

Phenyl Acrylates and Divinyl Benzene Cross-Linked Copolymers as Basic Novel Supports: Synthesis and Characterization

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SYNOPSIS

Suspension copolymerization of glycidyl methacrylate (GMA), phenyl methacrylate (PhMA), 2,4,6-tribromophenyl acrylate (TBPA), and 4-acetylphenyl acrylate (APA) with divinyl benzene (DVB) was carried out at $80 \pm 1^\circ\text{C}$ in aqueous medium, as basic supports for possible applications in polymer-supported chemistry. The resulting copolymer beads were characterized with various techniques. The identification of monomers in the copolymer was attempted using FTIR and ^{13}C -CP/MAS-NMR spectroscopic techniques. The optical and scanning electron microscopic methods were used to study the shape, size, and surface morphology of the beaded copolymers. The particle-size distribution was measured, and the average particle size of the particulate copolymers were carried out using a Malvern particle-size analyzer. The decomposition temperatures and energy of activation involved in the thermal degradation were studied with thermogravimetry. The solvent imbibition of the polymer supports in various solvents was carried out with a centrifuge method.

INTRODUCTION

Merrifield's concept of solid-phase peptide synthesis (SPPS) revolutionized the field of peptide synthesis and also generated much interest in the possible applications of polymer supports in other areas of chemistry.¹⁻⁴ Since then, the studies on the significance of cross-linked copolymers based on vinyl monomers as basic supports have increased.⁵ It was realized earlier that the polymer support itself plays an important role in supported organic synthesis. Some of the problems associated with Merrifield's earlier technique were explained on the basis of the chemical nature of the support used and the interactions between the peptide chain and the support, and the need for improved types of supports was emphasized.⁶ Sheppard demonstrated elegantly the role of the polymer support by synthesizing a peptide, which otherwise was giving problems with a

conventional resin (styrene-divinyl benzene) on polar hydrophilic supports.⁷ Although some work has been carried out with glycidyl methacrylate-based resins, their use in SPPS is not known.⁸⁻¹⁰ Activated acrylates are the recent addition as basic supports in supported organic synthesis, metal ion separation, etc.¹¹⁻¹³ The present paper reports the synthesis and characterization of phenyl acrylates cross-linked with divinyl benzene as basic supports in aqueous suspension medium for their possible applications in supported synthesis.

EXPERIMENTAL

Materials

Phosphoric acid, anhydrous phosphorus pentoxide, 2-butanone, triethylamine (TEA), chloroform, chlorobenzene, methacrylic acid, benzoyl chloride, 2,4,6-tribromophenol, and 4-hydroxy acetophenone (Sico-chem) were used as such without further purification. Benzoyl peroxide (Fluka) was purified by recrystallization. Glycidyl methacrylate (GMA) (Fluka) was distilled under vacuum before use.

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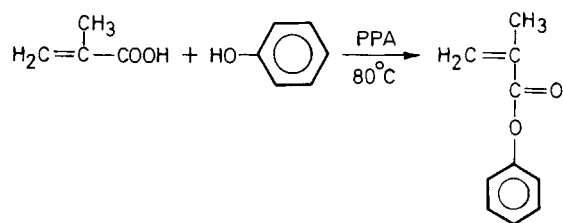
Polyvinylpyrrolidone (MW 360,000) (Fluka) was used as received. Divinyl benzene (DVB) (Fluka) was washed with 5% aqueous sodium hydroxide solution before use.

Synthesis of Monomers

Polyphosphoric acid was prepared by mixing equimolar quantities of phosphoric acid and anhydrous phosphorus pentoxide. Phenyl methacrylate (PhMA) was synthesized by reacting phenol with methacrylic acid in the presence of polyphosphoric acid as reported in the literature¹⁴:

IR (cm⁻¹): 3030, 2920, 1736, 1635, 1590, 1290, 1130, 700

¹³C-NMR (ppm): 135.68 (=C), 126.69 (=CH₂), 150.79 (¹C), 120.06 (³C and ⁵C), 125.36 (⁴C), 121.34 (²C and ⁶C), 175.19 (C=O), 16.00 (CH₃).



Scheme 1 Synthesis of PhMA.

Acryloyl chloride was prepared by following the procedure of Stampel et al.¹⁵ 2,4,6-Tribromophenyl acrylate (TBPA) and 4-acetylphenyl acrylate (APA) were synthesized by treating the acryloyl chloride (0.125 mol) with the corresponding phenols (0.125 mol) in the presence of TEA (0.125 mol) at 0°C in chloroform. The unreacted phenols were removed by washing with 5% sodium hydroxide solution. The resulting solutions were treated with anhydrous magnesium sulfate and the solvent removed by rotary evaporation. The crude solid monomers thus obtained were purified by recrystallization:

TBPA mp 75–76°C

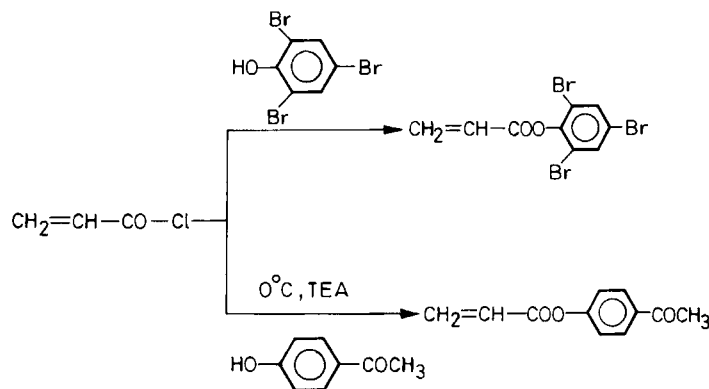
IR (cm⁻¹): 3020, 1740, 1650, 1630, 1550, 1290, 1140, 860

¹³C-NMR (ppm): 134.17 (=CH₂), 126.45 (=CH), 161.49 (C=O), 145.20 (¹C), 118.49 (²C and ⁶C), 134.81 (³C and ⁵C), 119.84 (⁴C)

APA mp 72–74°C

IR (cm⁻¹): 3010, 1750, 1675, 1630, 1595, 1400, 1290, 1130, 820

¹³C-NMR (ppm): 163.70 (O–C=O), 197.00 (–C=O), 154.22 (¹C), 132.95 (=CH₂), 127.49 (=CH), 129.78 (³C and ⁵C), 121.57 (²C and ⁶C), 134.74 (⁴C), 26.30 (CH₃)



Scheme 2 Synthesis of TBPA and APA.

