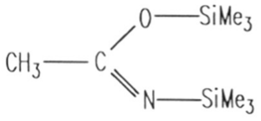
It is observed that due to the presence of both the tautomers, the NMR spectrum of MTBDMSAm took on a complicated shape. The assignments were made based on the NMR spectra of similar compounds like the TBDMSAm and N-methylacrylamide.

3.3.2. Monomer structure: amide-imidate equilibrium in disilylated amide compounds.

One of the interesting features of the amide derivatives bearing trimethylsilyl and tert-butyldimethylsilyl groups is their ability to exist in tautomeric forms. This is particularly well illustrated by the stereochemical non-rigidity of the popular silylating agent bis(trimethylsilyl)acetamide (BSA). Although this compound has been reported to have the amide structure (A)[8] and the imidate structure (B)[9], the imidate assignment has been confirmed by a spectroscopic study of the ^{15}N derivative[10].



A

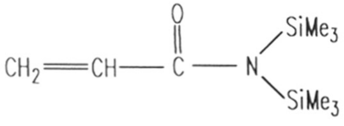


B

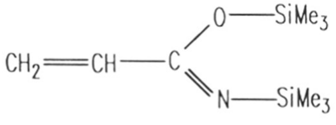
The NMR spectrum of BSA at room temperature (27-31°C) contains a singlet in the trimethylsilyl region which splits into a doublet as the temperature decreases. This behavior is attributed to a temperature-dependent intramolecular exchange of trimethylsilyl groups[2,11].

^{1}H NMR of BTSAm shows two distinct signals at 0.20 and 0.35 ppm indicating that at room temperature, the monomer exists exclusively in the imidate structure (D). The repeat unit of the homopolymer of BTSAm has a molecular structure which is analogous to that of acetamide, but still the polymer exists in the imidate form as evidenced by the ^{29}Si CP-MAS spectrum of poly(BTSAm) (Chapter 4, Fig.4.2). Chemical shifts for the silicons are -9.55 ppm and 16.41 ppm, close to the same for BSA silicons at -5.5 ppm and 16.6 ppm[11]). Reason may be that in solid phase this kind of tautomerism is more restricted.

The electronic differences between the amide forms of the bis silylated acetamide and bis silylated acrylamide is that in the former (A) the carbonyl-nitrogen π-character is more than that in the latter (C).



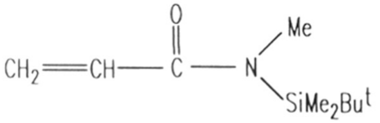
C



D

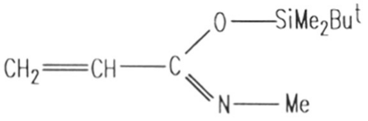
In acrylamide, the carbonyl group is conjugated with the vinylic double bond. Therefore, in (D) the contribution of the canonical forms having carbon-nitrogen double bond is less compared to the same in acetamide. Reportedly a decrease in the carbonyl-nitrogen π-character results in a decrease in the relative stability of the amide form[2]. Higher amide content is therefore expected for BSA and relatively less for BTSAm, since the π-electron density over the carbonyl-nitrogen linkage is more in the former and less in the latter.

It has been reported that the N-methyl,N-tert-butyldimethylsilyl acetamide exists in the amide form[12]. However, we found that the acrylamide analog of the same, i.e. MTBDMSAm exists as an equilibrium mixture of the amide (E) and the imidate (F) forms (shown below) at room temperature as indicated by the >C=O and -C=N- carbon peaks of almost equal intensity at 166.45 and 155.02 ppm respectively in the ^{13}C NMR.



$CH_2{=}CH{-}C({=}O){-}N(Me)(SiMe_2Bu^t)$

E



$CH_2{=}CH{-}C(O{-}SiMe_2Bu^t){=}N{-}Me$

F

3.4. Conclusion

In this chapter, the syntheses and characterizations of the silylated acrylamide monomers are described. All the monomers were hydrolytically unstable, but were stable to storage under inert conditions and could be conveniently used for further manipulations using cannula and benchtop inert atmosphere techniques. The silylated acrylamides are shown to exist in an equilibrium mixture of the amide and imidate forms.

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CHAPTER - IV

CHAPTER - IV:

SOLUTION HOMOPOLYMERIZATION OF SILYLATED ACRYLAMIDES:

4.1 Introduction: The solution polymerization of various silylated acrylamides were studied in benzene, wherein the chain transfer to solvent is negligible. The silylated polymers were quantitatively hydrolyzed and precipitated in acidulated methanol in the form of poly(acrylamide) for an accurate determination of the conversion. In the following sections the solution homopolymerization of BTSAm and TMSAm and their kinetics will be discussed.

4.2: Experimental:

4.2.1: Polymerization:

4.2.1.1: Materials: Benzoyl peroxide (BPO; from BDH, England) was recrystallized from methanol-chloroform. 2,2'-azobisisobutyronitrile (AIBN) was recrystallized from methanol. BTSAm was distilled and stored at 0-10°C about 6h. prior to use. TMSAm was recrystallized from dry hexane. Benzene was purified over blue sodium benzophenone ketyl radical. An initiator solution was made by dissolving an accurately weighed quantity of BPO in benzene.

4.2.1.2: Solution polymerization of N,O-bis(trimethylsilyl)acrylamide (BTSAm):

BTSAm is a liquid at room temperature and is miscible with benzene in all proportions. The monomer was polymerized using AIBN and BPO at a 70°C and 80°C respectively. The polymerizations were carried out in sealed ampoules. The monomer, benzene and the required quantity of initiator solution were transferred into ampoules through a cannula under a positive pressure of argon. The ampoules were sealed in vacuo and the contents were polymerized with BPO or AIBN for about 6 h. The contents of the ampoules were transferred under argon into a round bottom flask. The solvent was removed under vacuum and the residue was washed with dry hexane to remove any unreacted monomer.

^{1}H NMR ($CDCl_3$) (Fig. 4.1):	δ = 0.0-0.5 (m, 18H, $-OSi(CH_3)_3$ and $=N-Si(CH_3)_3$, 1.5-2.5 (two humps, 3H, $-CH_2-CH<$).
^{29}Si NMR ($CDCl_3$) (Fig. 4.2):	(solid state, MAS at 3.0 kHz, Me_4Si standard, taken without proton decoupling): δ = -9.55 ($=NSi(CH_3)_3$), 16.41 ($-OSi(CH_3)_3$).

The nitrogen content in poly(BTSAm) was found to be 6.38%. The calculated value is 6.50%.

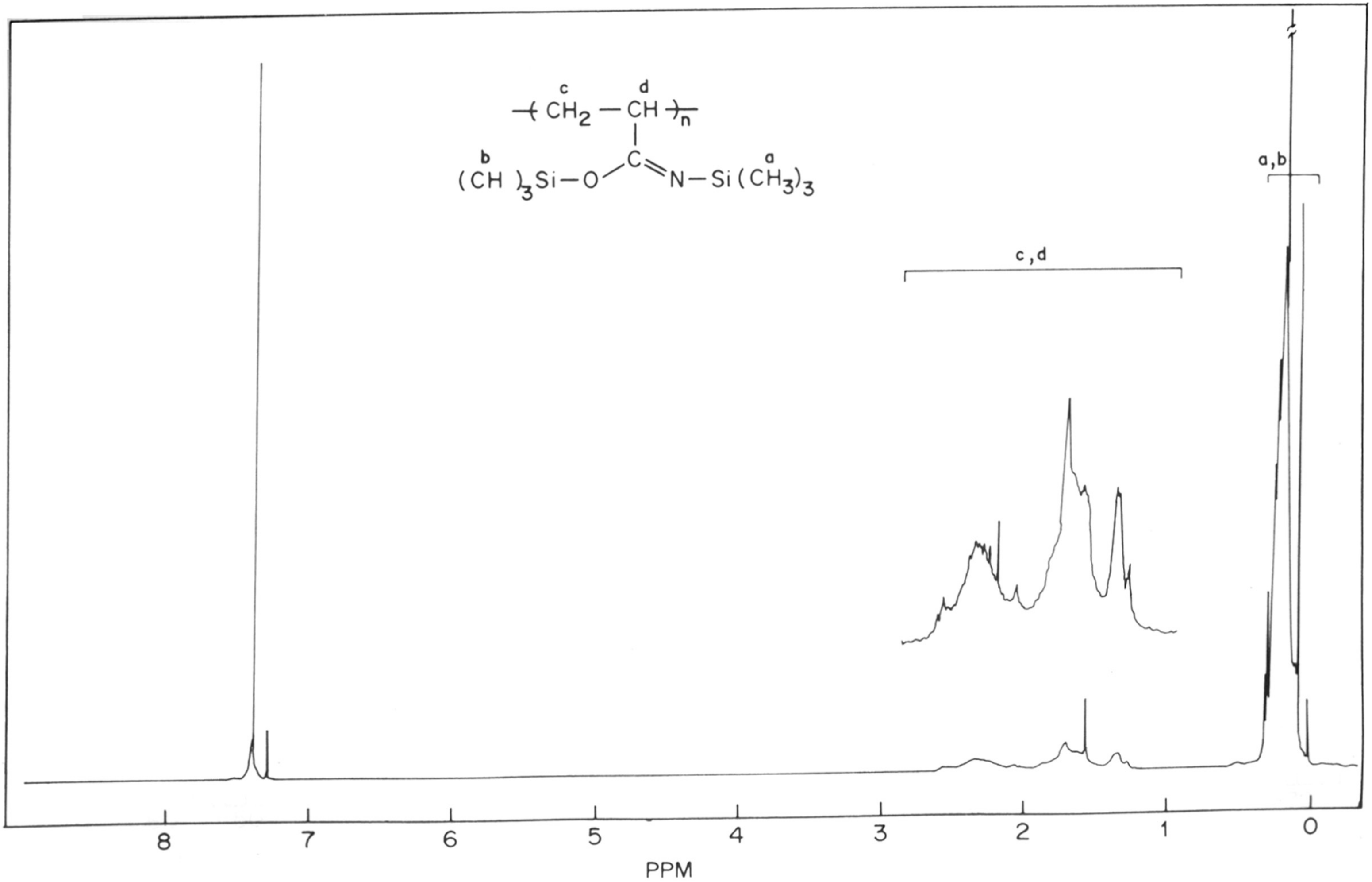

Fig. 4.1 ^{1}H NMR spectrum of poly[N,O-bis(trimethylsilyl) acrylamide]

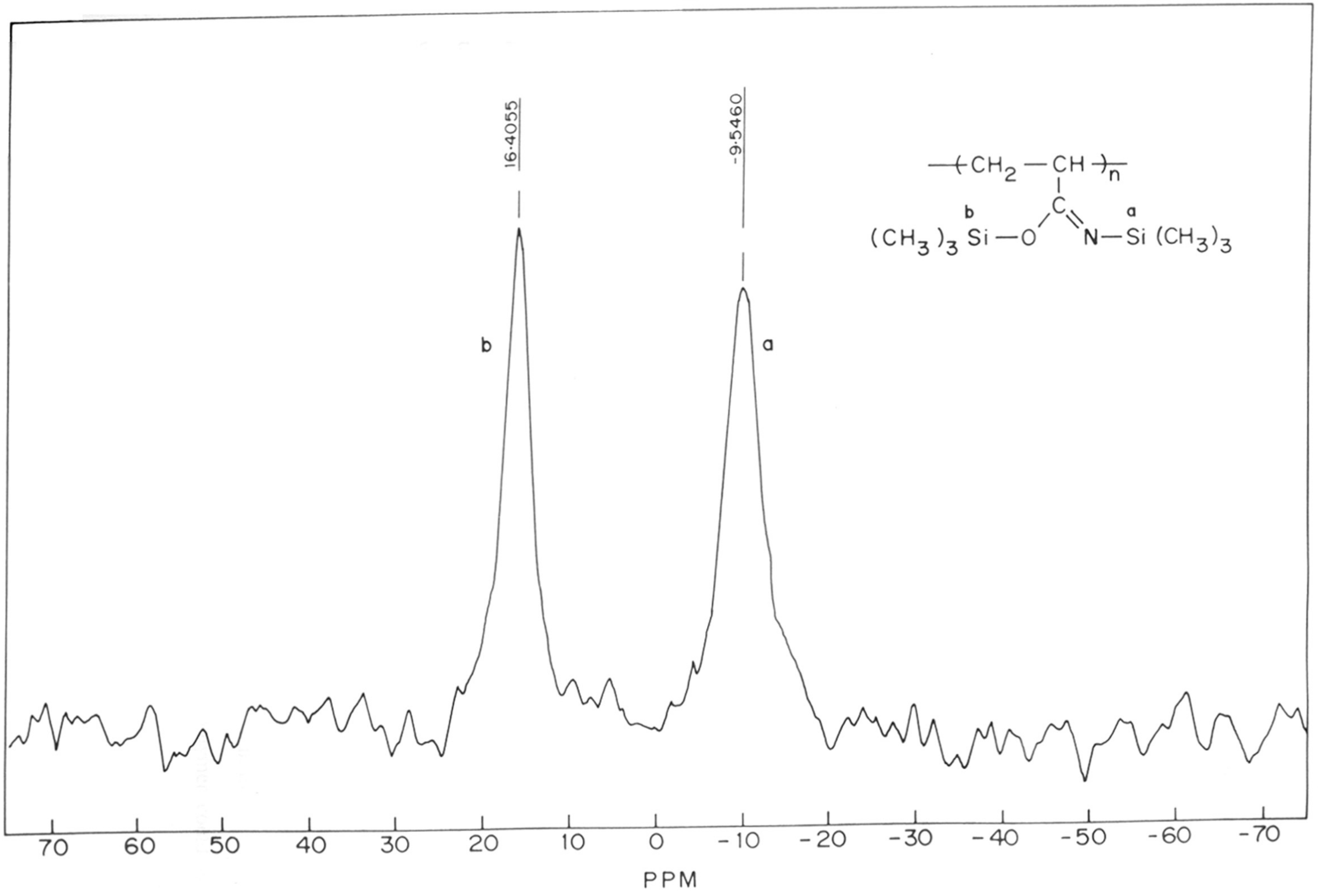

Fig. 4.2 ^{29}Si NMR spectrum of poly[N,O-bis(trimethylsilyl) acrylamide]

Solubility: The poly(BTSAm) was soluble in benzene and THF and also in methanol. It was found to be insoluble in hexane.

Stability: The polymers were highly unstable hydrolytically. However, if stored under an inert atmosphere, they were stable for an indefinite period of time.

4.2.1.3: Solution polymerization of N-trimethylsilylacrylamide (TMSAm):

TMSAm is a solid at room temperature and was highly soluble (more than 55% at ambient temperature) in benzene. The monomer was polymerized in benzene using AIBN and BPO at a temperature range of 40-80°C. The polymerizations were carried out in sealed ampoules. The monomer solution, benzene and the required quantity of initiator solution were transferred into ampoules through a cannula under a positive pressure of argon. The ampoules were sealed in vacuo and the contents were polymerized at 40°C and 70°C with AIBN and 50°C and 80°C with BPO for 2-3h. The contents of the ampoules were transferred under Argon into a round bottom flask, solvent was removed under vacuum and the residue was washed with dry hexane to remove any unreacted monomer.

^{1}H NMR: (Fig.4.3)	δ = 0.5, >N-Si(CH_3)$_3$ protons of polymer; 1-3 three humps, -CH_2-CH- backbone protons, 5.5-6.9, hump, deuterium exchangeable, >CONH- proton.

Solubility: The polymer was found to be soluble in benzene, tetrahydrofuran and also in methanol.

Stability: The polymer was stable indefinitely under inert atmosphere. However it underwent hydrolysis if kept in the open.

4.2.2: Hydrolysis: Treatment of an aliquot of the benzene solution of poly(TMSAm) or poly(BTSAm) with a 2N solution of HCl in methanol results in complete hydrolysis of the silyl groups as well as precipitation of the polymer. Alternatively the benzene was removed by evacuation and the residue was stirred with a minimum volume of a solution of 0.5N HCl/tetrahydrofuran (1:1, v/v) when two layers were separated. The polymer could be precipitated in methanol.

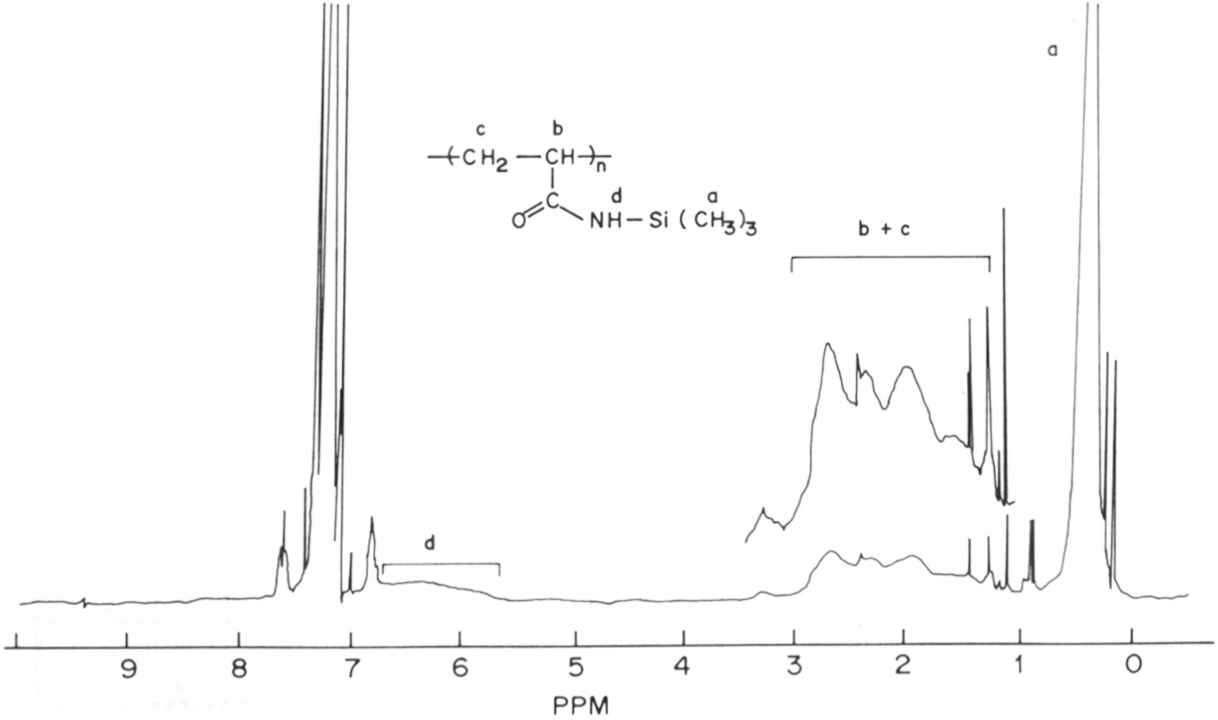

Fig. 4.3 ^{1}H NMR spectrum of poly[N-trimethylsilyl acrylamide]

Table-4.1
Polymerization of N,O-Bis(trimethylsilyl)acrylamide in Benzene

Exp. No.	[M] (mol/L)	[I] (mol/L)	conv. to poly(BTSAm) (%)	$[\eta]^a$ of poly(BTSAm) dL/g.	conv. to polyacrylamide (%)	$[\eta]^b$ of polyacrylamide in dL/g.	silyl content after wash (%)
Initiator AIBN							
1.	0.40	0.02	75	0.11	75	0.12	99
2.	0.40	0.01	74	0.12	74	0.13	95
3.	2.00	0.02	100		100	0.46	
Initiator BPO							
4.	0.40	0.02	74	0.14	74	0.21	96
5.	0.40	0.01	70	0.14	73	0.24	96
6.	2.00	0.02	100		100	0.52	

[a] Measured in benzene at 30±0.1°C
[b] Measured in water at 30±0.1°C

Table-4.2
Polymerization of N-trimethylsilylacrylamide in Benzene

Exp. No.	[M] (mol/L)	[I] (mol/L)	Temp. in °C	Time in h.	conversion in (%)	$[\eta]^a$ of polyacrylamide in dL/g.	M_v of polyacrylamide x 10^{-5}
				Initiator AIBN			
1.	2.0	0.02	40	3.0	100	5.74	23.5
2.	2.0	0.02	70	2.0	95	1.37	3.84
3.	1.0	0.01	40	3.0	100	3.41	12.2
4.	1.0	0.01	70	2.0	100	0.74	1.76
				Initiator BPO			
5.	2.0	0.02	50	3.0	94	2.31	7.44
6.	2.0	0.02	80	2.0	100	0.89	2.22
7.	1.0	0.01	50	3.0	100	2.05	6.40
8.	1.0	0.01	80	2.0	100	0.52	1.13

a) Measured in water at 30±0.1°C

4.2.3: Kinetics of Solution homopolymerization of TMSAm and BTSAm: Kinetics of solution homopolymerization was studied to understand the effect of monomer concentration [M], initiator concentration [I], and temperature on the rates of polymerization of TMSAm and BTSAm. In one set of experiment the monomer, initiator and solvent were taken in an apparatus shown below (Fig.4.4) and from time to time aliquots of the reaction mixture were syringed out and precipitated in a 2N HCl solution in methanol in gooch crucibles.

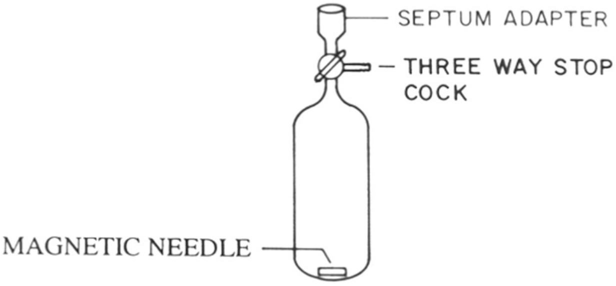

FIG. 4·4

In another set of experiments, a number of ampoules were filled with monomer, solvent and initiator solutions, sealed under vacuum and dipped in an oil bath heated to the temperature of polymerization. From time to time the ampoules were taken out of the oil bath and dipped into liquid nitrogen to quench the reaction. Subsequently, the ampoules were cut opened, the polymer dissolved by adding dry tetrahydrofuran and transferred into a beaker. To this a 2N HCl/THF solution was added and the mixture was slowly stirred when two layers separated. The entire solution was then poured into a large volume of MeOH with stirring to precipitate the polyacrylamide. The mixture was then filtered through a G-4 gooch crucible and the residue dried at 40°C until no further weight loss. The conversions were determined based on the initial feed of the monomer. BTSAm is a liquid and the neat monomer has a concentration of about 4.0 M. TMSAm could be dissolved to make solution as concentrated as 3.5 M. It was found that for both monomers use of a concentration more than 2.0 M results in the formation of a highly viscous solution or gel within an hour. Experiments were therefore performed at conditions at which for a considerable span of time the polymer solution could be syringed out and the conversions could be easily followed.

4.3: Results and Discussion:

4.3.1: Homopolymerization of BTSAm: Polymerization of BTSAm was carried out using AIBN and BPO as the initiators. The poly(BTSAm) samples were isolated under careful exclusion of moisture and characterized by ^{1}H and ^{29}Si NMR as well as by intrinsic viscosity in benzene. The ^{1}H NMR spectrum of the polymer washed with hexane to remove unreacted monomer is shown in Fig.4.1. The fact that the silyl groups were intact in the polymer after polymerization and work up was confirmed by estimation of the silyl content from NMR (Table-4.1). The ^{29}Si NMR spectrum of the polymer in the solid state shows two distinct silicon peaks of almost equal intensity (Fig.4.2) which indicates that the polymer also exists in the imidate form like the monomer.

The polymer is stable indefinitely as long as protected from moisture. Poly(BTSAm) could be quantitatively deprotected under mild conditions to poly(acrylamide).

4.3.2: Homopolymerization of TMSAm: Polymerization of TMSAm has been carried out using AIBN and BPO as the initiators. The poly(TMSAm) samples were isolated under careful exclusion of moisture and characterized by ^{1}H NMR (Fig. 4.3). The fact that the silyl groups were intact in the polymer after polymerization was confirmed from the ratio of the relative integration of the vinyl and silyl protons of the polymer, which was found to be 1:3 as expected. Poly(TMSAm) could be quantitatively deprotected under mild conditions.

4.3.3: Kinetic Aspects of Solution homopolymerization: In all the time-conversion experiments, the time-conversion plots were found to be a straight line up to a certain time after which the curves levelled off. In most of the cases, an induction period of 3-5 min. was noticed. At low concentrations and/or lower temperatures, a longer induction period (about 30 min.) were observed. The rate of polymerizations were calculated based on the linear part of the time conversion curve.

In order to compare the polymerization data for TMSAm and BTSAm with those for the other conventional monomers like acrylates and acrylamide derivatives an assumption was made that the reaction follows classical radical kinetics with termination by disproportionaltion and no transfer. These assumptions allow a calculation of the ratio $k_p/k_t^{1/2}$ in the classical equation for the ideal radical polymerizations which is,

$$R_p = \left(\frac{k_p}{k_t^{\frac{1}{2}}} \right) [M] \, (2fk_d[I])^{\frac{1}{2}} \text{.............}(4.1)$$

where R_p is the rate of polymerization, [M] is monomer concentration, [I] is the initiator concentration, k_p, k_t, k_d are the rate constants for propagation, termination, and initiator decomposition respectively and 'f' is the initiator efficiency. Having obtained $k_p/k_t^{1/2}$ values from the measured R_p values, one can then calculate the expected values of M_n using the equations:

$$P_n = \nu_n = \left(\frac{K_p}{K_t^{\frac{1}{2}}} \right) \frac{[M]}{(2fk_d[I])^{\frac{1}{2}}} \text{..............}(4.2)$$

and

$$M_n = P_n \times m \text{...........}(4.3)$$

where P_n is the number average degree of polymerization, ν_n is the kinetic chain length and 'm' is the molecular weight of the monomer unit. In deriving equations 4.1 and 4.2, the termination step, -d[R]/dt has been defined as $k_t[R]^2$ rather than as $2k_t[R]^2$ so as to produce $k_p/k_t^{1/2}$ values that can be directly compared with those in the literature which have mostly been derived assuming the former convention[1]. For the decomposition of BPO at 60°C, 70°C and 80°C, the k_d values have been assumed to be 2.14×10^{-6}, 1.21×10^{-5} and 4.01×10^{-5} respectively. For the decomposition of AIBN at 50°C, 60°C and 70°C the k_d value has been assumed to be 2.30×10^{-6}, 8.80×10^{-6} and 3.47×10^{-5} respectively. These values are the averages of those given in reference 2 for decomposition of BPO and AIBN at the relevant temperatures in benzene.

The values of 'f' have been assumed to be 1.0 and 0.6 for BPO and AIBN respectively[3].

4.3.3.1: Dependence of the polymerization rate on initiator concentration:

Equation 4.1 shows that the polymerization rate is dependent on the square root of the initiator concentration. For both BTSAm and TMSAm this dependence has been confirmed as shown in the plot of $[I]^{1/2}$ versus R_p in Fig.4.5 and Fig.4.6 respectively.

4.3.3.2: Dependence of the polymerization rate on monomer concentration: The rate expression in equation (4.1) also requires a first order dependence of the polymerization rate on the monomer concentration. This is indeed found to be the behavior for both TMSAm and

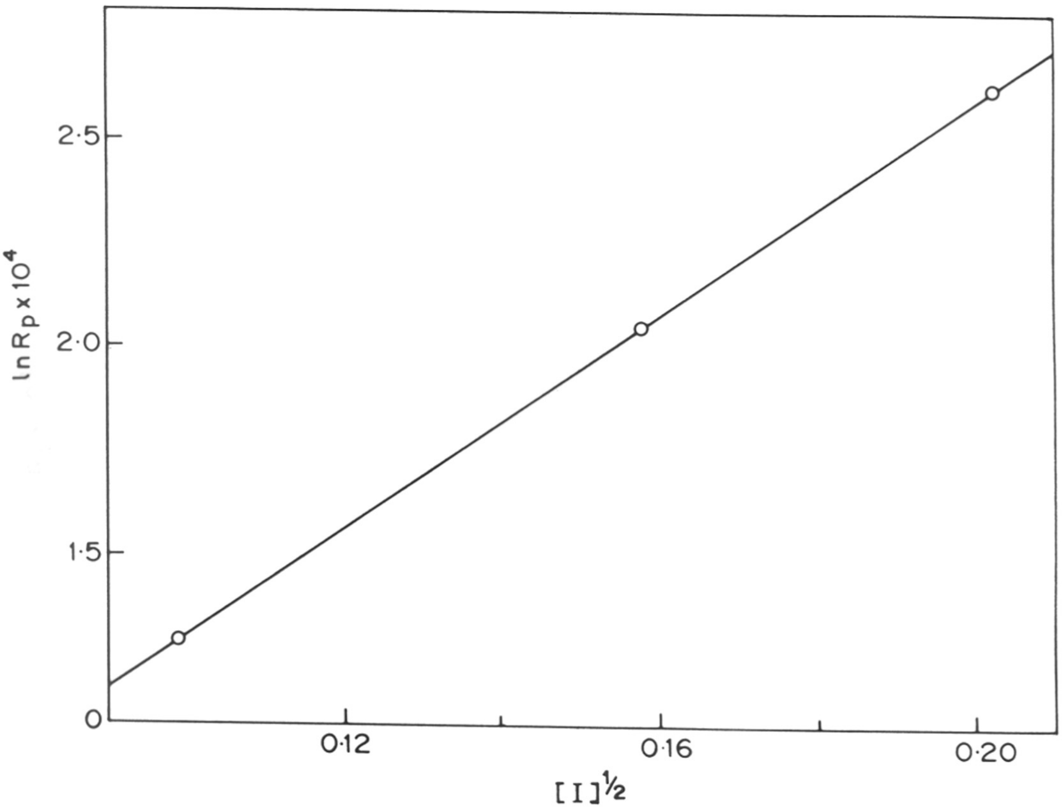

Fig. 4.5 Dependence of rate of polymerization of BTSAm on initiator concentration

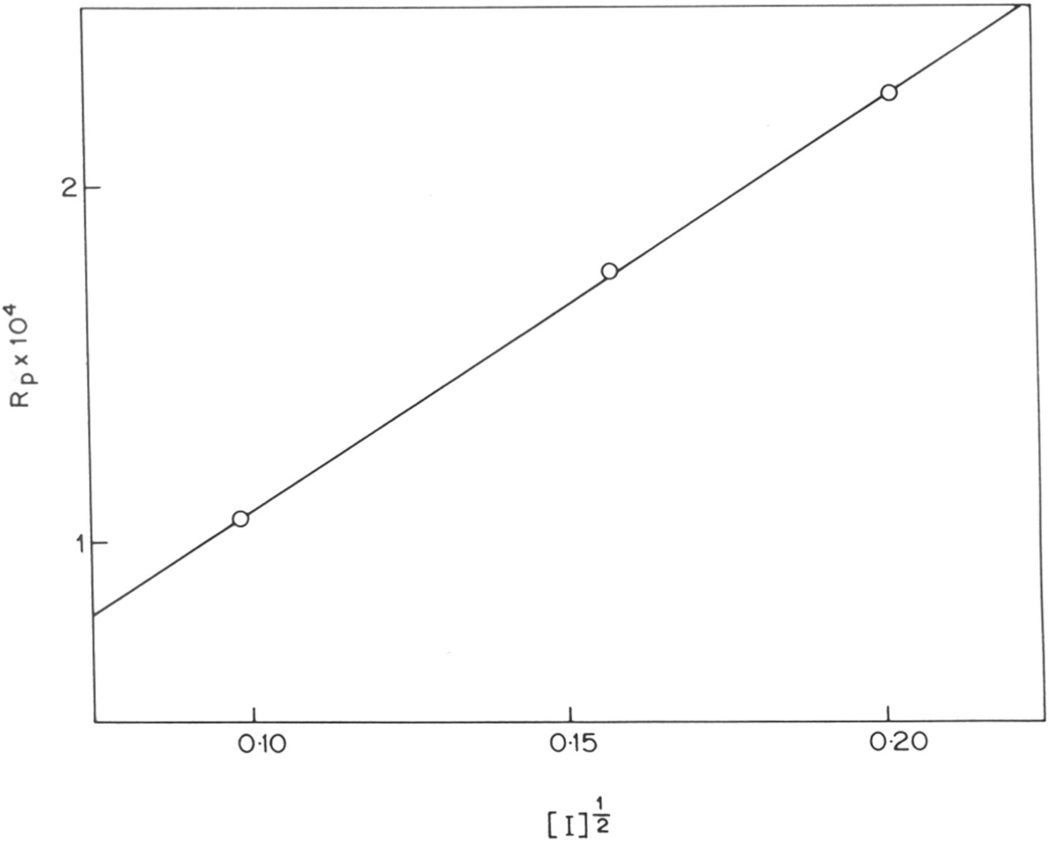

Fig. 4.6 Dependence of rate of polymerization of TMSAm on initiator concentration

