CHAPTER - 5

PREPARATION, CHARACTERIZATION AND PROPERTIES OF STYRENE-ACRYLIC ESTER AND VINYL ACETATE-ACRYLIC ESTER POLYMERS

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5.1 Preview

Homopolymers of styrene has been shown to have number of properties leading to a variety of industrial applications. Of growing importance are those fields which are related to their use in packaging, molded household wares, containers, machine housing, electrical equipment, toys, water coolers and so on[1]. However, molecular inflexibility leaves the pure homopolymers unable to withstand high rates of mechanical loading, making it brittle under impact and causing stress-cracking. By copolymerising styrene with other monomers like acrylates, the deficiencies of polystyrene are tempered with, and desirable properties can be obtained[2,3]. Copolymers of hydrophobic monomers like styrene, alkyl acrylates, acrylonitrile and small amounts (1-10%) of polar unsaturated carboxylated monomers like acrylic acid, methacrylic acid, and itaconic acid are products of commercial interest due to their applications in paints, adhesives, binders, thickeners etc.[4]. Adhesive tape prepared by applying a mixture of 2-ethyl hexyl acrylate (EHA), methacrylic acid and methyl methacrylate (MMA) copolymer emulsion with other additives, on polypropylene (PP), has been reported[5]. The terpolymerization of maleic anhydride-methyl methacrylate-styrene has been extensively studied and modified by tributyltin oxide to yield terpolymers of biological interest[6].

A wide variety of chemical or physical strategies including copolymerization, polymer blend formation, and cross linking network formation have been explored to provide multifunctional polymers[7]. The combination of durability,

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versatility and the ability to tailor molecules relatively easily to specific application have made acrylic and methacrylic esters main candidates for numerous and diverse applications[8,9]. Homo and copolyacrylates are of great interest in many industrial applications because of the wide range of physical and chemical properties that can be covered by an appropriate choice of the side groups and copolymer system[10]. Acrylates are the most outstanding products widely used in building blocks (polymethyl methacrylate) for a variety of polymers, controlled drug release matrices (polyhydroxymethacrylate), contact lenses (polyhydroxy acrylates), electro-active polymers (polyphenyl acrylate), varnishes (polymethyl acrylate) and many others[11,12]. The polyacrylates have acquired prime importance in industrial applications and are also used in various fields such as thin films, fibres, filaments, coatings, lithography, lacquers, adhesives, printing inks, binder etc.[13-16].

A number of alkyl fumarate-vinyl acetate copolymers were reported as flow improvers for high waxy Borhalla crude oil[17]. Graft copolymers prepared by the polymerization of poly (ethylene oxide) macromonomers with acrylic and vinyl comonomers have been extensively studied as semi-permeable membranes for biomedical applications, as well as support systems for the preparation of microcapsules and nanoparticles[18]. Soundararajan et al.[19] reported co/terpolymers of butyl acrylate, styrene and/or maleic anhydride as top coats lacquers in leather industries. Adhesive properties of terpolymers of ethyl acrylate, ethyl α-cyanocinnamate and styrene were investigated by Angelovici and Kohn[20].

On the otherhand polyvinyl acetate (PVAc) is one of the most important of all the synthetic thermoplastic adhesives with wide range of industrial applications[21]. It also finds widespread use as the intermediate for the commercial production of (i) polyvinyl alcohol and (ii) polyvinyl acetal and as a sizing material for paper and textiles. Application in gum industry (chewing gum) is also popular[22].

The ability to produce polymers containing long sequences of two or more different monomers has led to new products with unique and valuable properties depending on the constitution and ratio of monomeric units and also on the method of preparation[23,24]. Free-radical copolymerization is a method of modifying the properties of polymers. Knowledge of copolymer composition is an important step in the evaluation of their utility. The accurate estimation of the copolymer composition and the determination of monomer reactivity ratios are important for tailor making copolymers with required physico-chemical properties[25]. NMR spectroscopic technique is well established as a convenient method for determining composition ratio of constituent monomer units in copolymer[23,26]. Viscosity of dilute polymer solution gives an insight of the conformation adopted by polymer chain. Theories based on viscosity also account for the influences of variables such as temperature and solvent on conformational changes in solution[27,28]. In this regard the present study reports synthesis and characterization of a series of styrene-acrylate and vinyl acetate-acrylate copolymers. The change in properties as a function of composition and constitution of monomers and determination of reactivity ratios of monomers were also studied and presented in detail.

5.2 Materials

The monomers styrene (S, Fluka, Switzerland), vinyl acetate (VAc, Fluka, Switzerland), ethyl acrylate (EA, BDH, Poole, England), methyl acrylate (MA), *n*-butyl acrylate (BuA) and methyl methacrylate (MMA, National Chemicals, Baroda, India) (Figure 5.1) were distilled at reduced pressure. The middle fraction of the distillate was collected and used. The purity of other monomers *n*-hexyl acrylate, (HA, 99.0%), cyclohexyl acrylate (CA, 92.9%) and benzyl acrylate (BA, 99.8%) was checked by Gas Chromatography. These were gifted by Indian Petrochemical Corporation Limited, Baroda, India and were used without any further treatment. Technical grade azobisisobutyronitrile (AIBN) was recrystallized from warm methanol and benzoyl peroxide (BPO, Fluka) was purified by dissolving it in chloroform at room temperature and reprecipitating it by adding methanol, before it was used. The solvents were all freshly distilled before use.

5.3 Experimental Techniques

The FTIR spectrum of the polymers were recorded on a Nicolet FTIR, Impact 400D spectrophotometer. For FTIR spectra, the solid polymers and KBr (spectroscopic grade) were thoroughly mixed and this mixture was pressed to form a pellet, whereas liquid polymers were spread over the NaCl cells and the spectra were recorded. ^{1}H and ^{13}C-NMR spectra of homo and copolymers were recorded under standard conditions at room temperature in deuterated chloroform ($CDCl_3$) on a JEOL JNM FX-100, FT-NMR spectrometer operating at 100 and 25 MHz respectively, for ^{1}H-NMR and ^{13}C-NMR. TMS was used as an internal reference and $CDCl_3$ as an internal lock.

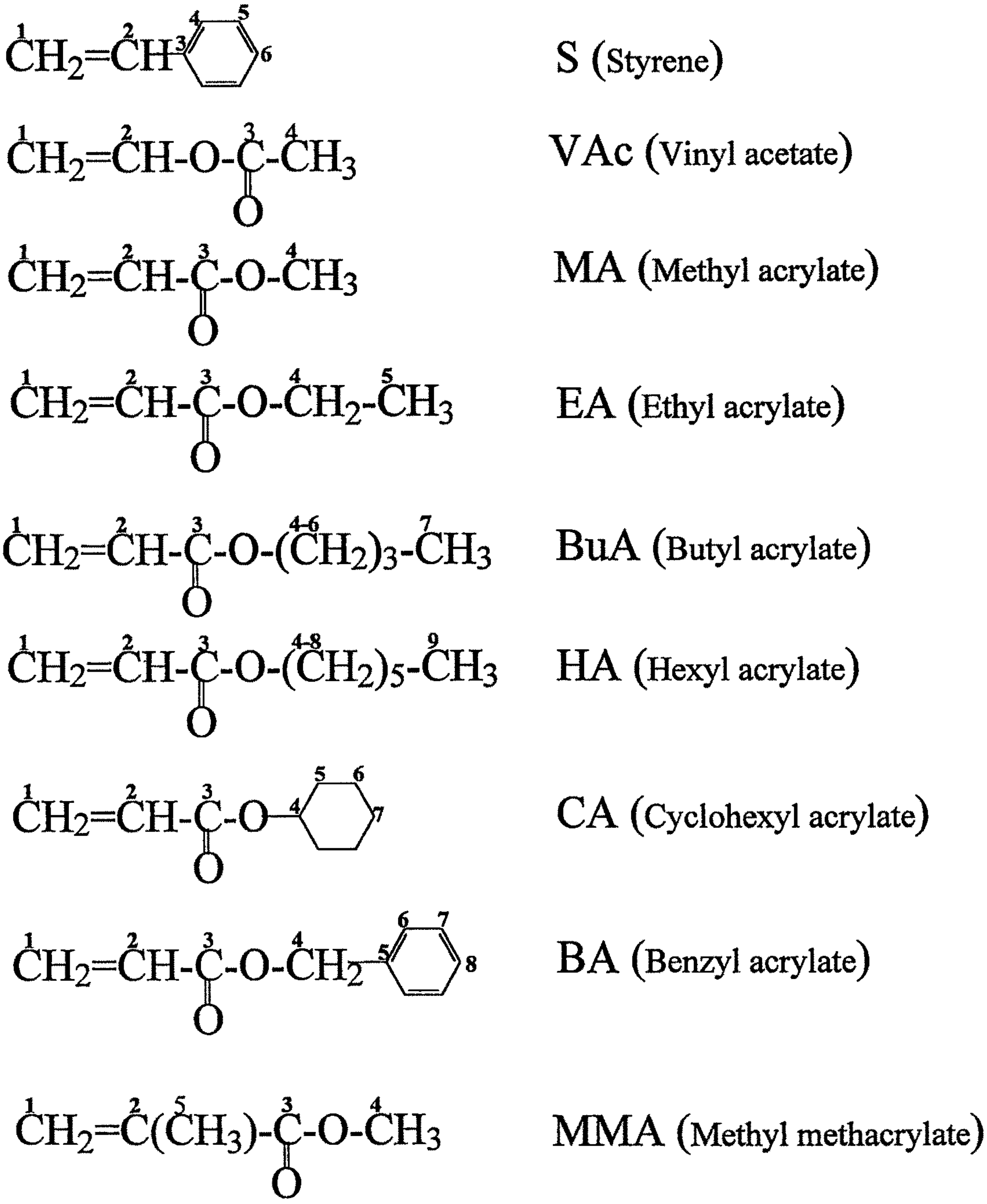


Figure 5.1 Molecular structure for the monomers used in the experiments.

Thermal analysis of the polymers were studied using TGA and DSC measurements. The TGA of the polymer samples was recorded on a Shimadzu thermal analyzer DT-30B at a heating rate of 10° C min^{-1} in the presence of air. DSC measurements were carried out for polymers from -75 to 200^0C using the modulated differential scanning calorimetry (MDSC) ($MDSC^{TM}$, TA Instruments Inc., USA). DSC 2910 system at a heating rate of 10^0 C min^{-1} under nitrogen atmosphere.

Molecular weights (M_n and M_w) and molecular weight distribution (M_w/M_n) were determined with respect to standard polystyrene by gel permeation chromatography (GPC). The Waters associates system used was equipped with a Waters 700 satellite wise injector, a Waters 510 HPLC solvent pump, three columns packed with styrogel of nominal pore sizes of 500, 1000 and 10,000 Å connected in series, and a RI detector. The elution rate of toluene was 0.8 mL min^{-1}. The GPC was calibrated with standard polystyrene samples of molecular weights in the range 15,000 - 4,70,000.

Viscosity measurements of the dilute solution of the homo and copolymers in 1,4-dioxane were carried out using an Ubbelohde dilution viscometer suspended in a thermostated bath at the required temperature (± 0.05°C). Measurements for each solution were repeated five to six times. Densities of the solutions at different temperatures were assumed to be those of solvent at that temperature[21].