Suspension Copolymerization

Copolymerization of GMA, PhMA, TBPA, and APA was carried out in aqueous suspension medium. In a representative experiment, a four-necked reaction kettle fitted with a stirrer, nitrogen inlet, water condenser, and an addition funnel, containing 250 g of distilled water with 1.5 g of polyvinylpyrrolidone and very small amounts of calcium sulfate and phosphate. The kettle was kept in a thermostatic water bath, and the temperature was maintained at 80 ± 1°C. Twenty-six grams of PhMA, 3 g of DVB, and

0.68 g of benzoyl peroxide were dissolved in 30 mL of chlorobenzene (diluent), and the monomer mixture was thoroughly flushed with nitrogen and was added to the vessel through the addition funnel while stirring the aqueous solution with a Teflon blade stirrer at 600 rpm. The polymerization was allowed to proceed for 12 h. After that, the suspension mixture was taken into water and stirred with a glass rod for few minutes, allowed to settle, and then decanted. The beads were washed with distilled water,

acetone, ethyl acetate, chloroform, dioxan, and dichloromethane to remove stabilizers, unreacted monomer, and soluble polymers. Finally, the beaded copolymers were filtered through a sintered glass funnel by applying suction and were dried in a vacuum oven overnight at room temperature.

Measurements

The FTIR spectra of the copolymer samples were run on a Nicolet-20 DXB using a KBr pellet. The ^{13}C -CP/MAS-NMR was conducted on Bruker 300 MSL CP/MAS instrument operating at 75.47 MHz at the Indian Institute of Science, Bangalore. The spectra were run with fine powders of glassy beads at room temperature, and the Kel-F rotor was employed for MAS. The samples were rotated with a spectral width of 25,000 Hz, the CP time was 22 ms, and the number of scans was in the range of 150–750. Each sample was rotated with two different spin rates, and by comparing the resultant spectra, the spinning side bands were eliminated.

Optical photographs of the copolymer beads were taken using a Nikon phase-contrast microscope. The unsieved samples were spread on glass slide, and photographs were taken with 100 \times magnification.

Scanning electron micrographs of the copolymer beads were taken on a Jeol-JSM 35 CF instrument. Specimens were prepared by placing the dry powder on a round cover glass that was mounted with double-faced adhesive tape on a stud and then coated with a thin layer of gold under vacuum to observe the size and shape of the bead copolymer.

Perkin-Elmer model 3700 with a TGS-7 computer was used to run thermograms. Experiments were carried out under nitrogen atmosphere at the flow rate of 200 mL/min, and the rate of heating was maintained at 20°C/min.

Solvent imbibition of the cross-linked copolymer beads was carried out using a centrifuge method. A sample of the resin (1 g) was introduced into a glass disc of porosity no. 3. The sample in the glass tube was weighed, and then 15 mL of solvent was added to the tube, which was closed with a rubber cerum cap to prevent solvent evaporation. It was kept at room temperature for 1 h to allow the solvent to imbibe into the bead. Then, the sample was centrifuged at 500 rpm for 5 min using a laboratory centrifuge. After removing the excess solvent, the filter tube was weighed. By using this procedure, the swelling of the copolymer beads in chloroform, dimethyl formamide, dioxan, and ethyl acetate was carried out. The amount of the solvent imbibed into the copolymer beads was expressed as gram/gram.

RESULTS AND DISCUSSION

Cross-linked copolymer beads of GMA, TBPA, APA, and PhMA with DVB were prepared in aqueous suspension medium at $80 \pm 1^\circ\text{C}$ (Table I). Suspension was maintained by mechanical stirring with a Teflon-bladed stirrer and with the help of suspension stabilizers. The resulting beaded copolymers were dried in vacuum and were sieved with mechanical sieves. Generally, the range obtained was 100–500 mesh (BSS). The copolymer-beaded supports were characterized with FTIR, ^{13}C -CP/MAS-NMR, optical microscopy, SEM, particle-size analyzer, thermogravimetry, and solvent imbibition studies.

Characterization

An attempt was made to identify the incorporation of monomers in the cross-linked copolymer. The

Table I Suspension Copolymerization of PhMA and GMA with DVB

Copolymer	Monomer (g)	Cross-Linking		Diluent ^b (g)	Initiator ^c (g)	Water ^d (g)	Stabilizer (g)	Stirring Rate (rpm)
		Agent ^a (g)						
GMA-DVB	30	2.80		39	0.90	270	1.60	600
PhMA-DVB	30	3.00		33	0.60	240	1.45	600
TBPA-DVB	30	8.00		44	0.76	305	1.83	600
APA-DVB	30	4.00		100	0.68	280	1.60	600

^a DVB.

^b Chlorobenzene was used as diluent.

^c Benzoyl peroxide was used as free radical initiator.

^d Polyvinylpyrrolidone (MW 360,000)

characteristic absorptions and chemical shifts of the monomer involved in the copolymerization were studied by infrared and ^{13}C -NMR (solid) spectroscopy.

Infrared Spectroscopy

Infrared spectroscopy is the most widely employed technique not only for following the chemical reactions carried out on cross-linked polymers but also for structure identification.¹⁶ Letsinger and Kalus¹⁷ demonstrated the quantitative use of this technique for determining the extent of hydrogen bonding. Figure 1 shows the FTIR spectra of GMA-DVB cross-linked copolymer. The spectra show the bands at 2990 and 2928 cm^{-1} due to methylene and methyl-stretching vibrations. The appearance of a very sharp band at 1730 cm^{-1} is due to the ester carbonyl of the GMA unit. The appearance of a bending vibration at 907 cm^{-1} not only explains the incorporation of the GMA unit, but also shows the intactness of the epoxy group in the copolymerization process. The FTIR spectra of the PhMA-DVB copolymer is shown in Figure 2. The $-\text{C}-\text{H}$ stretch-

ing vibrations of aromatic, backbone methylene, and methyl groups of PhMA were observed at 3024, 2968, 2925, and 2832 cm^{-1} , respectively. The ester carbonyl gave a sharp band at 1747 cm^{-1} , and the aromatic skeletal absorption was observed at 1591 cm^{-1} . Because of the monosubstituted pattern of the PhMA, bending vibrations were seen at both 688 and 743 cm^{-1} . The FTIR spectra of the APA-DVB copolymer are shown in Figure 3. The $-\text{C}-\text{H}$ stretching vibrations of aromatic, methyl, backbone methylene, and methine groups of the APA unit appeared at 3010, 2944, 2905, and 2831 cm^{-1} , respectively. The sharp bands at 1756 and 1683 cm^{-1} are due to the ester carbonyl and the keto carbonyl groups of the APA unit, respectively. The aromatic $-\text{C}=\text{C}-$ vibrations of acetylphenyl ring appeared at 1597 cm^{-1} .