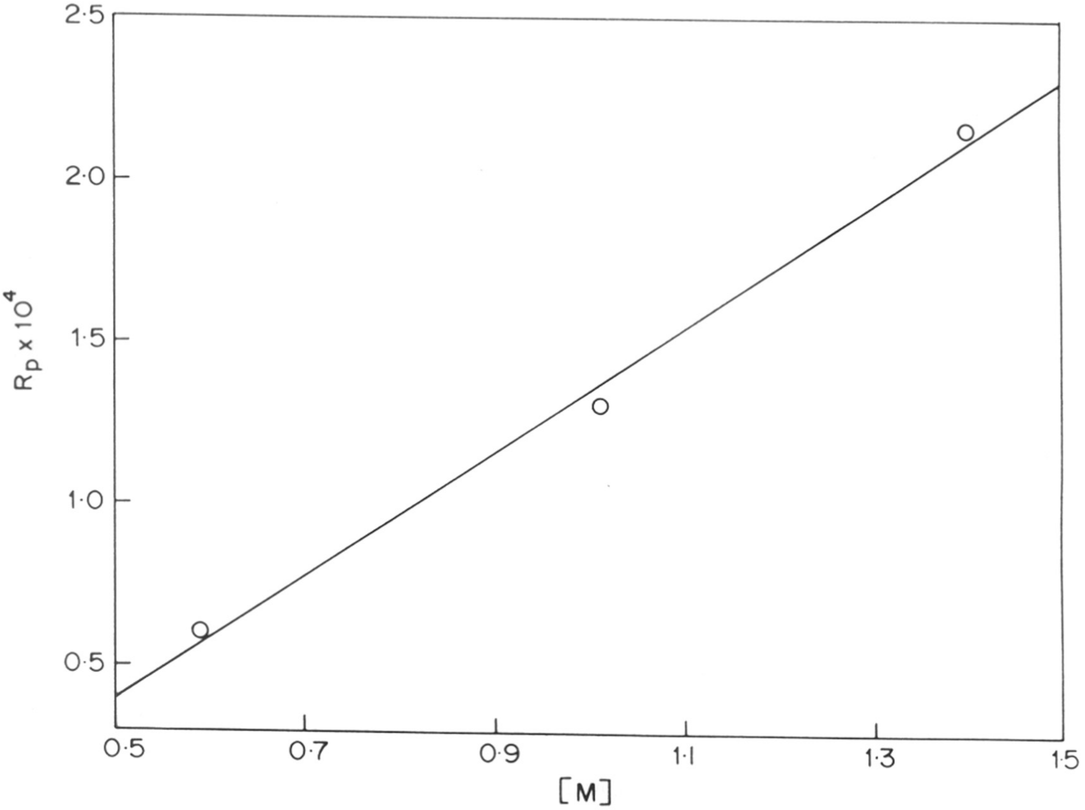

Fig. 4.7 Dependence of rate of polymerization of BTSAm on monomer concentration

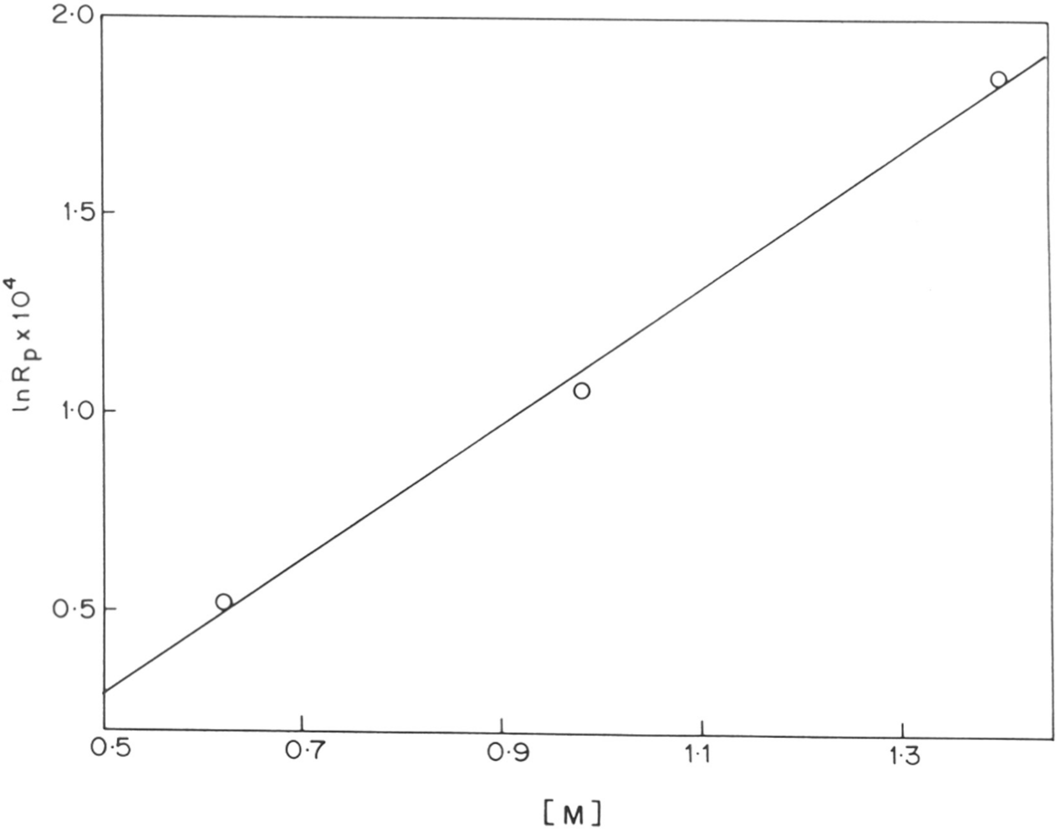

Fig. 4.8 Dependence of rate of polymerization of TMSAm on monomer concentration

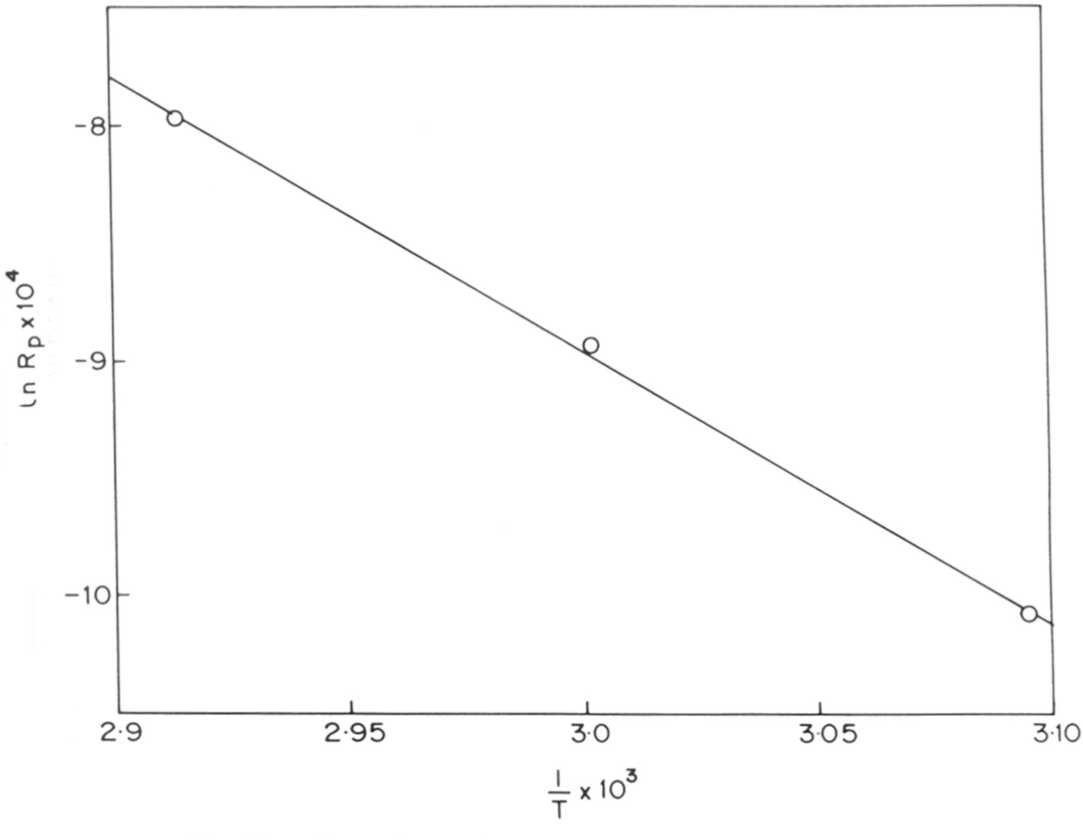

Fig. 4.9 Dependence of rate of polymerization of TMSAm on temperature

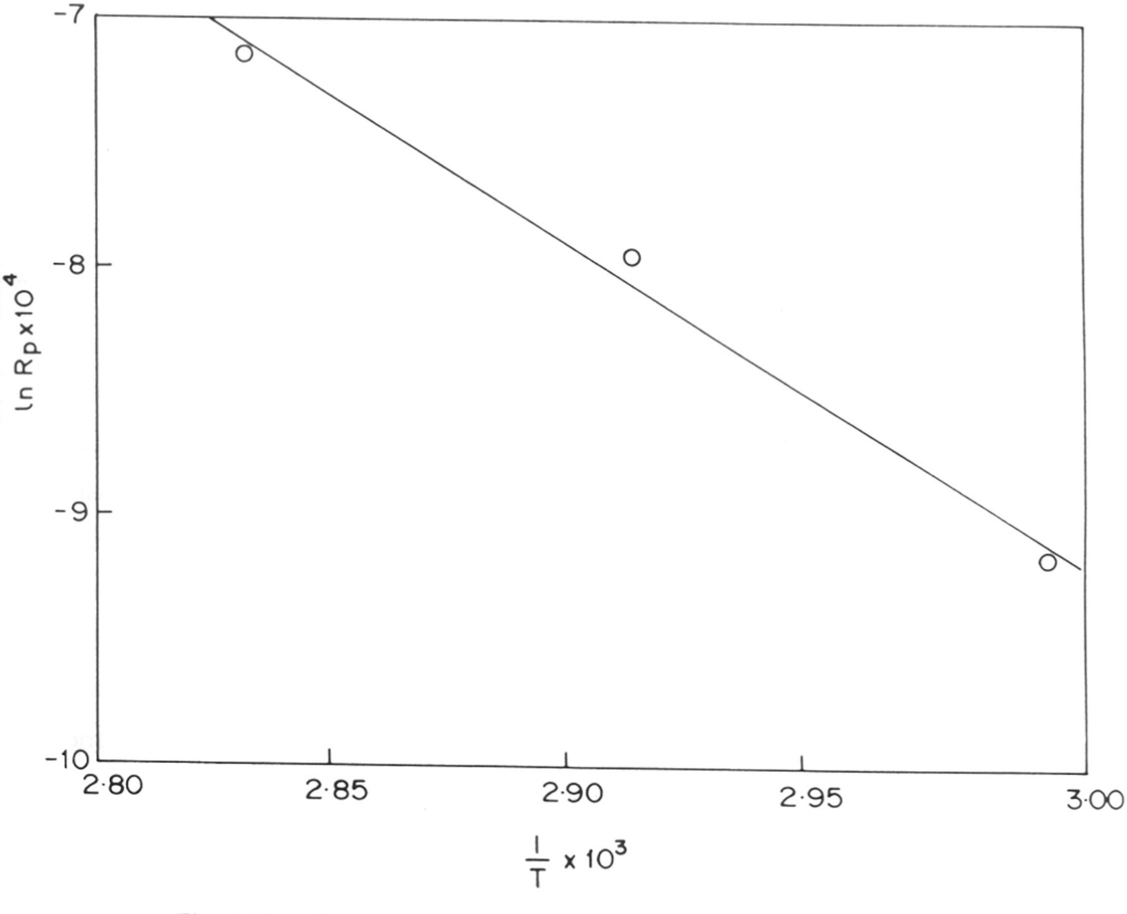

Fig. 4.10 Dependence of rate of polymerization of BTSAm on temperature

BTSAm. The variation of rate of polymerization of both BTSAm and TMSAm have been plotted against monomer concentration in Fig. 4.7 and Fig. 4.8. The points fall close to a straight line as expected.

4.3.3.3: Dependence of the polymerization rate on temperature: The temperature dependence of the rate of polymerization can be described by the equation:

$$\ln\left[2^{\frac{1}{2}}k_p\left(\frac{k_d}{k_t}\right)^{\frac{1}{2}}\right]=\ln\left[2^{\frac{1}{2}}A_p\left(\frac{A_d}{A_t}\right)^{\frac{1}{2}}\right]-\frac{E_p-\frac{E_t}{2}+\frac{E_d}{2}}{RT}\text{.............}(4.4)$$

or,

$$\ln R_p=\ln\left[2^{\frac{1}{2}}A_p\left(\frac{A_d}{A_t}\right)^{\frac{1}{2}}\right]+\ln\left[f[I]^{\frac{1}{2}}[M]\right]-\frac{E_R}{RT}\text{..........}(4.5)$$

where,

$$E_R=E_p-\frac{E_d-E_t}{2}$$

Here A_p, A_t and A_d are the entropy factors (also called pre-exponential factors) and E_p, E_t and E_d are the activation energies for chain propagation, termination and initiator decomposition. A plot of ln R_p against 1/T should give a straight line from the slope of which one can find out the value of (E_p-E_t/2) (provided the value of E_d is available). E_R is called the "overall" activation energy for the rate of polymerization. For BTSAm the plot of the measured R_p values (as obtained using AIBN as the initiator) at three different temperatures namely at 50°C 60°C and 70°C against the corresponding 1/T (T in Kelvin) is shown in Fig.4.9. For TMSAm, the measured R_p values at temperatures 60°C, 70°C and 80°C (as obtained using BPO as the initiator) have been plotted against the corresponding 1/T (Fig.4.10). The slope of the lines gives the values of E_p-1/2E_t to be 32.2 kJ/mol for BTSAm and 31.2 kJ/mol for TMSAm. In this calculations, values of E_d have been taken as 128.4 kJ/mol for AIBN and 133.9 kJ/mol for BPO[3].

The intrinsic viscosities of the polymer samples obtained on maximum conversion were determined in water at 25°C. The weight average molecular weights were calculated based on the [η] values using the following correlation[4]:

$$[\eta]=1.00\times10^{-4}\times[M_w]^{0.755}\text{...............}(4.6)$$

where [η] is in dL/g.

Table-4.3
Solution Polymerization of N,O-Bis(trimethylsilyl)acrylamide in benzene using AIBN as the Initiator:

[M] mol l^{-1}	[I] mol l^{-1}x10^{-2}	Temp. (°C)	R_p (mol$l^{-1}s^{-1}$x10^4)	$k_p/k_t^{1/2}$ ($l^{1/2}mol^{-1/2}sec^{-1/2}$)	M_n of Polyacrylamide	$[\eta]^{a)}$ dL/g.	$M_w^{b)}$
0.59	0.61	60	0.60	0.4013	66300	0.69	120700
1.01	0.98	60	1.30	0.4009	89500	0.89	170000
1.40	1.41	60	2.15	0.3972	102400	0.92	179300
0.98	2.49	60	2.05	0.4076	55400	0.58	101300
0.97	4.10	60	2.62	0.4116	43100	0.49	76300
0.99	0.97	50	0.42	0.2592	111500	0.99	198400
1.02	1.01	70	3.44	0.5203	58200	0.62	106450

a) Measured in water at 25±0.1°C
b) Calculated using the equation (4.6)

Table-4.4
Solution Polymerization of N-trimethylsilylacrylamide
in benzene using BPO as the Initiator:

[M] mol l^{-1}	[I] mol l^{-1}x10^{-2}	Temp. (°C)	R_p (moll^{-1}s^{-1}x10^4)	$k_p/k^{1/2}$ ($l^{1/2}$mol$^{-1/2}$sec$^{-1/2}$)	M_n of Polyacrylamide	[η][a] dL/g.	M_w[b]
0.62	0.61	60	0.521	0.5196	141700	1.16	240919
1.40	1.42	60	1.85	0.5371	216800	1.73	411900
0.98	0.97	60	1.06	0.5293	180950	1.48	334800
1.102	2.49	60	1.76	0.5313	117100	1.09	222400
0.99	4.11	60	2.25	0.5412	90802	0.88	168000
1.02	0.99	70	3.50	0.7011	103850	0.98	193150
1.00	1.02	80	7.88	0.8712	68500	0.76	136900

[a] Measured in water at 25±0.1°C
[b] Calculated based on equation (4.6)

The values of the kinetic parameters and molecular weights are shown in Table 4.3 and 4.4. The rate of polymerizations are comparable to the conventional monomers like acrylates and methacrylates. 'Dead-end' characteristics were not noticed. Reasonably high $k_p/k_t^{1/2}$ values allow one to conduct polymerizations of TMSAm and BTSAm at temperatures at which their half-lives are in the range around 10 h. This means that AIBN may be employed at 60°C-70°C when the $t_{1/2}$ for AIBN is in the range of 22h. and 4.8h. and BPO may be employed at 70°C-80°C when the $t_{1/2}$ for BPO is between 7.3 h. and 5 h. The molecular weight of the polymer is controlled largely by the rato of [I] to [M] in the usual way. The preparation of high molecular weight polymers will require low [I] and hence relatively long polymerization time. Under these circumstances polymerizations should be carried out at relatively lower temperatures (say, at 40°C-50°C for AIBN and 50°C-60°C for BPO).

4.4: Conclusion:

N-trimethylsilylacrylamide and N,O-bis(trimethylsilyl)acrylamide are two organic soluble precursors of acrylamide which can be conveniently polymerized in a non-polar organic medium like benzene to give polymers with a wide range of molecular weights. The silylated polymers can be hydrolyzed to poly(acrylamide) under mild conditions.

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CHAPTER - V

CHAPTER V:

SOLUTION COPOLYMERIZATION OF SILYLATED ACRYLAMIDES:

5.1 Introduction:

One of the objectives of synthesizing silylated acrylamides was to make them organic soluble. Acrylamide as such has a very poor solubility in non-polar solvents (0.036% in benzene). This has prevented its use in copolymerization with a variety of lipophilic monomers. Literature reveals that copolymerization of acrylamide with hydrophobic monomers in organic solvents produces blocky copolymers which are compositionally inhomogeneous[1]. It is believed that the properties of copolymers, in particular, of those containing polar and non-polar monomers, can be improved by decreasing their compositional inhomogeneity[2a]. Compositional inhomogeneity is also known to cause microphase separation resulting in loss of transparency[2b]. We reasoned that large solubility difference could be one of the reasons for r_1, r_2 values of greater than unity, generally observed for acrylamide copolymers with lipophilic comonomers. Lipophilicity of acrylamide can be improved by substituting one or both the hydrogens with a non-polar group (e.g. alkyl, aryl etc.). However, the parent monomer, acrylamide cannot be regenerated from such substituted acrylamides. On the otherhand substituting hydrogens in acrylamide with a trimethylsilyl or tert-butyldimethylsilyl group could increase its lipophilicity and yet offer the advantage of easy desilylation after polymerization to regenerate the amide functionality. To examine the validity of this hypothesis we studied the copolymerizability of the monomers N-trimethylsilylacrylamide (TMSAm) , N-tert-butyldimethylsilylacrylamide (TBDMSAm), and N,O-bis(trimethylsilyl)acrylamide (BTSAm) with styrene in benzene using benzoyl peroxide as the free radical initiator. The copolymers from all the three precursors could be hydrolyzed under mild conditions to give random copolymers of styrene and acrylamide. Characterization of the styrene-acrylamide copolymers were performed using a combination of ^{1}H and ^{13}C NMR spectroscopy, FTIR spectroscopy, TGA, DTG, and DSC.

Experimental:

5.2.1 Materials: Benzoyl peroxide (BPO; from BDH, England) was recrystallized from methanol-chloroform. Benzene, hexane and styrene were purified as usual. Acrylamide (BDH, India) was recrystallized from chloroform. DMSO (SD Fine chemicals, Bombay) was distilled over calcium hydride at 60°C under reduced pressure. N-trimethylsilylacrylamide, and

N-tert-butyldimethylsilylacrylamide were recrystallized from dry hexane. N,O-Bis(trimethylsilyl)acrylamide was distilled prior to use and stored under a positive pressure of argon between 0 to 10°C.

5.2.2 Instruments: The ^{1}H NMR spectra of the styrene-acrylamide copolymers were recorded using a Bruker AC-200 MHz spectrometer at 200 MHz and 298K, by using DMSO-d_6 as a solvent and locking agent. Elemental analyses were performed on a Carlo-Erba model CHNS-O EA 1008 elemental analyzer. Analysis for C,H and N were performed using helium as the carrier gas. Intrinsic viscosities were determined using an Ubbelohde viscometer in a Schott-Gerate model CK-100/CT-1450/AVS-440 automatic viscometer. FTIR spectra were scanned using a Perkin-Elmer PC-16 FTIR spectrometer. TGAs were scanned using a Perkin Elmer TGA 7 thermal analyzer and DSCs were scanned in a Perkin Elmer DSC 7 instrument. Glass transition temperatures were determined from thermograms at the points of inflection.

5.2.3. Copolymerization of TMSAm, BTSAm and TBDMSAm with styrene:

5.2.3.1 Copolymerization Procedure: Accurately weighed quantities of TMSAm, and TBDMSAm were dissolved in weighed volumes of benzene to make the solution of the two monomers. The solutions of the two monomers and BTSAm (liquid at room temperature) could be conveniently transferred into the reactor ampoules using a cannula under positive pressure of argon. The required volumes of styrene and the initiator (benzoyl peroxide) solution were also introduced into the ampoules. Weights before and after the introduction of each component were taken to calculate the exact amount of the components introduced. Each of the ampoules was frozen in liquid nitrogen and was evacuated under a vacuum of 10^{-3} mbar to remove the dissolved air. The reaction mixture was then melted and the process of freezing and evacuation was repeated twice. For TMSAm and BTSAm, the polymerizations were carried out at both 50°C and 80°C and for TBDMSAm, polymerizations were done at 80°C. Polymerizations were done for a short period of time to ensure a conversion of less than 10%. Each reaction was terminated by freezing the ampoule in liquid nitrogen. The solvent was then evacuated and the residue dissolved in acidulated (1.0N HCl) DMSO. The solution was stirred for about 30 min and the hydrolyzed polymer precipitated in acetone or water. The process was repeated two times to ensure complete desilylation. The polymers which were precipitated in water (containing less than 40 mol% of acrylamide in the copolymer) were redissolved in neutral THF and precipitated in hexane. All copolymers were white to yellow powders.

Table - 5.1(A): Copolymerization of TMSAm (M_1) with styrene (M_2)

Expt. No.	Monomer(M_1) feed (mol%)	Time (min.)	Conversion (%)[a]	Nitrogen content (% by weight)	Incorporation of acrylamide (m_1) (mol%)	Intrinsic viscosity (η)[b]
Copolymerization temperature = 50°C						
1.	8.20	80	3.5[c]	1.77	12.6	-
2.	18.5	75	4.0[c]	3.51	24.1	0.22
3.	37.6	75	4.2[c]	4.93	32.9	0.28
4.	56.3	60	3.0[c]	5.85	38.2	0.23
5.	70.9	55	4.8[d]	8.65	53.4	0.22
6.	80.7	35	4.2[d]	10.34	61.8	0.30
7.	90.8	25	3.0[d]	11.99	69.5	0.43

a) Determined by gravimetry after hydrolysis and precipitation
b) Determined in DMSO at 30±0.1°C
c) soluble in chloroform and dimethylsulfoxide
d) soluble in dimethylsulfoxide

Table - 5.1(B): Copolymerization of TMSAm (M_1) with styrene (M_2)

Expt. No.	Monomer(M_1) feed (mol%)	Time (min.)	Conversion (%)[a]	Nitrogen content (% by weight)	Incorporation of acrylamide (m_1) (mol%)	Intrinsic viscosity (η)[b]
Copolymerization temperature = 80°C						
1.	27.2	45	8.8[c]	3.27	22.6	0.17
2.	32.9	40	9.7[c]	4.96	33.0	0.16
3.	50.1	45	10.2[c]	5.11	33.9	0.20
4.	87.2	20	7.0[d]	11.78	68.5	0.29

[a] Determined by gravimetry after hydrolysis and precipitation
[b] Determined in DMSO at 30±0.1°C
[c] soluble in chloroform and dimethylsulfoxide
[d] soluble in dimethylsulfoxide

Table - 5.2(A): Copolymerization of BTSAm (M_1) with styrene (M_2)

Expt. No.	Monomer(M_1) feed (mol%)	Time (min.)	Conversion (%)[a]	Nitrogen content (% by weight)	Incorporation of acrylamide (m_1) (mol%)	Intrinsic viscosity (η)[b]
Copolymerization temperature = 50°C						
1.	9.6	120	4.0[c]	1.90	13.5	0.21
2.	20.3	110	4.0[c]	4.23	28.6	0.23
3.	25.7	110	3.5[c]	5.29	35.0	0.23
4.	37.8	100	5.0[c]	6.30	40.8	-
5.	50.1	80	2.5[d]	7.17	45.6	0.44
6.	59.0	80	5.0[d]	8.19	51.0	0.39
7.	69.5	60	3.5[d]	9.20	56.2	0.36
8.	79.0	45	3.0[d]	10.05	60.4	0.40
9.	88.3	40	5.0[d]	12.92	73.6	0.42
10.	92.8	30	4.5[e]	15.66	85.0	-

[a] Determined by gravimetry afterhydrolysis and precipitation
[b] Determined in DMSO at $30\underline{+}0.1$°C
[c] soluble in chloroform and dimethylsulfoxide
[d] soluble in dimethylsulfoxide
[e] soluble in a mixture of CD_3CN/D_2O (7/3, v/v)

Table - 5.2(B): Copolymerization of BTSAm (M_1) with styrene (M_2)

Expt. No.	Monomer(M_1) feed (mol%)	Time (min.)	Conversion (%)[a]	Nitrogen content (% by weight)	Incorporation of acrylamide (m_1) (mol%)	Intrinsic viscosity (η)[b]
Copolymerization temperature = 80°C						
1.	25.4	45	8.7[c]	3.96	26.9	0.18
2.	28.7	40	9.2[c]	4.31	29.1	0.20
3.	62.9	50	10.0[c]	11.07	43.2	0.21
4.	82.3	40	9.7[d]	11.97	69.4	0.27
5.	91.2	35	8.5[d]	12.42	71.4	0.31

[a] Determined by gravimetry after hydrolysis and precipitation

[b] Determined in DMSO at 30±0.1°C

[c] soluble in chloroform and dimethylsulfoxide

[d] soluble in dimethylsulfoxide

Table - 5.3: Copolymerization of TBDMSAm (M_1) with styrene (M_2)

Expt. No.	Monomer(M_1) feed (mol%)	Time (min.)	Conversion (%)[a]	Nitrogen content (% by weight)	Incorporation of acrylamide (m_1) (mol%)	Intrinsic viscosity (η)[b]
Copolymerization temperature = 80°C						
1.	11.5	60	8.5[c]	1.75	12.5	0.18
2.	15.4	45	5.8[c]	2.89	20.1	0.15
3.	31.1	40	5.0[c]	4.81	32.1	0.19
4.	52.1	42	5.5[c]	5.01	33.3	0.16
5.	67.8	35	6.5[d]	7.03	44.8	0.30
6.	88.6	30	7.0[d]	10.22	61.2	0.30

[a] Determined by gravimetry after hydrolysis and precipitation
[b] Determined in DMSO at 30±0.1°C
[c] soluble in chloroform and dimethylsulfoxide
[d] soluble in dimethylsulfoxide

5.2.3.2 Microstructural Analysis: For microstructural analysis, ^{13}C NMR spectra were recorded at 75.48 MHz (Bruker MSL-300) spectrometer at 373K. The sample concentration was 12% w/v DMSO-d_6. Spectra were obtained by using BROADBAND decoupling and pulse delay of 10s, accumulating 6000 scans with a digital resolution of 0.4 Hz/point, corresponding to a spectral width 25000 Hz and a data length of 8 K. The flip angle and acquisition time were 45° and 1.3s respectively. Monomer sequence placements were determined by comparing the relative peak areas of the proton or carbon atoms involved. In performing quantitative NMR measurements via compositionsl or configurational sequence placements, one must take into account difference in Nuclear Overhauser Effects and spin-lattice relaxation times (T_1). No NOE or T_1 values have been determined but one additional ^{13}C NMR experiment was performed on a copolymer with M-50 with a much longer delay (15s) and gating off the decoupler to remove the NOE. The results are identical with those obtained via ^{13}C NMR spectra with the standard method. Implicitly, we assumed that no diffential T's are present for compositional triads (AAA, AAS, SAS, SSS etc.) in the ^{13}C NMR spectra. No differential ^{1}H NOEs were condidered to occur. Within these limits relative peak areas were proportional to the numbers of proton and carbon atoms involved. Peak areas were determined by deconvolution method using Bruker WIN-NMR software.

5.2.3.3 Characterization: Copolymers from all the three monomers on hydrolysis yielded styrene-acrylamide copolymers. Therefore the features of the NMR, FTIR and thermograms were similar.

^{1}H NMR of styrene-acrylamide copolymers (Fig. 5.1-5.3): ($CDCl_3$ or dimethyl sulphoxide-d_6): δ ppm. = 0.75-2.5 (two humps; 3H, -CH_2-CH-, backbone protons contributed by both monomers), 6.25-7.5 (two humps; 5H, C_6H_5-, phenyl ring protons of styrene).

I.R. of copolymers (Fig. 5.4-5.6) (KBr) cm^{-1}: 1662 cm^{-1} - 1666 cm^{-1}, Overlap C=O stretch from Acrylamide ; 1600, 1492, 1452 cm^{-1}, Ring C-C stretch, styrene. 758 cm^{-1}, Out-of-plane C-H bend, styrene; 700 cm^{-1}, out of plane C-C bend, styrene.

^{13}C NMR of styrene-acrylamide copolymers (Fig. 5.7-5.14): (dimethyl sulphoxide-d_6, 100°C): δ ppm. = 142-144, multiplate at ipso-Carbon of styrene; 174-176, amide carbonyl carbon from acrylamide moieties.