5.4 Polymer Synthesis

The synthesis of homopolymers were done as reported earlier[21,29]. Polyvinyl acetate (PVAc) synthesis was carried out as given in Chapter 4. Homopolymer polyacrylate(s) were synthesised as follows : 20.0 mL of acrylate(s) in 60.0 mL of DMF (except cyclohexyl acrylate where solvent was 1,4-dioxane) and 0.1% (w/v) of BPO as an initiator were taken in a three necked flask under a nitrogen atmosphere. The reaction mixture was stirred at 85°C for a period of 9h. The three-necked flask was equipped with a water condenser and was placed in a thermostated water bath at 85°C. The reaction mixture after polymerization was poured into an excess of doubly distilled water to precipitate out the polymer(s). The polymer thus obtained was purified by reprecipitation from a solvent system into a non-solvent system and finally dried in *vacuo* before characterization.

Synthesis of styrene homopolymer and styrene-acrylate copolymers were carried out in benzene medium : 20.0 mL [50:50 (v/v) of styrene and an acrylate] of total monomer in 30.0 mL of benzene was taken in a three-necked flask. The reaction set up was similar to that used for synthesis of polyacrylate(s). AIBN (0.2 g) was used as the initiator. The reaction mixture was stirred for a period of 9 h under a nitrogen atmosphere at 70°C. Polymers were obtained by pouring the reaction mixture into the non-solvent, methanol, except for P(styrene-methyl acrylate) and P(styrene-ethyl acrylate) [i.e. P(S-MA) and P(S-EA)] copolymers, respectively. These polymers were precipitated in excess of n-hexane. The precipitated products were further purified by removal of the respective homopolymers in selective solvent-nonsolvent systems.

Copolymerization of styrene (S) with cyclohexyl acrylate (CA) and benzyl acrylate (BA) were also carried out in different feed 90:10, 75:25, 60:40, 40:60 and 20:80 (v/v) styrene and acrylate(s) respectively. The recipe for the synthesis of copolymer 75:25 (v/v) of styrene and acrylate(s) was as follows :

7.5 mL styrene, 2.5 mL acrylate(s) and 0.1 g AIBN were taken in 15.0 mL benzene. The polymerization reaction was carried out under nitrogen atmosphere at 70°C. The reaction set up remains the same as described in earlier paragraph. The copolymerization was stopped at low conversion (below 10%). Then the resulted copolymers were precipitated by a large quantity of methanol. The homopolymer, PS, is insoluble in acetone although the copolymers are soluble. The precipitate was then treated with acetone to remove polystyrene homopolymer. The homopolymers PBA and PCA are soluble in warm nitromethane, hence, these polymers were separated from the copolymers using warm nitromethane. The copolymers were washed well with methanol and dried in vacuo before characterization.

Copolymers of vinyl acetate with various acrylate(s) were prepared in DMF (60.0 mL) using benzoyl peroxide as the free radical initiator at 85°C. For each polymer, the initial total monomer concentration was 20.0 mL [50:50 (v/v) of vinyl acetate and acrylate], and that of the initiator was 0.2 g. Appropriate amounts of monomers, initiator and solvent were mixed in a three necked flask under nitrogen atmosphere. The reaction mixture was stirred at 85°C for a period of 9 h. The three necked flask was equipped with a water condenser and was placed in a thermostated water bath at 85°C. The reaction mixture after polymerization was poured into an excess of doubly distilled water to precipitate out the polymers. The precipitated products were further purified by removal of the respective homopolymers in selective solvent - nonsolvent system, as described below.

Copolymerization of vinyl acetate (VAc) with cyclohexyl acrylate (CA) and benzyl acrylate (BA) were also carried out in different feed ratios of the two monomers. The ratios chosen for study were 80:20, 60:40, 50:50, 40:60 and 20:80 (v/v) of vinyl acetate and acrylate(s), respectively. The recipe for the synthesis of copolymer 80:20 (v/v) of VAc and acrylate(s) was as follows : 6.0 mL VAc, 1.5 mL acrylate(s) and 0.075 g AIBN were taken in 22.5 mL 1,4-dioxane. The polymerization reaction was carried out under nitrogen atmosphere at 85°C. The reaction set up remains the same as described earlier. The conversion was restricted to below 10% in order to satisfy the usual copolymerization equation (approximately 1 h). After the desired time, copolymers were precipitated by pouring the mixture in excess of distilled water. The homopolymer, polyvinyl acetate, is soluble in methanol. The precipitate was then treated with methanol to remove PVAc homopolymer. The homopolymer PCA and PBA are soluble in *p*-xylene and hence these polymers were separated from the copolymers. The copolymers were washed well with methanol and dried in *vacuo* before characterization.

5.5 Results and Discussion

(a) FTIR analysis :

FTIR spectra of various homopolymers [Fig. 5.2, PMA and PCA] and copolymers [Fig. 5.3, P(S-MA) and P(S-BA)] are presented. All the polymers showed characteristic IR absorptions which agreed very well with those reported in the literature[20,30]. The homopolymers (Fig. 5.2) show characteristic absorption bands due to ester group (C=O stretch) at 1733 cm^{-1}. C-O-C symmetric and assymmetric stretches were observed at 1266 and 1176 cm^{-1}, respectively. The symmetrical and assymmetrical bending vibrations of $C-CH_3$ were also seen at 1452 and 1374 cm^{-1}, respectively, whereas an out-of-plane C-H bend was observed at 760 cm^{-1}. Other prominent absorption peaks were at 2937 and 2860 cm^{-1}. These are due to aliphatic (C-H) stretches of $-CH_2$ and $-CH_3$. The FTIR spectra of various copolymers (Fig. 5.3) showed characteristic absorption bands due to their respective acrylate monomer units. Besides, additional absorptions due to the benzene ring of the styrene monomer units were also observed at 1501, 1602 and 3037 cm^{-1} [20,31].

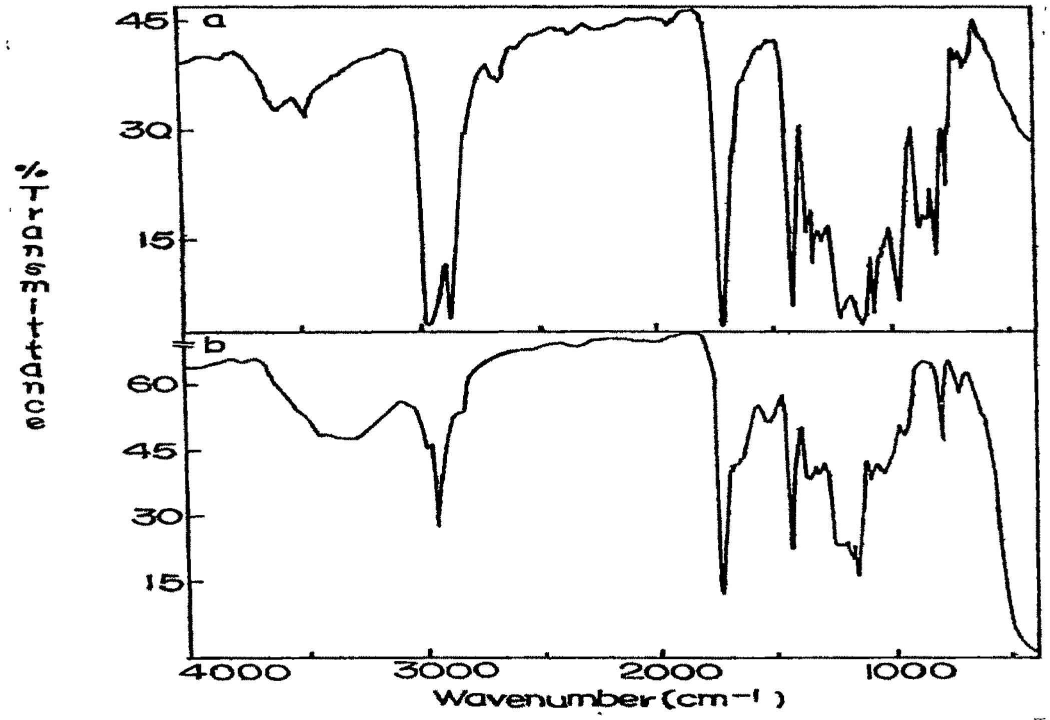


Figure 5.2 : Representative FTIR spectrum of homopolymers (a) PCA and (b) PMA.

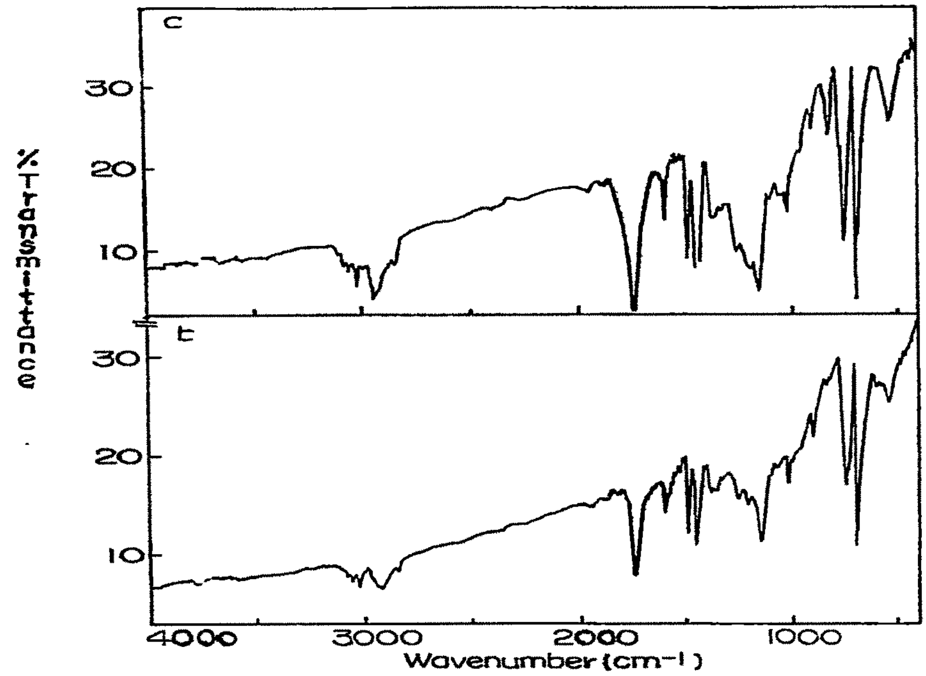


Figure 5.3 : Representative FTIR spectrum of copolymers (a) P(S-MA) and (b) P(S-BA).

The structures of VAc-acrylate copolymers were deduced from FTIR spectra of polymer films spread over the NaCl cell. FTIR spectra of copolymers (Fig. 5.4) show band at 610 cm^{-1}, characteristic of vinyl acetate unit due to the out-of-plane CH_2-CO_2 bend [21]. The C=O stretching of ester group was observed at higher frequency (1750 cm^{-1}) than normal carboxyl absorption. C-CH_3 symmetric and asymmetric bending vibrations were observed at 1451 and 1370 cm^{-1}, respectively. Other prominent absorption peaks due to symmetrical (ν_s O-C-O) and asymmetrical stretching (ν_{as} O-C-O) vibration were observed at 1246 and 1180 cm^{-1}, respectively, whereas an out-of-plane C-H bend of acrylate moieties was observed at 773 cm^{-1}. Besides this, aliphatic stretching absorption of C-H, due to -CH_2 and -CH_3 appears at 2942 and 2861 cm^{-1}. The assignments were done with the help of the literature data[30,31].