^{13}C -CP/MAS-NMR spectroscopy

In recent years, high-resolution solid-state NMR (^{13}C -CP/MAS) has been found to have many applications in the characterization of polymers in the solid state.¹⁸⁻²² Ford et al.^{23,24} recently demonstrated

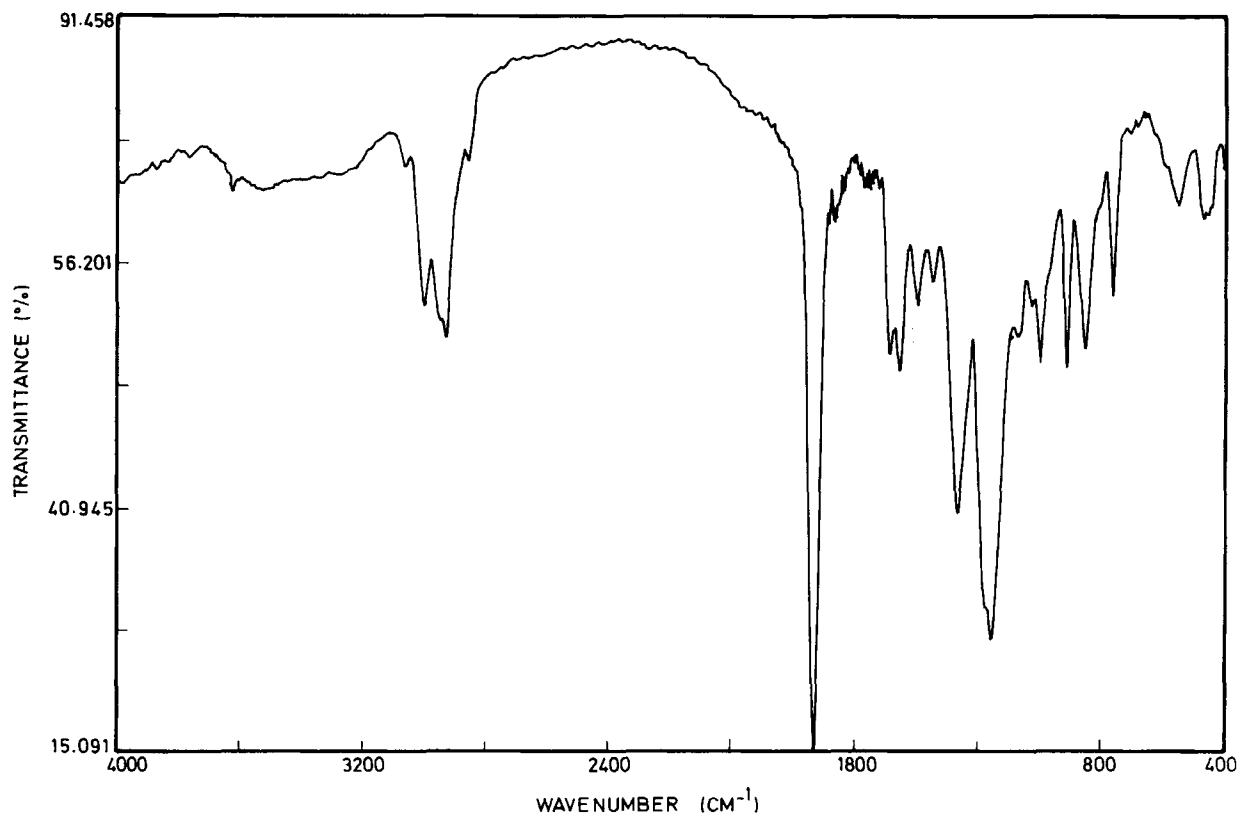


Figure 1 FTIR spectra of GMA-DVB copolymer.

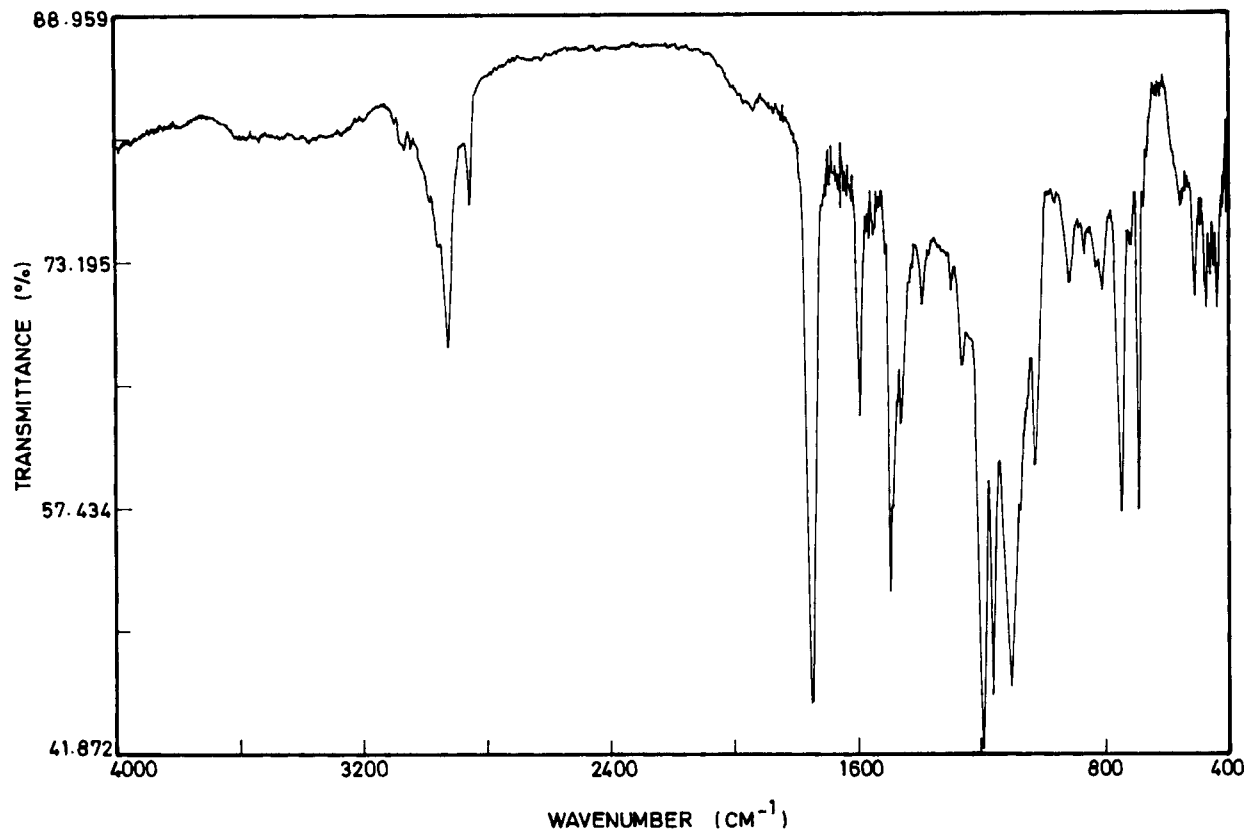


Figure 2 FTIR spectra of PhMA-DVB copolymer.