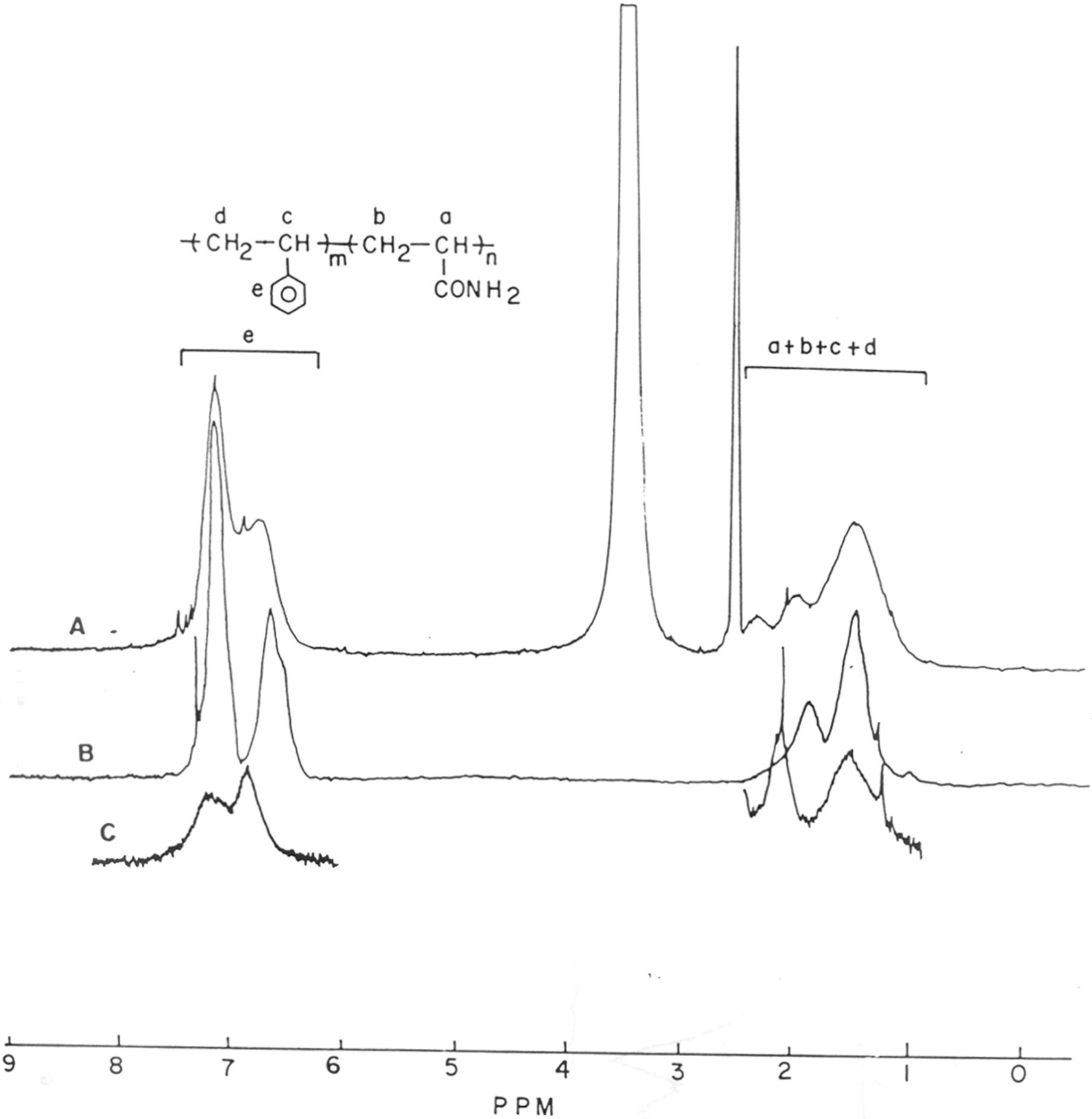


Fig. 5.1 ^{1}H NMR spectrum of S/A copolymers from TMSAm; A: Feed mole ratio TMSAm : styrene = 56.3 : 43.7 (DMSO-d_6). B: Feed mole ratio TMSAm : styrene = 8.2 : 91.8 ($CDCl_3$); C: Feed mole ratio TMSAm : styrene = 90.8 : 9,2 (DMSO-d_6)

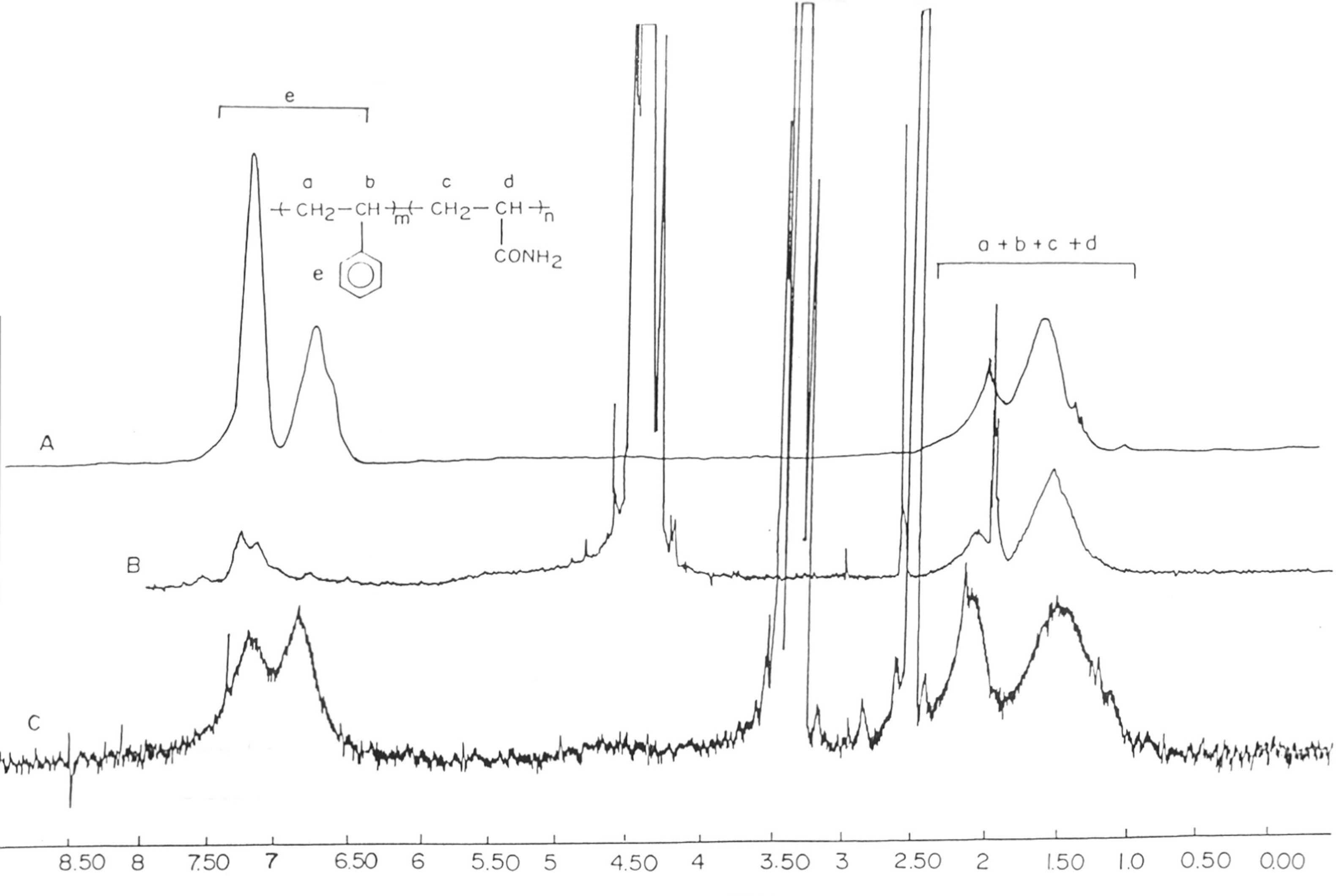


Fig. 5.2 ^{1}H NMR spectrum of S/A copolymers from BTSAm; A: Feed mole ratio BTSAm : styrene = 9.6 : 90.4 ($CDCl_3$). B: Feed mole ratio BTSAm : styrene = 92.8 : 7.2 (CD_3CN/D_2O, 3:7, v/v); C: Feed mole ratio BTSAm : styrene = 79 : 21(DMSO-d_6).

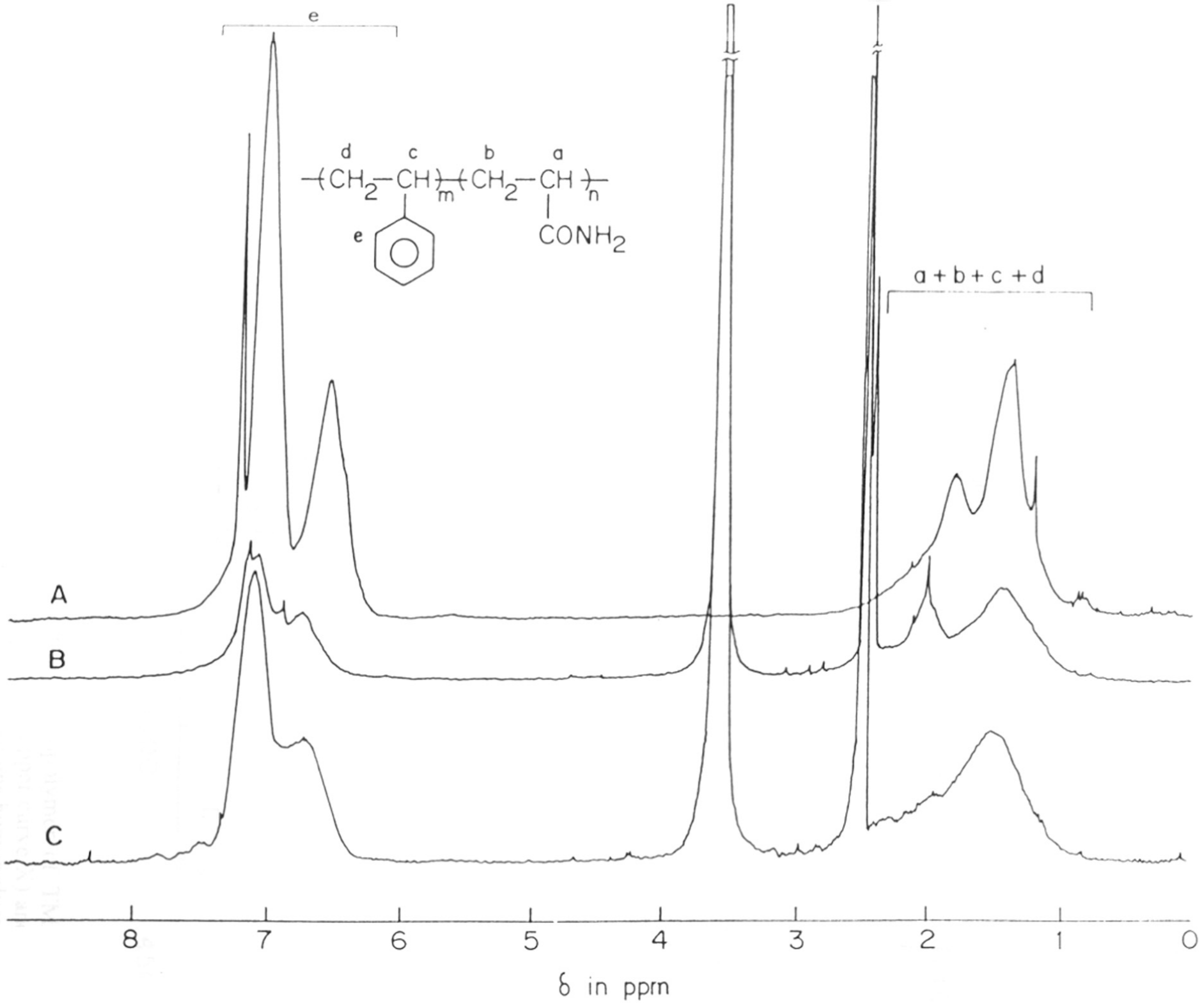


Fig. 5.3 ^{1}H NMR spectrum of S/A copolymers from TBDMSAm; A: Feed mole ratio TDBMSAm : styrene = 15.4 : 84.6 ($CDCl_3$). B: Feed mole ratio TBDMSAm : styrene = 88.6 : 11.4 (DMSO-d_6); C: Feed mole ratio TMSAm : styrene = 52.1 : 47.9 (DMSO-d_6).

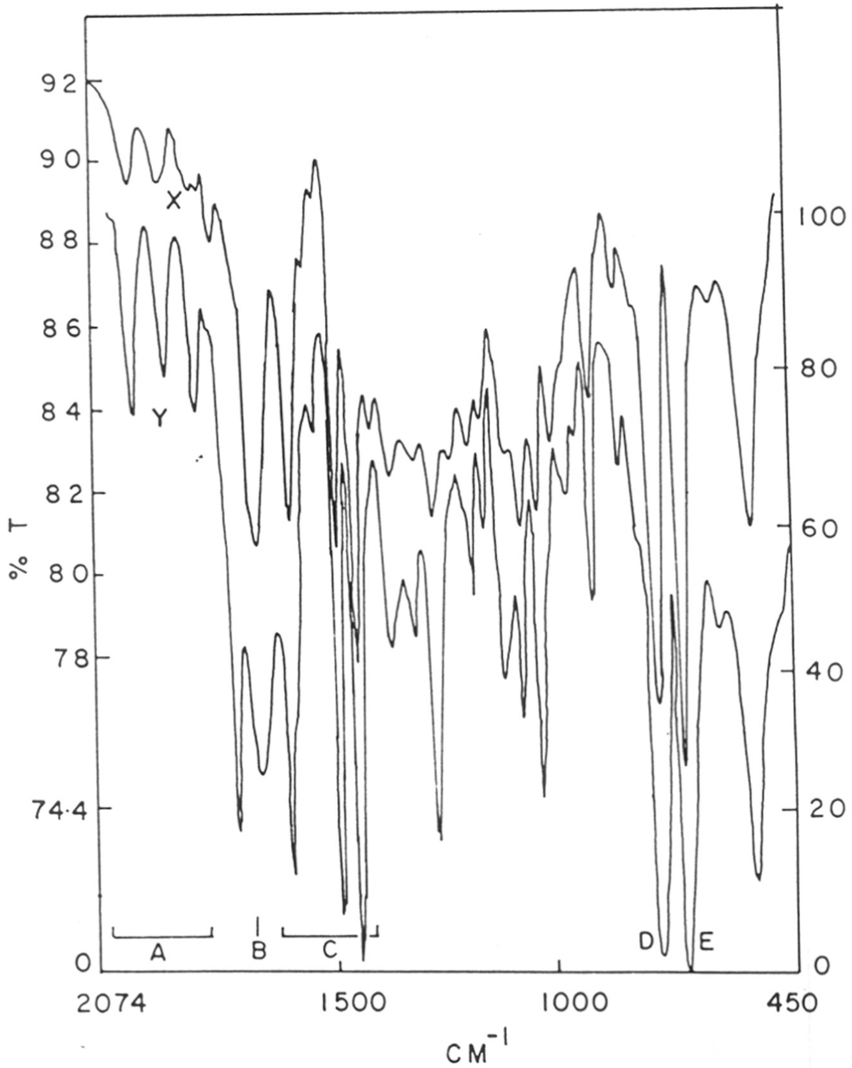


Fig. 5.4 FTIR spectra of a hydrolyzed copolymer of TMSAm: Styrene = 18.5 : 81.5 mole ratio (upper curve X) and of a mixture of polyacrylamide : polystyrene homopolymers of 20 : 80 mole ratio (lower curve Y).

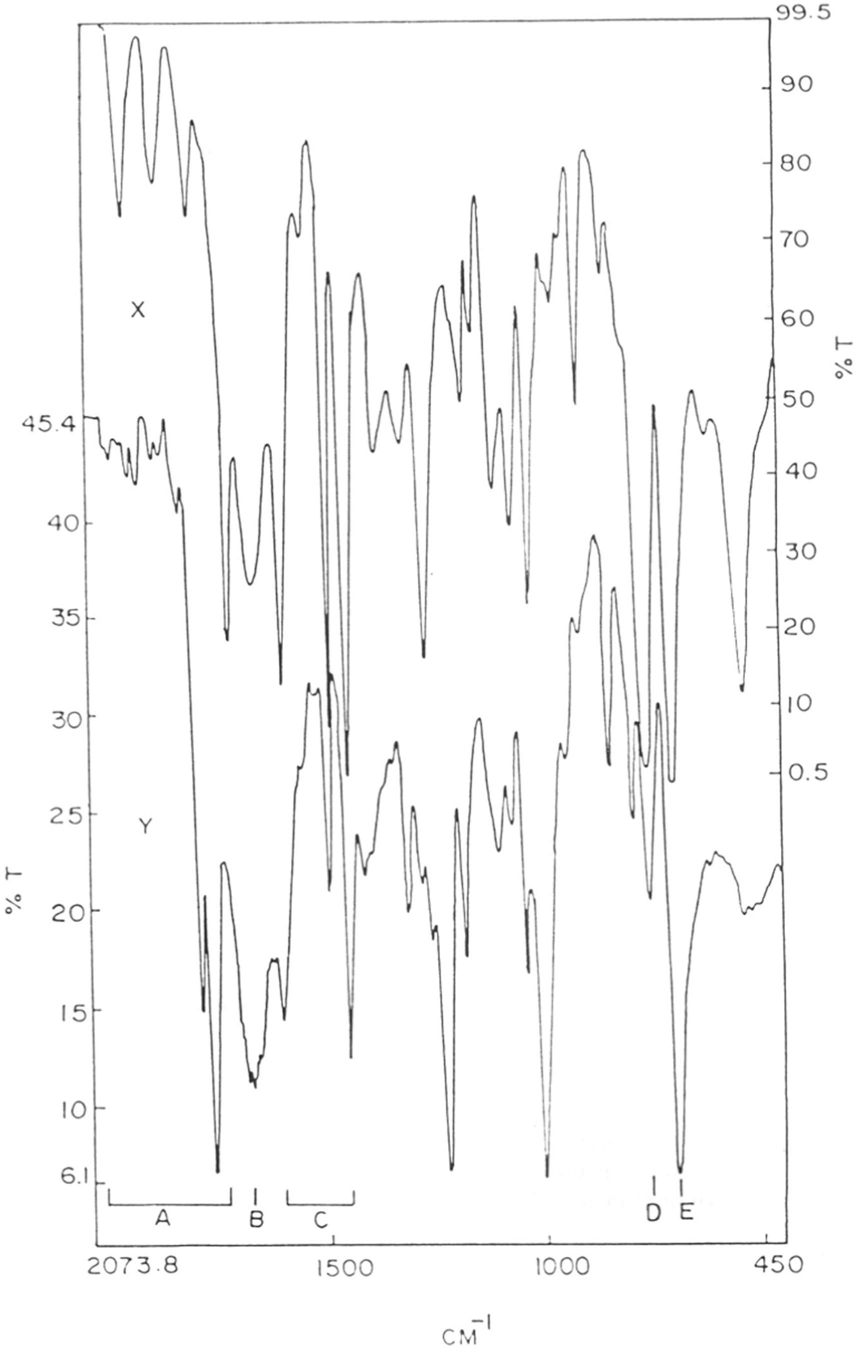


Fig. 5.5 FTIR spectra of a synthetic mixture of poly(acrylamide)-poly(styrene) (20:80 mole ratio) (X) and of the hydrolyzed copolymer of BTSAm : styrene = 25.7 : 74.3 mole ratio (Y).

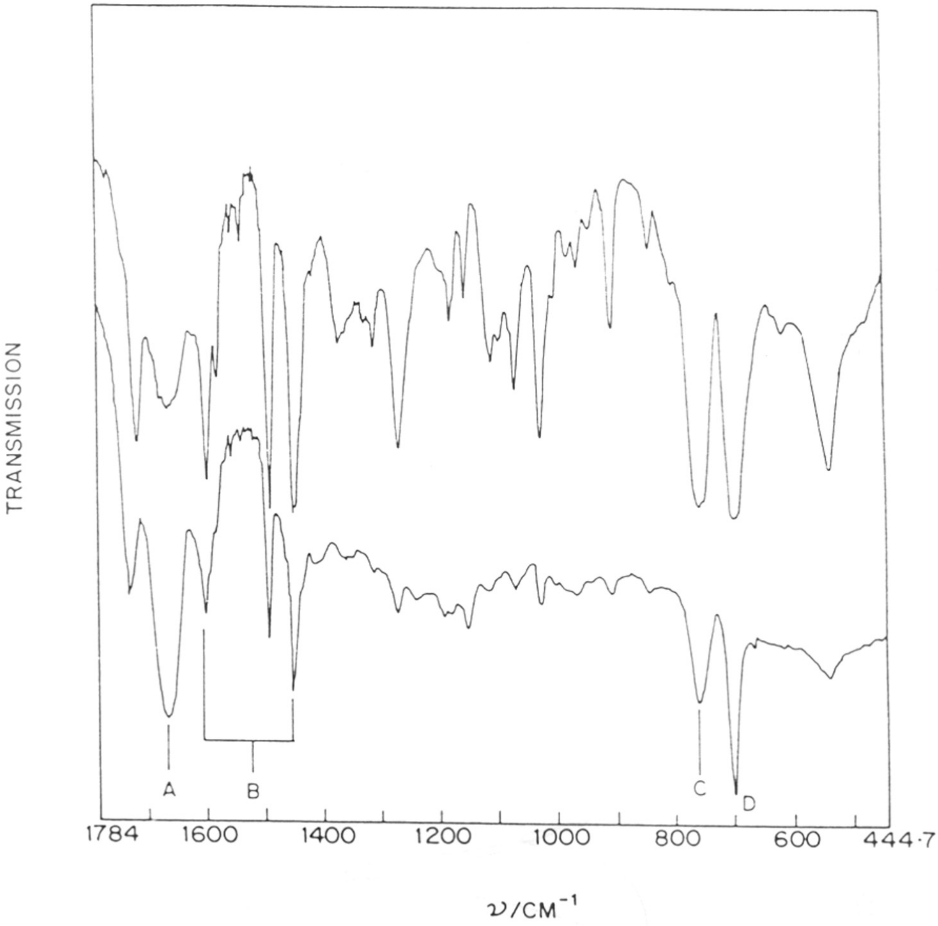


Fig. 5.6 FTIR spectra of a hydrolyzed copolymer of TMSAm: Styrene = 52.1 : 47.9 mole ratio (lower curve) and of a mixture of polyacrylamide : polystyrene homopolymers of 30 : 70 mole ratio (upper curve).

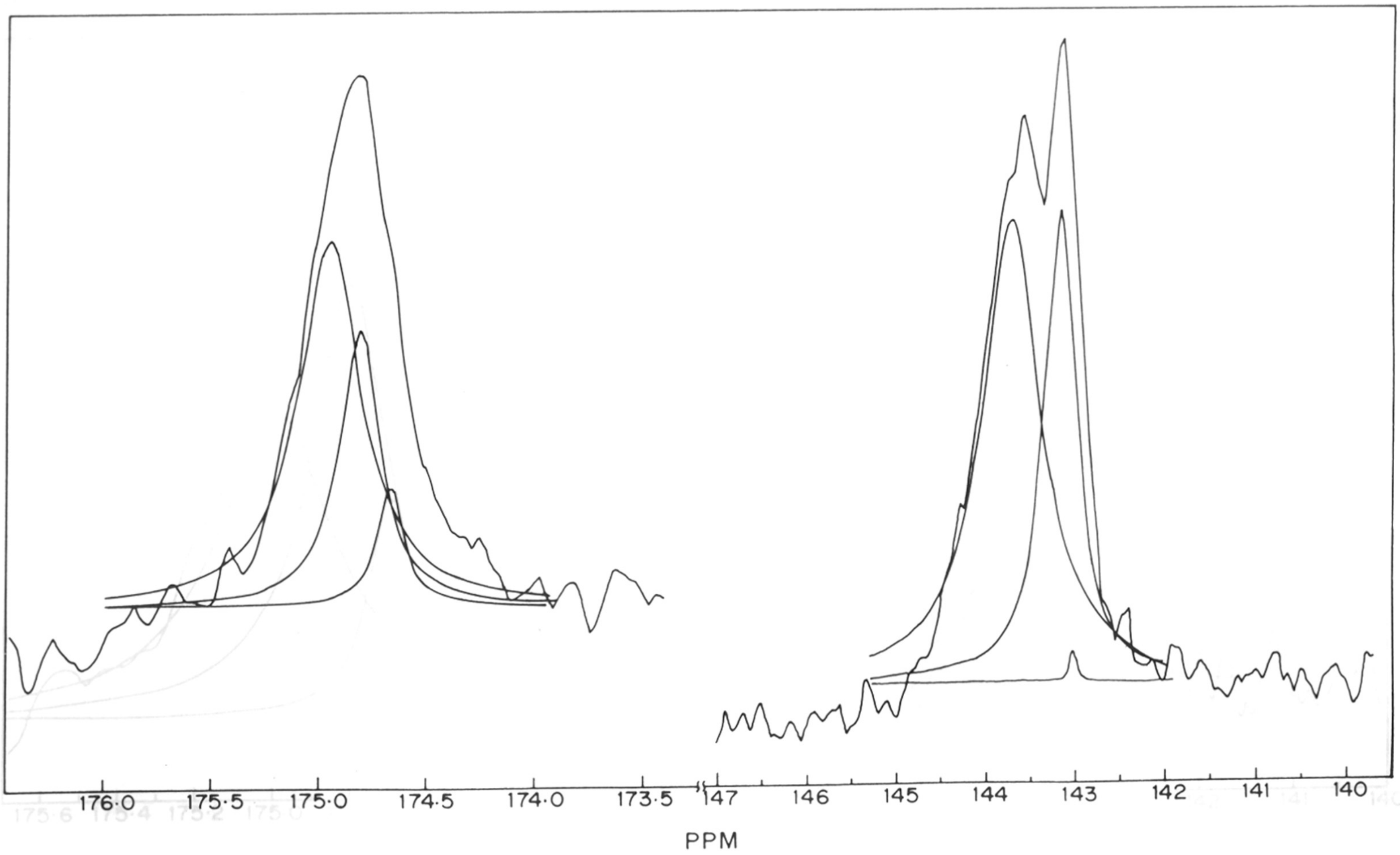


Fig. 5.7 Deconvoluted amide carbonyl (left) and ipso carbon (right) peaks of the ^{13}C NMR spectrum of S/A copolymer obtained using TMSAm precursor; sample no. M-27

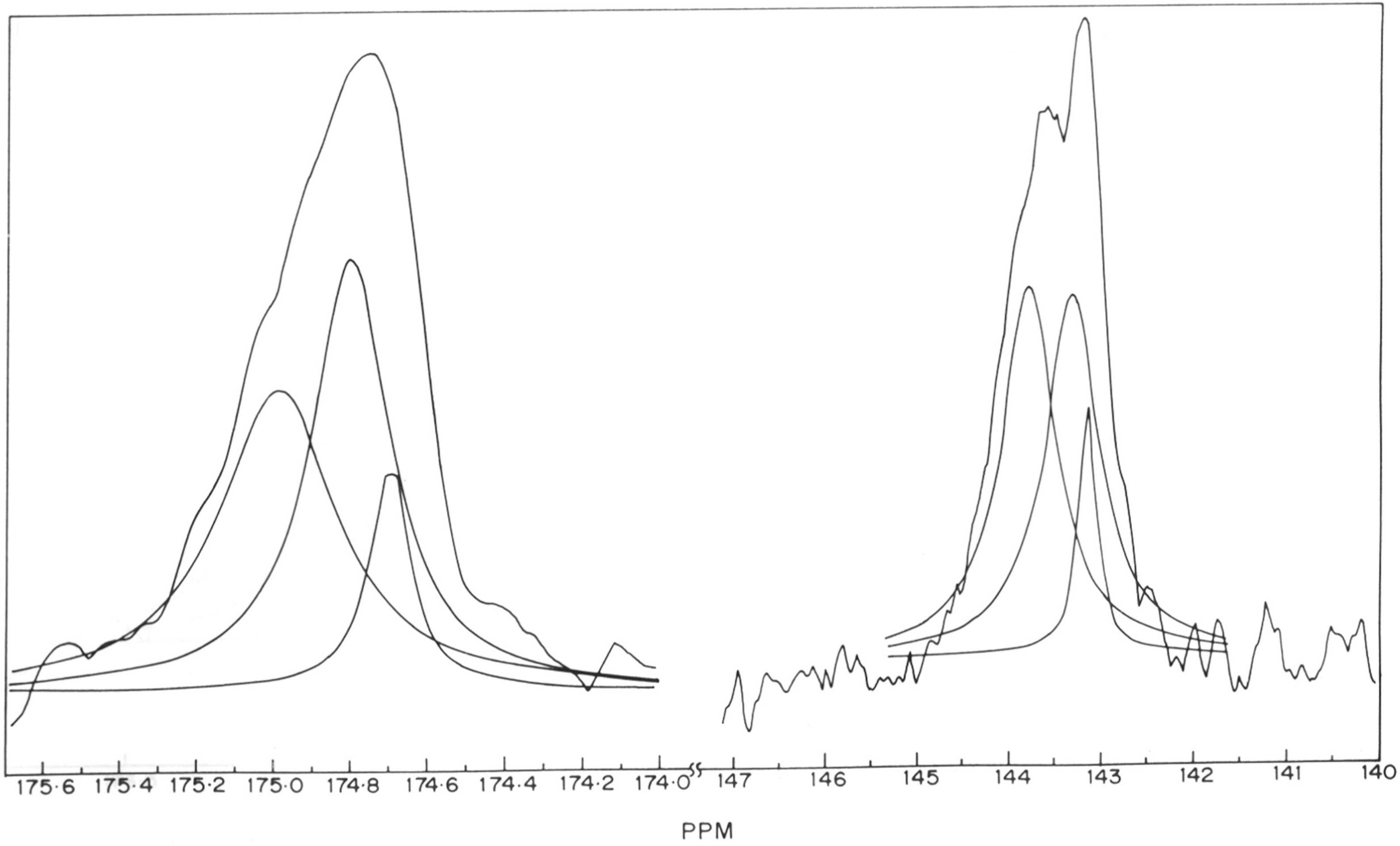


Fig. 5.8 Deconvoluted amide carbonyl (left) and ipso carbon (right) peaks of the ^{13}C NMR spectrum of S/A copolymer obtained using TMSAm precursor; sample no. M-33