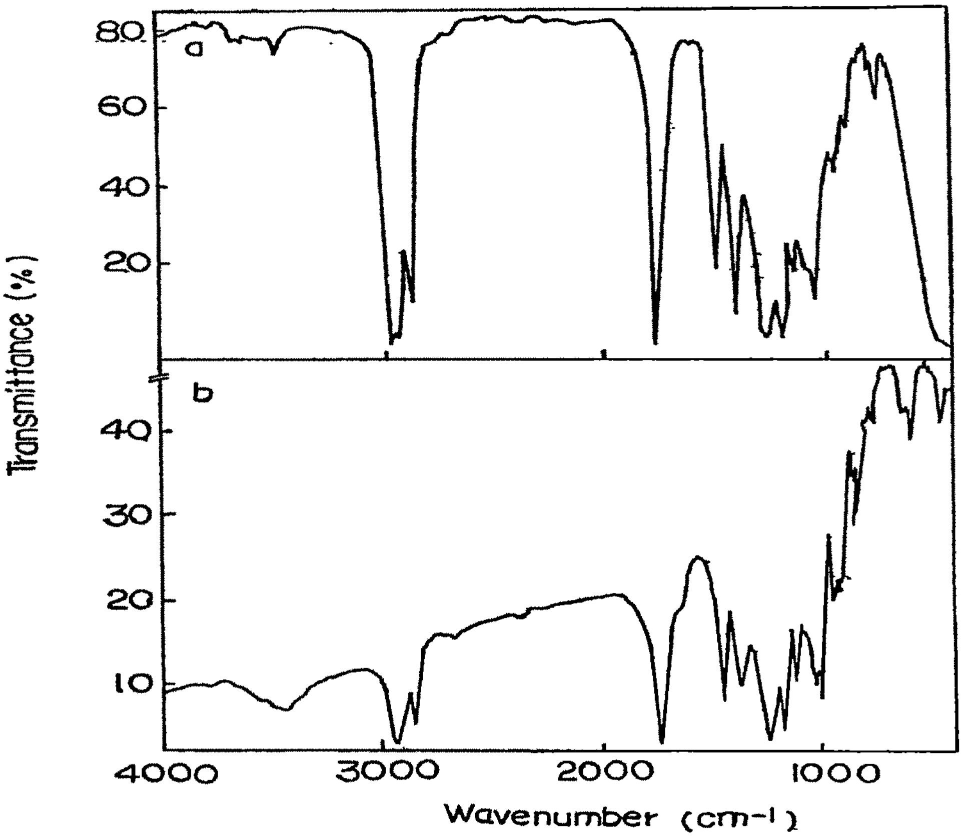


Figure 5.4 Representative FTIR spectra of copolymers (a) P(VAc-HA) and (b) P(VAc-CA)

(b) ^{1}H-NMR analysis :

The ^{1}H-NMR spectra of the homopolymers [Fig. 5.5 : (a) PS, (b) PCA and (c) PBA] and copolymers [Fig. 5.6 : (a) SCA-2 and (b) SBA-5] along with assignments of various resonance signals are shown. ^{1}H-NMR spectra show the resonance signals corresponding to their structures (Fig. 5.1).

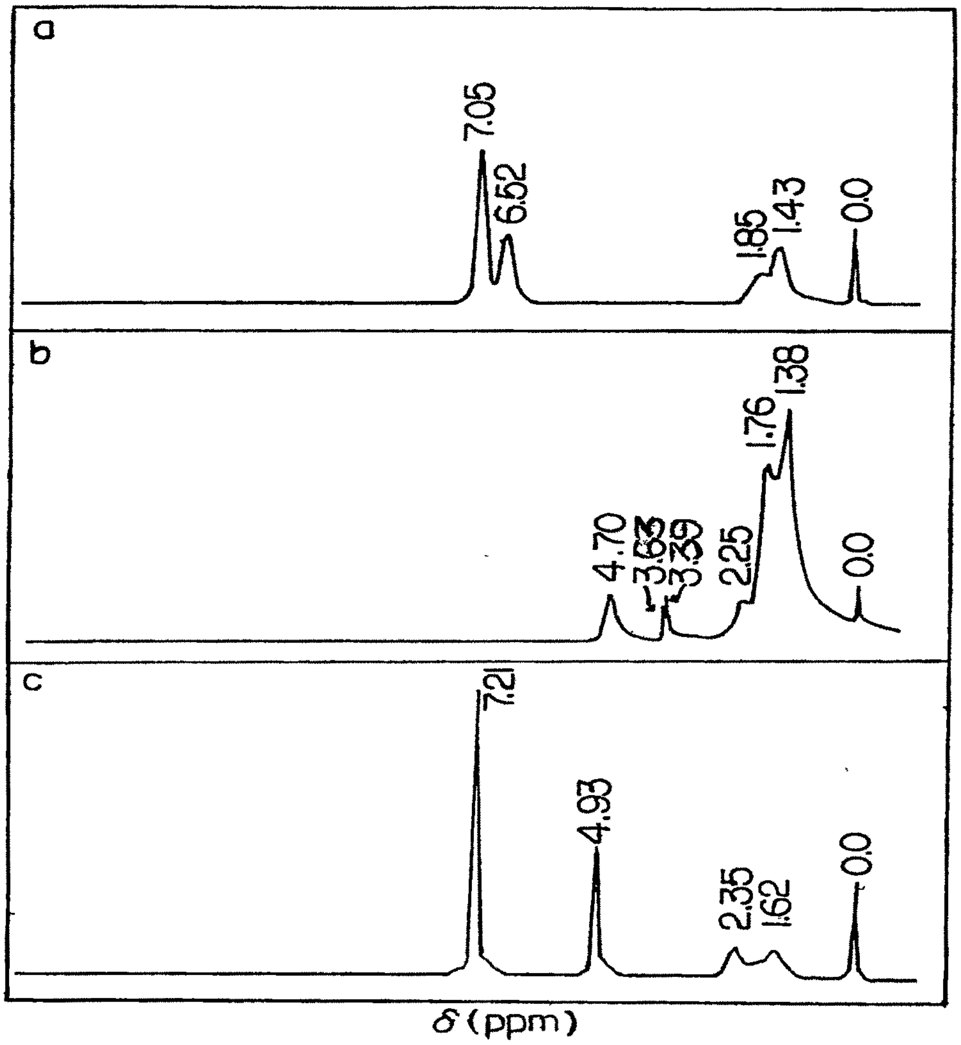


Figure 5.5 : Representative ^{1}H-NMR spectrum of homopolymers (a) PS, (b) PCA and (c) PBA in $CDCl_3$.

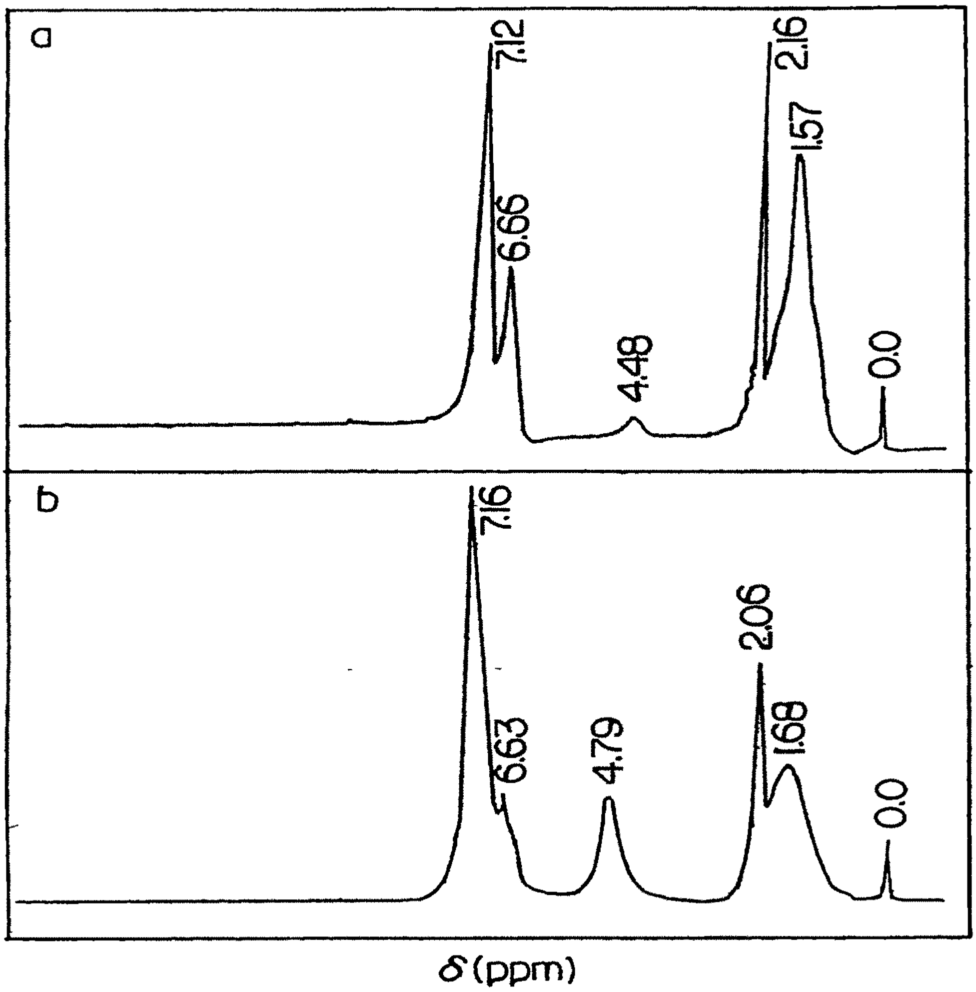


Figure 5.6 : Representative ^{1}H-NMR spectrum of copolymers (a) P(S-CA), i.e. SCA-2 [CA=20.0 mol% in the feed] and (b) P(S-BA), i.e. SBA-5 [BA=75.0 mol% in the feed] in $CDCl_3$.

Polystyrene homopolymer [Fig. 5.5(a)] resonance signals appeared at 7.05-6.52 (benzene ring), 1.85 (αCH- connected with benzene ring), and 1.43 ppm (βCH_2-backbone protons)[31], whereas 7.21 (benzene ring), 4.93 (-CH_2-adjacent to phenyl group), 2.35 (αCH-) and 1.62 ppm (βCH_2-) are the resonance signals corresponding to poly benzyl acrylate (PBA) [Fig. 5.5(c)]. Figure 5.5(b) represents the signal, around δ=4.70 ppm associated with protons of -OCH group and resonance signals appeared at 1.76 and 2.25 ppm are due to five methylene groups. The methine backbone proton (αCH-) and backbone methylene proton (βCH_2-) resonate between δ=3.69-3.63 and 1.38 ppm, respectively[30].

The ^{1}H-NMR spectra of the VAc containing copolymers are shown in Figure 5.7. Assignments of ^{1}H-NMR signals based on comparisons with previously published spectra of homopolymers[29,32] allowed determination that the product contained vinyl acetate (VAc) and acrylate repeat units. The resonance signals appearing at δ = 1.71-1.83 and 1.35 ppm are corresponding to methylene backbone protons of VAc and CA, respectively. The methine backbone proton (αCH-) of the VAc and CA monomeric units resonate as broad signals at δ = 4.95 - 4.58 and 3.69 - 3.63 ppm, respectively. The methine backbone signal (αCH-) of VAc unit overlapped with signal associated with proton of -OCH group of CA unit (appeared at around 4.70 ppm) and -CH_2- adjacent to phenyl group of BA (appeared at around 4.93 ppm) and hence could not be distinguished. The aromatic protons of BA unit give distinct signal at δ = 7.25 ppm whereas the signal around δ = 1.97 ppm is associated with acetoxy protons (-$OCOCH_3$) of VAc unit.