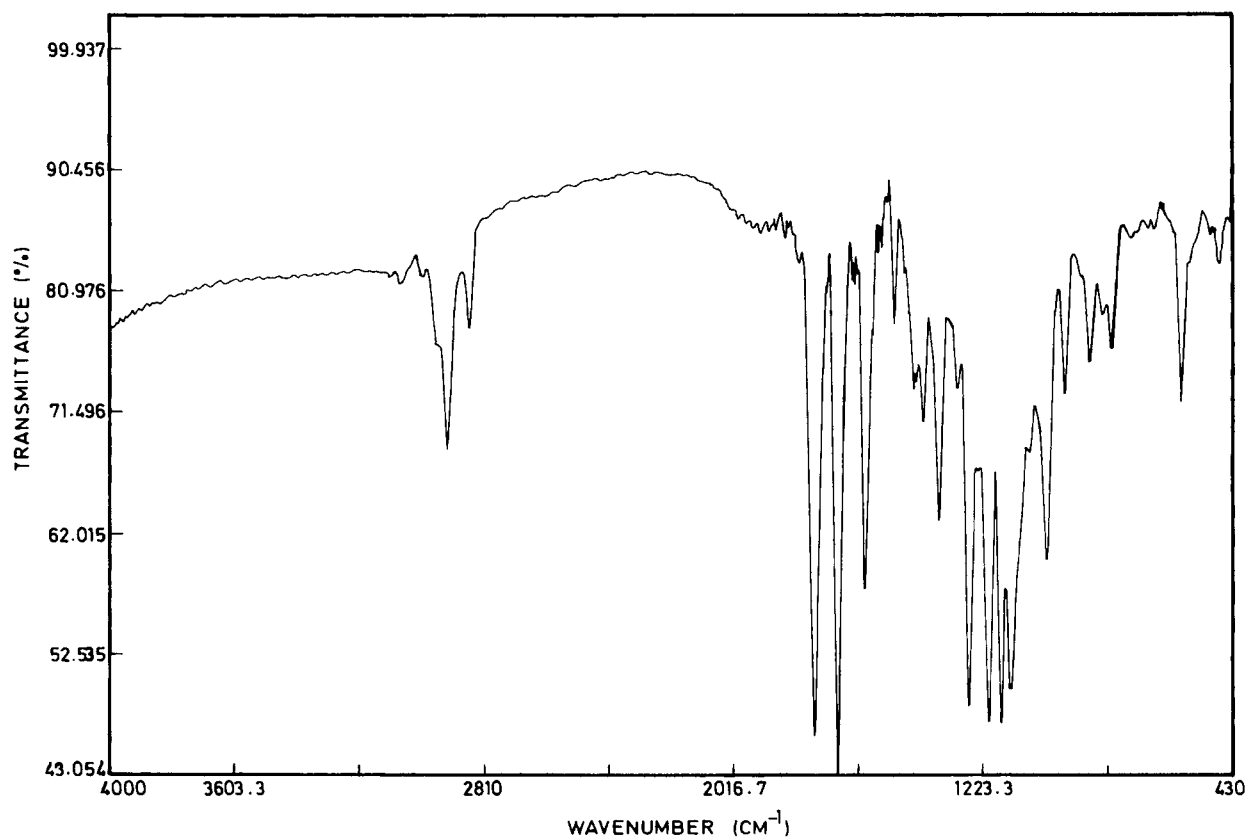


Figure 3 FTIR spectra of APA-DVB copolymer.

the potential use of CP/MAS for quantitative evaluation of unreacted double bonds in styrene cross-linked with DVB copolymers. In the present study, the CP/MAS-NMR spectra of the cross-linked copolymers are compared with their soluble homopolymer analogs and are discussed. Figure 4(B) shows the CP/MAS-NMR of GMA cross-linked copolymer. The methyl group of the GMA unit appeared at 14.55 ppm as a broad unresolved peak in cross-linked systems, whereas in the homopolymer, it appeared as a sharp peak at 16.97–18.97 ppm [Fig. 4(A)]. The backbone $-\text{CH}_2$ group of GMA gave a sharp line at 43.27 ppm for the copolymer and at 44.59–45.10 ppm for the homopolymer. The backbone tertiary carbon appeared as a shoulder peak in the cross-linked system at 48.79 ppm as a sharp line. The $-\text{OCH}_2$ appeared as a sharp line at 65.86 ppm for the homopolymer and as a broad peak at 65.04 ppm for the copolymer. The epoxy carbons appeared as a small peak for the homopolymer at 52.29 ppm and as a shoulder peak for the cross-linked copolymer at 54.00 ppm.

The ^{13}C solid and solution NMR of homo- and copolymers of PhMA–DVB are shown in Figures 5 (A) and (B). In both systems, the splitting pattern is the same. The α -methyl group of copolymer appeared as a broad peak at 17.40–20.65, and in homopolymer, as three sharp lines at 16.00–19.93 ppm. The backbone $-\text{CH}_2$ of both systems were seen at 45.61 and at 44.31 as a high intense peak. The tertiary carbon of the homo- and cross-linked copolymers appeared at 53.80 and 54.00 ppm, respectively. The $-\text{O}^{13}\text{C}$ of the phenyl ring of the homopolymer gave a sharp line at 150.42 ppm, and that of the copolymer gave a broad peak at 149.33 ppm. The remaining carbons of the phenyl ring gave well-resolved lines in the homopolymer at 129.20 (^3C and ^5C), 120.79 (^2C and ^6C), and 125.66 (^4C) ppm. A similar type of spectrum was observed in the cross-linked system, but the peaks are not well resolved. The $^2\text{C}/^6\text{C}$ was seen at 119.55 and the $^3\text{C}/^5\text{C}$ at 127.79 as broad peaks in the copolymer. The ^4C of cross-linked system appeared as a shoulder at 125.00 ppm.

Optical Microscopy

The optical micrograph of the unsieved copolymer beads is shown in Figure 6. Based on the visual appearance, beads were classified as (i) transparent, (ii) translucent, and (iii) opaque. Albright²⁵ explained the visual appearance of polymer beads with respect to the cluster formation of microgels. The

optical photograph of the PhMA–DVB copolymer shows the spherical nature of the beads. It can be seen from the figure that different sizes of the particles are formed in the course of polymerization. The small-size particles are seen in greater number, as the stirring rate employed was 600 rpm during the polymerization. The translucent nature of the beads obtained in the present experimental conditions demonstrates *that* the diluent employed in the synthesis of copolymer is a good solvent. Albright explained the translucent nature of the beads, which are made up of smaller clusters.