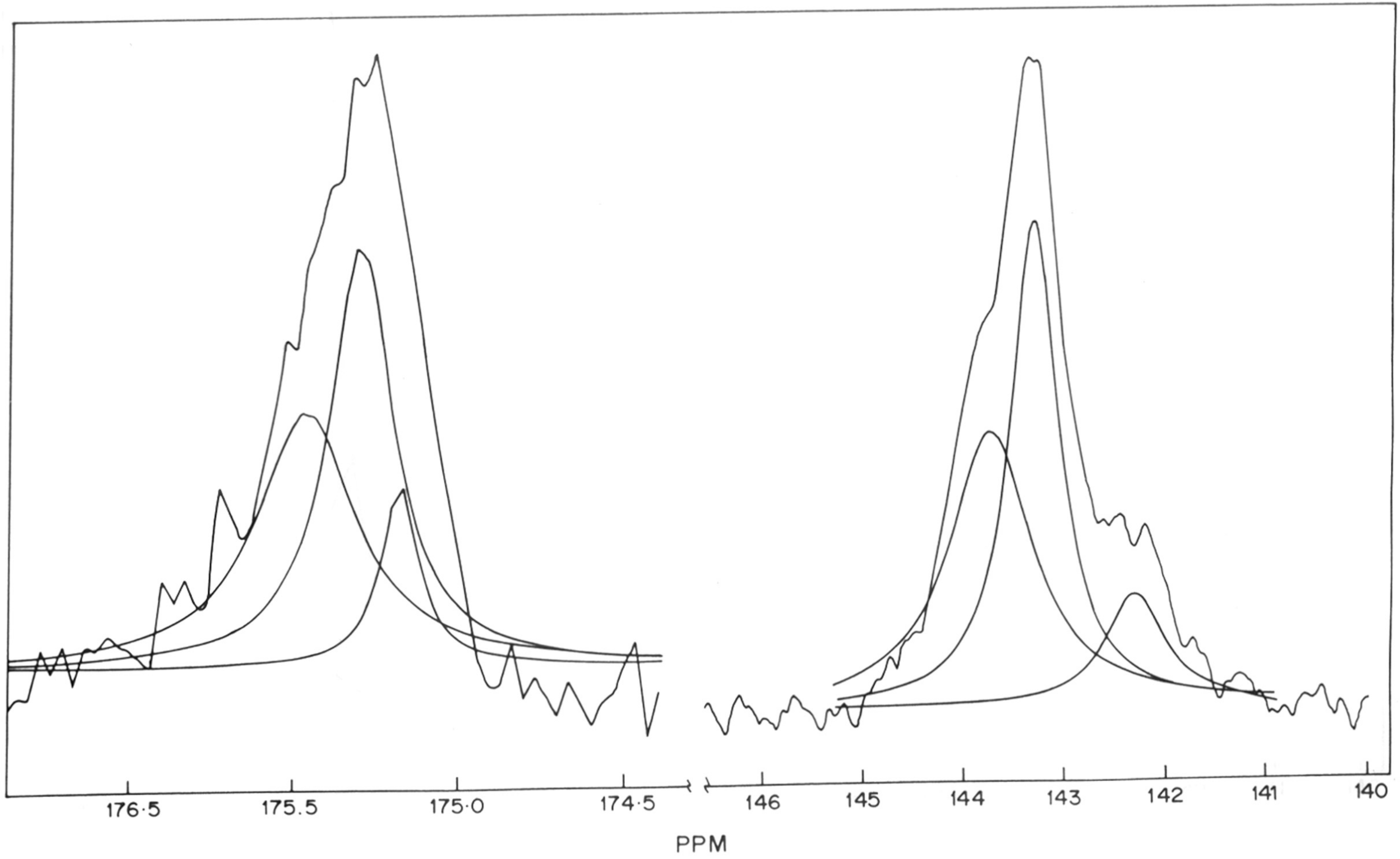


Fig. 5.9 Deconvoluted amide carbonyl (left) and ipso carbon peaks (right) of the ^{13}C NMR spectrum of S/A copolymer obtained using TMSAm precursor; sample no. M-50

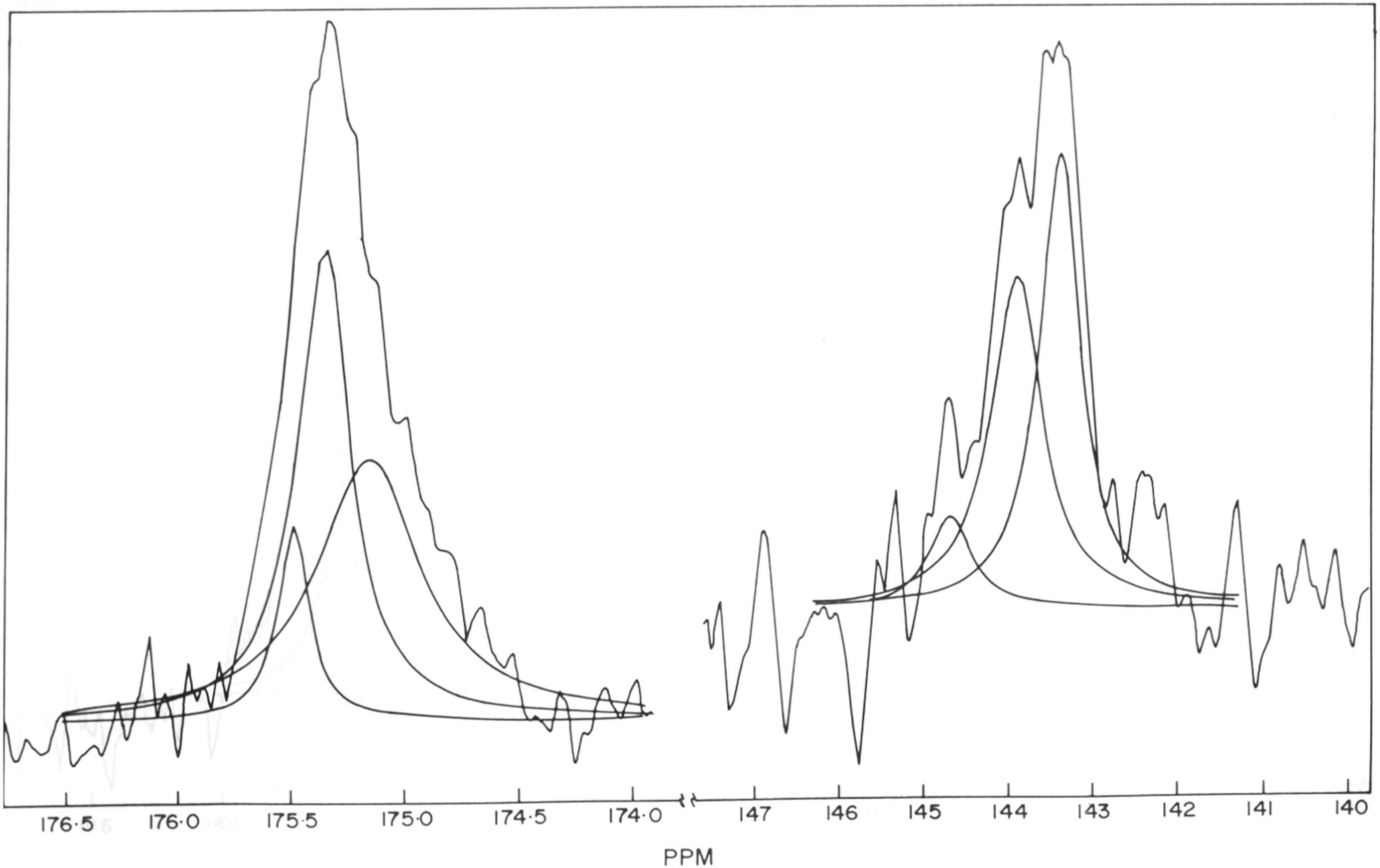


Fig. 5.10 Deconvoluted amide carbonyl (left) and ipso carbon (right) peaks of the ^{13}C NMR spectrum of S/A copolymer obtained using TMSAm precursor; sample no. M-87

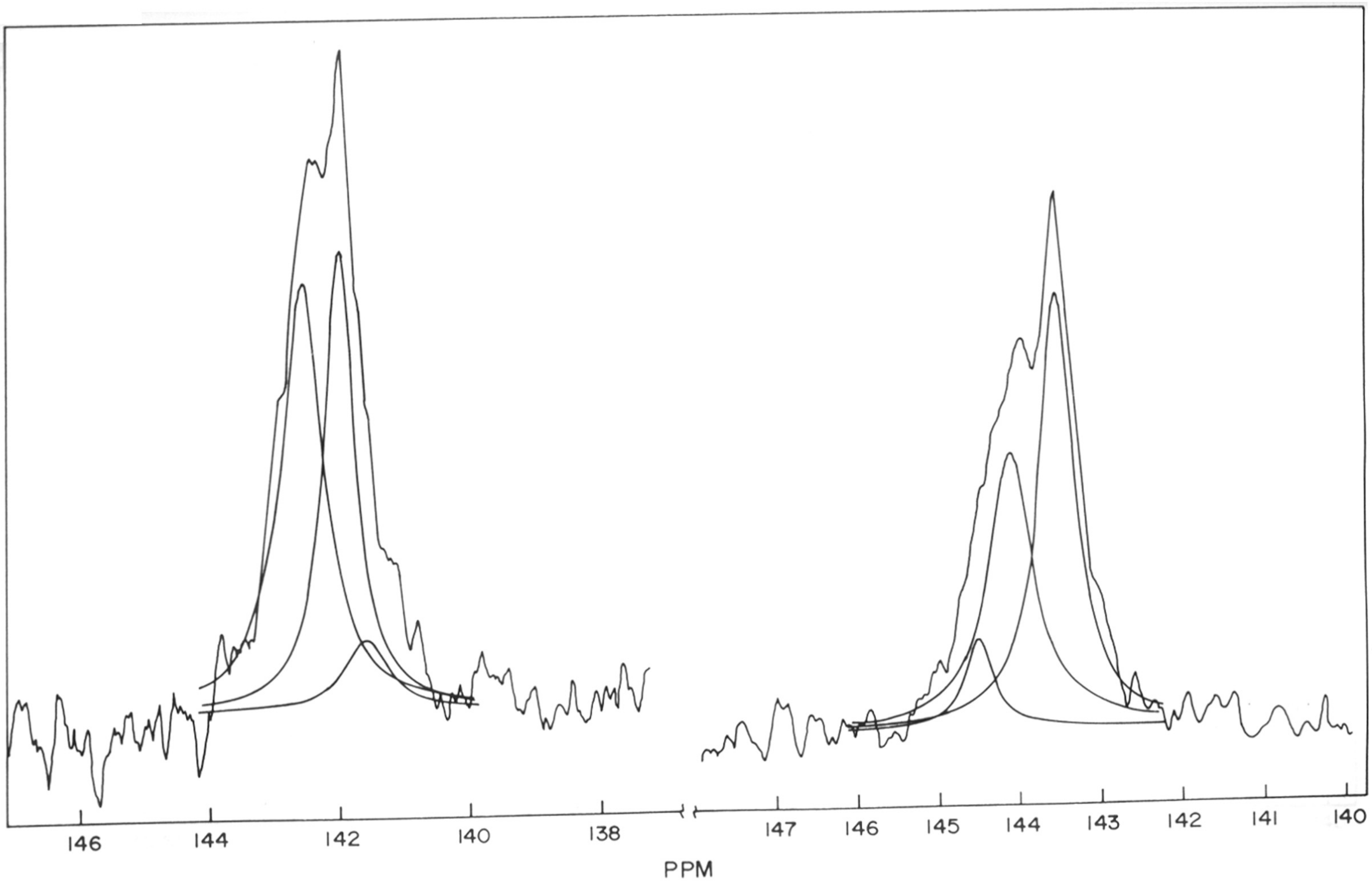


Fig. 5.11 Deconvoluted ipso carbon peaks of the ^{13}C NMR spectrum of S/A copolymer obtained using BTSAm precursor; sample no. B-25 (left) and B-91 (right)

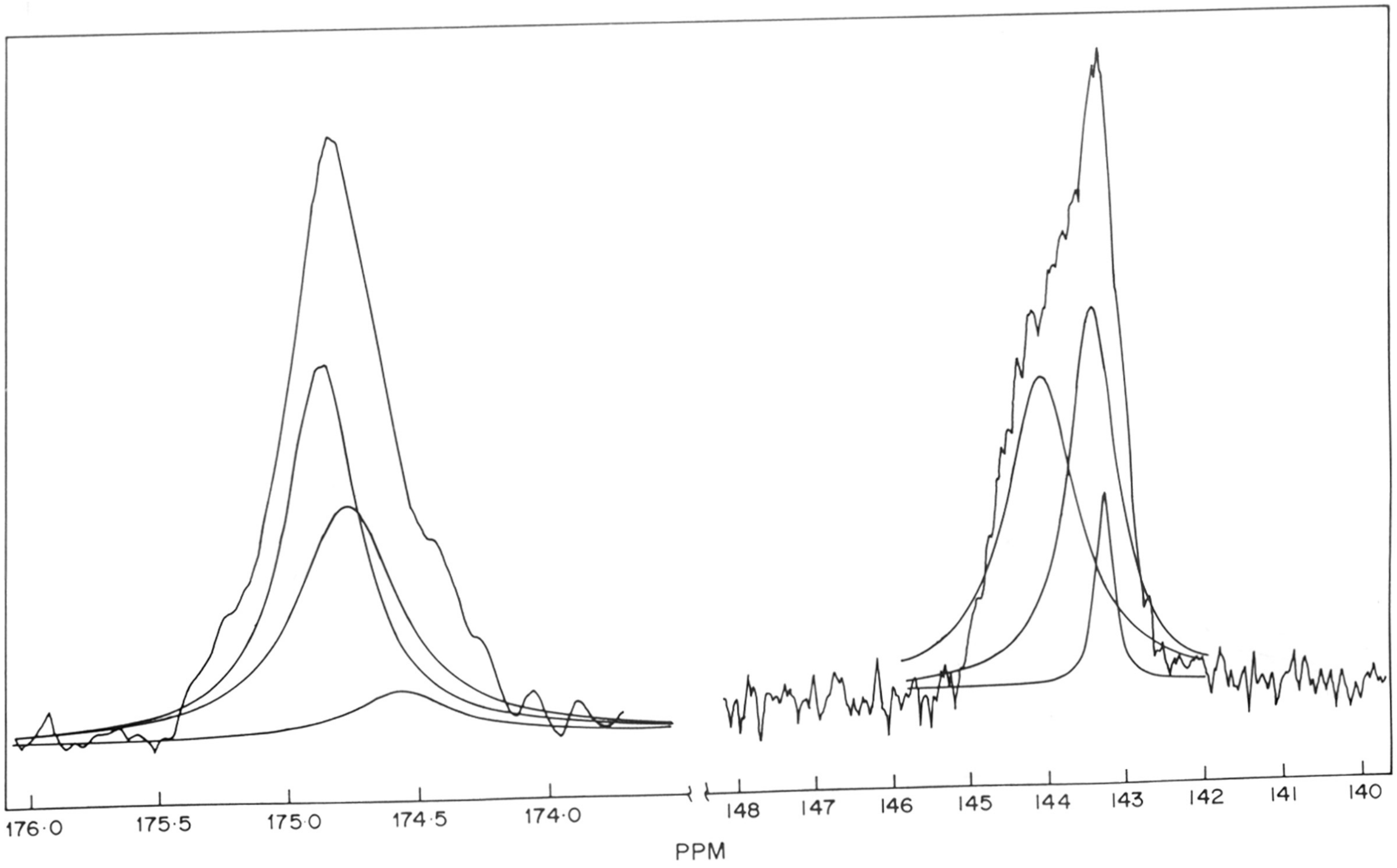


Fig. 5.12 Deconvoluted amide carbonyl (left) and ipso carbon (right) peaks of the ^{13}C NMR spectrum of S/A copolymer obtained using BTSAm precursor; sample no. B-30

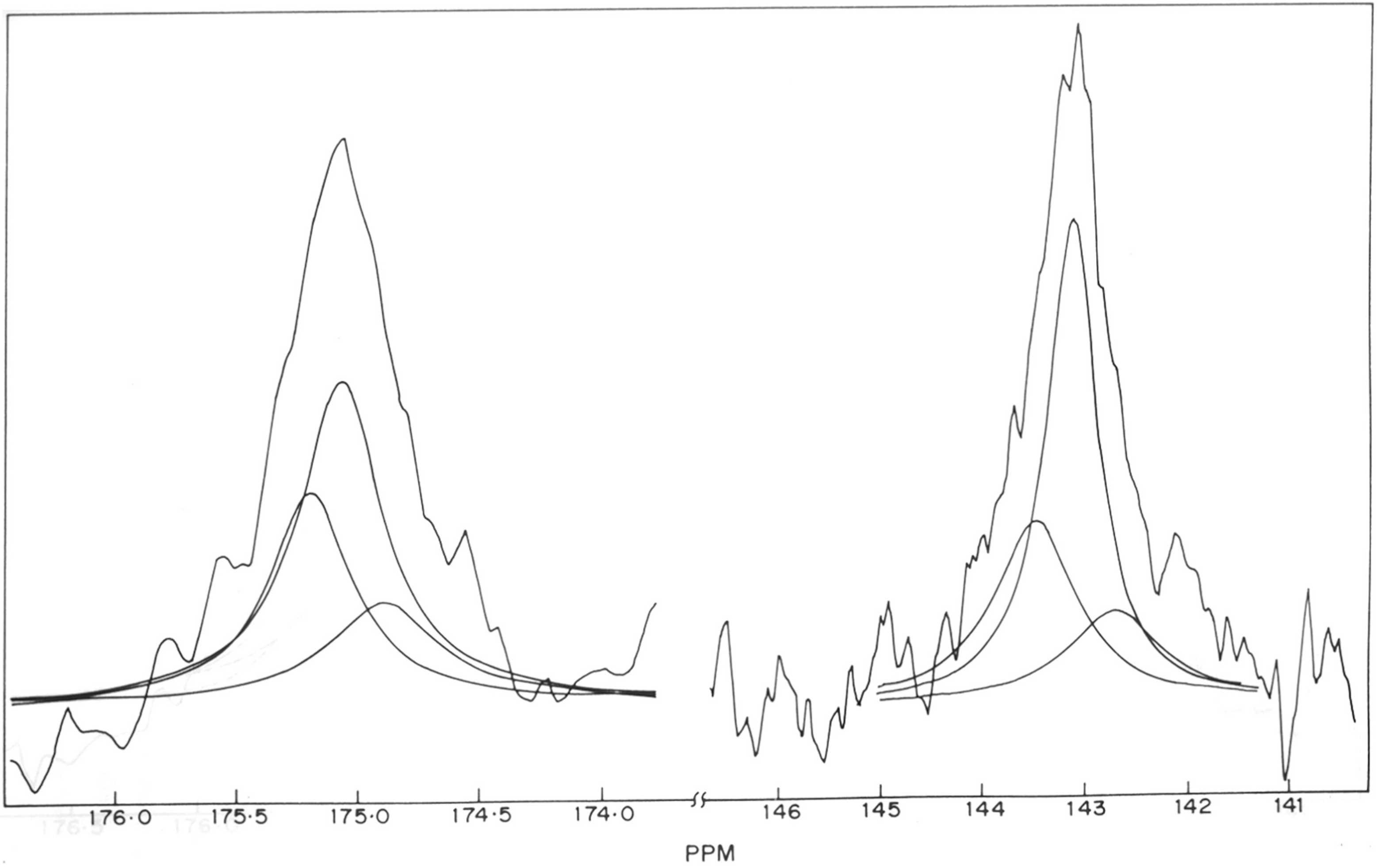


Fig. 5.13 Deconvoluted amide carbonyl (left) and ipso carbon (right) peaks of the ^{13}C NMR spectrum of S/A copolymer obtained using BTSAm precursor; sample no. B-63

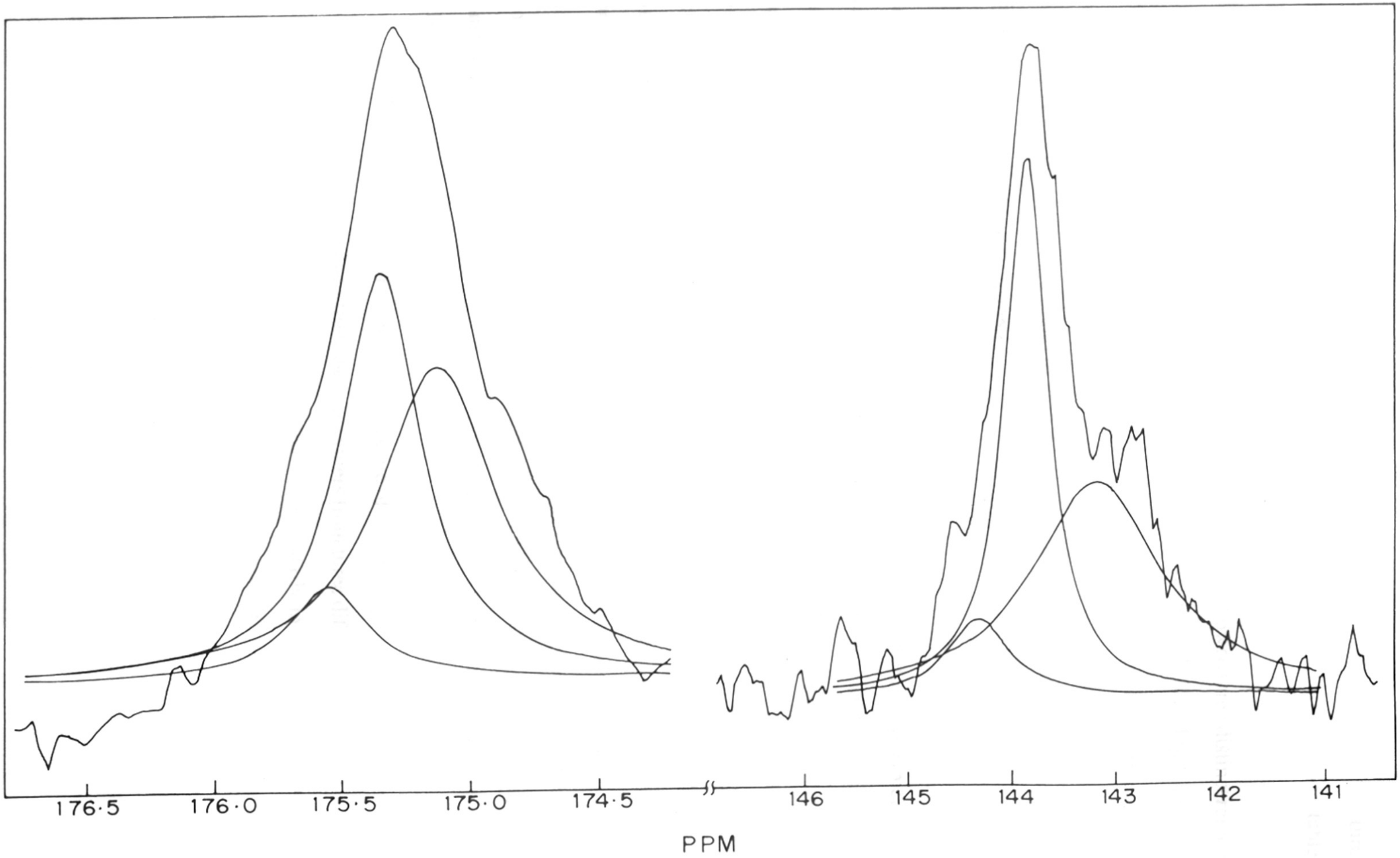


Fig. 5.14 Deconvoluted amide carbonyl (left) and ipso carbon (right) peaks of the ^{13}C NMR spectrum of S/A copolymer obtained using BTSAm precursor; sample no. B-82

Elemental Analysis: The nitrogen analysis reports of the samples obtained from the three acrylamide precursors namely TMSAm, BTSAm and TBDMSAm are shown in the tables 5.1-5.3.

TGA of Copolymers (Fig. 5.15-5.17): The TGA of the copolymers showed three distinct regions of degradation, as supported by the presence of three distinct peaks in the DTGs (Fig.5.18-5.20).

DSC of Copolymers (Fig 5.21-5.23): Each sample was annealed at 160°C for five minutes, then cooled to 50°C and again scanned for the DSC thermogram. The DSC of the copolymers showed a single T_g values of which were found to vary depending on the composition of the samples.

5.3 RESULTS AND DISCUSSION:

5.3.1 Determination of Copolymer Composition:

The synthesis of compositionally homogeneous styrene-acrylamide copolymers was accomplished using three silylated acrylamide precursors. The monomers BTSAm, TMSAm and TBDMSAm were copolymerized with styrene using BPO as the initiator. The copolymer compositions were determined from nitrogen analysis and peak area in ^{1}H NMR spectra. Comparison of the peak area in the region $\delta = 0.75$ to 2.5 due to vinylic protons contributed by both monomers (either of the silylated acrylamides and styrene) with the area of the protons due to the aromatic group appearing in the region $\delta = 6.25$-7.5 enables the estimation of the copolymer composition. Samples obtained from mole ratios of acrylamide precursor : styrene = 15:85 to 50:50 after hydrolysis were soluble in $CDCl_3$. NMR of copolymers containing more than 40 mol% acrylamide were recorded in dimethyl sulfoxide (DMSO-d_6) (Fig.3). Copolymer compositions were also calculated from the nitrogen analysis. The results are shown in Tables 5.1-5.3.

In Fig. 5.4, 5.5 and 5.6 the FTIR spectra of a mixture of two homopolymers are compared with those of the copolymers obtained from the copolymers from three different precursors. Changes in the relative absorbances at different wavelengths, particularly in the region 1300-900 cm^{-1}, is most likely due to the vibrational coupling occuring because of frequent alternation of the comonomer moieties in the polymeric chain[3].

On the basis of the copolymer compositions (Fig.5.24, 5.25, 5.26, 5.27, and 5.28), the reactivity ratios for BTSAm, TMSAm or TBDMSAm (M_1) and styrene (M_2) were determined using the Kelen Tudos method[4] (Table 5.1-5.3). At both 50°C and 80°C, the reactivity ratios for the three monomers and the comonomer (styrene) are calculated to be less than unity indicating the

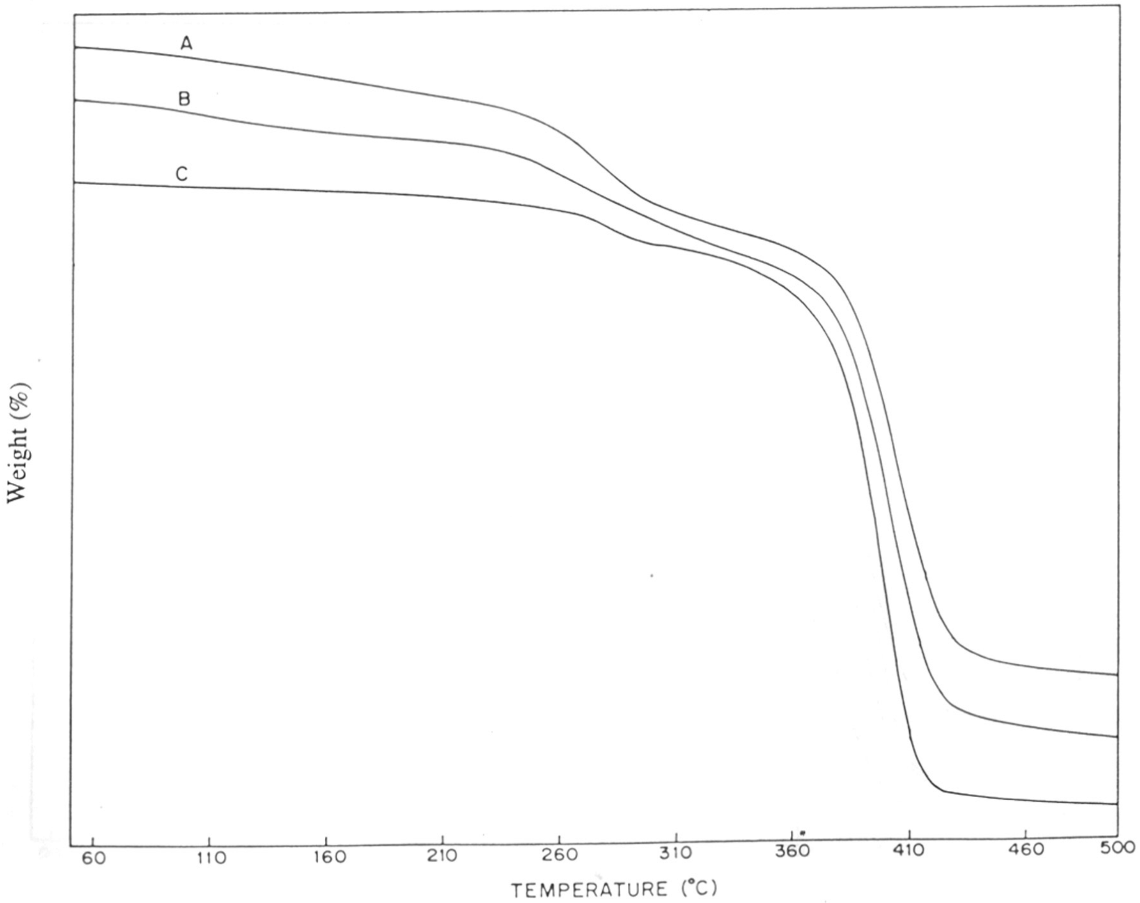


Fig. 5.15 Thermogravimetric Analysis:thermograms of the samples M-87 (A), M-67 (B) and M-50 (C).

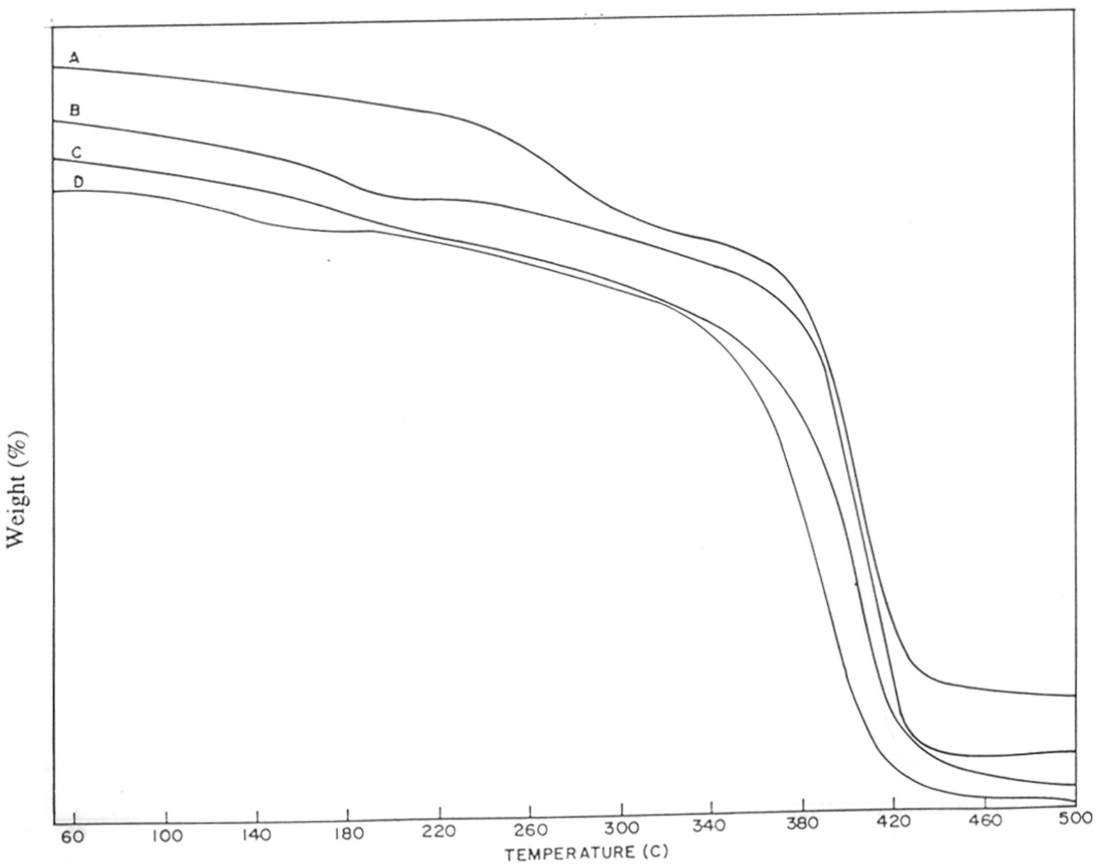


Fig. 5.16 Thermogravimetric Analysis:thermograms of the samples B-91 (A), B-82 (B), B-63 (C) and B-25 (D).