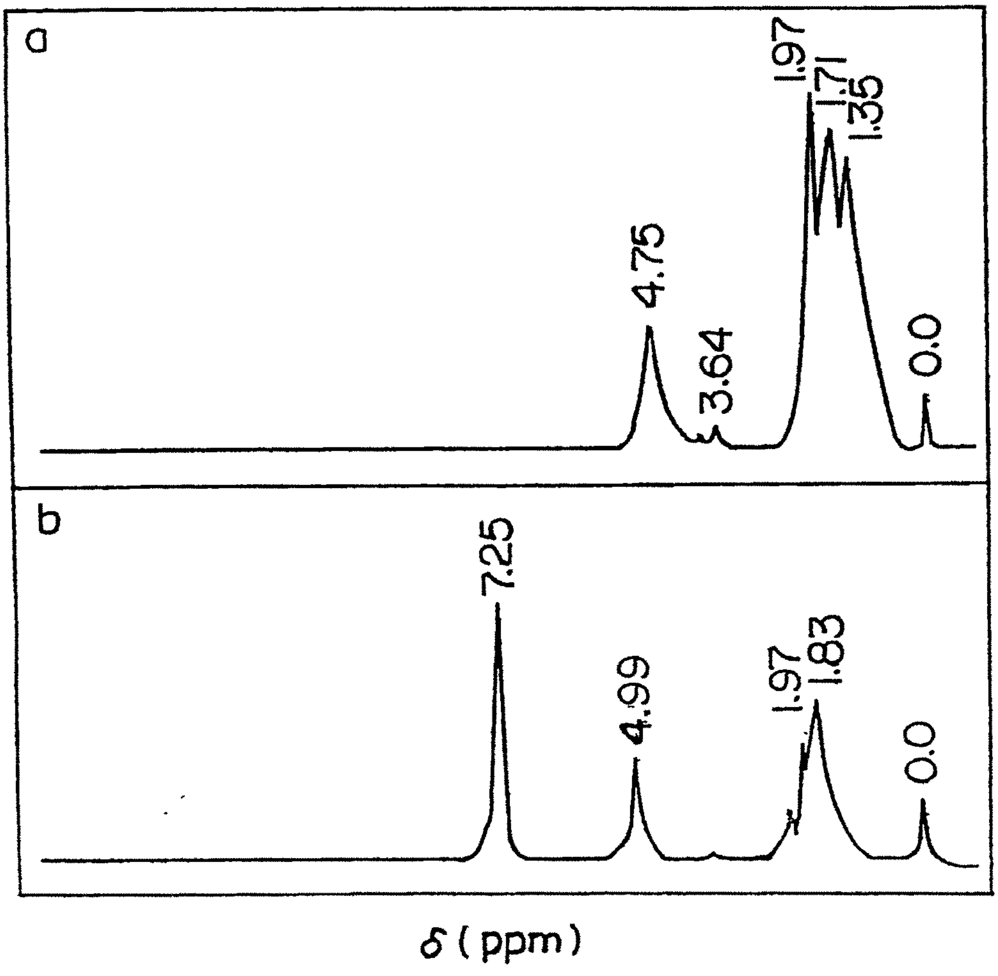


Figure 5.7 : Representative ^{1}H-NMR spectra of copolymers P(VAc-CA) [CA = 63.0 mol % in the feed] and (b) P(VAc-BA) [BA = 29.4 mol % in the feed] in $CDCl_3$.

The copolymer compositions were determined by ^{1}H-NMR spectra [Fig. 5.6: (a) and (b)]. The distribution of protons in the two units is important in distinguishing the monomers in the copolymer chain[25]. The αCH- and βCH_2-protons of styrene, CA and BA as well as phenyl protons of styrene and BA are almost indistinguishable. Hence, in the present study aromatic protons (~7 ppm) of styrene and -OCH proton (~4.48 ppm) of CA are chosen for the estimation of styrene composition in the P(S-CA) copolymer. The mole fraction of styrene (m_1) in the copolymer P(S-CA) was determined using the following relation :

$$m_1 = \frac{A_{ph}}{A_{ph} + 5A_{-OCH}} \qquad (1)$$

where A_{ph} and A_{-OCH} represents the ^{1}H-NMR resonance peak areas of protons on phenyl and -OCH groups, respectively. The styrene composition in the P(S-BA) copolymer was evaluated using the distinct peaks of methylene protons (~4.57 ppm, adjacent to phenyl group) and the peak intensity corresponds to the total number of protons of a particular group. The mole fraction of the copolymer was calculated by the following equation[25] :

$$\frac{\text{Intensity of methylene protons } (I_{CH2})}{\text{Intensity of total protons } (I_T)} = \frac{2\,m_2}{10\,m_2 + 8\,m_1} \qquad (2)$$

The equation (2) is based on the fact that there are 10 protons in BA and 8 protons in styrene and BA with 2 methylene protons gives distinct resonance peak for methylene group at 4.57 ppm. From this and $m_1 = 1\text{-}m_2$, the following equation was derived.

$$m_2 = \frac{4I_{CH2}}{I_T - I_{CH2}} \qquad (3)$$

Integrated peak intensities were employed for this calculation. So, m_2 is the mole fraction of BA and m_1 ($=1\text{-}m_2$) is that of styrene. Based on equation 3, the mole fraction of styrene was calculated by measuring the intensities of methylene protons and total protons from the spectra of all copolymer samples.

The mole fraction calculated for styrene in P(S-CA) and P(S-BA) copolymers of various compositions, are listed in Table 5.1.

The average copolymer composition [mole fraction of vinyl acetate, m_{VAc} in P(VAc-CA) copolymer] can be readily obtained by using the equation

$$m_{VAc} = \frac{I\,(\text{-OCOCH}_3)}{I\,(\text{-OCOCH}_3) + 3I\,(\alpha\text{CH-})} \qquad (4)$$

where I (-OCOCH$_3$) and I(αCH-) represent the total peak intensities of the proton resonances of -OCOCH$_3$ of VAc unit and of the αCH- of the CA unit, respectively. The acetoxy protons of VAc resonates at ~ 1.97 ppm, whereas αCH- proton of CA resonates at 3.69-3.63 ppm. The composition of copolymers as determined by ^{1}H-NMR along with the feed composition is given in Table 5.2.

The vinyl acetate mole fraction (m_{VAc}) in P(VAc-BA) copolymer was calculated using the peak intensity of methylene group of VAc unit and phenyl group of BA unit using the following relation

$$m_{VAc} = \frac{5I\,(\beta\text{CH}_2\text{-})}{5I\,(\beta\text{CH}_2) + 2I\,(\text{Ph})} \qquad (5)$$

where, I (βCH$_2$-) and I (Ph) represent the peak intensities of the methylene protons of VAc unit and of phenyl protons of BA unit, respectively. The mole fractions of monomers in the relevant copolymers of various compositions calculated by using ^{1}H-NMR are listed in Table 5.2.

Table 5.1 : Composition of Monomers in Feed and in Copolymers and Fineman-Ross Parameters

Samples	M_1[a]	m_1[b]	$X = \frac{M_1}{M_2}$	$Y = \frac{m_1}{m_2}$	$G = \frac{X(Y-1)}{Y}$	$F = \frac{X^2}{Y}$
SCA-1[c]	0.925	0.927	12.33	12.70	11.98	11.36
SCA-2	0.804	0.740	4.10	2.85	5.91	2.66
SCA-3	0.672	0.675	2.05	2.08	2.02	1.06
SCA-4	0.477	0.596	0.91	1.48	0.56	0.29
SCA-5	0.255	0.457	0.34	0.84	0.14	-0.06
SBA-1	0.923	0.909	11.99	9.99	14.39	10.79
SBA-2	0.800	0.798	4.00	3.95	4.05	2.99
SBA-3	0.667	0.670	2.00	2.03	1.98	1.02
SBA-4	0.471	0.642	0.89	1.79	0.44	0.39
SBA-5	0.250	0.575	0.33	1.35	0.11	0.12

[a] M_1 is the mole fraction of styrene in feed.

[b] m_1 is the mole fraction of styrene in copolymer, determined by ^{1}H-NMR spectroscopy.

[c] SCA is copolymer of styrene with cyclohexyl acrylate and SBA is the copolymer of styrene with benzyl acrylate.

Table 5.2 : Composition of Monomer in Feed and in Copolymers and Kelen-Tudos Parameters

Samples	M_1[a]	m_1[b]	$X = M_1/M_2$	$Y = m_1/m_2$	$G = X(Y-1)/X$	$F = X^2/Y$	$\varepsilon = F/\alpha + F$[c]	$\theta = G/\alpha + F$
VCA-1[d]	0.872	--	6.813	--	--	--	--	--
VCA-2	0.719	0.385	2.259	0.626	-0.374	8.152	0.656	-0.030
VCA-3	0.630	0.293	1.703	0.414	-0.586	7.005	0.620	-0.052
VCA-4	0.532	0.223	1.127	0.286	-0.714	4.441	0.509	-0.082
VCA-5	0.299	0.075	0.427	0.081	-0.919	2.251	0.344	-0.141
VBA-1	0.869	0.656	6.634	1.907	3.155	23.078	0.894	0.122
VBA-2	0.714	0.569	2.497	1.320	0.605	4.723	0.634	0.081
VBA-3	0.625	0.488	1.667	0.953	-0.082	2.916	0.517	-0.015
VBA-4	0.469	0.428	0.883	0.748	-.0297	1.042	0.367	-0.079
VBA-5	0.294	0.350	0.416	0.538	-0.357	0.322	0.106	-0.117

[a] M_1 is the mole fraction of vinyl acetate (VAc) in feed ($M_1 + M_2 = 1$).

[b] m_1 is the mole fraction of vinyl acetate (VAc) in the copolymer ($m_1 + m_2 = 1$).

[c] $\alpha = \sqrt{F_{min}.F_{max}} = 4.28$ [for P(VAc-CA)] and 2.73 [for P(VAc-BA)].

[d] VCA represents P(VAc-CA) copolymer systems and VBA represents P(VAc-BA) copolymer systems.

Monomer reactivity ratios r_1(S or VAc) and r_2(CA or BA) could thus be calculated graphically using the equation proposed by Fineman and Ross (F.R.)[33]

$$X(Y-1)/Y = r_1 X^2/Y - r_2 \qquad (6)$$

where $X = M_1/M_2$ and $Y = m_1/m_2$ (as defined in Table 5.1 & 5.2). On plotting $X(Y-1)/Y$ versus X^2/Y (Fig. 5.8), the slope and intercept yielded r_1 (S or VAc) and r_2 (CA or BA). The values obtained for r_1 and r_2 are r_1(S) = 0.930 and r_2 (CA) = 0.771 for styrene and CA in P(S-CA) copolymers, whereas r_1(S) = 0.755 and r_2 (BA) = 0.104 for styrene and BA in P(S-BA) copolymer and r_1 (VAc) = 0.089 and r_2 (CA) = 1.109 for VAc and CA in P(VAc-CA) copolymer, whereas r_1(VAc) = 0.155 and r_2 (BA) = 0.390 for VAc and BA in P(VAc-BA) copolymer.