Scanning Electron Microscopy

Scanning electron micrographs of the typical copolymer beads are shown in Figure 7. The bead size, shape, and surface can be observed from these micrographs. Scanning electron microscopy was used for the determination of porosity characteristics of ion-exchange resins, and the results were compared with the direct measurement methods like BET adsorption and mercury porosimetry.²⁶ Guyot et al.^{27–29} extensively used the SEM technique for studying the morphological features and the mechanism of formation of the beads. The micrographs show that all particles are perfectly spherical and almost uniform in their sizes and that the surface is even and smooth. The sizes of the particles were calculated from the micrographs, and the values are in agreement with the values determined by particle-size analysis. The even and smooth surface of the particles also demonstrates that the monomer diluent is a good solvent for the resulting support and the beads are microporous in nature, which was also confirmed by the measurement of the surface area using the BET method.

Particle-Size Analysis

The successful reproducibility of the suspension copolymerization is visually tested by measuring the average particle size of the beads.³⁰ Among the parameters that control the particle size in suspension polymerization are the nature and the amount of the stabilizer, geometry of the vessel, the stirrer, and the stirring rate.³¹ The particle-size distribution of typical copolymer beads was determined by using a Malvern particle-size analyzer. By keeping the parameters such as water-to-monomer ratio, geometry of the vessel, and stirring rate constant, the formation of the particles with almost uniform size was observed. The particle-size distribution curves for

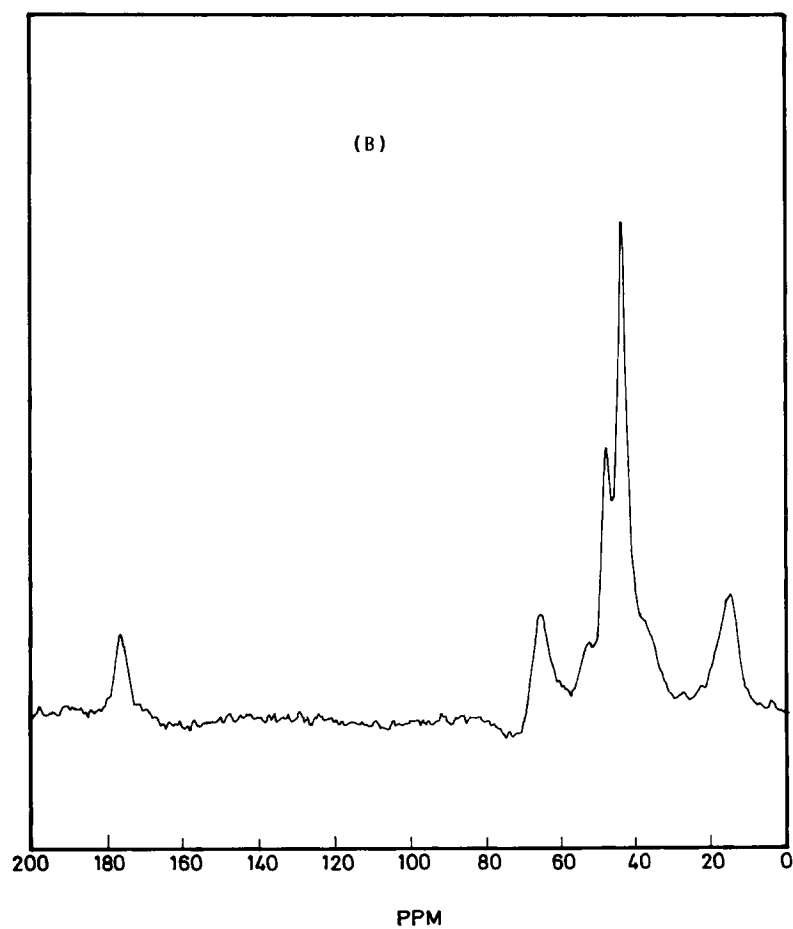
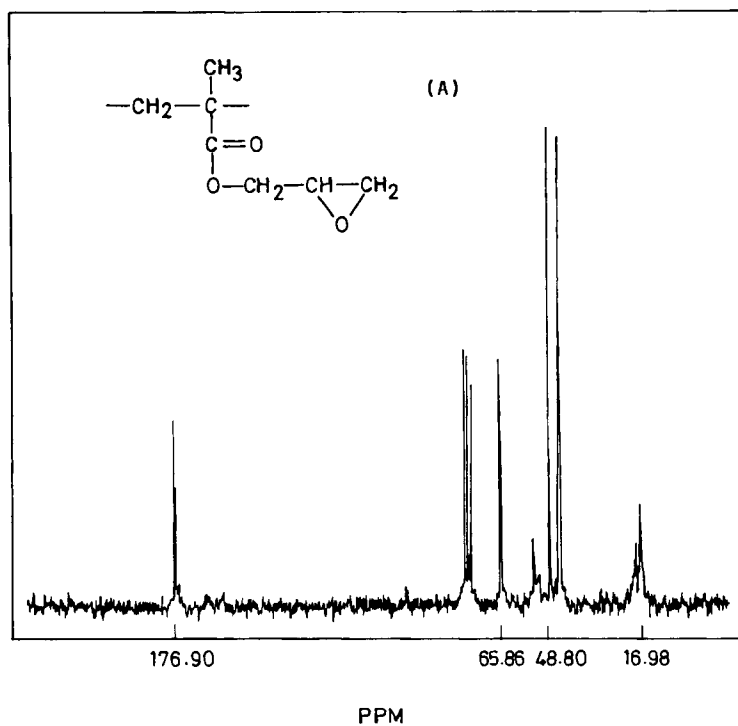


Figure 4 (A) Proton decoupled ^{13}C -NMR spectra of poly(GMA), (B) ^{13}C -CP/MAS-NMR spectra of cross-linked GMA copolymer.