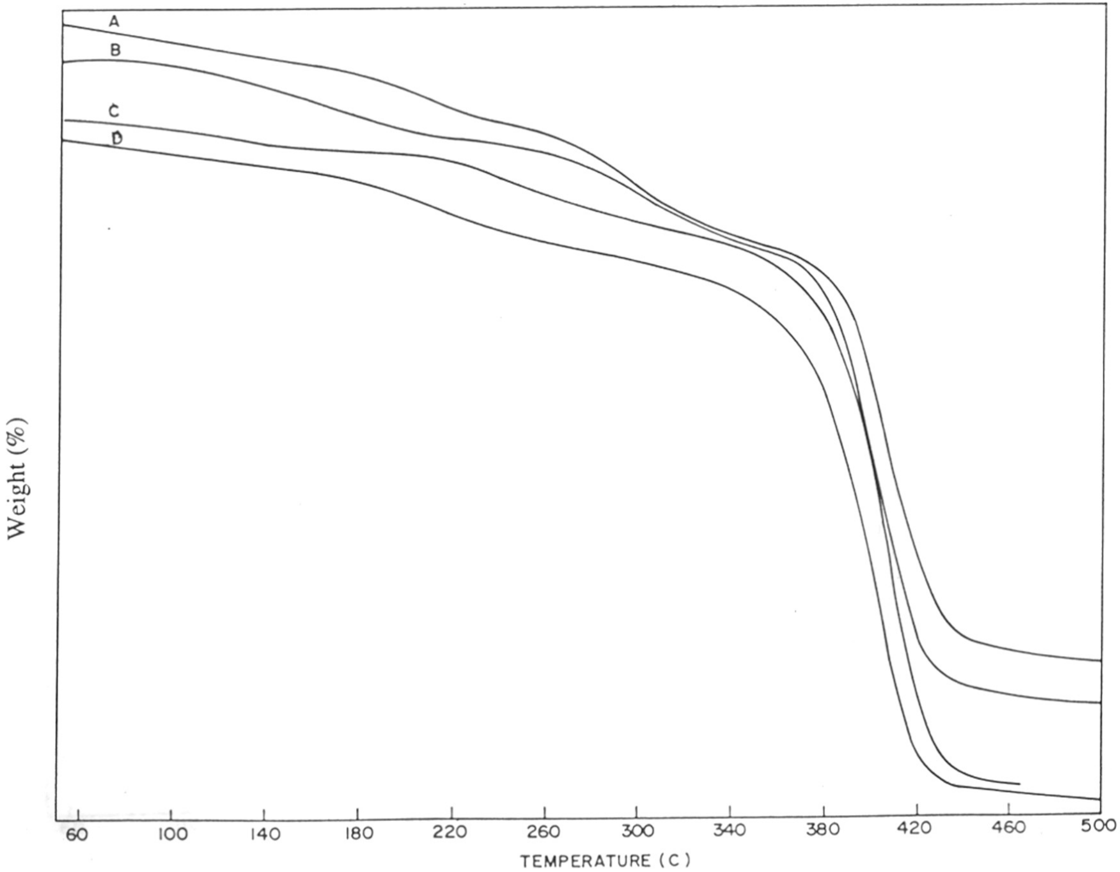


Fig. 5.17 Thermogravimetric Analysis: thermograms of the samples TB-89 (A), TB-68 (B), TB-52 (C) and TB-15 (D).

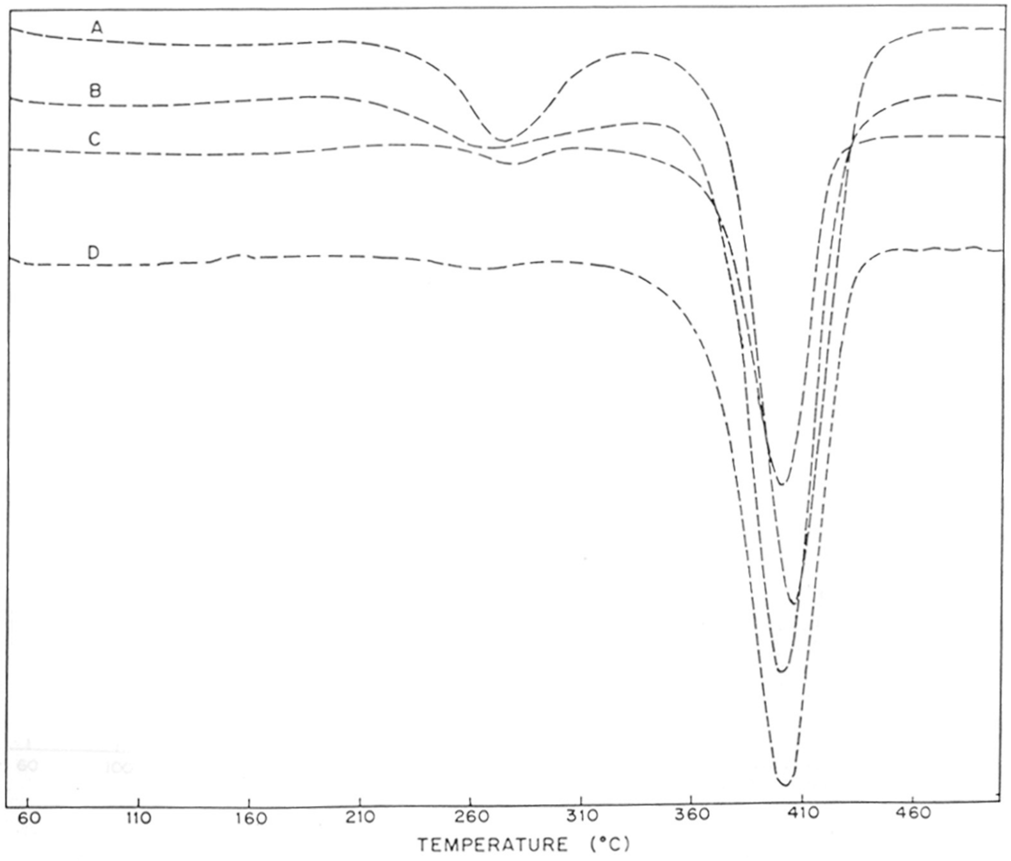


Fig. 5.18 DTG curves of the samples M-87 (A), M-67 (B) M-50 (C) and M-27 (D).

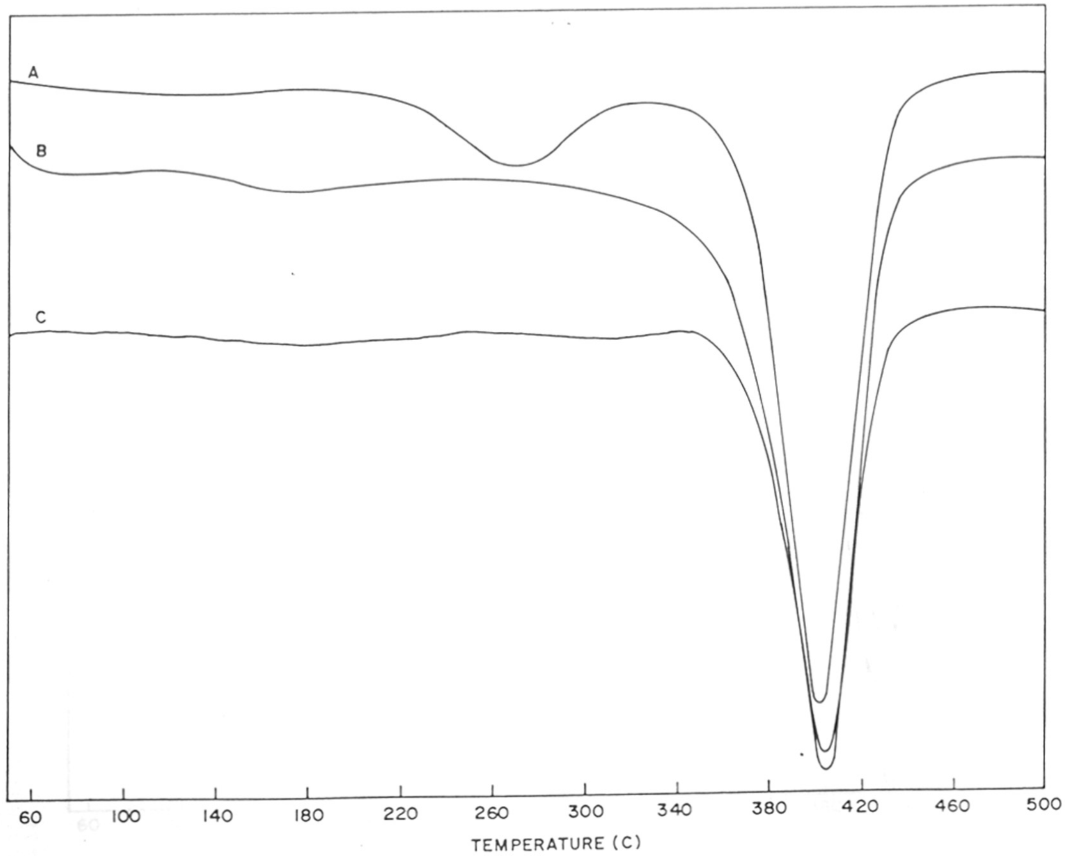


Fig. 5.19 DTG curves of the samples B-91, (A), B-63 (B) B-82(C).

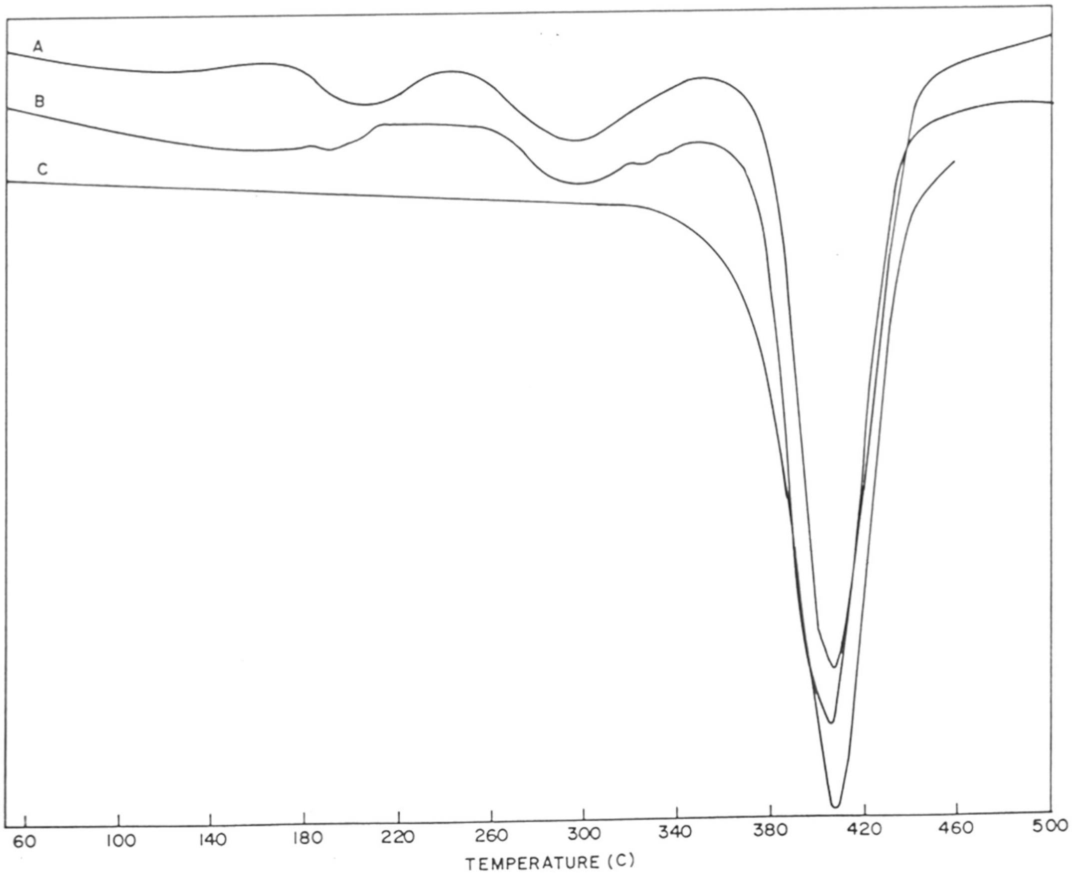


Fig. 5.20 DTG curves of the samples TB-89 (A), TB-68 (B), and TB-52 (C).

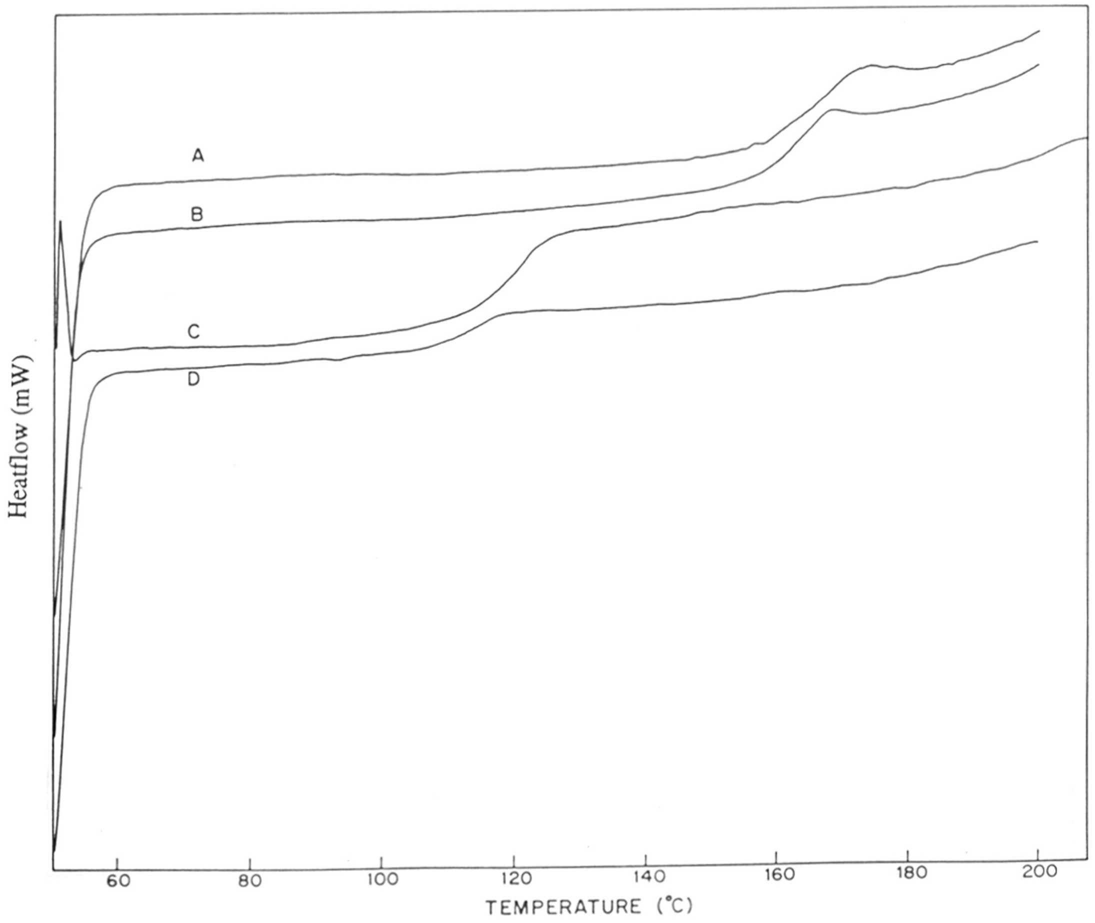


Fig. 5.21 DSC curves of the samples M-87 (A), M-50 (B) M-33 (C) and M-27 (D).

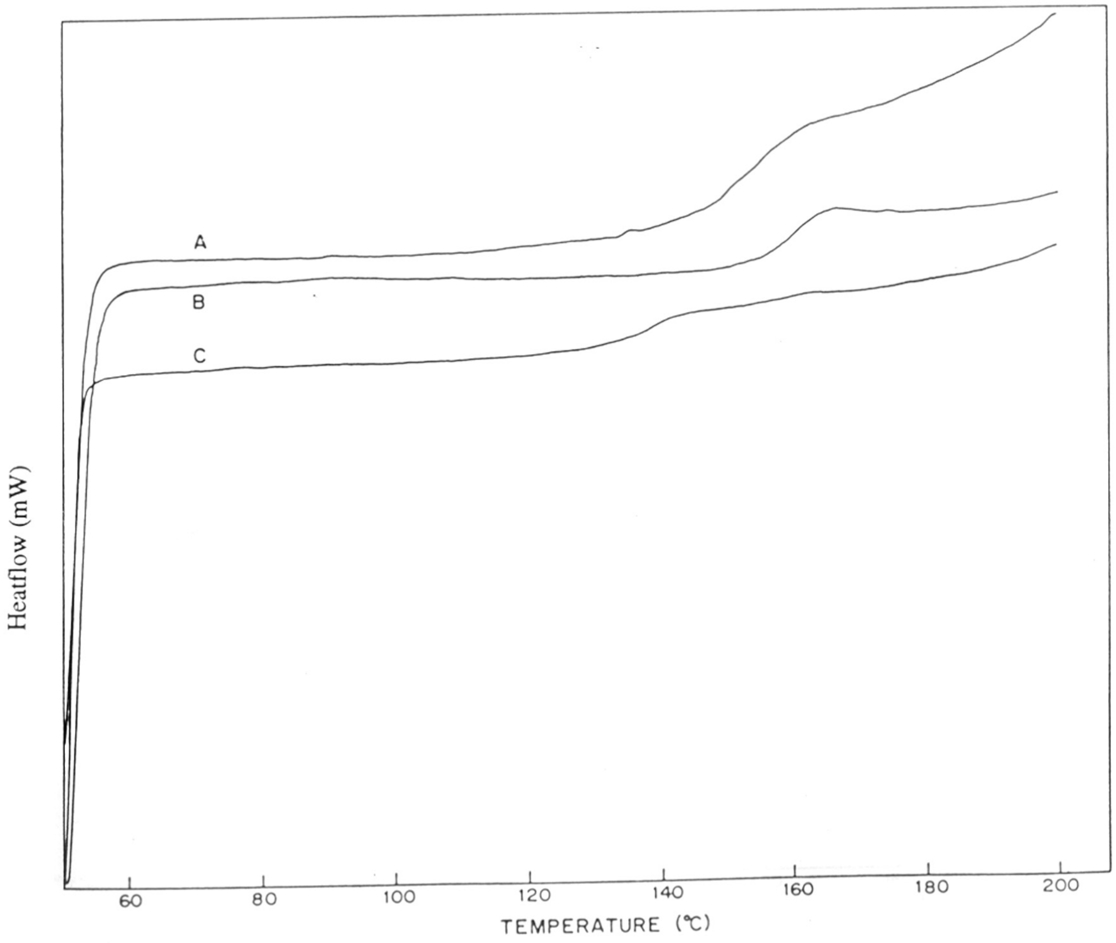


Fig. 5.22 DSC curves of the samples B-91 (A), B-82 (B) B-25 (C).

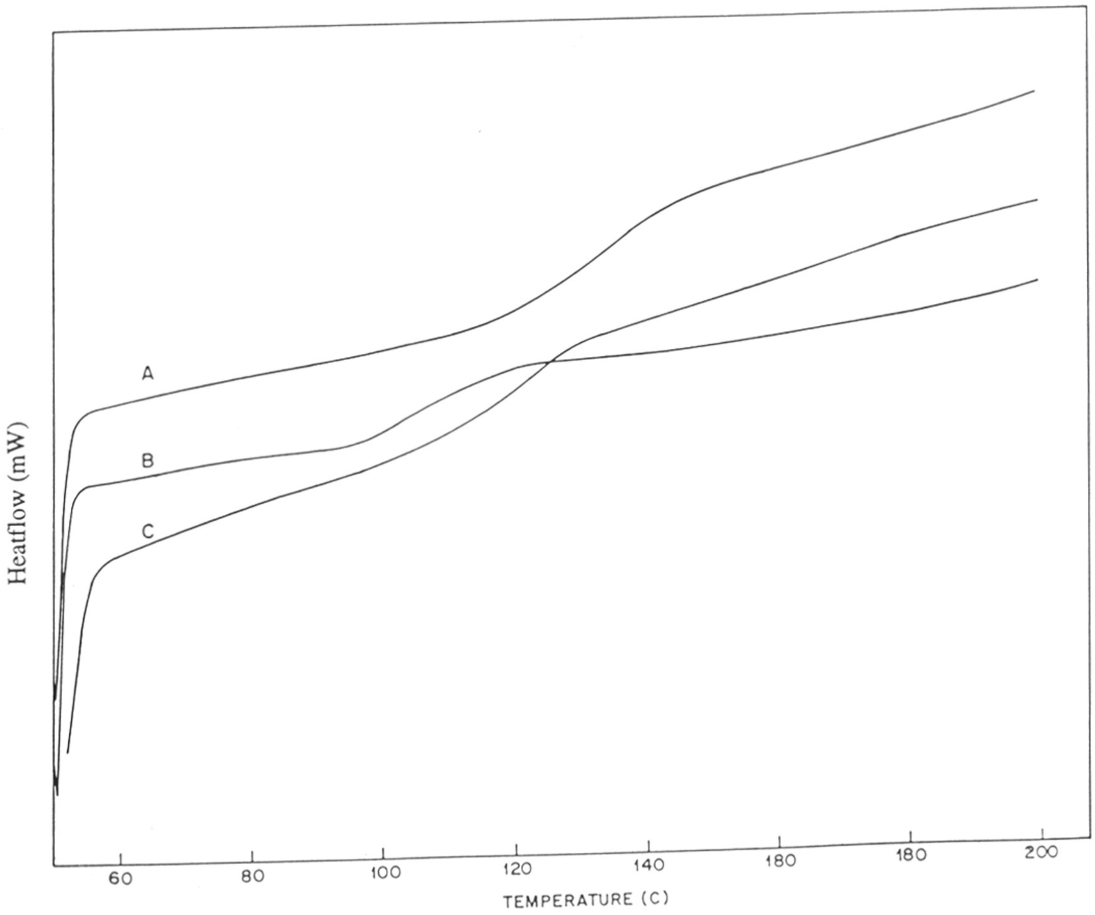


Fig. 5.23 DSC curves of the samples TB-89 (A), TB-31 (B), and TB-52 (C).

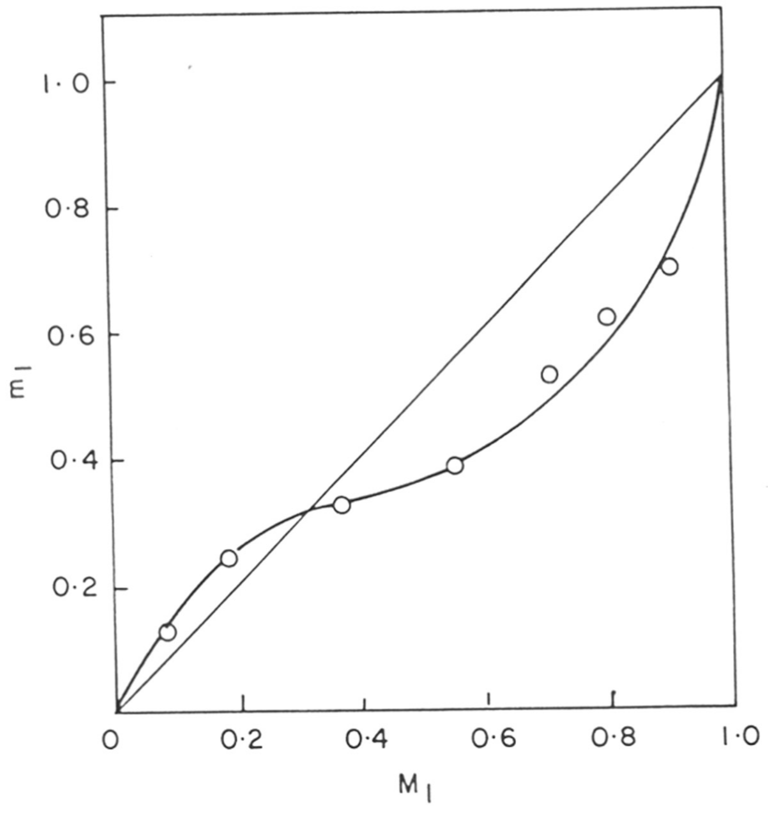


Fig. 5.24 Plot of the mole fraction of acrylamide in the instantaneously formed copolymer (m_1) vs. the mole fraction of TMSAm in the feed (M_1). Conditions: solvent, benzene; initiator, BPO; [M] = 2.0 mol/L; [I] = 0.02 mol/L; temp. 50°C.

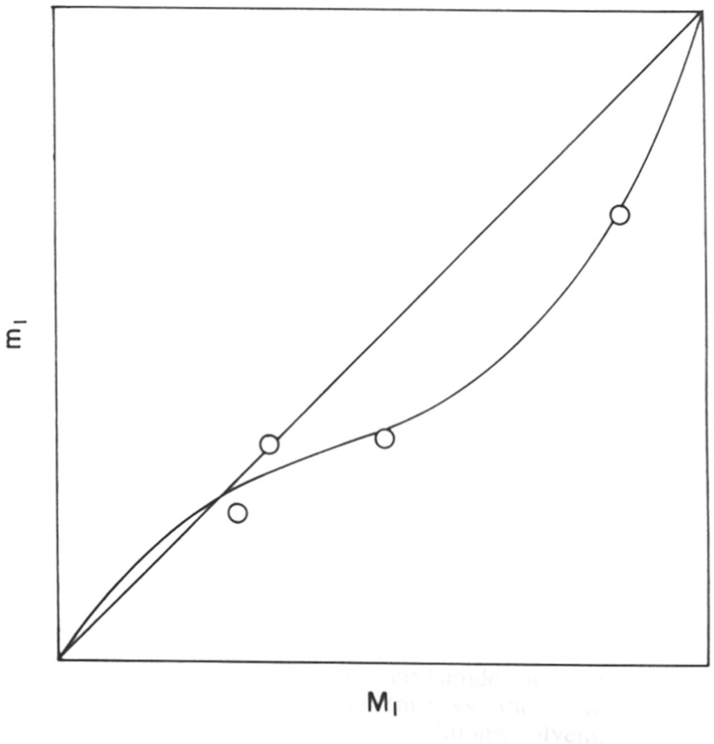


Fig. 5.25 Plot of the mole fraction of acrylamide in the instantaneously formed copolymer (m_1) vs. the mole fraction of TMSAm in the feed (M_1). Conditions: solvent, benzene; initiator, BPO; [M] = 0.60 mol/L; [I] = 0.036 mol/L; temp. 80°C.

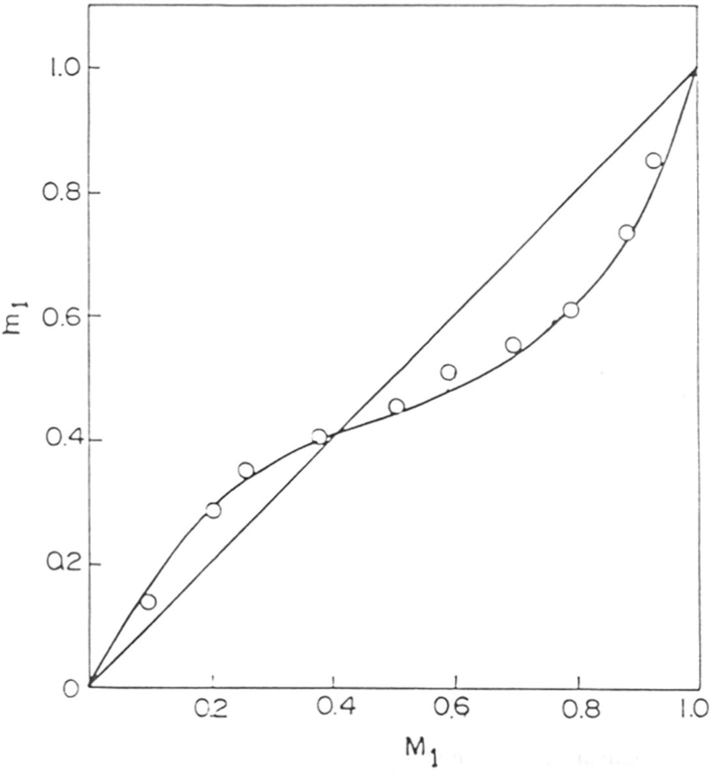


Fig. 5.26 Plot of the mole fraction of acrylamide in the instantaneously formed copolymer (m_1) vs. the mole fraction of BTSAm in the feed (M_1). Conditions: solvent, benzene; initiator, BPO; [M] = 2.0 mol/L; [I] = 0.02 mol/L; temp. 50°C.

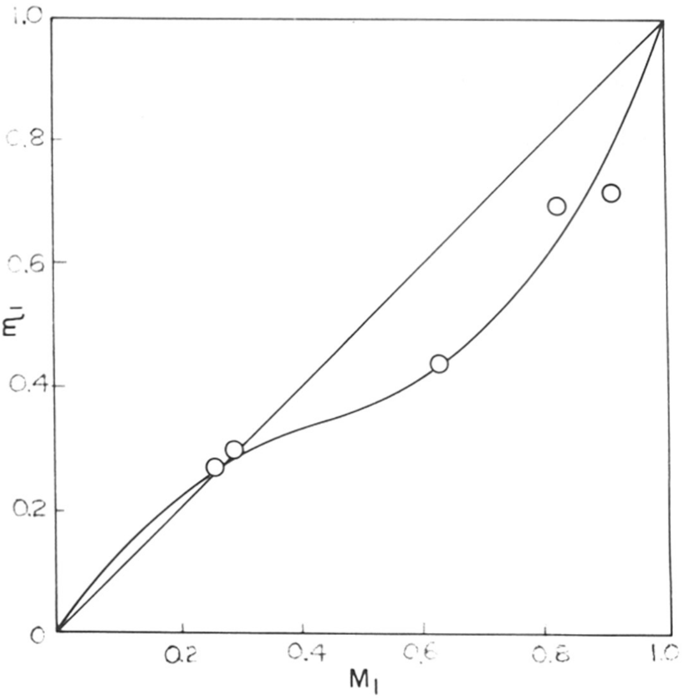


Fig. 5.27 Plot of the mole fraction of acrylamide in the instantaneously formed copolymer (m_1) vs. the mole fraction of BTSAm in the feed (M_1). Conditions: solvent, benzene; initiator, BPO; [M] = 0.60 mol/L; [I] = 0.036 mol/L; temp. 80°C.

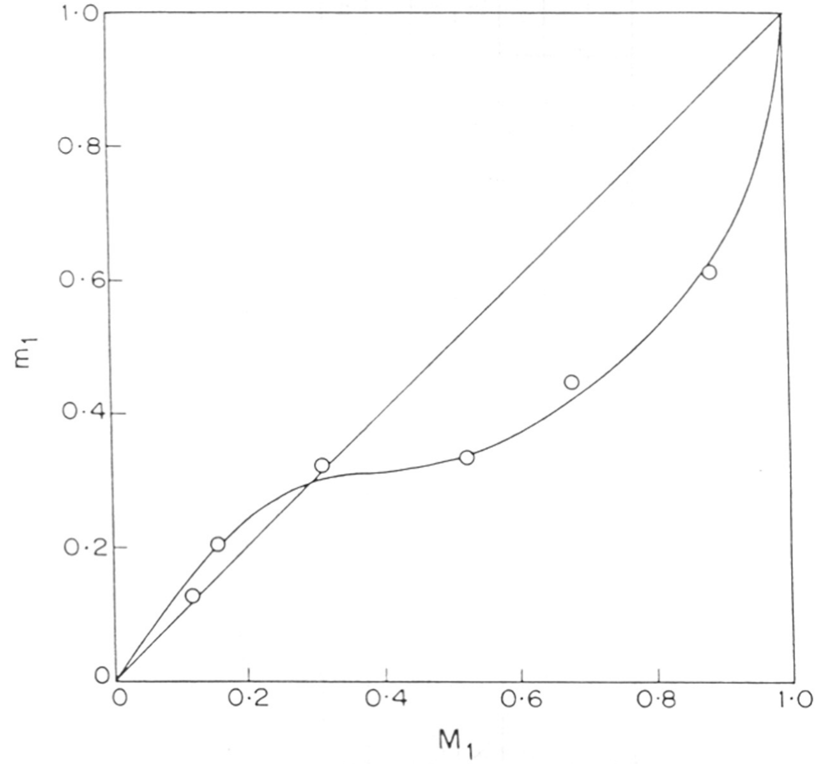


Fig. 5.28 Plot of the mole fraction of acrylamide in the instantaneously formed copolymer (m_1) vs. the mole fraction of TBDMSAm in the feed (M_1). Conditions: solvent, benzene; initiator, BPO; [M] = 0.50 mol/L; [I] = 0.005 mol/L; temp. 80°C.