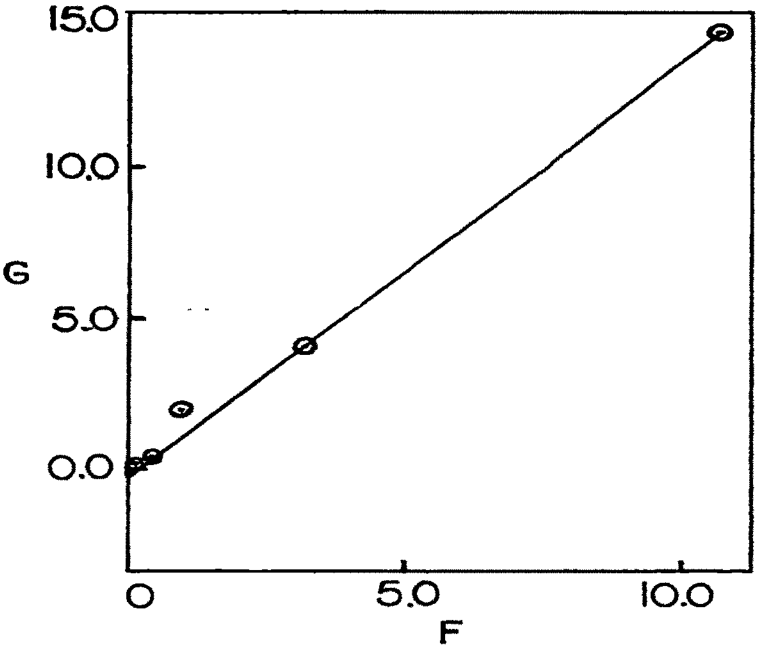


Figure 5.8 : Fineman-Ross plot for copolymerization of styrene with benzyl acrylate.

The reactivity ratios were also determined according to Kelen-Tudos (K.T.) procedure[33]. The resulting values of reactivity ratios estimated were r_1 (VAc) = 0.083 and r_2 (CA) = 1.109 and r_1 (VAc) = 0.164 and r_2 (BA) = 0.461, for VAc with CA and BA in P(VAc-CA) and P(VAc-BA) copolymer, respectively. The value obtained by the method of F.R. and K.T. agree very well with each other.

The r_1r_2 value (Table 5.3) of S-CA copolymer is 0.717 indicates that the copolymer should have random distribution of monomeric units with a tendency toward alternation, whereas the low value of 0.079 of r_1r_2 for S-BA system indicates alternate distribution of monomeric units[34]. Several values of r_1 and r_2, depending on temperature and reaction conditions, are reported in the literature[35] for the various monomer pairs and are presented in Table 5.3.

The nature of the copolymer sequence of P(VAc-CA) and P(VAc-BA) copolymer systems are alternating[13]. The systems are lying in the range of $0< r_1r_2 < 1$. Since the product r_1r_2 [0.092 and 0.076 for P(VAc-CA) and P(VAc-BA) copolymer respectively, r_1 and r_2 were used from K.T. method] are close to zero than to unity, there is a great tendency for M_1 and M_2 to alternate in the polymeric chain[13,21].

The copolymer composition vs initial monomer composition plot (Fig. 5.9 & 5.10) was sigmoidal and it crossed the ideal line at the point where $M_1{=}m_1$ = 0.766 and 0.785 for P(S-CA) and P(S-BA) copolymer respectively, and for P(VAc-BA) copolymer it crossed the ideal line at the point 0.390, indicating the azeotropic copolymer composition for these systems[13]. Theoretically the values were obtained from the following equation which was very close to the experimental value.

Table 5.3 : Reactivity Ratios of Styrene (r_1) with Different Acrylates (r_2)

Styrene (1) / Acrylates (2)	Methyl Acrylate (MA)	Ethyl Acrylate (EA)	Butyl Acrylate (BuA)	Cyclohexyl Acrylate (CA)	Benzyl Acrylate (BA)
r_1	0.750[a]	0.800[a]	0.698[a]	0.930 (0.885)[a]	0.755 (0.534)[a]
r_2	0.180[a]	0.200[a]	0.164[a]	0.771 (0.254)[a]	0.104 (0.248)[a]
$r_1 r_2$	--	--	--	0.717	0.079

[a] Ref.35.

$$M_{1\,critical} = m_{1\,critical} = \frac{1 - r_2}{2 - r_1 - r_2} \qquad (7)$$

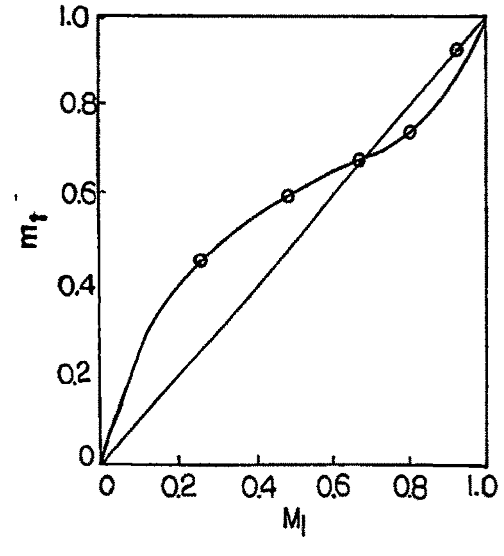


Figure 5.9 : Copolymer composition (m_1) Vs initial monomer composition (M_1) plot for P(S-CA) copolymers.

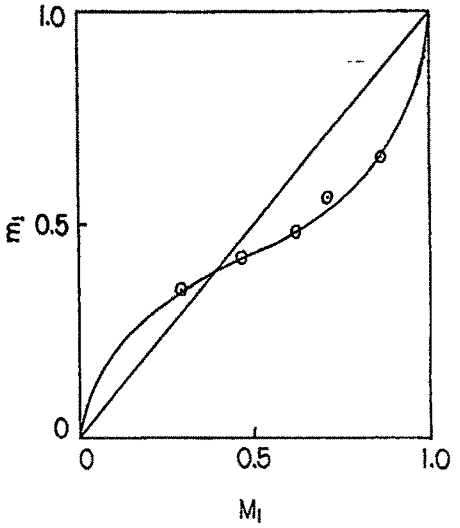


Figure 5.10 : Copolymer composition (m_1) Vs initial monomer composition (M_1) plot for P(VAc-BA) copolymers.

The Q and e values of Alfrey-Price Q, e scheme[13] for CA and BA were determined by using experimentally obtained values of the corresponding reactivity ratios. The values of $e_2 = -0.8$ and $Q_2 = 1.0$ from the literature were used for styrene and e_1 and Q_1 were evaluated for CA and BA using the following equations

$$e_1 = e_2 \pm (|\ln r_1 r_2|)^{½} \qquad (8)$$

$$Q_1 = Q_2/ r_2 \exp [e_2 (e_1 - e_2)] \qquad (9)$$

The values found to be $e_1 = 1.38$ and $Q_1 = 0.19$ for CA and $e_1 = 0.80$ and $Q_1 = 0.37$ for BA respectively.

(c) ^{13}C-NMR analysis :

The proton decoupled ^{13}C-NMR spectrum of all the polymers shows characteristic resonance signals at their respective positions corresponding to their constituent monomeric unit/s. The ^{13}C-NMR spectrum of homopolymers recorded in $CDCl_3$ at room temperature, are shown in Figure 5.11. In ^{13}C-NMR signals due to the carbons of long alkyl side chains were observed in the region 14-42 ppm. The assignment of various resonance peaks due to different carbon atoms were done using the additive shift parameters for hydrocarbons[29,30]. In such calculations, an assumption was made for that the ester groups do not influence the chemical shifts of the methylene groups, but are only affected by

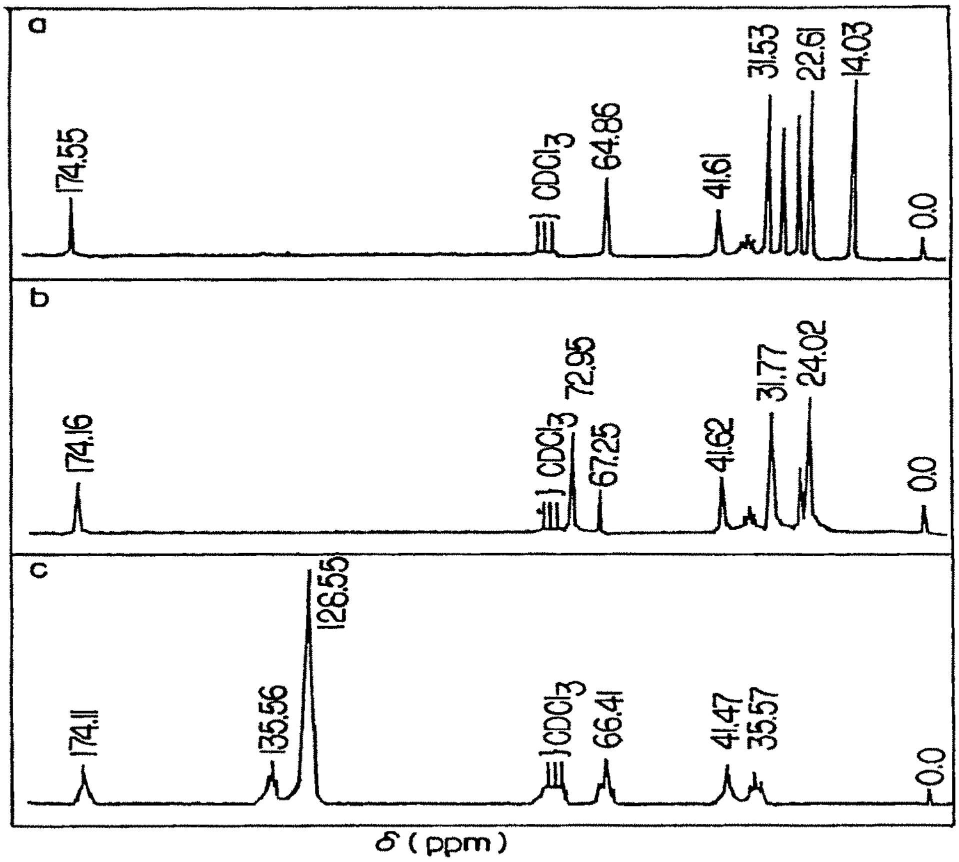


Figure 5.11 : Representative ^{13}C-NMR spectrum of homopolymers (a) PHA, (b) PCA and (c) PBA in $CDCl_3$.

substitutions as far removed as the δ position (i.e. α effect of +9.1, β = +9.4, γ = -2.5 and δ = +0.3 ppm). The calculations of shift were done using the formula, the predicted shift parameter, δ = 2.5 + Σ*nA*, where *A* is the additive shift parameter; and *n* is the number of carbon atoms for each shift parameter (methane adsorbs at 2.5 ppm upfield from TMS whereas alkane groups unsubstituted by heteroatoms absorbs downfield from TMS to about 60 ppm).

For PHA, δ should be predicted for all the five side-chain carbon atoms. Beginning with terminal methyl, the predicted shift parameters were 13.8, 22.9 and 32.0 ppm. The $-OCH_2$-group absorbs at 64.9 ppm. The observed values were in good agreement with the calculated values. The δ_5 and δ_6 shows little downfield values due to the influence of heteroatoms. Besides this absorptions, the methine (αCH-) absorbs at 41.6 ppm and methylene (βCH_2-) group at 35.6 ppm, whereas C=O resonated at 174.4 ppm[4,26]. In all these polyacrylate(s), the carbonyl carbon do not show any splitting but the methylene carbons show splitting due to configurational effects (Fig. 5.11). In case of PS and PBA, the methylene and methine carbons of phenyl ring are resonated at 126.0, 128.6, 132.0 and 135.6 ppm, whereas cyclohexyl group methylene and methine of PCA also absorb at their respective positions as shown in Figure 5.11.