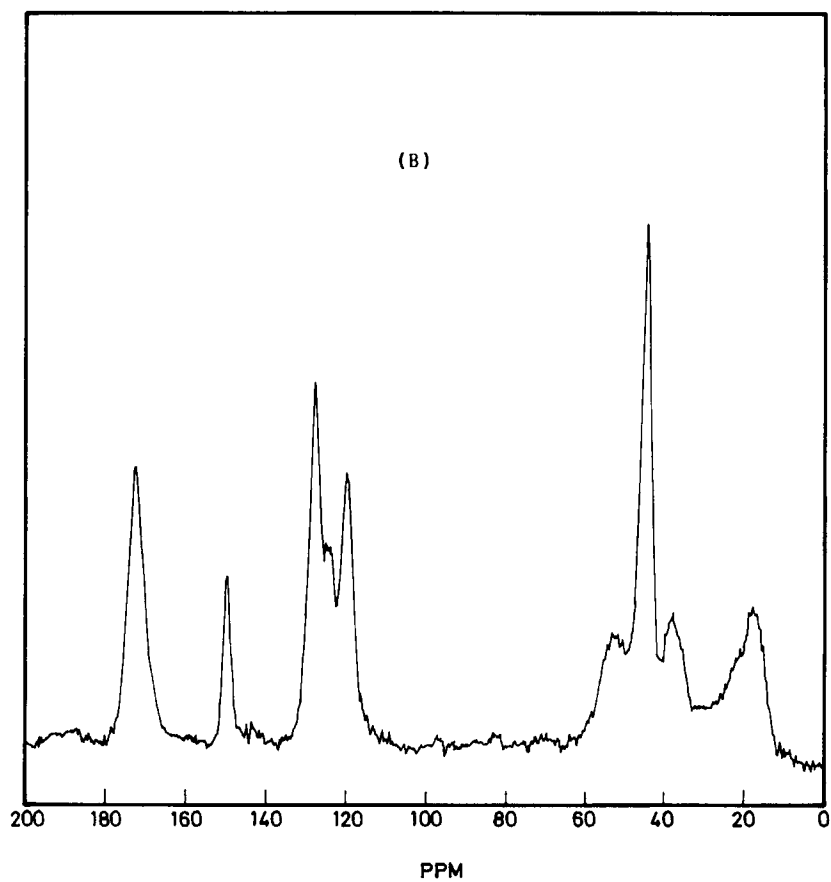
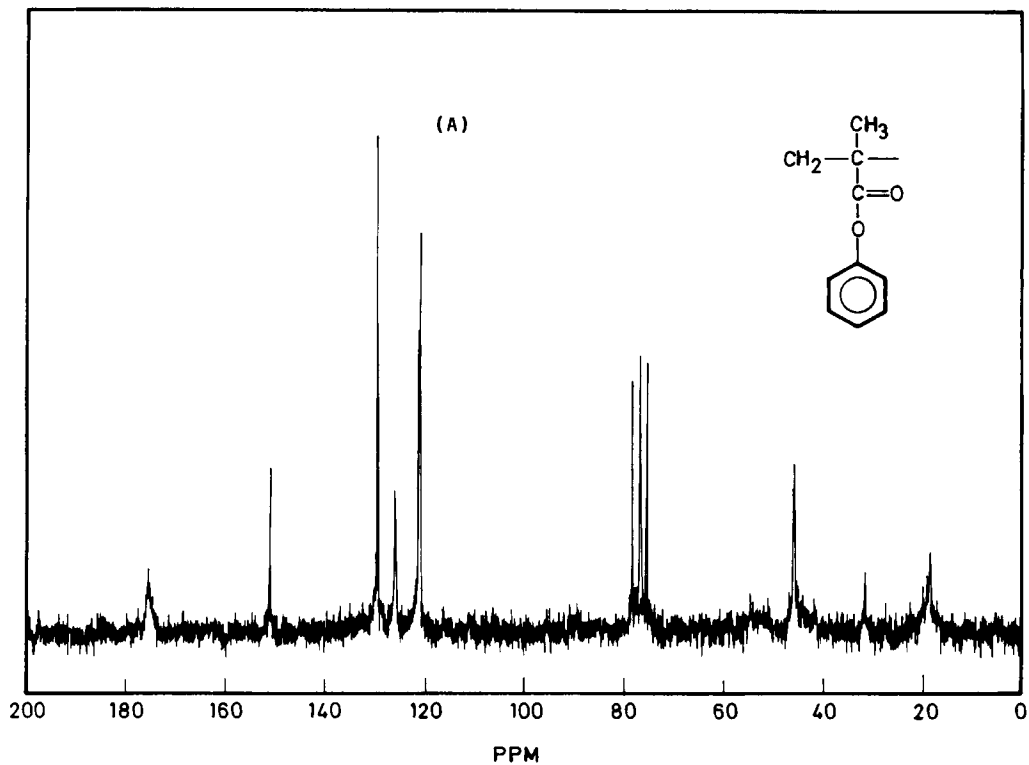


Figure 5 (A) Proton-decoupled ¹³C-NMR spectra of poly(PhMA), (B) ¹³C-CP/MAS-NMR spectra of cross-linked PhMA copolymer.

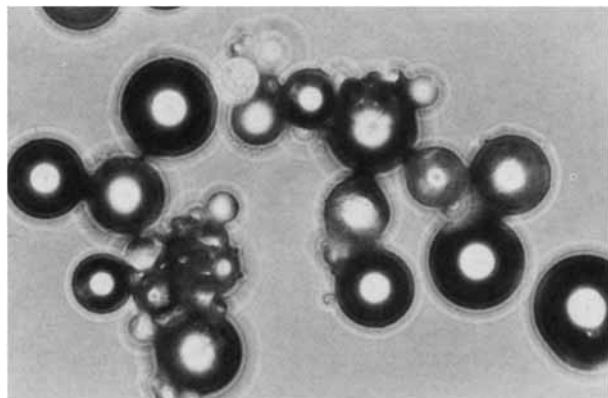


Figure 6 Optical photograph of PhMA cross-linked with DVB (4%) copolymer $\times 100$.

GMA and PhMA cross-linked with DVB are shown in Figures 8 and 9. The distribution curve of the GMA-DVB copolymer beads is narrow, and the maximum number of particles are seen around $61.6 \mu\text{m}$. The average particle size of the beads is $66.2 \mu\text{m}$. Similar conditions were employed for synthesizing the PhMA-co-DVB polymer beads. The distribution curve of these copolymer beads is symmetrical with a small peak at $39.5 \mu\text{m}$. The maximum number of particles is seen around $71.4 \mu\text{m}$, whereas the average bead diameter is $68.9 \mu\text{m}$, which is almost equal to the average particle size of the GMA-co-DVB system.

Thermogravimetric Analysis

The thermogravimetric curves of the cross-linked copolymers are shown in Figure 10. The decomposition temperature (DT) and the energy of activation involved in the degradation process were determined by the Coats and Redfern³² and Doyle methods.³³ The initial decomposition temperature (T_i) of the GMA-DVB copolymer was noted at 244.35°C , whereas final decomposition temperature (T_f) was 477.43°C . The 30, 50, and 70% weight losses were observed at 333.20 , 353.30 , and 379.90°C , respectively. The activation energy of the degradation of the copolymer was 16.2 K cal/mol . In the case of the PhMA-DVB copolymer, the onset of decomposition was observed at 233.68°C and T_f at 434.72°C . The degradation of the copolymer occurred in a single stage having E_a as 29.11 K cal/mol . The 50% of the copolymer was degraded at 354.62°C , whereas 70% weight loss was observed at 371.92°C . The thermogram of the TBPA-DVB copolymer shows the onset of the decomposition tem-

perature at 283.49°C and T_f at 424.94°C , and the degradation occurred in a single stage. The 50% weight loss was observed at 394.53°C , and the corresponding activation energy of the degraded co-