Table-5.4(A)
Parameters for determination of reactivity ratio of copolymerization between TMSAm (M_1) and styrene (M_2) in benzene using BPO at 50°C

M_1	M_2	m_1	m_2	X	Y	G	F	η	ξ
8.20	91.8	12.6	87.4	0.089	0.144	-0.529	0.055	-0.333	0.035
18.5	81.5	24.1	75.9	0.227	0.318	-0.487	0.162	-0.287	0.096
37.6	62.4	32.9	67.1	0.60	0.49	-0.62	0.735	-0.273	0.324
56.3	43.7	38.2	61.8	1.29	0.62	-0.79	2.684	-0.187	0.637
70.9	29.1	53.4	46.6	2.44	1.15	0.32	5.18	0.048	0.772
80.7	19.3	61.8	38.2	4.18	1.62	1.6	10.78	0.130	0.876
90.8	9.2	69.5	30.5	9.87	2.28	5.54	42.7	0.125	0.965

$\alpha = 1.532$

$r_1 + r_2/\alpha = 0.51$; $-r_2/\alpha = -0.381$

Therefore, $r_1 = 0.13$ and $r_2 = 0.58$

Table-5.4(B)
Parameters for determination of reactivity ratio of copolymerization between TMSAm (M_1) and styrene (M_2) in benzene using BPO at 80°C

M_1	M_2	m_1	m_2	X	Y	G	F	η	ξ
27.2	72.8	22.6	77.4	0.374	0.292	-0.907	0.479	-0.247	0.130
32.9	67.1	33.0	67.0	0.490	0.492	-0.506	0.487	-0.137	0.132
50.1	49.9	33.9	66.1	1.0	0.513	-0.949	1.949	-0.184	0.379
87.2	12.8	68.5	31.5	6.81	2.17	3.672	21.37	0.149	0.870

$\alpha = 3.1995$

$r_1 + r_2/\alpha = 0.461$; $-r_2/\alpha = -0.279$

Therefore, $r_1 = 0.18$ and $r_2 = 0.89$

Table-5.5(A)
Parameters for determination of reactivity ratio of copolymerization between BTSAm (M_1) and styrene (M_2) in benzene using BPO at 50°C

M_1	M_2	m_1	m_2	X	Y	G	F	η	ξ
9.60	90.4	13.5	86.5	0.11	0.16	-0.595	0.078	-0.374	0.049
20.3	79.7	28.6	71.4	0.255	0.40	-0.383	0.163	-0.229	0.0973
25.7	74.3	35.0	65.0	0.346	0.538	-0.297	0.223	-0.171	0.129
37.8	62.2	40.8	59.2	0.608	0.689	-0.274	0.537	-0.134	0.262
50.1	49.9	45.6	54.4	1.00	0.838	-0.193	1.193	-0.071	0.441
59.0	41.0	51.0	49.0	1.44	1.041	0.057	1.99	0.016	0.568
69.5	30.5	56.2	43.8	2.28	1.28	0.499	4.06	0.0896	0.729
79.0	21.0	60.4	39.6	3.76	1.53	1.302	9.24	0.121	0.859
88.3	11.7	73.6	26.4	7.55	2.79	4.84	20.43	0.221	0.931
92.8	7.2	85.0	15.0	12.89	5.67	10.62	29.3	0.345	0.951

$\alpha = 1.512$

$r_1 + r_2/\alpha = 0.594$; $-r_2/\alpha = -0.317$

Therefore, $r_1 = 0.28$ and $r_2 = 0.48$

Table-5.5(B)
Parameters for determination of reactivity ratio of copolymerization between BTSAm (M_1) and styrene (M_2) in benzene using BPO at 80°C

M_1	M_2	m_1	m_2	X	Y	G	F	η	ξ
25.4	74.6	26.9	73.1	0.34	0.37	-0.579	0.312	-0.146	0.079
28.7	71.3	29.1	70.9	0.40	0.41	-0.576	0.39	-0.142	0.096
62.9	37.1	43.2	56.8	1.70	0.76	-0.537	3.8	-0.072	0.509
82.3	17.7	69.4	30.6	4.65	2.27	2.6	9.52	0.197	0.722
91.2	8.8	71.4	28.6	10.36	2.50	6.22	42.9	0.133	0.921

$\alpha = 3.66$

$r_1 + r_2/\alpha = 0.387$; $-r_2/\alpha = -0.186$

Therefore, $r_1 = 0.20$ and $r_2 = 0.68$

Table-5.6
Parameters for determination of reactivity ratio of copolymerization between TBDMSAm (M_1) and styrene (M_2) in benzene using BPO at 80°C

M_1	M_2	m_1	m_2	X	Y	G	F	η	ξ
11.5	88.5	12.5	87.5	0.130	0.143	-0.779	0.118	-0.347	0.053
15.4	84.6	20.1	79.9	0.182	0.252	-0.540	0.131	-0.239	0.058
31.1	68.9	32.1	67.9	0.451	0.473	-0.502	0.430	-0.196	0.168
52.1	47.9	33.3	66.7	1.09	0.499	-1.094	2.381	-0.243	0.528
67.8	32.2	44.8	55.2	2.11	0.812	-0.489	5.483	-0.064	0.721
88.6	11.4	61.2	38.8	7.77	1.577	2.843	38.283	0.0704	0.947

$\alpha = 2.125$

$r_1 + r_2/\alpha = 0.349$; $-r_2/\alpha = -0.314$

Therefore, $r_1 = 0.04$ and $r_2 = 0.67$

tendency of the monomers towards forming random copolymers. A basic structural difference between TMSAm and BTSAm is that the former exists in the amide form and the latter exists in the imidate form. However this does not seem to have much effect in the reactivity of the monomers. At 80°C, a lower value of r_1 was observed for TBDMSAm when compared to TMSAm. This indicates a reduced reactivity of TBDMSAm towards its own monomer, presumably on account of the bulkier substitution on silicon.

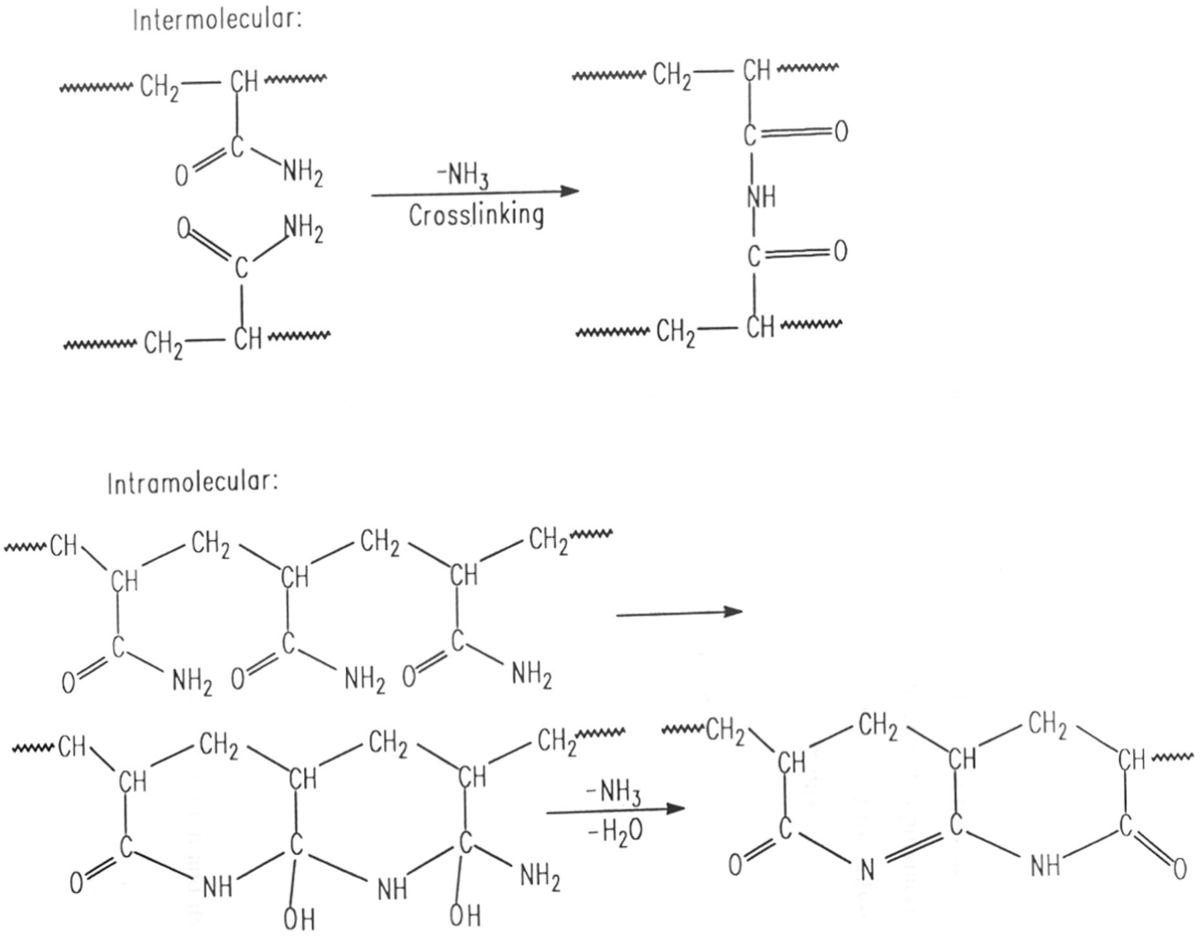
5.3.2 Thermal Analysis:

Since the copolymers consist of acrylamide and styrene fragments, the thermal behavior is expected to be an average of the two depending on the composition. When heated (heating rate of 5 - 20°C min^{-1}), undried samples of polyacrylamide decompose in three stages[5]. The first stage (20 - 220°C) corresponds to loss of bound water, and the second stage (220 - 340°C) is the loss of ammonia due to imidization (intra and intermolecular) and H_2O by dehydration. The third stage (>340°C) represents mainchain scission. A probable mechanism for the imidization process is shown in scheme 5.1[5,6]

Polystyrene breaks down statistically primarily by a process of random scissions yielding lower molecular weight products. It is generally believed that decomposition, such as this, proceed in two steps. In the first, it is assumed that random thermal scissions break the polymer chain at the weak points resulting from factors such as head-to-head linkages, chain branches and segments depolymerize into volatile products consisting mainly of trimers and tetramers). it is during this second step that the major portion of weight loss occurs in the decomposition process. However, in the reported TGA of polystyrenes and of the samples we made, two visibly distinct regions of degradation were not observed and the DTG curves also show only one peak[7].

From the TGA and DTG of the styrene-acrylamide copolymers it has been observed that the extent of retaining water is less in the styrene-acrylamide copolymers as compared to the same for a polyacrylamdide sample, and that there is a steady decrease in the affinity towards water with increasing styrene content in the copolymers.

In the region 220-340°C, the characteristics of the TGA and DTG thermograms vary depending on the copolymer composition (Fig. 5.15 - 5.20). Imidization is reported to occur on a poly(acrylamide) chain both intra- as well as intermolecularly[5,6]. This appears to be true also for the styrene-acrylamide copolymers. Occurrence of imidization upon heating was confirmed from the FTIR spectra of a sample [precursor: BTSAm, feed mol ratio, BTSAm : styrene = 82.3



Scheme -5.1

: 17.7; incorporation, acrylamide : styrene = 69.4 : 30.6] before and after heating at a temperature of 240°C for 12 min. under vacuum. There is a clear shift of the peak maxima corresponding to $CONH_2$, appearing at 1660 cm^{-1} (before heating) to a maxima at 1698 cm^{-1} (Fig.5.29) corresponding to the imide carbonyl stretch.

In case of copolymers containing lower mol% acrylamide, the probability of existence of adjacent acrylamide fragments are less. Yet TGA show the imidization occurs even in such samples. This must occur via an intermolecular process. With higher mol% acrylamide, the extent of imidization also increases. Both intermolecular imidization and intramolecular imidization may occur in this case.

The final stage of degradation involves the breakdown of the main chain. For poly(acrylamide) samples made using the same precursors under conditions similar to that of copolymerization, the onset of main chain scission was found to take place at about 290°C, and for polystyrene, the temperature was found to be about 265°C. For all the copolymers the main chain breakdown occured in a similar temperature range. (Fig. 5.15-5.17).

DSC measurements showed a steady increase of T_g with increasing mole% of acrylamide in the copolymer. The presence of only one glass transition is evidence for the absence of macroscopic phase separation and therefore implies that the copolymer samples are fairly homogeneous[8,9].

5.3.3. Copolymer microstructure:

Molecular spectroscopy is an important tool for the analysis of chemical structure, morphology, orientation and molecular dynamics of a polymer chain[10]. These have an effect on the property of the polymer. The properties of a copolymer depends both on the chemical nature of the repeating units and on their arrangement within the polymer chains (microstructure)[18,19]. There are prior reports in the literature on the compositional triad and cotacticity parameters of acrylamide-acrylic acid copolymers, obtained by alkaline hydrolysis[11], by direct copolymerization[12], and by inverse microemulsion[13]. The sequence distribution and its effect on glass transition temperature of poly(ahnydride-co-amide) also has been reported recently[14]. The triad distribution and tacticity parameter of styrene-co-methyl acrylate polymer made by solution and emulsion polymerization[15] and those of styrene-co-methacrylonitrile polymers made by bulk polymerization[16] have been studied using ^1H and ^{13}C NMR. However, there is no prior report on microstructural analysis of styrene-acrylamide copolymers. It was therefore of interest to examine the microstructure of the styrene-acrylamide copolymers using

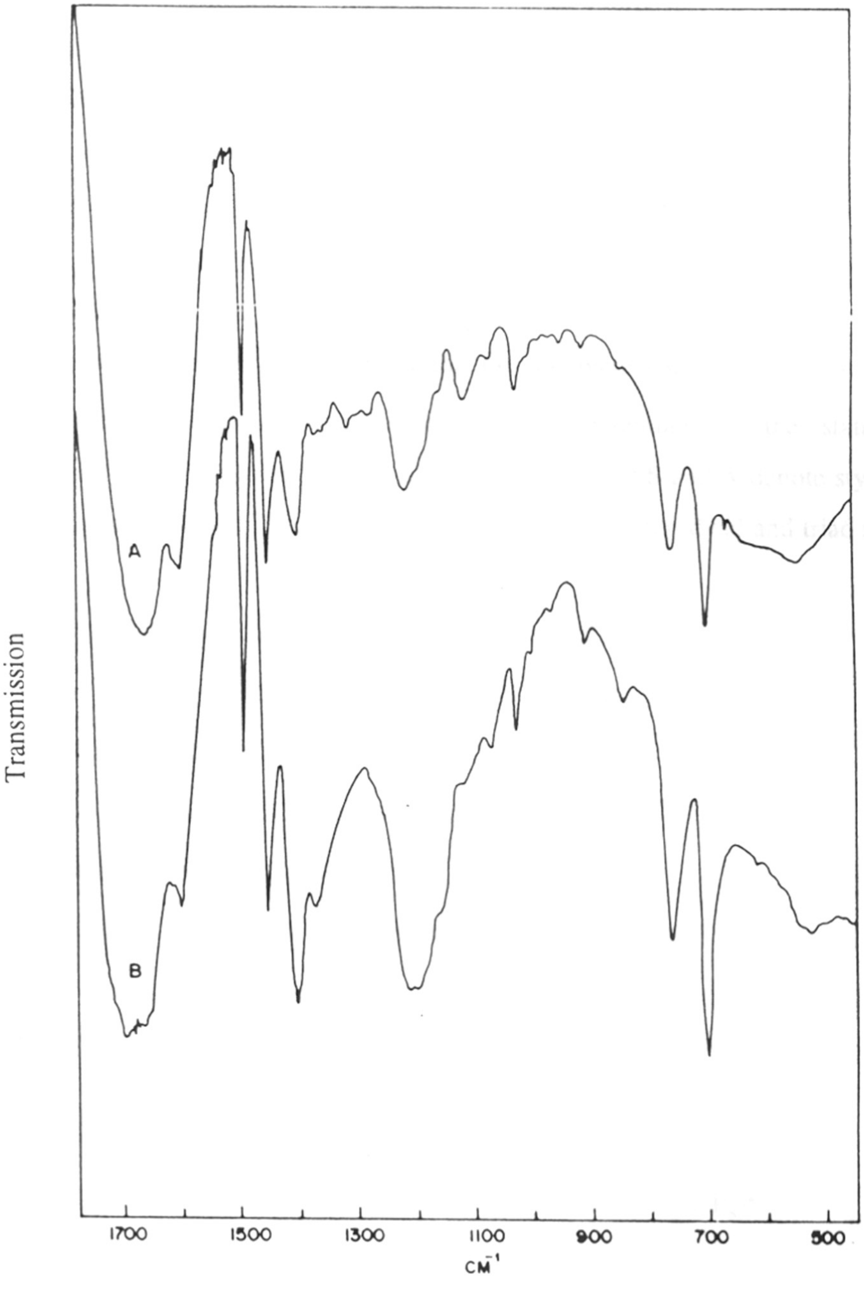


Fig. 5.29 Comparison of FTIR spectra of B-82 before and after heating to a temperature of 240°C. Imidization of the amide group results in the shift of the amide peak (A) towards higher wave number (B).

carbon-13 NMR spectroscopy. Analysis of the monomer sequence distribution up to triad level were done and the results compared with statistical models. Moreover, from the experimental dyad concentrations calculated from the ^{13}C NMR spectra, the glass transition temperatures (T_g) of a series of copolymers were determined using Barton's equation. These T_g values are in good agreement with the values measured by DSC technique.

Copolymers obtained using TMSAm: The reactivity ratios of TMSAm (r_A) and styrene (r_S) copolymerized in benzene at 50°C are found to be 0.13 and 0.57 respectively as determined by Kelen-Tudos method[4]. At 80°C the values, determined using the same method, were $r_A = 0.18$ and $r_S = 0.89$[17]. These reactivity ratios indicate that the copolymers are random in nature.

Theory: For convenience, we summerize here the essentials of the statistics of copolymerization[20,21], with reference to the present problem. Let **S** and **A** denote styrene and acrylamide units respectively. The relative proportions of monomer, dyad and triad sequence are related by,

$$\mathbf{(S) = (SS) + 1/2(SA) = (SSS) + (SSA) + (ASA)}$$

$$\mathbf{(A) = (AA) + 1/2(SA) = (AAA) + (AAS) + (SAS)}$$

$$\mathbf{(SS) = (SSS) + 1/2(SSA)}$$

$$\mathbf{(SA) = (SSA) + 2(ASA) = (AAS) + 2(SAS) = (AAS) + 2(SAS)}$$

$$\mathbf{(AA) = (AAA) + 1/2(AAS)}$$

[Note that the relative intensity of an unsymmetrical sequence, e.g., (SSA), also include the inverse (ASS)].

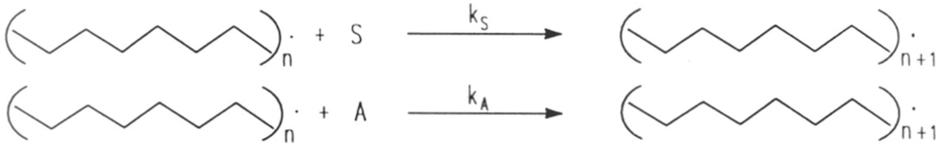
In the Bernoullian model there is one independent probability, that of adding, say, an S unit, P_S. Necessarily, $P_S + P_A = 1$. The monomer and triad intensities are related to P_S by

$$\mathbf{(SSS) = P_S^3} \qquad \mathbf{(SAS) = P_S^2(1\text{-}P_S)}$$

$$\mathbf{(SSA) = 2P_S^2(1\text{-}P_S)} \qquad \mathbf{(AAS) = 2P_S(1\text{-}P_S)^2}$$

$$\mathbf{(ASA) = P_S(1\text{-}P_S)^2} \qquad \mathbf{(AAA) = (1\text{-}P_S)^3}$$

This model implies the existence of only two propagation steps.



giving

$$\mathbf{P_S = rf_S/[1 + f_S(r\text{-}1)]}$$

where $r = k_S/k_A$ and f_S is the mole fraction of S in the comonomer feed.

In the first-order Markov model, the addition probability depends on the end unit of the growing chain. There are four conditional probabilities, P_{XY}, where X denotes the end unit and Y the added unit (X,Y = S or A). Only two probabilities are independent since necessarily $P_{SS} + P_{SA} = P_{AA} + P_{AS} = 1$.

Defining $u = P_{SA}$ and $w = P_{AS}$, one obtains,

$$\mathbf{(SSS) = w(1\text{-}u)^2/(u+w)}$$

$$\mathbf{(SSA) = 2uw(1\text{-}u)/(u+w)}$$

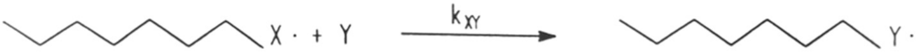
$$\mathbf{(AAS) = 2uw(1\text{-}w)/(u+w)}$$

$$\mathbf{(ASA) = u^2w/(u+w)}$$

$$\mathbf{(AAA) = u(1\text{-}w)^2/(u+w)}$$

$$\mathbf{(SAS) = uw^2/(u+w)}$$

This model corresponds to four distinct propagation steps of general form:



giving

$$\mathbf{u = (1\text{-}f_S)/[1+f_S(r_S - 1)] \quad and \quad w = f_S/[r_A+f_S(1\text{-}r_A)]}$$

where r_S and r_A (the reactivity ratios) are equal to k_{SS}/k_{SA}, and k_{AA}/k_{AS}, respectively. If $r_S = r_A = 1$ (and hence $P_{SA} + P_{AS} = 1$), first-order Markov statistics reduces to the Bernoullian case.

The percentage of monomer feeds in copolymers (mol%) obtained using TMSAm and BTSAm (experiments done at 80°C) are shown in Table-5.1(B) and 5.2(B) respectively.

A number of organic solvents such as chloroform, tetrahydrofuran, dioxane, acetonitrile, dimethylformamide and mixtures of any two of these in various proportions were tried to dissolve all the S/A copolymers with various monomer compositions shown in Table-5.1(B) and 5.2(B). However, it was found impossible to get a homogeneous solution. The only solvent giving clear solution for a wide range of copolymer compositions was dimethyl sulfoxide (DMSO). The compositional effects were considered to be more sensitive than the configurational effect since the peaks sensitive to the configurational effect overlapped in the region (30-40 ppm) with the DMSO-d_6 (solvent) peaks. For sequence analyses, the resonance signals of homopolymers, poly(styrene) (PS), poly(acrylamide) (PA) and copolymers S/A were considered.

Previous NMR studies[11,22,23] of acrylamide (A) homopolymer have shown that the C=0 peak is essentially unaffected by tacticity, whereas CH and CH_2 resonances are split into several peaks. Similarly, NMR of styrene homopolymers have shown that C_α(-CH) and C_β(-CH_2) resonances are very close (38-48 ppm) and that the methine carbon (higher field part of this region) is not affected by configurational effet[24] whereas the C_1 carbon (quarternary carbon of the aromatic ring) exhibits complex configuational effects[24,25] with pentad chemical sensitivity. Based on this, peak assignments were done in case of poly(styrene) and poly(acrylamide) homopolymer used in the present study. The aromatic carbon atoms in PS show splitting according to their environment. The S/A copolymers of various compositions, obtained using TMSAm, exhibit a highly complex aromatic ring-carbon resonance patterns around 142.26 - 143.72 ppm. No splitting was observed for ortho, meta and para carbon which appeared around 128.58, 126.87 and 124.58 ppm respectively. Similarly, C-1 of copolymers from BTSAm occurs around 142.69 - 144.47 ppm., while no splitting was observed for ortho, meta, and para carbon; for S/A copolymers the resonance δ 127.77, 126.74 and 124.45 ppm respectively. Signals around 30 - 38 ppm were assigned to $(CH)_A$, $(CH_2)_A$, but could not be used for sequence analysis because of overlapping with the signals of the solvent. The signals in the region 38 - 42 ppm are assigned to $(CH)_A$, $(CH)_S$ and $(CH_2)_S$ but can not be used for sequence analysis due to the overlap of the signals from both monomeric units. The sharp singlets around 128.0, 126.0 and 124.0 ppm can be attributed to ortho, meta and para-carbon atoms of the phenyl ring respectively, indicating their insensitivity towards different compositional sequences.

The C-1 carbon of the styrene unit appeared as a well resolved multiplet in the region 142 to 144 ppm, indicating sensitivity towards different monomer placements. The carbonyl carbon signal in the S/A copolymer appeared as a multiplet around 174 to 176 ppm indicating sensitivity towards different compositional sequences. In case of the S/A copolymer, a shift in the position of various functional groups of the units from S and A was observed (in comparison to homopolymers). This is due to the change in the nature of adjacent monomeric units in the copolymer which changes the chemical shift of S and A centered triads.

The carbonyl $(C{=}O{<})_A$ (A) and $(C\text{-}1)_S$ carbon (B) regions of S/A copolymers are shown in Figures: 5.7(A,B) - 5.13 (A,B). C-1 of B-25 and B-91 are shown in 5.14 (A,B). The chemical shift difference within the resonance signals and the splitting pattern shows its sensitivity toward different monomer sequences and cotacticity in the carbonyl carbon resonances. Poly(acrylamide) exhibits a singlet around 174.0 ppm. As the concentration of styrene in the sample increases, signal characteristics of the homopolymer decreases, whereas a set of downfield signals centred between 175.0 and 175.5 starts to appear. Three sets of signals, the intensities of which change with copolymer composition, can be assigned to the carbonyl carbon atom of the central unit from A in SAS, SAA (AAS) and AAA triad sequences from low to high field. In the case of A-centered triads, introduction of a unit from S in AAA signals (by $\delta = 0.50$ ppm). Van Doremaela et.al.[15] have reported a similar type of assignment for styrene/methyl acrylate copolymers. Concentration of various A-centered triads can be calculated from the relative areas of respective signals.

Poly(styrene-co-acrylamides) were prepared at low conversions (10%). The characteristics of the samples are given in Table-5.1(B) and 5.2(B). The mole fraction of styrene in the feed (f_S) and that in the final copolymer (F_S) are reported together with the percentage conversion (Y). The results shown in M-27 and M-33 are in excellent agreement between f_S and F_S in case of TMSAm. The results for samples B-25 and B-30, obtained from BTSAm, also show an excellent agreement between f_s and F_s values. Such agreement is expected logically for Y=100%. For a more detailed insight into the copolymerization kinetics, the sequence distribution as revealed by the triad proportions was examined.

Figure - 5.7-5.10 shows the development of the carbonyl resonance of acrylamide and ipso carbon C-1 of styrene with increasing acrylamide content for the copolymers obtained using TMSAm precursor namely, M-27, M-33, M-50 and M-87 respectively and Fig. 5.11-5.13 shows the development of the carbonyl resonance of acrylamide and ipso carbon C-1 of styrene for the samples got using BTSAm. namely, B-30, B-63 and B-82. The development in ipso carbon resonance in peaks of B-25 and B-91 are shown in Fig. 5.14. The spectra of the homopolymers, poly(styrene) (PS) and poly(acrylamide) (PAM) are also shown for comparison, and the triad assignment is indicated on the spectrum of M-50. This assignment has been deduced directly from the dependence of the component resonancess on copolymer composition and a comparison with the homopolymer chemical shifts. The assignment is also in agreement with those reported previously for radical poly(acrylamide-co-acrylates) prepared in water[11] and in inverse microemulsions using oil-water systems[13].

Figures 5.31-5.34 show the comparison for all copolymers between the experimental triad proportions and the theoretical distribution curves for Bernoullian statistics calculated by using the relationship $P_S = F_S$. The literature values of reactivity ratios differ from unity. However, there is surprisingly good agreement between experiment and theory for this model. However, Truong et.al.[12] has also shown that for high degree of conversion an apparent distribution close to that of Bernoulli could be obtained when taking into account the compositional heterogeneity of poly(acrylamide-co-acrylates) with reactivity ratios $r_A = 0.3$ and $r_M = 0.95$.

A proper determination of the reactivity ratios of monomers requires therefore a sequence distribution analysis of copolymers with various compositions and degrees of conversion, particularly, in the low conversion range (10%), where the average copolymer composition and the instantaneous composition are similar.

Figures 5.31 and 5.33, the theoretical triad distribution curves, matches very well with the figures 5.32 and 5.34, the experimental triad distribution curves, respectively. This confirm the random character of the monomer placement. The numerical values are shown in Table-5.7 (A-B). Similarly, the fraction of triads determined from C-1 and C=O group carbon resonance of the copolymer samples from TMSAm and BTSAm compare well with theoretical values. The discrepancy in this case is quite marked and outside experimental error. This result agrees with that of other authors[11-13,26] who found that the sequence distribution of acrylamide/acrylate and acrylamide/sodium acrylate copolymers prepared by alkaline hydrolysis of polyacrylamide is characterized by autoretarded kinetics and very different from Bernoullian behavior.