The representative ^{13}C-NMR spectrum of the VAc-acrylate copolymers [in 1:1 (v/v) of the two monomers] recorded in $CDCl_3$ at room temperature are shown in Figure 5.12. The assignment of various resonance peaks due to different carbon atoms were done using the literature data[30-32] as well as comparison with the previously published spectra of the homopolymers[14]. The chemical shift values corresponding to various carbon atoms present in the homopolymers and copolymers are listed in Tables 5.4-5.6. Unlike in the homopolymers of acrylates, the carbonyl carbon in all these copolymers shows splitting. Also various splitting patterns are observed in resonances of backbone methylene · and methine. The splitting is influenced by the composition of the copolymers and is due to configurational and sequence distribution effects.

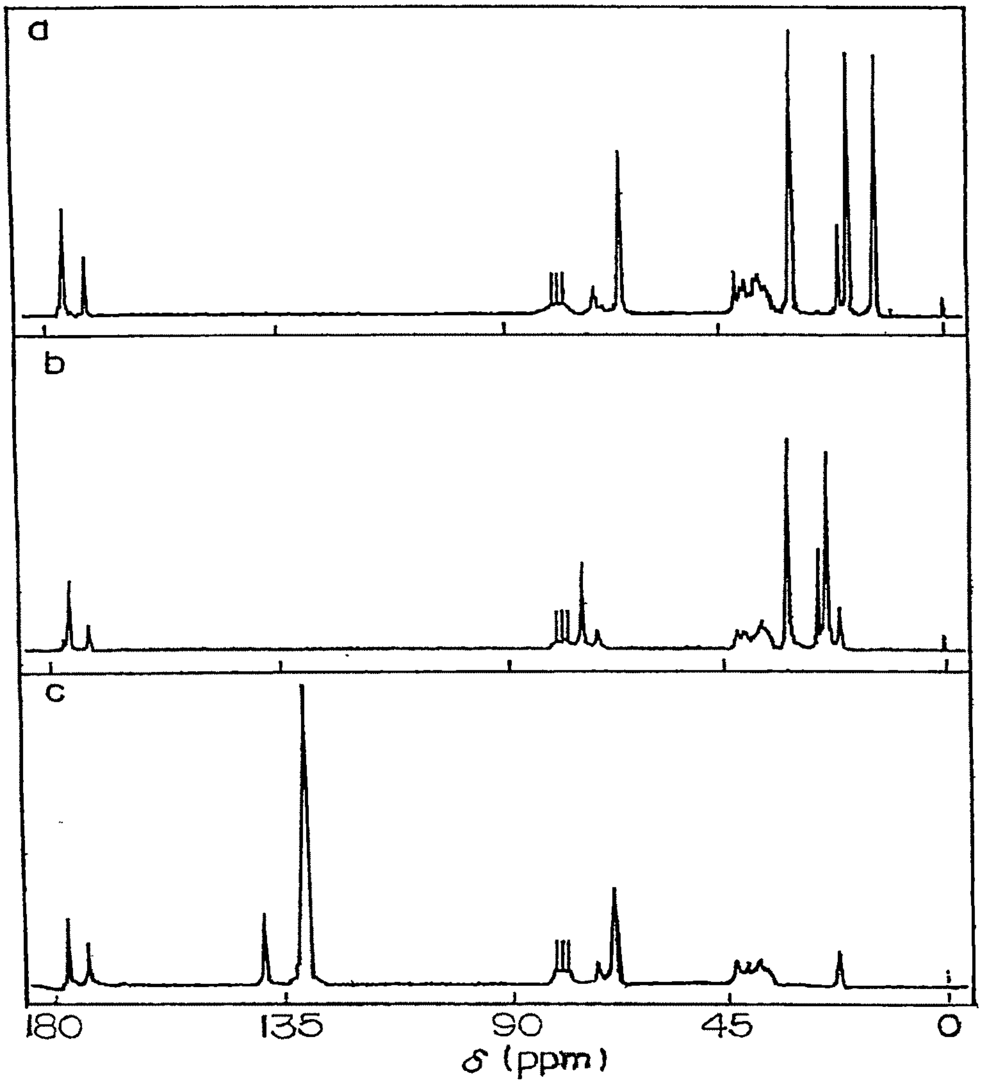


Figure 5.12 : Representative ^{13}C-NMR spectrum of (a) P(VAc-BuA), (b) P(VAc-CA) and (c) P(VAc-BA) in $CDCl_3$.

Table 5.4 : Chemical Shifts (δ_{ppm}) of the Carbon Peaks in ^{13}C-NMR for the Various Homopolymers

PVAc	PMA	PEA	PBuA	PHA	PCA	PBA	PMMA
C_1 170.26	C_3 174.65	C_3 174.31	C_3 174.26	C_3 174.55	C_3 174.16	C_3 174.11	C_3 177.77
							176.84
C_2 67.05	C_4 51.56	C_4 60.33	C_4 64.27	C_4 64.68	C_4 72.95	C_5 135.56	C_1 54.24
67.15							
68.22							
C_1 39.67	C_2 41.13	C_2 41.23	C_2 41.37	C_2 41.61	C_2 41.62	C_{6-8} 128.55	C_4 51.75
C_4 21.05	C_1 34.74	C_1 34.99	C_1 35.28	C_1 35.57	C_1 35.62	C_4 66.41	C_2 44.88
							44.54
							43.81
		C_5 13.99	C_5 30.51	C_5 31.53	C_5 31.77	C_2 41.47	C_5 18.81
							16.37
			C_6 19.01	C_6 28.60	C_6 25.58	C_1 35.57	
			C_7 13.60	C_7 25.58	C_7 24.02		
				C_8 22.61			
				C_9 14.03			

Table 5.5 : Chemical Shifts (δ) of the Carbon Peaks in ^{13}C-NMR for the Various P(S-Acrylate) Copolymers

P(S-MA)		P(S-EA)		P(S-BuA)		P(S-HA)		P(S-CA)		P(S-BA)	
C_3(MA)	175.96 175.43	C_3(EA)	175.43 174.89	C_3(BuA)	175.63 174.79	C_3(HA)	175.63 174.77	C_3(CA)	174.85 174.55	C_3(BA)	175.18 174.11
C_3(S)	142.78	C_3(S)	143.36	C_3(S)	144.06	C_3(S)	143.71	C_3(S)	143.99	C_3(S)	143.27
C_{4-6}(S)	128.16 126.21	C_{4-6}(S)	128.01 126.02	C_{4-6}(S)	127.96 126.11	C_{4-6}(S)	127.96 126.97	C_{4-6}(S)	128.11 126.06	C_4(BA)	135.91
C_4(MA)	51.17	C_4(EA)	59.34	C_4(BuA)	63.79	C_4(HA)	64.13	C_4(CA)	72.22	C_{4-6}(S) + C_{6-8} (BA)	128.06 126.02
C_2(S+MA)	41.03	C_2(S+EA)	40.79	C_2(S+BuA)	41.08	C_2(S+HA)	40.98	C_2(S+HA)	41.13	C_2(S+BA)	41.03
C_1(S+MA)	39.52	C_1(S+EA)	38.79	C_2(S+BuA)	30.55	C_1(S+HA) + C_7(HA)	31.38	C_1(S+HA)	31.58	C_1(S+BA)	39.96
		C_5(EA)	13.94	C_5(BuA)	19.05	C_5(HA)	28.41	C_5(CA)	25.44	C_5(BA)	65.54
				C_6(BuA)	13.69	C_6(HA)	25.53	C_6(CA)	23.83		
						C_8(HA)	22.51	C_7(CA)	17.94		
						C_9(HA)	14.03				

Table 5.6 : Chemical Shifts (δ_{ppm}) of the Carbon Peaks in ^{13}C-NMR for the Various P(VAc-Acrylates) Copolymers

P(VAc-MA)		P(VAc-EA)		P(VAc-BuA)		P(VAc-HA)		P(VAc-CA)		P(VAc-BA)		P(VAc-MMA)	
C_3(MA)	174.79	C_3(EA)	174.35	C_3(BuA)	174.50	C_3 (HA)	174.50	C_3(CA)	173.77	C_3(BA)	174.07	C_3 (MMA)	177.57
													176.69
C_3(VAc)	170.07	C_3 (VAc)	170.02	C_3(VAc)	170.11	C_3(VAc)	170.11	C_3(VAc)	169.97	C_3(VAc)	170.11	C_3(VAc)	169.58
C_2(VAc)	69.73	C_2 (VAc)	69.54	C_2(VAc)	69.78	C_2(VAc)	69.75	C_2(CA)	72.75	C_5(BA)	135.56	C_2(VAc)	66.71
C_4(MA)	51.56	C_4(EA)	60.43	C_4 (BuA)	64.42	C_4(HA)	64.76	C_4(VAc)	69.49	$C_{6\text{-}8}$(BA)	128.31	C_1(MMA)	54.33
C_2(MA)	41.08	C_2(EA)	41.23	C_2(BuA)	41.37	C_2(HA)	41.27	C_2(CA)	41.57	C_2(VAc)	69.63	C_4(MMA)	51.61
C_1(VAc)	39.13	C_1(VAc)	39.27	C_1(VAc)	39.52	C_1(VAc)	38.01	C_1(VAc)	40.01	C_4(BA)	66.32	C_2(MMA)	44.65
													44.34
													43.81
C_1(MA)	36.89	C_1(EA)	36.79	C_1(BuA)	37.43	C_1(HA)	35.59	C_1(CA)	36.50	C_2(BA)	41.32	C_1(VAc)	39.72
	34.65		35.13		35.28		35.13		35.67				
C_4(VAc)	20.66	C_4(VAc)	20.66	C_5(BuA)	30.55	C_5(HA)	31.29	C_5(CA)	31.38	C_1(VAc)	39.37	C_4(VAc)	20.91
		C_5(EA)	13.94	C_4(VAc)	20.81	C_6(HA)	28.36	C_6(CA)	25.24	C_1(BA)	37.13	C_5(MMA)	18.81
											35.18		16.42
				C_6(BuA)	19.05	C_7(HA)	25.34	C_7(CA)	23.68	C_4(VAc)	20.71		
				C_7(BuA)	13.64	C_8(HA)	22.57	C_4(VAc)	20.69				
						C_4(VAc)	20.71						
						C_9(HA)	13.84						

As shown in Figure 5.12 and Table 5.6, ^{13}C-NMR spectrum of all the copolymers showed two distinct / well resolve carbonyl carbon resonances of the VAc as well as the acrylate monomeric units appearing, respectively, at δ = 169.97 - 170.11 and 174.07 - 174.79 ppm. These are singlets and do not show any tacticity or sequence distribution effect. However for P(VAc-MMA) triplet peaks showing compositional and configurational sensitivities are observed. The quaternary carbon of the MMA unit also appear as a multiplet at around δ = 43.81 - 44.65 ppm, showing its sensitivity to copolymer tacticity[31]. All the methylene, methine, methyl and methoxy carbons resonate at their respective positions as presented in Tables 5.4 - 5.6 for various homopolymers and for copolymers, respectively.