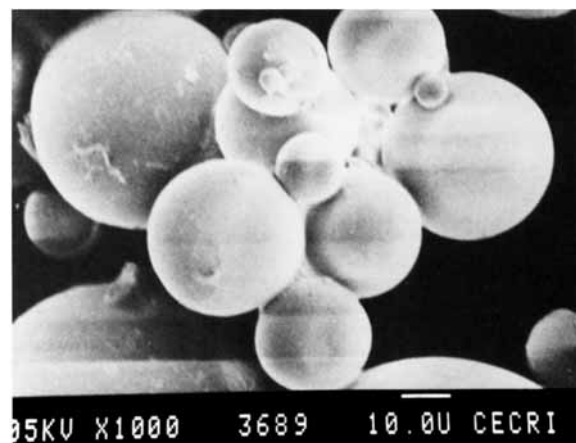
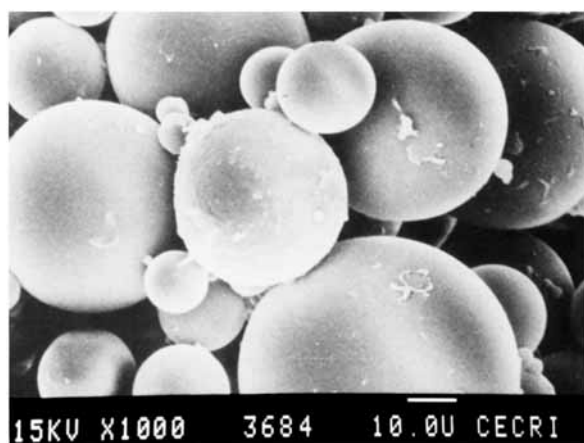
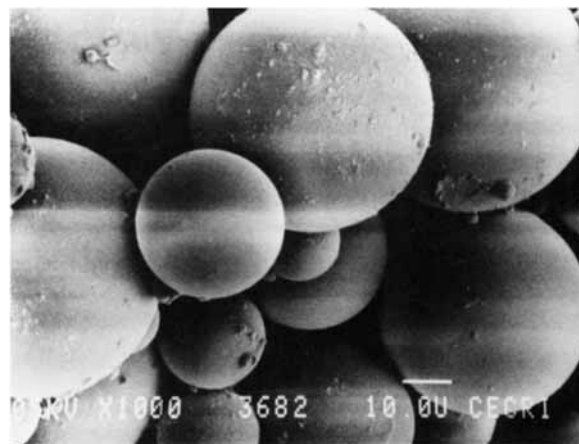


Figure 7 Scanning electron micrographs of cross-linked copolymer beads: (A) GMA-DVB (3682); (B) PhMA-DVB (3684); (C) TBPA-DVB (3689).

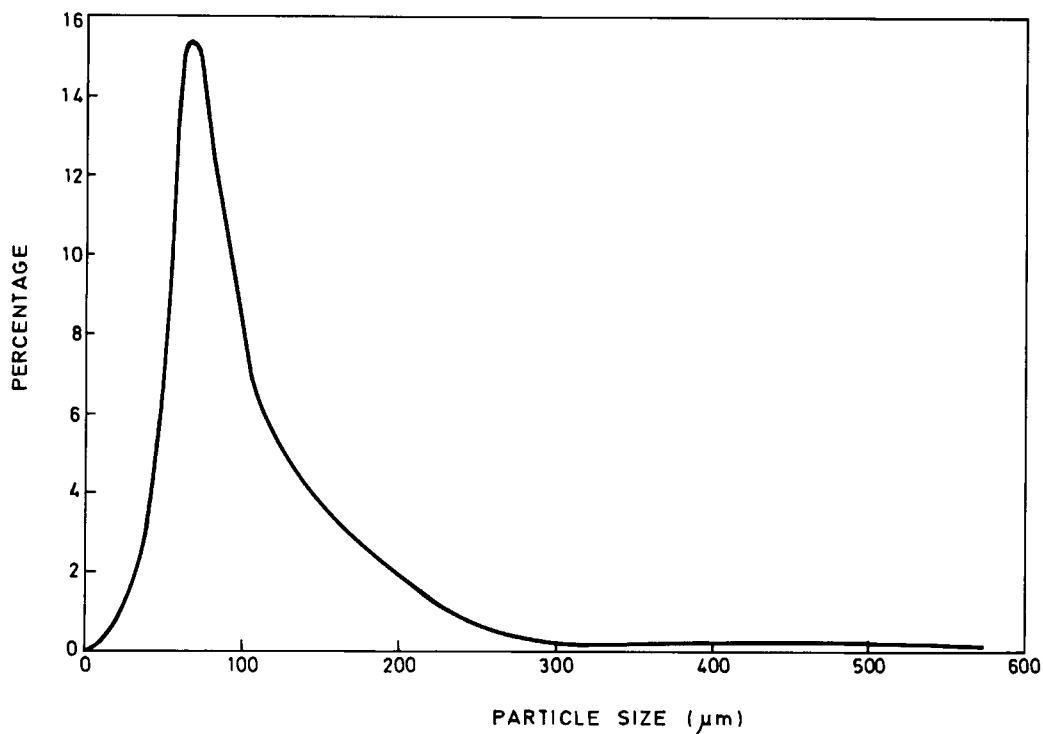


Figure 8 Particle-size distribution curve of GMA cross-linked with DVB copolymer beads.