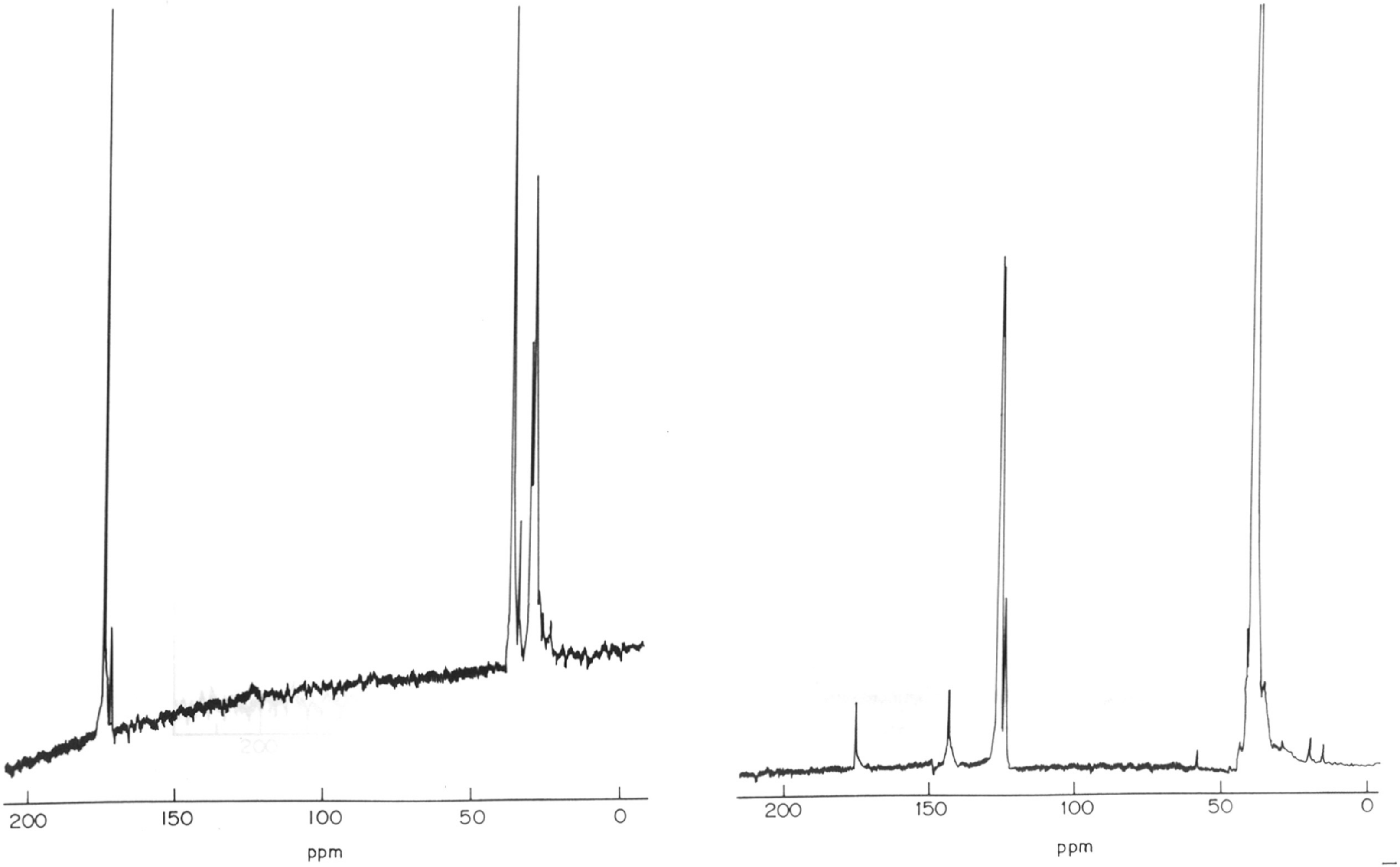


Fig. 5.30 a) ^{13}C NMR spectrum of poly(acrylamide) (recorded in D$_2$O) (left); ^{13}C NMR spectrum of M-50 (recorded in DMSO-d$_6$) (right)

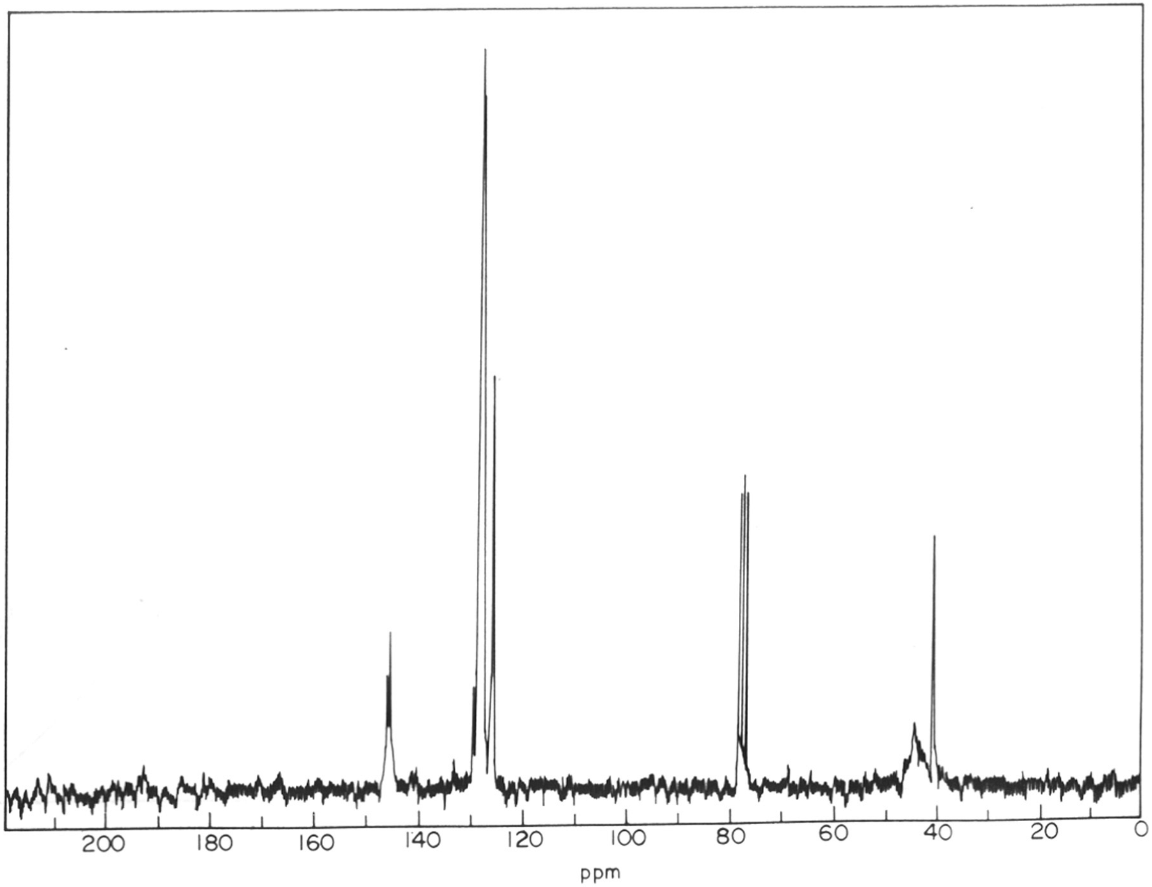


FIG. 5·30

b) ^{13}C NMR spectrum of poly(styrene) (recorded in $CDCl_3$)

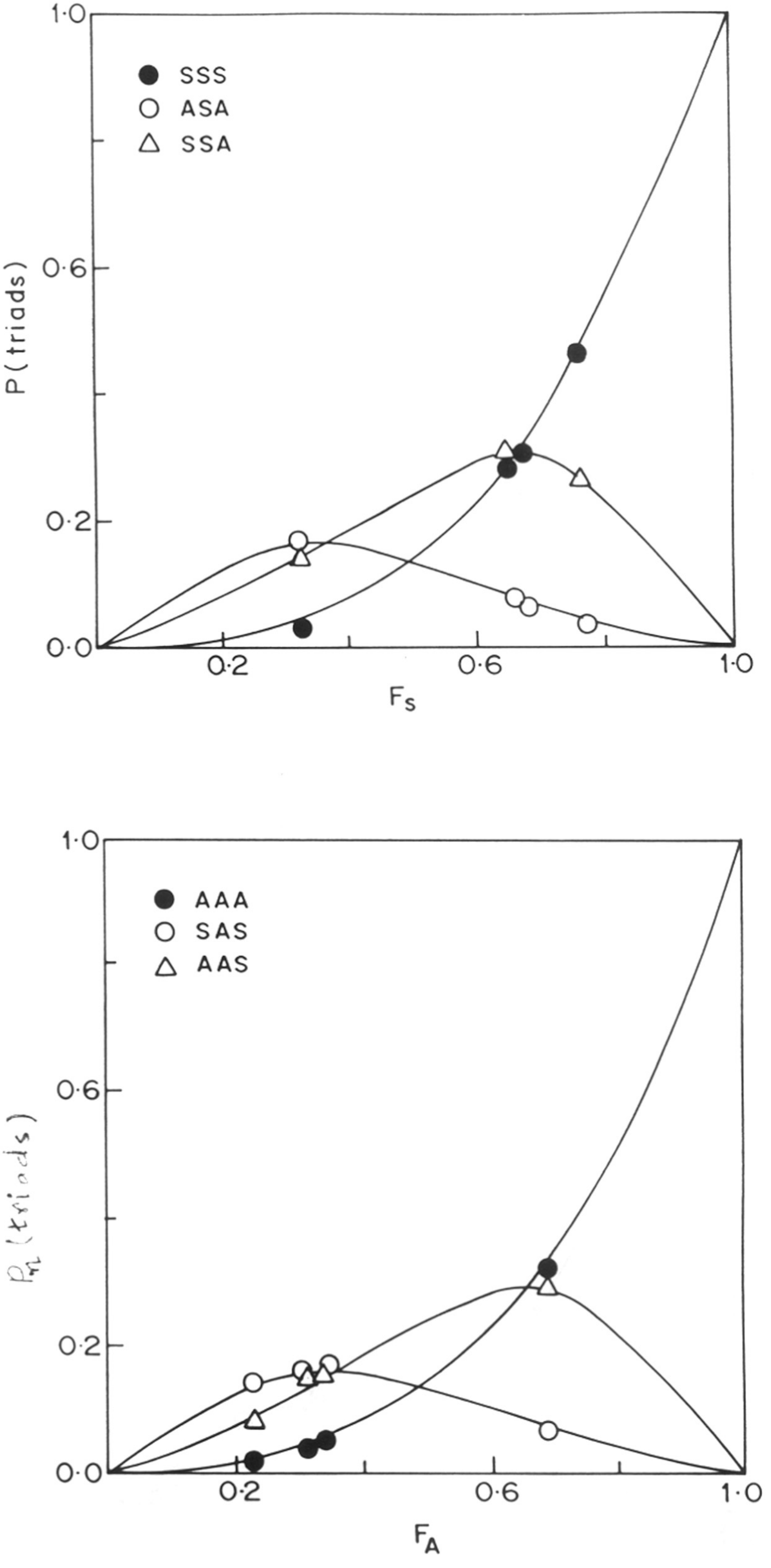
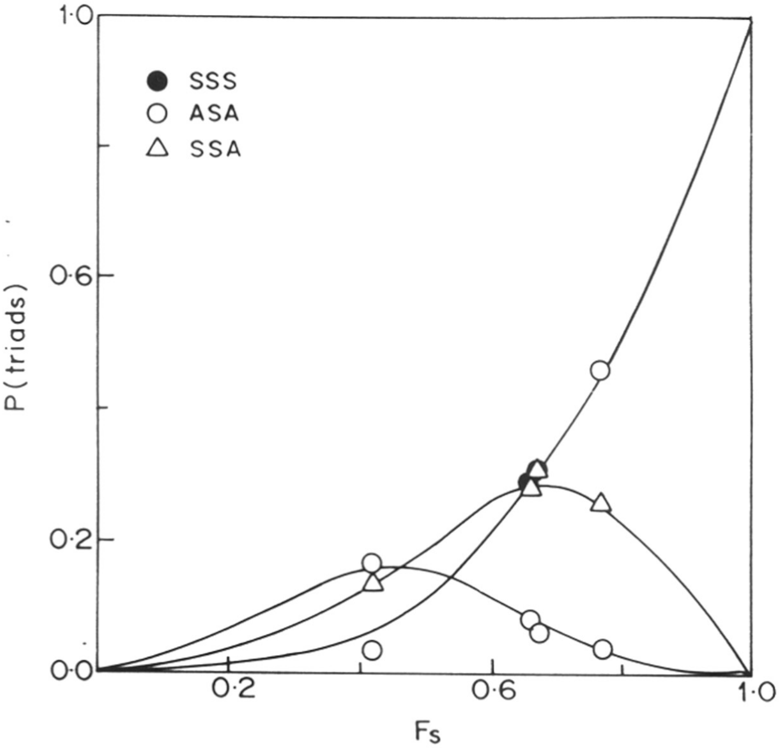


Fig. 5.31 Theoretical triad proportions (symbols), calculated for Bernoullian statistics with $P_s = F_s$ (curves), for S/A copolymers obtained using TMSAm.



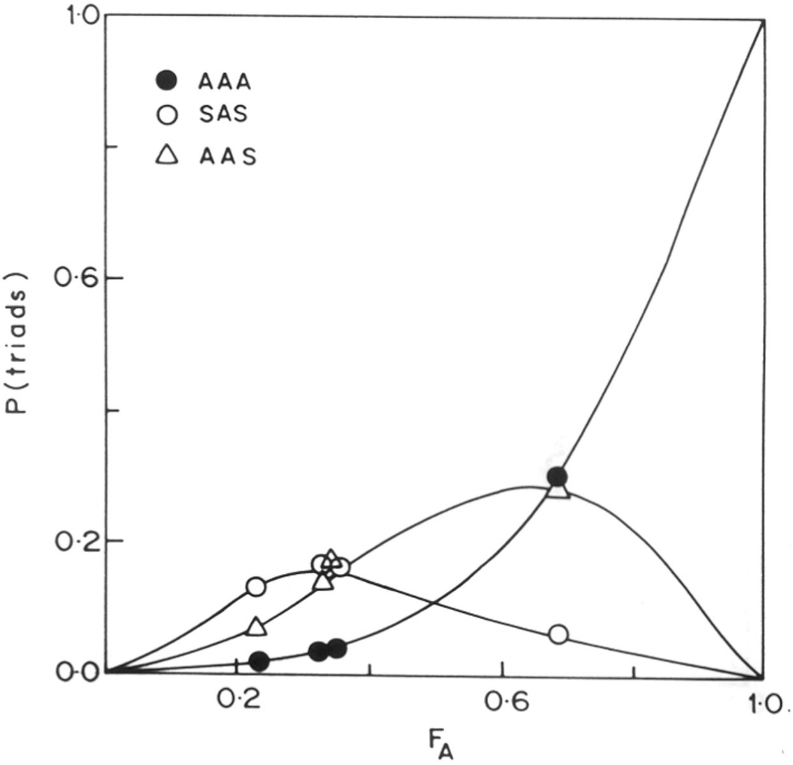


Fig. 5.32 Experimental triad proportions (symbols) from C-1 and C=O group carbon resonance of the S-A copolymers obtained using TMSAm

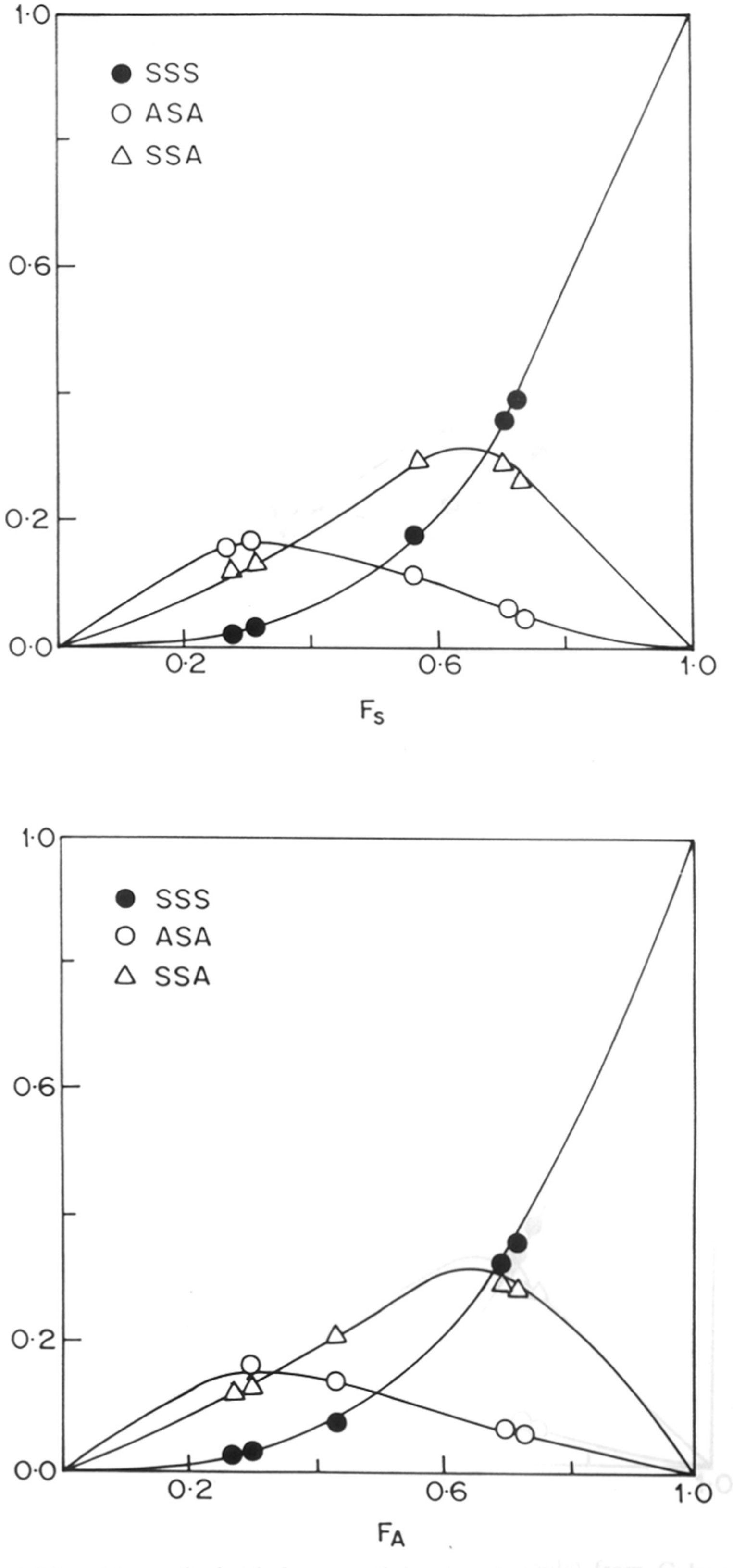


Fig. 5.33 Theoretical triad proportions (symbols), calculated for Bernoullian statistics with $P_s=F_s$ (curves), for S/A copolymers obtained using BTSAm.

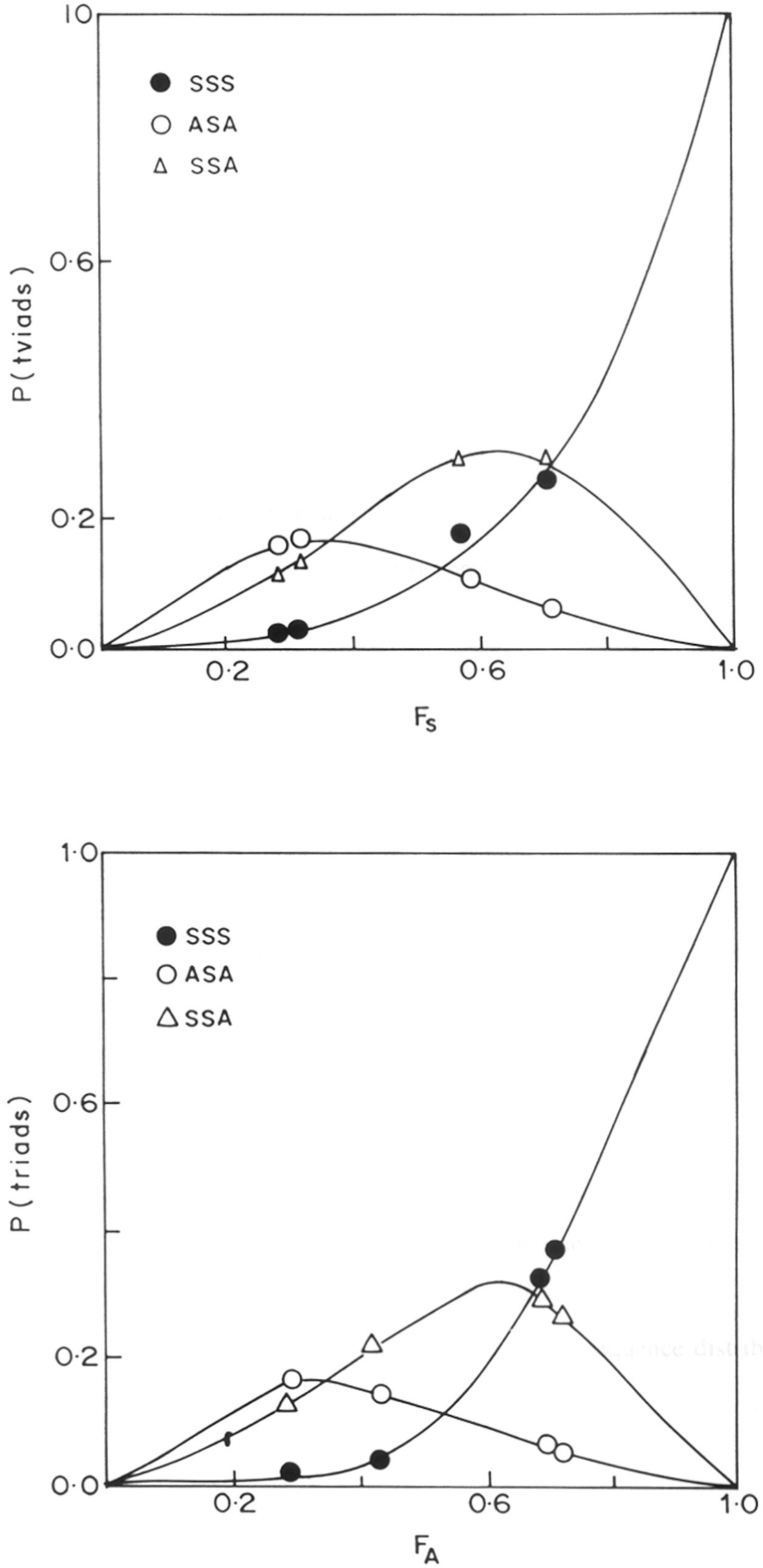


Fig. 5.34 Experimental triad proportions (symbols) from C-1 and C=O group carbon resonance of the S-A copolymers obtained using BTSAm

Errors and further statistical analysis: Experimental errors were not quoted above in order to avoid excessively complex tables and figures. The value of F_S simply obtained from the areas of the S and A signals and is therefore determined with relatively small error of about 3% because of the clear resolution of the S and A regions. However, the triad intensities are more reliable in case of ipso C-1 atom of styrene and less reliable in case of carbonyl group of acrylamide because of spectral overlap. Estimates of the errors arising from uncertainties in division of the integrals range from 5% for the better resolved peaks of high intensity, such as AAA in sample M-87 of figure 1, to 20% for poorly resolved peaks of low intensity such as SAS in sample M-50 of Figure-5.30. The agreement with Bernoullian statistics is well within these limits, indicating that the reactivity ratios are both close to unity.

In principle, on the basis of the reactivity ratios for styrene/acrylamide system in other solvents one would have expected deviations from Bernoullian statistics significantly greater than the experimental errors. We have analyzed the triad intensities in the low-conversion samples (10%) further in terms of first-order Markov statistics in order to compare with the Bernoullian model. The experimental and calculated proportions are given in Table-5.7 and Markov probabilities and reactivity ratios in Table-5.8. The improvement in agreement of the intensities is marginal and it is found that P_{SS} P_{AS}, P_{AA} P_{SA} and $P_{SA} + P_{AS}$ 1. Taking the experimental errors and the scatter of the reactivity ratios between samples into account, we conclude in this system in case of M_{27} and M_{33}, the r_A is 0.90 ± 0.18 and $r_S = 0.98 \pm 0.09$. The r_A and r_S values deviate from unity incase of M-50 and M-87 samples. The monomer feed compositions do not correspond closely with the incorporation monomer composition F_S in polymer which was obtained by ^{1}H NMR spectroscopy, although these copolymers were synthesized at low conversion (<10%). However all experimental triad sequences (SSS, SSA, ASA, SAS, AAS & AAA) matches with both Bernoullian and first-order Markov statistics. A similar discrepancy was obtained in case of BTSAm and is shown in Table-5.7(B). In comparison, the experimental values of triad sequences are more closer to Bernoullian than 1st-order Markov statistics.

The block character (η) is an adequate way to characterize the sequence distribution in the copolymers. It is given by the expression[27],

$$\eta = [SA]/2[S][A]$$

TABLE - 5.7(A)

Composition of Styrene (f_S), copolymer composition (F_S), Degree of Conversion (Y), and Triad Relative Intensities for the Hydrolyzed Copolymers from styrene-N-trimethylsilylacrylamide copolymers:

								RELATIVE INTENSITY					
System	Y%	f_S	f_A	F_S	F_A	T_1°C[a]		SSS	SSA	ASA	SAS	AAS	AAA
M-27	8.8	0.728	0.272	0.774	0.226	100	exptl.	0.463	0.262	0.038	0.138	0.067	0.019
							B[b]	0.463	0.271	0.039	0.135	0.079	0.012
							M[c]	0.453	0.274	0.041	0.137	0.083	0.012
M-33	9.7	0.671	0.329	0.670	0.330	100	exptl.	0.301	0.293	0.067	0.148	0.143	0.037
							B[b]	0.301	0.296	0.073	0.148	0.146	0.036
							M[c]	0.298	0.294	0.074	0.149	0.145	0.035
M-50	10.2	0.499	0.501	0.661	0.339	100	exptl.	0.288	0.293	0.082	0.143	0.154	0.039
							B[b]	0.288	0.296	0.076	0.148	0.152	0.039
							M[c]	0.285	0.296	0.077	0.148	0.154	0.040
M-87	7.0	0.128	0.872	0.315	0.685	100	exptl.	0.031	0.140	0.151	0.068	0.289	0.311
							B[b]	0.031	0.136	0.148	0.068	0.296	0.321
							M[c]	0.033	0.143	0.152	0.074	0.298	0.297

[a]Temperature of NMR Spectrum scanning, [b]Bernoullian [c]Markov

TABLE - 5.7(B)

Composition of Styrene (f_S), copolymer composition (F_S), Degree of Conversion (Y), and Triad Relative Intensities for the Hydrolyzed Copolymers from styrene-N,O-bis(trimethylsilyl)acrylamide copolymers:

								RELATIVE INTENSITY					
System	Y%	f_S	f_A	F_S	F_A	T_1 °C[a]		SSS	SSA	ASA	SAS	AAS	AAA
B-25	8.7	0.746	0.254	0.731	0.269	100	exptl.	0.326	0.258	0.054	-	-	-
							B[b]	0.391	0.287	0.053	0.144	0.106	0.019
							M[c]	-	-	-	-	-	-
B-30	9.2	0.713	0.287	0.709	0.291	100	exptl.	0.356	0.294	0.056	0.146	0.125	0.023
							B[b]	0.356	0.293	0.060	0.146	0.120	0.025
							M[c]	0.356	0.292	0.059	0.145	0.122	0.025
B-63	10.0	0.371	0.629	0.568	0.432	100	exptl.	0.183	0.296	0.107	0.139	0.220	0.084
							B[b]	0.183	0.279	0.106	0.139	0.212	0.081
							M[c]	0.193	0.277	0.099	0.131	0.213	0.087
B-82	9.7	0.177	0.823	0.306	0.694	100	exptl.	0.026	0.125	0.147	0.066	0.296	0.334
							B[b]	0.029	0.130	0.147	0.065	0.295	0.334
							M[c]	0.025	0.124	0.151	0.065	0.296	0.336
B-91	8.5	0.088	0.912	0.286	0.714	100	exptl.	0.023	0.114	0.144	0.058	0.268	0.367
							B[b]	0.023	0.117	0.146	0.058	0.292	0.364
							M[c]	0.022	0.118	0.151	0.062	0.295	0.349

[a] Temperature of NMR Spectrum scanning, [b] Bernoullian [c] Markov

TABLE - 5.8(A)

First order Markov Addition Probabilities, Reactivity Ratios, Block Character (η) and Run number (R) for Styrene-Acrylamide copolymers obtained using TMSAm as the acrylamide precursor.

System	P_{SA}	P_{AA}	P_{SS}	P_{AS}	P_{SA+AS}	$r_A.r_S(M)^a$	(η)	R
M-27	0.232	0.232	0.768	0.768	1.000	0.996	0.98	35.02
M-33	0.333	0.327	0.667	0.673	1.006	0.975	0.99	44.25
M-50	0.342	0.342	0.658	0.658	1.000	1.000	0.99	44.84
M-87	0.679	0.666	0.321	0.334	1.013	0.938	0.99	43.10

[a] Markov

$0<r_1r_2<1$ lies between the ideal and alternating systems

TABLE - 5.8(B)
First order Markov Addition Probabilities, Reactivity Ratios, Block Character (η) and Run number (R) for Styrene-Acrylamide copolymers obtained using BTSAm as the acrylamide precursor.

System	P_{SA}	P_{AA}	P_{SS}	P_{AS}	P_{SA+AS}	$r_A.r_S(M)^a$	(η)	R
B-30	0.291	0.295	0.709	0.705	0.996	1.024	0.984	41.27
B-63	0.417	0.449	0.583	0.551	0.968	1.138	0.998	49.09
B-82	0.709	0.694	0.291	0.306	1.015	0.930	0.986	42.67
B-91	0.720	0.702	0.280	0.298	1.018	1.114	0.984	40.84

[a] Markov
$0 < r_1r_2 < 1$ lies between the ideal and alternating systems.

TABLE - 5.9(A)
Comonomer Triad Ratios of Styrene-Acrylamide Copolymers obtained using TMSAm as the Acrylamide Precursor

Samples	AAS/ASA		SSA/SAS	
	Observed	Calculated[a)]	Observed	Calculated[a)]
M-27	1.76	2.00	1.90	2.00
M-33	2.12	2.00	1.98	2.00
M-50	1.87	2.00	2.05	2.00
M-87	1.91	2.00	2.06	2.00

a)Calculated from Bernoullian Statistics

TABLE - 5.9(B)
Comonomer Triad Ratios of Styrene-Acrylamide Copolymers obtained using BTSAm as the Acrylamide Precursor

Samples	AAS/ASA		SSA/SAS	
	Observed	Calculated[a)]	Observed	Calculated[a)]
B-30	2.22	2.00	2.01	2.00
B-63	2.05	2.00	2.12	2.00
B-82	2.01	2.00	1.89	2.00
B-91	1.86	2.00	1.96	2.00

a)Calculated from Bernoullian Statistics

TABLE - 5.10(A)

Number Average Sequence Length for 'Styrene' (η_S)[a)]

Samples	Observed	Calculated from	
		Bernoullian Statistics	First-Order Markov Statistics
M-27	4.42	4.42	4.31
M-33	3.03	3.03	3.0
M-50	2.95	2.95	2.92
M-87	1.46	1.46	1.14

[a)] Copolymers obtained from TMSAm

TABLE - 5.10(B)

Number Average Sequence Length of Acrylamide (A) (η_A)[a)]

Samples	Observed	Calculated from	
		Bernoullian Statistics	First-Order Markov Statistics
M-27	1.29	1.29	1.30
M-33	1.49	1.49	1.49
M-50	1.51	1.51	1.51
M-87	3.18	3.18	2.91

[a)] Copolymers obtained from TMSAm

TABLE - 5.11(A)

Number Average Sequence Length of Styrene (S) (η_S)[a)]

Samples	Observed	Calculated from	
		Bernoullian Statistics	First-Order Markov Statistics
B-30	3.436	3.436	3.436
B-63	2.314	2.314	2.398
B-82	1.420	1.440	1.410
B-91	1.400	1.400	1.388

[a)] Copolymers obtained from BTSAm

TABLE - 5.11(B)

Number Average Sequence Length of Acrylamide (A) (η_A)[a)]

Samples	Observed	Calculated from	
		Bernoullian Statistics	First-Order Markov Statistics
B-30	1.410	1.410	1.418
B-63	1.760	1.760	1.814
B-82	3.267	3.267	3.267
B-91	3.496	3.496	3.356

[a)] Copolymers obtained from BTSAm

TABLE - 5.12(A)

Glass Transition Temperature (T_g) and diad composition data from S/A copolymers obtained using TMSAm precursor

Serial No.	S mole fraction in feed	Diad fractions	T_g(°C)	
			Calculated from Barton's Equation	Obtained from DSC
M-27	0.7	[SS]=0.60	122	113
		[AA]=0.06		
		[AS]=0.34		
M-33	0.6	[SS]=0.45	138	120
		[AA]=0.11		
		[AS]=0.44		
M-50	0.5	[SS]=0.43	142	163
		[AA]=0.11		
		[AS]=0.46		
M-87	0.1	[SS]=0.11	166	166
		[AA]=0.46		
		[AS]=0.43		

TABLE - 5.12(B)

Glass Transition Temperature (T_g) and diad composition data from S/A copolymers obtained using BTSAm precursor

Serial No.	S mole fraction in feed	Diad fractions	T_g(°C)	
			Calculated from Barton's Equation	Obtained from DSC
B-30	0.7	[SS]=0.50	137.71	138.55
		[AA]=0.10		
		[AS]=0.40		
B-63	0.4	[SS]=0.32	156.74	155.03
		[AA]=0.19		
		[AS]=0.49		
B-82	0.2	[SS]=0.10	160.56	159.80
		[AA]=0.48		
		[AS]=0.42		
B-91	0.1	[SS]=0.10	159.60	154.52
		[AA]=0.50		
		[AS]=0.40		

where [SA] is the mole fractions of SA dyad and [S], [A] are the mole fractions of S and A monomers in the copolymers. The value of $0 \leq \eta < 1$ reflects more block character; n=1 for random copolymers; the copolymer tends to alternate in the polymer structure if $1 \leq \eta < 2$. Table-5.8(A) and Table-5.8(B) show that the value of η for S/A copolymer obtained from TMSAm and BTSAm approaches to 1.0, indicating that S/A copolymers have greater tendency towards random copolymerization.