(d) TGA analysis :

Thermal behaviour of the homopolymers and copolymers were studied by thermogravimetry. The nature of the thermograms of all the homopolymers and styrene containing copolymers were found to be similar showing one step decomposition (Fig. 5.13a). Most of the polymer samples were stable upto 300°C and started loosing weight above this temperature (Table 5.7). The thermal behaviour of VAc-acrylates copolymer e.g. P(VAc-CA), P(VAc-BA) and P(VAc-EA) copolymers are given in Figure 5.13b. The nature of the thermograms of all the copolymers were also found to be similar showing single step decomposition. Most of these copolymers were stable upto 388°C though PVAc and other homopolymers show lower initial decomposition temperature[14]. The decomposition observed in the temperature range of 320-590°C is perhaps due to the break down of polymer initiated from the weak sites (e.g. unsaturated chain ends, branching, head-to-head linkages etc.) as observed earlier[36]. The activation energy of decomposition (E_a) values (Table 5.7) showed that PMA exhibited lowest thermal stability than PEA, whereas the other polymers i.e. PBuA and PHA exhibited higher thermal stability at a heating rate of 10°C min^{-1}. All the copolymers also followed the similar pattern i.e. with increasing linear chain length of the pendant group present in the copolymers, thermal stability increases.

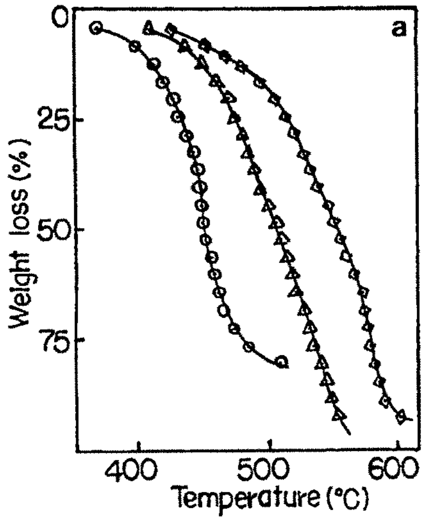


Figure 5.13(a) : Representative TGA plots of (7) P(S-EA), (Δ) P(S-CA) and (O) PCA at heating rate of 10 K min^{-1} in air.

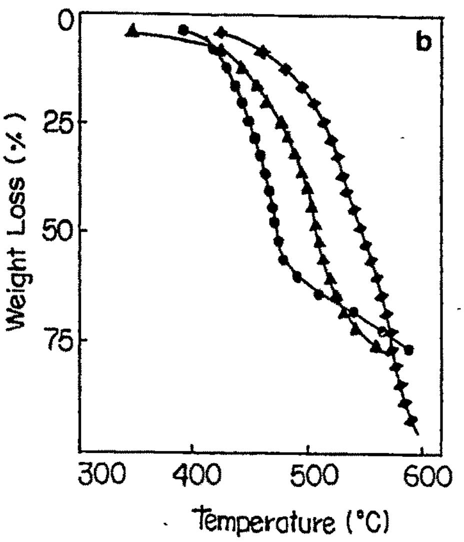


Figure 5.13(b) : Representative TGA plots of (●) P(VAc-CA), (▲) P(VAc-BA) and (◆) P(VAc-EA) at heating rate of 10 K min^{-1} in air.

The data listed in Table 5.7 give the initial decomposition temperature (IDT), maximum rate of decomposition (T_{max}), complete decomposition temperature (FDT) and also the activation energies (E_a) calculated using standard relations suggested by Broido[21].

$$\ln \ln (1/Y'') = -E_a/R\,(1/T) + \text{constant} \qquad (10)$$

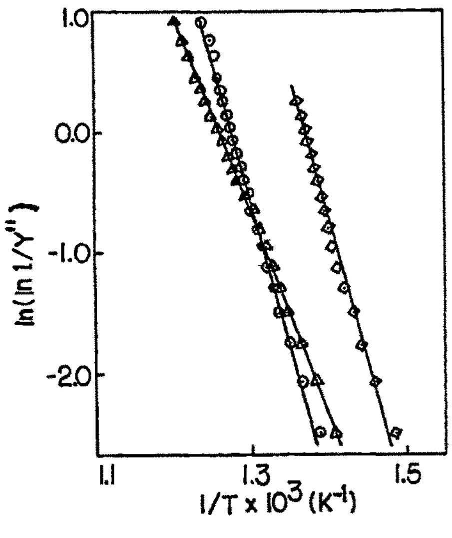
Table 5.7 : Thermal Analysis Results for Various Homopolyers and Copolymers

Polymer Samples	IDT (°C)	T_{max} (°C)	FDT (°C)	Weight Loss (%)	E_a[b] (kJ mol^{-1})	T_g (°C)
PMA[a]	320	--	500	89	92.0	19.5
PEA[a]	380	--	510	87	136.3	-3.0
PBuA[a]	360	--	530	90	141.3	--
PCA	400	445	508	80	174.8	12.6
PBA	435	503	535	80	188.2	12.5
PS	408	501	553	80	124.7	100.2
P(S-MA)	430	518	567	92	129.3	48.0
P(S-EA)	481	546	589	92	141.0	17.4
P(S-BuA)	428	519	549	84	153.2	-0.3
P(S-HA)	460	515	558	88	153.3	--
P(S-CA)	438	505	557	92	139.9	46.4
P(S-BA)	435	510	535	80	188.2	--
P(VAc-MA)	390	468	538	76	114.5	--
P(VAc-EA)	446	503	567	68	114.0	--
P(VAc-CA)	388	455	490	60	142.0	--
P(VAc-BA)	426	497	533	68	119.5	--

[a] Ref. : R.Joseph, Ph.D. Thesis submitted to M.S.University of Baroda, 1992, p.62.

[b] Calculated using Broido method at a heating rate of 10°C/min in air.

where Y” [= $(W_o - W_t) / (W_o - W\infty)$] is the fraction of the number of initial molecules not yet decomposed; W_t, W∞ (=0) and Wo are the weight at time ‘t’, the weight at infinite time, and the initial weight respectively. A plot of ln ln (1/Y”) versus (1/T) [eq.10] gives an excellent approximation to a straight line over a range of 0.999<Y”>0.001. The slope is related to the activation energy. Representative plots are shown in Figures 5.14(a & b). E_a values for vinyl acetate copolymer systems are almost same except the copolymer with CA unit.



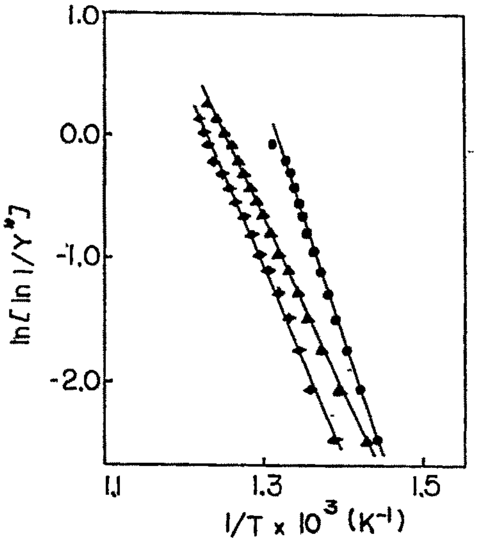


Figure 5.14(a) : Representative Broido plots for (a) (7) P(S-EA), (Δ) P(S-CA) and (O) PCA.

Figure 5.14(b) : Representative Broido plots for (●) P(VAc-CA), (▲) P(VAc-BA) and (◆) P(VAc-EA).

(e) DSC analysis :

DSC curves for PS and polyacrylates are shown in Figure 5.15. From the DSC curves, the glass transition temperature (T_g) of polymers were obtained. Polyacrylates have low values of T_g but as the styrene unit is incorporated in the copolymers of acrylates their T_g values increase (Table 5.7). The T_g values obtained for all these polymers agree well with those reported in literature[29,37]. The onset T_g, T_g at point of inflection and peak T_g values are 93.5, 100.2 and 104.7°C respectively for PS and are mentioned in Figure 5.15.

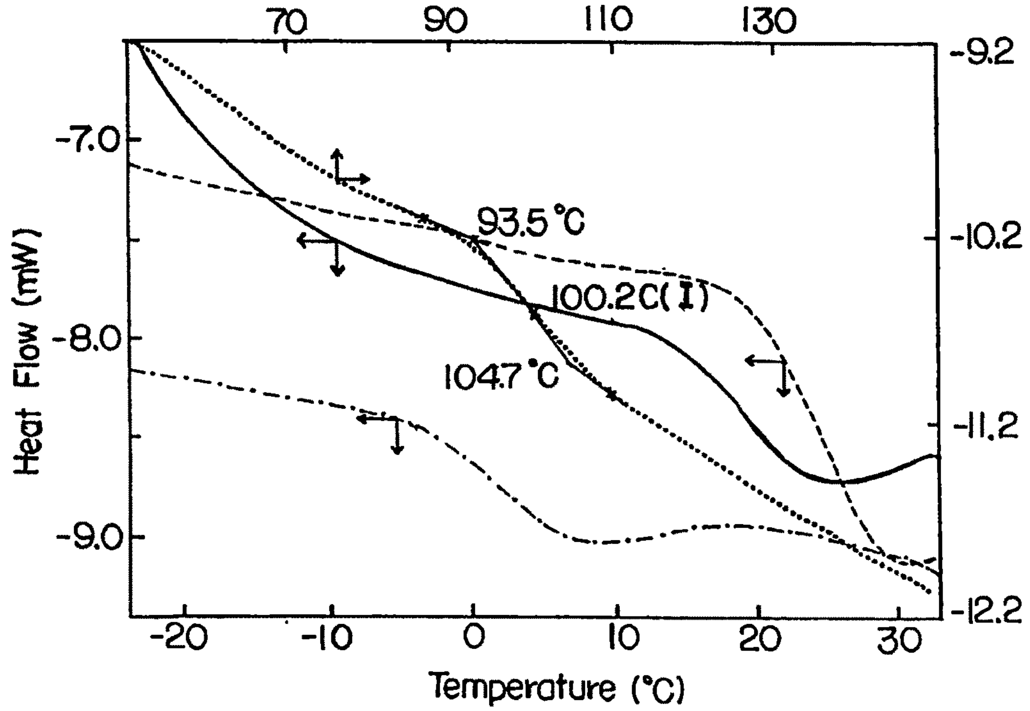


Figure 5.15 :Representative DSC thermogram of homopolymers: (......) PS, (—) PCA (-----) PMA and (-.-.-) PEA at heating rate 10 K min^{-1} in N_2 atmosphere.

(f) GPC studies :

The approximate number average (M_n), weight average (M_w), Z-average (M_z) and viscosity average (M_v) molecular weights of homopolymers poly(cyclohexyl acrylate) (PCA) and polybenzyl acrylate (PBA), determined by gel permeation chromatography (Fig. 5.16) are 2.24 x 10^5, 2.42 x 10^5, 2.59 x 10^5 and 2.42 x 10^5 for PCA and 8.72 x 10^4, 1.67 x 10^5,2.62 x 10^5 and 1.67 x 10^5 for PBA, respectively. The molecular weight distribution (MWD) were found to be 1.08 and 1.91 for PCA and for PBA respectively.