The run number (R) of the copolymer is defined as the average number of the segments of either type per 100 monomer units. This may be written as[28]

$$\mathbf{R = 200/(N_S+N_A)}$$

where N_S and N_A are the number average sequence lengths of S and A monomer units in the copolymers shown in Table-5.10(A) (for copolymers from TMSAm) and Table-5.11 (for copolymers from BTSAm). In case of S/A copolymers the values of R lies in the range 35.02-43.10. Table 5.8(A) (for TMSAm) and table 5.8(B) (for BTSAm) depicts all the copolymerization parameters. The product of the two reactivity ratios namely $r_S.r_A$ is close to unity which also confirms the random nature of the copolymers [Tables 5.8(A) and 5.8(B)].

Markovian triad ratios AAS/ASA and SSA/SAS are given in Table-5.9(A) and Table-5.9(B). An examination of the triad distribution shows a good agreement with Bernoullian and 1st-order Markovian statistics in all polymers.

Number average sequence lengths for samples obtained using TMSAm are shown in Tables 5.10(A) and 5.10(B). The number average sequence length for styrene (η_S) decreases from 4.42 to 1.46, while number average sequence length of acrylamide (η_A) increases from 1.29 to 3.18 with variation of monomer feed composition from M-27 to M-87. Similarly for samples obtained using BTSAm, (η_S) decreases from 3.43 to 1.40, while (η_A) increases from 1.41 to 3.49 with variation of monomer feed composition from B-30 to B-91 [Tables 5.11(A) and 5.11(B)]. This shows that number average sequence for monomer is dependent on the concentration of that particular monomer. Number average sequence lengths appear to offer better conformity for both 1st-order Markovian and Bernoullian behavior.

Copolymerization may result in random, or alternating copolymers, which display one single glass transition temperature or in block or graft copoymers, which may exhibit two distinct glass transition temperatures. Furthermore, depending on the structural similarity of the two monomers (i.e. depending on the rotational barriers of an S-A linkage as compared to either an A-A or S-S linkage), a linear relationship or positive or negative deviations from ideality can be observed. Thus, much attention has been devoted to develop theoretical models relating the glass transition to molecular structure.

As reported earlier[29,30], sequence length distribution of comonomers has a large influence on the chemical and physical properties of copolymers, The most important parameter, T_g (glass transition temperature) is also affected by molecular weight, branching, intramolecular (triad distribution, tacticity) and intermolecular (chemical composition & molar mass distribution) copolymer microstructure[30]. Considering the direct correlation the T_gs of our (S-A) copolymers (M-27 to M-87) were determined from DSC and compared with the computed T_g values from the dyad sequence using Barton's equation[31] [Table 5.12(A)]. Similarly, T_gs of (S-A) copolymer (B-25 to B-91) were determined from DSC and compared with the computed T_g values from dyad sequence [Table 5.12(B)].

Barton and Johnston[32] described more precisely the effect of sequence distribution of monomeric unit in linear copolymers on its glass transition temperature (T_g) and considered the contribution of the dyad. Barton equation shows the dependence on sequence as follows:

$$\mathbf{T_{g,P} = N_{SS}, T_{g,SS} + N_{AA}, T_{g,AA} + (N_{SA} + N_{AS}) T_{g,SA}}$$

$T_{g,P}$ is the Tg of a copolymer containing mole fraction (N) of various dyads (SS, AA, SA, SA) $T_{g,SS}$ & $T_{g,AA}$ are the glass transition temperatures of polystyrene & polyacrylamide respectively. $T_{g,SA}$ is the glass transition temperature of the alternating copolymer and has not been reported in the literature so far. Therefore, we have calculated $T_{g,SA}$ by using experimental $T_{g,P}$ values from DSC of S-A copolymers in equation-3 and plotting ($T_{g,P}$-N_{SS}, $T_{g,SS}$-N_{AA},$T_{g,AA}$) against (N_{SA} + N_{AS}). For the copolymers obtained using TMSAm, the plots give two straight lines with zero intercept with slopes of 71.15 and 104.89°C respectively. Kumler et.al. have reported that T_g values of styrene/ethyl acrylate alternating copolymers containing >60% styrene are in the range of the reported values whereas the T_g of the same copolymer with <55% styrene are below 45°C. T_g of S/A alternative copolymers with >50% of styrene is 71.14 and <50% styrene is 104.89. These values of $T_{g,SA}$ were used for further calculation of $T_{g,P}$ from Barton's equation in Table 5.12(A) and Table-5.12(B). T_g s for poly(styrene) and poly(acrylamide) were 100 and 155.56°C respectively. The T_g obtained from dyad concentration values were found to be in good agreement with the values obtained from DSC [Table 5.12(A) and Table 5.12(B)]. For the copolymer samples obtained using BTSAm, a similar calculation gives the $T_{g,SA}$, value to be 91.63°C.

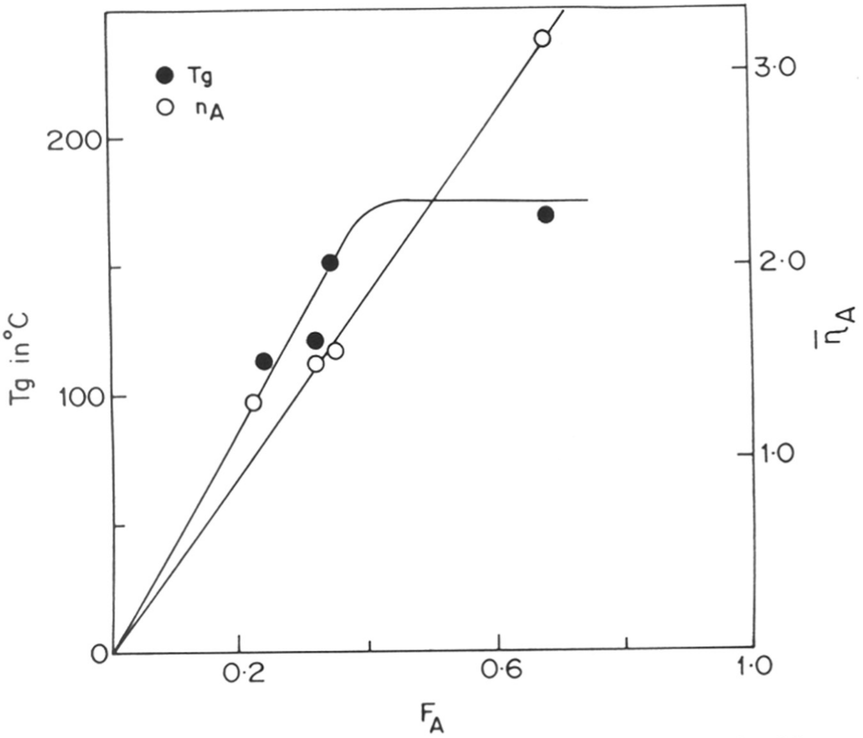


Fig. 5.35 a) Variation of $T_{g,P}$ and sequence length (η) with acrylamide incorporation (mol%) in the S/A copolymers obtained from TMSAm

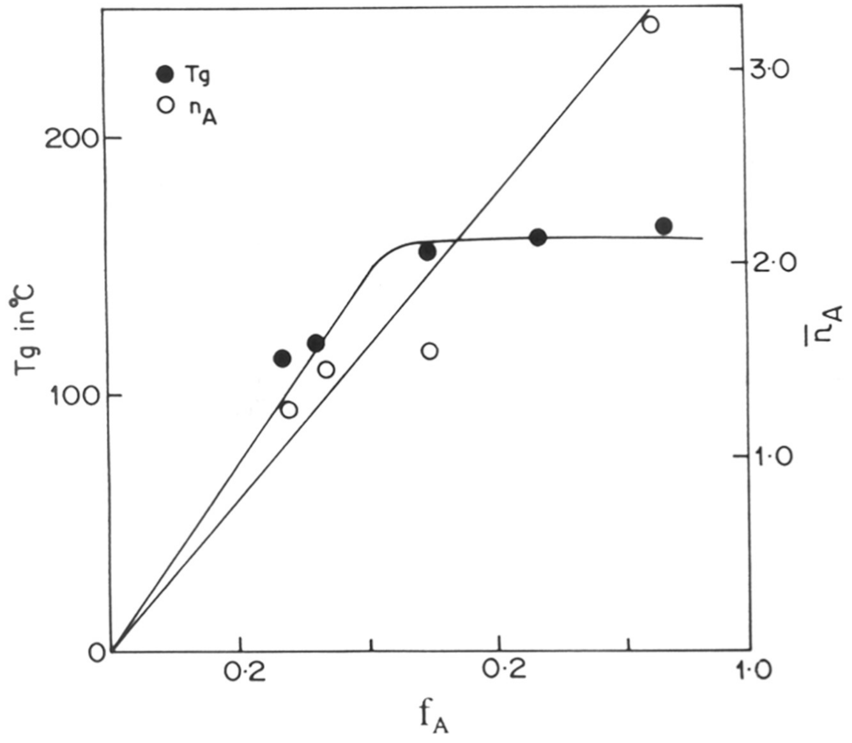


Fig. 5.35 b) Variation of $T_{g,P}$ and sequence length (η) with acrylamide feed (mol%) in the S/A copolymers obtained from TMSAm

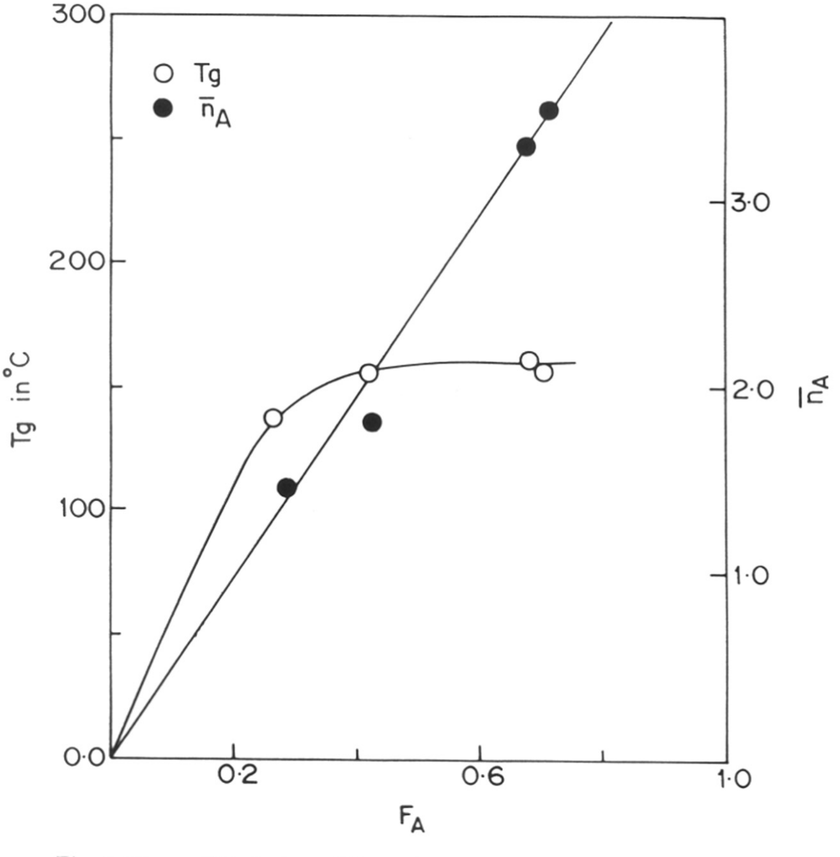


Fig. 5.36 a) Variation of $T_{g,P}$ and sequence length (η) with acrylamide incorporation (mol%) in the S/A copolymers obtained from BTSAm

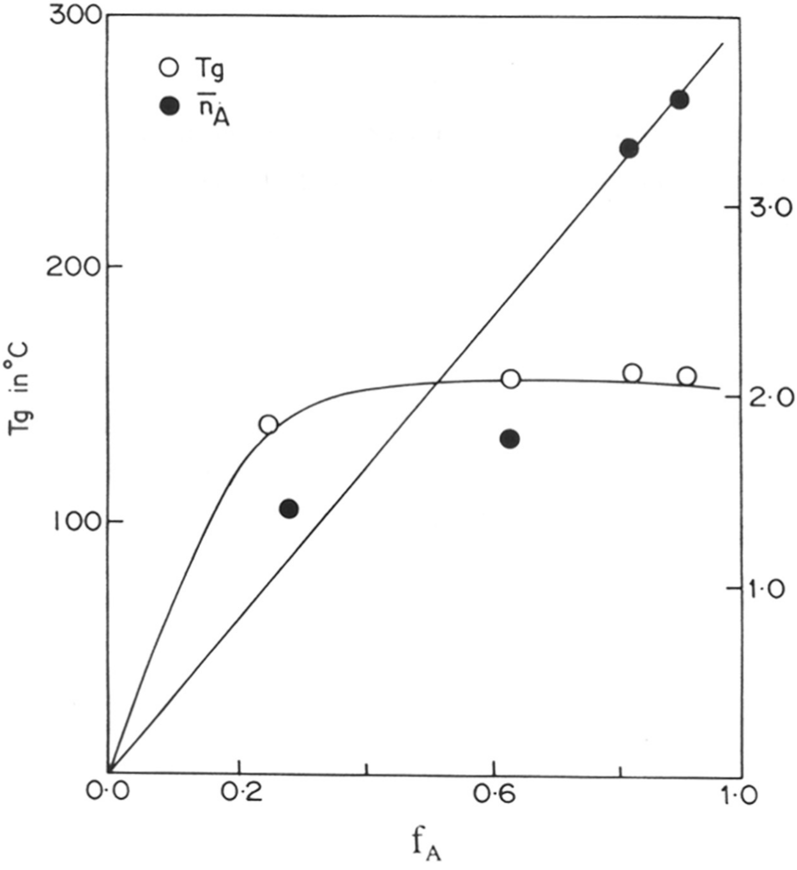


Fig. 5.36 b) Variation of $T_{g,P}$ and sequence length (η) with acrylamide feed (mol%) in the S/A copolymers obtained from BTSAm

The experimental $T_{g,P}$ are plotted against mole% acrylamide in copolymer and sequence lengths (Fig. 5.35). The $T_{g,P}$ increase linearly up to 45 mol% acrylamide and the curve levels off as it approaches the value for poly(acrylamide) homopolymer (155.56°C). Apparently the free volume required for the segmental motion increases rapidly as the copolymer composition approaches 45% of acrylamide. Above this composition the additional free volume required for segmental motion is small.

For the copolymers obtained using TMSAm (Table-5.35) T_g values increases and becomes steady with increasing A-A dyad concentration. Similarly T_g values initially decrease rapidly from M-87 to M-33 and then more slowly. This direct dependence of T_g on dyad concentration explains the agreement between the measured and predicted T_g values. Harris et.al.[30] observed the similar behavior in acrylonitrile-4-vinylpyridine copolymer system. Johnson's method of predicting T_g value[32] assumes that T_g of copolymer can be based on the components representing the $T_{g,S}$ of the various linkages (S-S, A-S, A-A) within the copolymers. Clearly there is a correlation between the T_g and the monomer sequence distribution for S-A copolymers. Average sequence length η_A increases with increase in T_g. This reveals T_g is also affected by η_A. Similar conclusions were drawm from Figure-5.36 when T_g and η_A are plotted against monomer feed composition of acrylamide in styrene-acrylamide copolymers.

5.4 Conclusion:

Novel random styrene-acrylamide copolymers could be synthesized by solution copolymerization ofstyrene with any of the silylated acrylamide monomers namely TMSAm, BTSAm and TBDMSAm in benzene followed by desilylation.

Compositions of the copolymers have been determined from ^{1}H NMR and nitrogen analysis. From the composition, the reactivity ratios of the monomers have been calculated which indicate a random nature of the copolymers. FTIR spectra of the copolymers also support the random nature.

The thermal degradation pattern of the S/A copolymers varied depending on the incorporation of the two monomers in the copolymer samples. A single glass transition temperature for a wide range of composition showed the compositional homogeneity of the copolymers.

The sequence distribution at triad level obtained from ^{13}C NMR matches with Bernoullian statistics more closely than 1st order Markovian statistics even in the lower conversion (10%).

The product of the reactivity ratio r_A and r_S calculated using ^{13}C NMR in both the cases for TMSAm and BTSAm approaches unity, strongly indicating a random nature of the copolymers.

The number average sequence length of either monomer (S,A) calculated from dyad and triad sequences is dependent on the concetration of that particular monomer.

The glass transition temperatures of the copolymers were theoretically estimated from the dyad sequence and compared with experimental $T_{g,P}$ values obtained from DSC. The agreement between the two T_g values was consistent.

The dyad sequence also enabled a calculation of $T_{g,SA}$ of alternating S,A copolymers.

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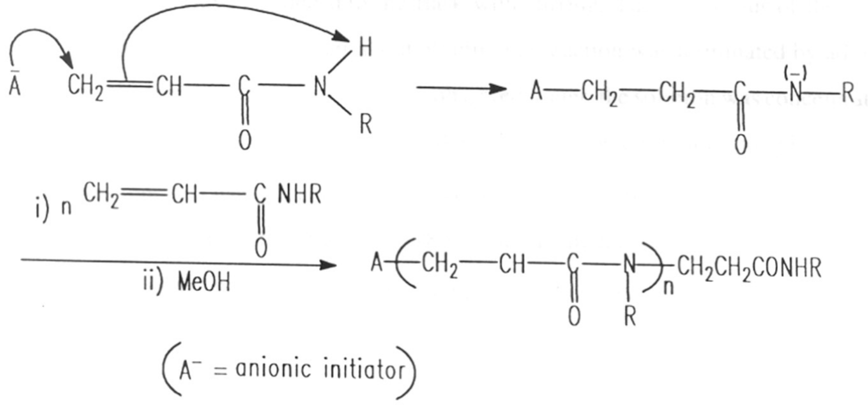
CHAPTER - VI

CHAPTER - VI:

ANIONIC POLYMERIZATION OF PROTECTED ACRYLAMIDES

6.1 Introduction:

Inspite of substantial research efforts towards synthesis of functional polymers via anionic polymerization, no attention has been paid towards the anionic polymerization of protected acrylamide monomers. Acrylamide and N-alkylacrylamides do not undergo vinyl polymerization in presence of anionic initiators. Instead, polymerization occurs by 'hydrogen transfer' to give poly(β-alanine)[1,2], (Scheme-6.1)



Scheme-6.1

It was thought that the protection of the amide hydrogens by easily deprotectable silyl functionalities might enable synthesis of poly(acrylamide)s by anionic initiators. The following sections describe attempts to perform anionic polymerization of N,O-bis(trimethylsilyl)acrylamide (BTSAm) and N-methyl,N-tert-butyldimethylsilylacrylamide (MTBDMSAm).

6.2 Experimental:

6.2.1 Anionic Polymerization of BTSAm and MTBDMSAm:

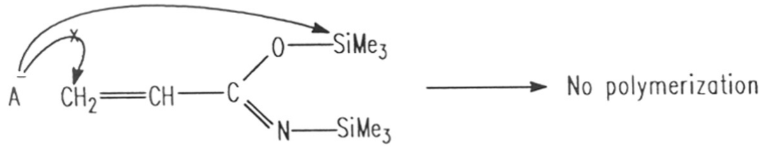
Materials: N,O-Bis(trimethylsilyl)acrylamide (BTSAm) was freshly distilled under reduced pressure prior to the reaction and was stored under a positive pressure of argon (0-10°C). MTBDMSAm was distilled first over calcium hydride and then over triisobutylaluminum. Tetrahydrofuran (THF) was dried over violet sodium-benzophenone ketyl radical and was distilled under static vacuum over oligostyryl lithium prior to use. The strength of n-BuLi solution in hexane was measured to be 0.33 M. α-Methylstyene was distilled over CaH_2. 1,1-diphenylethylene was distilled under static vacuum over few drops of butyllithium.

Procedure: A 250 mL round bottom flask containing a magnetic bar was conditioned by flame drying, repeated evacuation and filling with argon. About 50 mL of THF was placed in the cooled flask. A slight excess of α-methylstyrene was added to THF. Addition of the necessary amount of BuLi to this gave an instant red colour due to the formation of oligo α-methylstyryllithium. The colour was persistent indicating the livingness of the anionic initiator. The flask was placed over a dry-ice acetonitrile bath (-40°C). Under a positive pressure of argon, BTSAm was slowly added into the flask with stirring. The red colour of the THF solution disappeared immediately. After about 30 min. the reaction was terminated by adding 2N HCl/MeOH. No precipitation of polymer was observed. Later, the solution was concentrated to about 20 mL and was poured into 180 mL of MeOH. Still no precipitation took place.

The reaction was repeated using 1,1-diphenylhexyllithium (i.e. by using 1,1-diphenylethylene in place of α-methylstyrene) as the initiator at -78°C. Once again, no polymer could be isolated.

The polymerization of MTBDSAm was performed in a similar manner.

6.3 Results and Discussion: In section 1.3.5., we have referred the work done by Hirao et.al. and discussed why the trimethylsilyl enol ether of 4-vinylacetophenone could not be polymerized anionically. For BTSAm too a similar attack on the silyl group is possible as shown in scheme-6.2 below:



Scheme-6.2

The one other possibility could be the silyl group transfer (instead of hydrogen transfer which happens with the unprotected acrylamide) but this should have resulted in the formation of poly(β-alanine). Since no polymer could be found, this possibility can be ruled out.

The purity of the monomer N-methyl,N-tert-butyldimethylsilylacrylamide could not be improved better than 97%. This compound exists as a mixture of the amide and the imidate forms.

6.4 Conclusion:

Attempts to polymerize BTSAm or MTBDMSAm failed under the experimental conditions. The reason could be unwanted side reactions involving the cleavage of the silyl protection and/or the purity of the monomers.

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CHAPTER - VII

CHAPTER VII:

SUMMARY AND CONCLUSIONS:

7.1 Monomer synthesis and characterization:

A series of silylated acrylamide derivative have been synthesized and characterized. The monomers have been found to exist either in the amide or in the imidate form. The structure of the monomers have been established by ^1H and ^{13}C NMR spectroscopy. The amide form is the stable form for N-trimethylsilylacrylamide(TMSAm) and N-tert-butyldimethylsilylacrylamide (TBDMSAm); N,O-Bis(trimethylsilyl)acrylamide (BTSAm) has been found to exist exclusively in the imidate form; N-methyl, N-tert-butyldimethylsilylacrylamide exists as a mixture of the amide and the imidate forms. Predominance of one or the other tautomeric form has been explained in terms of the π-electron density over the carbon-nitrogen bond in the amide group. The silyl groups are hydrolytically unstable and the monomers are required to be handled under inert atmosphere.

7.2 Solution polymerization and kinetic studies:

A systematic study of the solution polymerization of the silylated acrylamides has been conducted. TMSAm and BTSAm were polymerized in benzene using benzoyl peroxide (BPO) and 2,2'-azobisisobutyronitrile (AIBN) as the free radical initiators. The monomers are highly soluble in benzene. The results show that the homopolymerization follows normal free radical polymerization kinetics wherein the rate of polymerization has a first order dependence on the monomer concentration and is proportional to the square root of the initiator concentration. From the temperature dependence of the rate of polymerization, the activation energies of polymerizations have been estimated.

7.3 Copolymerization and copolymer characterization:

The monomers BTSAm, TMSAm and TBDMSAm have been copolymerized with styrene in benzene using BPO as the free radical initiator. The styrene-acrylamide copolymers obtained upon hydrolysis of the copolymers have been found to be compositionally homogeneous. The copolymers were characterized by FTIR spectroscopy, ^1H NMR, ^{13}C NMR, nitrogen analysis and thermal analysis. FTIR spectra of the copolymers indicate the random nature of the copolymers. This is evident from the extent of vibrational coupling found in copolymers and comparison with the constituent homopolymers. The copolymer composition was estimated from nitrogen analysis and ^1H NMR.

The microstructure was determined from the ^{13}C NMR. The triad sequence distributions obtained compositionally from ipso carbon of styrene and C=O group of acrylamide in copolymers by ^{13}C NMR spectroscopy are close to the theoretical values calculated from Bernoullian as well as 1st order Markovian statistics for both TMSAm and BTSAm.

The mean sequence lengths of acrylamide and styrene residue, the block character (η) and run number were also calculated from ^{13}C NMR; η showed random nature of the S-A copolymers.

The glass transition temperature of the copolymers were theoretically estimated from the dyad sequence and compared with experimental $T_{g,P}$ values obtained from DSC. The agreement was satisfatory. The dyad sequence also enabled a calculation of $T_{g,SA}$ of alternating S-A copolymers.

7.4 Anionic polymerization:

Attempted anionic polymerization of BTSAm or MTBDMSAm failed. The reason could be unwanted side reactions involving the cleavage of the silyl group and/or the purity of the monomers.

In conclusion, a series of silylated acrylamide monomers have been synthesized and their free radical solution homo and copolymerization have been studied. This approach leads to novel random acrylamide copolymers containing nonpolar monomers in the polymer chain. The introduction of reactive silylamide functionalities as pendant groups may prove useful in post polymer functionalization reactions.

SYNOPSIS

Ever since Merrifield demonstrated the utility of polymeric supports for solid-phase peptide synthesis[1], reactive functional polymers are finding increasing applications in the areas of organic synthesis, catalysis, separation sciences, biotechnology etc[2]. This has given rise to widespread research interests in developing newer and efficient synthetic routes for obtatining functional polymers.

Among the different approaches for functional polymer synthesis, polymerization of protected functional monomers has attracted considerable attention in recent years. Protecting the functionality of a monomer by an easily deprotectable group prior to polymerization is important because of two reasons. Firstly, the polymerization technique may not be compatible with the unprotected monomer since the functional group may be reactive towards the initiator and/or the propagating end; and secondly, it may be possible to chemically modify the polymer obtained by polymerizing the protected monomer, which might not be feasible with the polymer formed from the unprotected one. Few examples of protection and polymerization of functional monomers are given in the following paragraphs.

Among the functional monomers which have been protected and polymerized by free radical polymerization are silyl enol ethers having a vinyl or dienyl groups[3-5], α-trimethylsilyloxystyrene, the silyl enol ether of acetophenone[6,7], and 2-trimethylsilyloxy-1,3-butadiene, the silyl enol ether of methyl vinyl ketone[8]. Such monomers exhibit an improved reactivity in radical copolymerization with various vinyl monomers, and also allow chemical modification utilizing the silyl functionality.

Organometallic polymerization catalysts such as Ziegler-Natta and olefin metathesis catalysts[9,10] possess only limited stability towards functional groups that contain heteroatoms such as O,S, and N. Chung et. al. have shown that ω-alkenyl-9-BBN (9-BBN:9 borabicyclononane) monomers are stable to Ziegler-Natta catalysts, can be homopolymerized[11,12] and copolymerized[13,14] with α-olefins and the borane groups can be easily converted into hydroxyl groups[15]. Thus, synthesis of polymer structures like poly(exo-5-hydroxynorbornene)[16,17], alternating ethylene-vinylalcohol copolymer[18] and telechelic 1,4-butadiene[19] have been made possible.

Anionic living polymerization of protected functional monomers have been extensively reviewed by Nakahama and Hirao[20,21]. Protection of the hydroxyl, thiol, keto, and amino group containing monomers, silyl substituted butadienes etc. have been well documented. Recently, maleimide has also been protected by silylation and anionically polymerized[22].

Inspite of the vigorous scientific activity in this area, relatively lesser attention has been paid to the controlled polymerization of acrylic amide monomers by anionic polymerization techniques. Acrylamide itself does not undergo vinyl polymerization in presence of anionic initiators. Instead, polymerization occurs by 'hydrogen transfer' to give poly(β-alanine)[23]. We therefore undertook the synthesis, and characterization of silyl substituted acrylamides as a class of protected acrylamide. Silylation may improve the liophilicity of acrylamide as well as enable polymerization by anionic initiators. Furthermore, silylation results in reduced hydrogen bonding which in turn improves the organic solubility and is likely to change the reactivity of the monomer in copolymerization. Literature reveals that copolymerization of acrylamide with hydrophobic monomers in organic solvents produce copolymers which are blocky i.e. compositionally inhomogeneous in nature[24]. It is believed that the properties of copolymers, in particular, of those containing polar and non-polar monomers can be improved by decreasing their compositional inhomogeniety[25a]. Compositional inhomogeniety is also known to cause microphase separation resulting in loss of transparency[25b].

The thesis entitled "Synthesis , Polymerization and Characterization of Protected acrylamides" deals with the synthesis of some mono- and di-substituted acrylamide monomers, their characterization and polymerization using free-radical and anionic initiators.

Objective of present investigation

1. To transform acrylamide, a hydrophilic monomer, into an organic soluble monomer by means of silylation and study the solution copolymerizability of the silylated acrylamides with organic soluble monomers in homogeneous phase. The copolymers obtained thereby, on deprotection, should produce compositionally homogeneous copolymers containing hydrophobic and hydrophilic moieties.

2. To protect the amide functionality of acrylamide by easily deprotectable silyl groups and study the anionic polymerizability of the protected monomers.

Chapter - I

This chapter provides a detailed and critical literature review on the protection and polymerization of functional monomers by several polymerization techniques like free radical, anionic, cationic, group transfer and Ziegler-Natta polymerizations.

Chapter - II

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

Chapter - III

This chapter deals with the synthesis and characterization of silylated acrylamide monomers. We have found that the monosilylation of acrylamide using trimethylsilylchloride or t-bytyldimethylsilylchloride in presence of triethylamine in benzene is a fairly easy process that takes place at room temparature, but introduction of the second silyl group requires a much harsher condition requiring the use of neat triethylamine as the medium, prolonged stirring at an elevated temparature for a long period of time. For example, for trimethylsilyl group it takes about 10h. and for t-butyldimethylsilyl group it takes almost 48h. The monomers have been characterized by ^{1}H and ^{13}C NMR and the purity established by GC and/or elemental analysis.

Chapter - IV

This chapter deals with the kinetics of the free radical solution homopolymerization of N-trimethylsilylacrylamide and N,O-Bis(trimethylsilyl)acrylamide in benzene, characterization of the homopolymers in the silylated form, and deprotection of the silylated amide functionality to get back poly(acrylamide)s.

Chapter - V

This chapter deals with the free radical solution copolymerization of silylated acrylamides with styrene, deprotection of the copolymers to generate styrene-acrylamide copolymers, determination of reactivity ratios, and characterization of the copolymers for compositions, microstructure, and thermal behavior.

Chapter - VI

This chapter deals with the studies on anionic polymerization of the protected acrylamide monomers using different types of anionic initiators and characterization of the polymers.

Chapter - VII

This chapter summarizes the results and describes the salient conclusions of the investigations reported in the thesis.

The study has resulted in an understanding of the methodologies for synthesis of silylated acrylamide monomers, there stability and reactivity towards copolymerization. A way of making a new host of random copolymers consisting of hydrophobic and hydrophilic moieties have been opened. Anionic polymerization of the protected acrylamides is likely to open a synthetic route for making several new block copolymers containing hydrophilic and hydrophobic blocks.

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LIST OF PUBLICATIONS

1. A.Dasgupta and S.Sivaram

   Synthesis and Polymerization of N,O-Bis(trimethylsilyl)acrylamide: A Protected Acrylamide

   Macromolecules, 27(6), 1665, (1994)

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   European Polymer Journal, (Submitted for Publication)

4. A.Dasgupta, B.Garnaik and S.Sivaram

   Microstructure of Styrene-Acrylamide Copolymers by Carbon-13 NMR

   (Manuscript under preparation)

5. A.Dasgupta and S.Sivaram

   Kinetic Studies on the Solution Polymerization of Silylated Acrylamides

   (Manuscript under preparation)

6. A.Dasgupta and S.Sivaram

   Monomer Precursors for Synthesis of Functional Polymers by Free Radical Polymerization: A Review.

   (Manuscript Under Preparation)