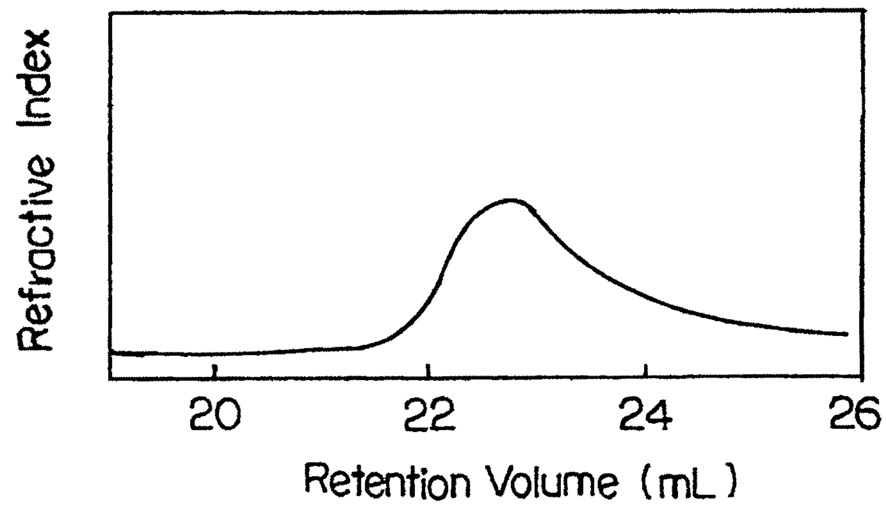


Figure 5.16 : Typical GPC chromatogram for polycyclohexyl acrylate.

(g) Viscosity measurements :

The intrinsic viscosity [η] is one of the most important source of information on the size and shape of polymer molecules[21]. The intrinsic viscosity [η] can be obtained by using the well known Huggins and Kraemer equations[21]. The [η] values of all the polymers are presented in Tables (5.8 & 5.9). It can be seen that [η] decreases as the temperature increases and [η] vs T plots are linear with negative slope[38]. This indicates that the swelling of the polymer chains is not much in these systems and the critical solution temperature are lower for these polymer solutions. This is due to the decreased thermodynamic affinity with increased temperature[38]. Moreover (Table 5.8) it can be recognized that the intrinsic viscosities of all the styrene containing copolymers having linear pendant group, increased with increasing chain length of the pendant group. However, in case of homopolymers, the intrinsic viscosities decreased with increase in chain length of the pendant group. From the values of intrinsic viscosity (Table 5.8), it is observed that the intrinsic viscosity in a solvent is

Table 5.8 : Intrinsic Viscosity '[η]', Hydrodynamic Volume 'V_E' and Shape Factor 'ν' of Various Polymers at Different Temperatures in 1,4-Dioxane

Polymer Samples	30°C			40°C			50°C		
	[η] (dL g^{-1})	V_E (dL g^{-1})	ν	[η] (dL g^{-1})	V_E (dL g^{-1})	ν	[η] (dL g^{-1})	V_E (dL g^{-1})	ν
PMA	0.330	0.1302	2.5	0.326	0.1288	2.5	0.323	0.1268	2.5
PEA	0.226	0.0898	2.5	0.224	0.0844	2.5	0.222	0.0880	2.5
PBuA	0.224	0.0893	2.5	0.223	0.0888	2.5	0.220	0.0879	2.5
PHA	0.161	0.0639	2.5	0.159	0.0629	2.5	0.157	0.0628	2.5
PCA	0.136	0.0540	2.5	0.135	0.0539	2.5	0.134	0.0532	2.5
PBA	0.478	0.1846	2.6	0.472	0.1828	2.6	0.466	0.1808	2.6
PS	0.188	0.0745	2.5	0.185	0.0740	2.5	0.182	0.0722	2.5
P(S-MA)	0.187	0.0747	2.5	0.185	0.0740	2.5	0.183	0.0728	2.5
P(S-EA)	0.188	0.0747	2.5	0.185	0.0728	2.5	0.183	0.0726	2.5
P(S-BuA)	0.197	0.0779	2.5	0.194	0.0774	2.5	0.192	0.0766	2.5
P(S-HA)	0.202	0.0800	2.6	0.200	0.0794	2.5	0.197	0.0785	2.5
P(S-CA)	0.162	0.0642	2.5	0.160	0.0631	2.5	0.158	0.0626	2.5
P(S-BA)	0.230	0.0920	2.5	0.226	0.0898	2.5	0.223	0.0885	2.5

Table 5.9 : Intrinsic Viscosity '[η]', Hydrodynamic Volume 'V_E' and Various Activation Parameters for Viscous Flow of the P(VAc-Acrylates) Copolymers at Different Temperatures in 1,4-Dioxane.

Samples	30°C		40°C		50°C		$\Delta H^{\neq}_{vis}$ (kJ. Mol^{-1})	$\Delta S^{\neq}_{vis}$ (J. mol^{-1} K^{-1})	$\Delta G^{\neq}_{vis}$ (40°C) (kJ. Mol^{-1})
	[η] (dL g^{-1})	V_E (dL g^{-1})	[η] (dL g^{-1})	V_E (dL g^{-1})	[η] (dL g^{-1})	V_E (dL g^{-1})			
P(VAc-MA)	0.167	0.066	0.165	0.065	0.163	0.064	10.2	2.6	9.4
P(VAc-EA)	0.178	0.071	0.175	0.070	0.172	0.068	10.3	2.7	9.5
P(VAc-BuA)	0.158	0.064	0.156	0.063	0.154	0.161	10.2	2.6	9.4
P(VAc-HA)	0.428	0.165	0.421	0.164	0.415	0.161	10.4	1.7	10.3
P(VAc-CA)	0.110	0.044	0.108	0.043	0.106	0.042	10.2	2.9	9.3
P(VAc-BA)	0.144	0.058	0.142	0.056	0.139	0.055	10.3	2.9	9.3
P(VAc-MMA)	0.135	0.058	0.134	0.053	0.132	0.052	10.2	2.7	9.5
PCA	0.136	0.054	0.135	0.054	0.134	0.053	10.9	2.6	9.4
PBA	0.478	0.185	0.472	0.183	0.466	0.181	10.5	1.5	10.0

depending on the interaction between polymer and solvent as well as among the polymer chains. Besides this, the chemical composition and constitution, the homogeneity and the length of sequences of chemically identical monomer units also affect the [η] value[38].

The intrinsic viscosity data were used to compute activation parameters of the viscous flow using the well known procedure suggested by Frenkel & Eyring[39 40]. It is observed that $\Delta H^{\neq}_{vis}$ of all the styrene containing systems in 1,4-dioxane are more or less constant and the average was found to be 15.6 ± 0.2 kJ mol^{-1}. The entropies of activation of the viscous flow ($\Delta S^{\neq}_{vis}$) were also low and positive 22 ± 1 J mol^{-1} K^{-1}. The values obtained for change in the free energy ($\Delta G^{\neq}_{vis}$), enthalpy ($\Delta H^{\neq}_{vis}$) and entropy ($\Delta S^{\neq}_{vis}$) of activation for the viscous flow for VAc-acrylate copolymers are listed in Table 5.9. It is observed that $\Delta H^{\neq}_{vis}$ and $\Delta S^{\neq}_{vis}$ of all the systems calculated at 0.8 g dL^{-1} concentration in 1,4-dioxane are more or less constant quantities, independent of temperature and the average was found to be 10.3 ± 0.1 k J mol^{-1} and 2.5 ± 0.2 J mol^{-1} K^{-1} respectively. These low values and constancy of $\Delta H^{\neq}_{vis}$ values signify that the systems are not cross-linked, whereas low and positive values of $\Delta S^{\neq}_{vis}$ indicate that the polymer structures were reasonably ordered in 1,4-dioxane. The $\Delta G^{\neq}_{vis}$ values can hence be computed for all these systems and was found to decrease with increase in temperature.

Voluminosity, V_E (i.e. a measured volume of solvated polymer) were evaluated by plotting χ against concentration C in g dL^{-1} where

$$\chi = \frac{[\eta_r^{0\,5} - 1]}{[C\,(1.35\,\eta_r^{0\,5} - 0.1)]} \qquad (11)$$

and η_r is the relative viscosity of the polymer solution.

The plot was linear and extrapolated to C = 0, and the intercept yielded V_E. It can be seen that V_E decreases with increase in temperature. This is due to the desolvation effect (Tables 5.8 & 5.9)[21].

The shape factor, 'ν' (which suggest conformation of macromolecules in solution) was obtained from the equation

$$[\eta] = \nu V_E \qquad (12)$$

The ν values were found to be 2.5 ± 0.1 for all the systems at three temperatures indicating polymer coils are spherical in nature and are not affected by temperature[33].

Some of the molecular parameters of polymers were calculated using solution viscosity data. The root-mean square end-to-end distances of homopolymers PCA and PBA chains were determined using the well-known relation[41]

$$[\eta] = \phi_0 < R^2 >^{3/2} / M_n \qquad (13)$$

where , ϕ_0 is universal constant, commonly known as the Flory- Fox constant and M_n is the number average molecular weight of the polymers. The calculated values of $<R^2>^{1/2}$ obtained at various temperatures are presented in Table 5.10. As temperature increases, $<R^2>^{1/2}$ values decrease indicating coiling of the polymer chain in solution.

The radius of the diffusing particle (r') was calculated from the well-known Einstein equation[27,42].

$$[\eta] = 10\pi N r'^3 / 3M_n \qquad (14)$$

Table 5.10 : Root Mean Square End-to-End Distance ($<R^2>^{1/2}$), Radius of the Diffusion Particle (r') and Diffusion Coefficient (D_0) of Homopolymers in 1,4-Dioxane

Polymers	30°C			40°C			50°C		
	$<R^2>^{1/2}.10^7$ (cm)	$r'.10^7$ (cm)	$D_0.10^7$ ($cm^2.Sec^{-1}$)	$<R^2>^{1/2}.10^7$ (cm)	$r'.10^7$ (cm)	$D_0.10^7$ ($cm^2.Sec^{-1}$)	$<R^2>^{1/2}.10^7$ (cm)	$r'.10^7$ (cm)	$D_0.10^7$ ($cm^2.Sec^{-1}$)
PCA	21.97	1.69	11.97	21.92	1.69	14.46	21.87	1.68	16.61
PBA	24.40	1.88	10.73	24.30	1.87	13.07	24.20	1.86	15.00

where N is Avogadro's number. The values of r' thus obtained for PAC and PAB homopolymers at different temperatures are listed in Table 5.10. These were found to be independent of temperature.

The quantitative relationship between the coefficient of diffusion D_0 and the radius of particles was obtained by Einstein equation[27,42]

$$D_0 = R\,T / 6\pi\,\eta_s r'N \qquad (15)$$

where η_s is the viscosity of 1,4-dioxane. The values of D_0 obtained are tabulated in Table 5.10. It is observed from the data that D_0 increases as the temperature increases.

5.6 Conclusion :

On the basis of the above mention results, it can be concluded that the free radical copolymerization reaction of S/VAc with CA/BA systems studied follows the classical copolymerization theory. FTIR, ^{1}H- and ^{13}C-NMR spectroscopy provided evidence for the structure and composition of the copolymers. The reactivity ratios measured via ^{1}H-NMR and calculated by Fineman-Ross and Kelen-Tudos methods agree very well with each other. The reactivity ratios of the monomers obtained by ^{1}H-NMR spectroscopy did show relatively higher reactivity of the styrene than that of respective acrylic esters. The values of r_1r_2 of monomers present in vinyl acetate- acrylate copolymers suggested great tendency for monomers to alternate in the polymeric chain. Single stage decomposition was observed for all copolymers. The activation energy of the decomposition for styrene copolymers increases as the linear alkyl chain length of the pendant group increased. The increase in pendant group chain length showed opposite effect on intrinsic viscosity i.e. for homopolymers it decreased whereas for copolymers with styrene it increased. The viscosity activation parameters indicate that the polymers in 1,4-dioxane solution are not cross linked and have reasonably ordered structure.

5.7 References

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