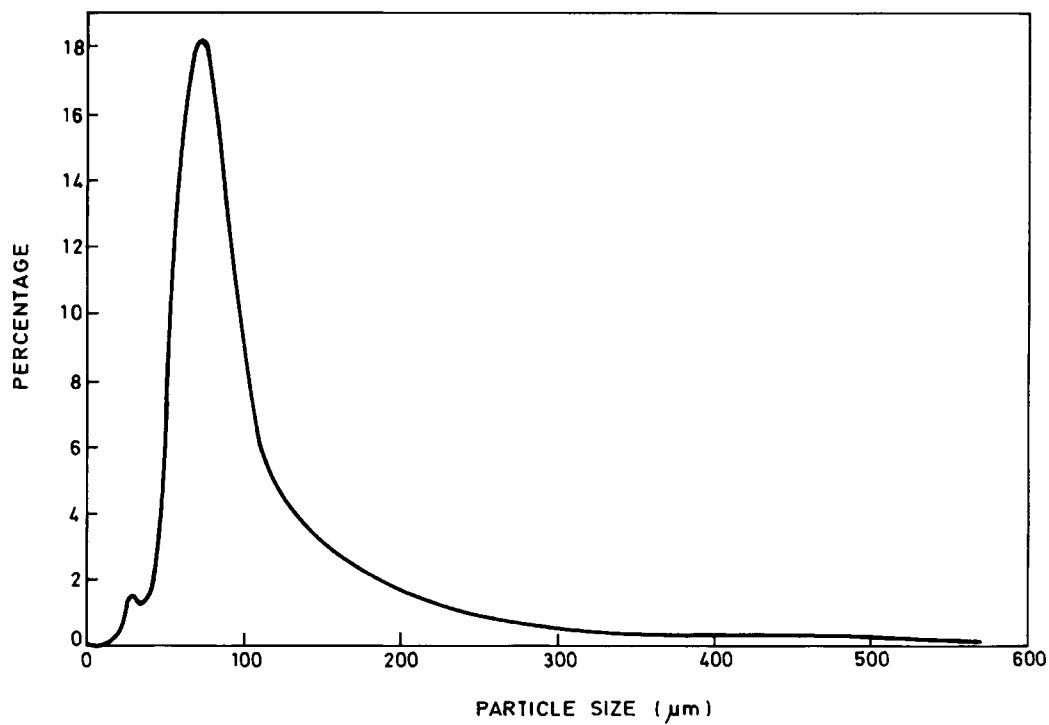


Figure 9 Particle-size distribution curve of PhMA cross-linked with DVB copolymer beads.

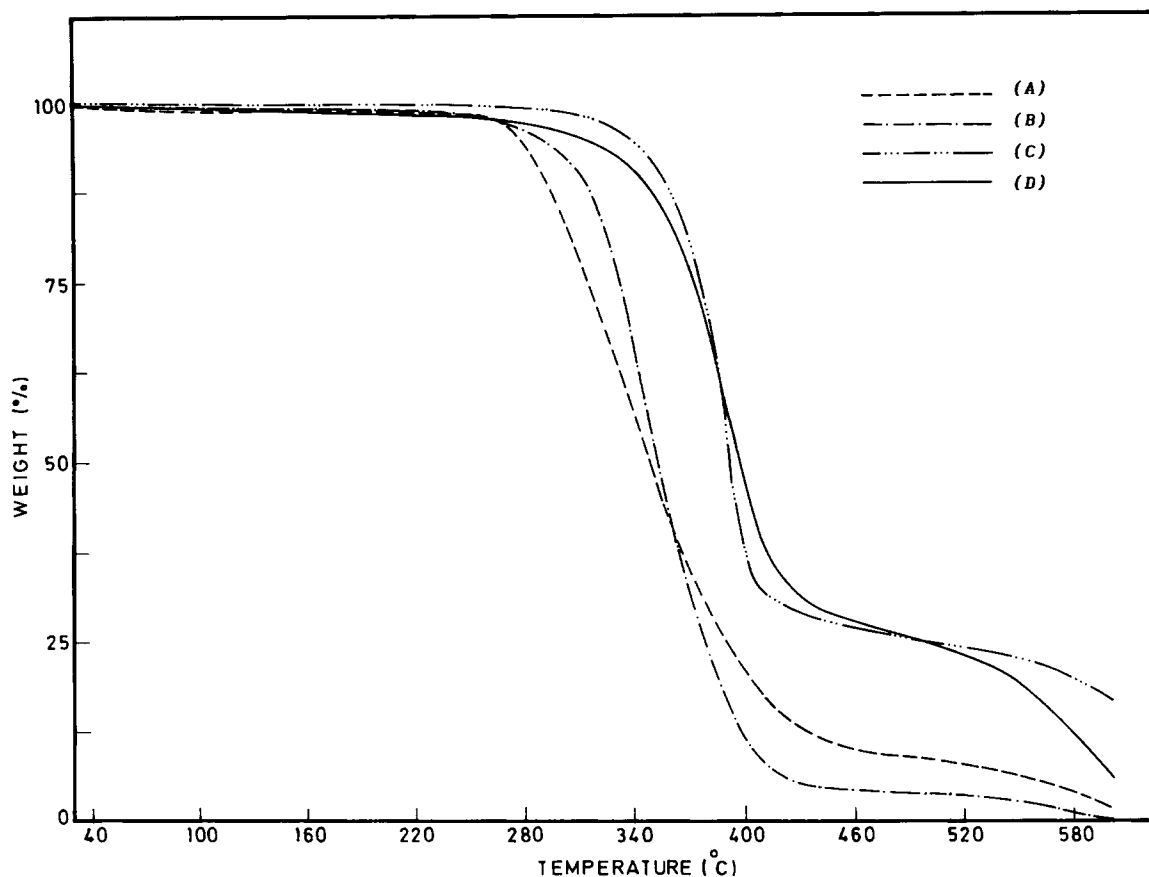


Figure 10 TGA thermograms of (A) GMA-DVB, (B) PhMA-DVB, (C) TBPA-DVB, and (D) APA-DVB copolymers.

polymer was 33.4 K cal/mol. The APA-co-DVB polymer decomposed in two stages. The first-stage decomposition was observed from 345.32 to 400.00°C, and the respective weight loss involved in this stage was 50% and the E_a of the process was

27.7 K cal/mol. The second-stage degradation of the copolymer was observed from 410.64 to 575.86°C with a weight loss of 40%, and the energy of activation was 5.6 K cal/mol. The comparison of activation energy values shows that the thermal stability

Table II Thermal Decomposition and Activation Energies of Cross-Linked Copolymers

Copolymer	Decomposition Temperature (DT) (°C)			Stages of Decomposition	Temperature Range (°C)	Coefficient of Correlation (r) and Energy of Activation (E_a)			
						CR		Doyle	
	30%	50%	70%			r	E_a (k cal/mol)	r	E_a (k cal/mol)
GMA-DVB	333.20	353.30	379.90	Single	293.30-402.66	0.98	13.7	0.99	16.2
PhMA-DVB	342.66	354.62	371.92	Single	317.24-385.22	0.98	23.8	0.99	29.1
TBPA-DVB	386.55	394.53	405.66	Single	345.32-405.66	0.96	30.9	0.97	33.4
APA-DVB	382.56	400.00	438.57	Stage 1	345.32-400.00	0.99	25.2	0.99	27.7
				Stage 2	400.00-575.86	0.97	3.6	0.97	5.6

Table III Swelling Studies

Copolymer	Chloro- form	Solvent (g)		Ethyl Acetate
		DMF	Dioxan	
GMA-DVB	2.404	1.976	1.992	1.602
PhMA-DVB	8.590	5.359	5.201	4.259
TBPA-DVB	2.160	2.250	1.834	1.382
APA-DVB	6.006	3.158	3.936	1.470

for the copolymers were TBPA-DVB > APA-DVB > PhMA-DVB > GMA-DVB (Table II).

Swelling Studies

The accessibility of functional groups present in the functionalized polymer supports for chemical modifications is an important parameter for deciding its utility.³⁴ Among the factors that influence the accessibility of functional groups in cross-linked copolymers is the phenomenon of swelling. Generally, the swelling properties of the polymer support depends on two factors: (i) cross-link ratio and (ii) chemical nature of the polymer support employed.³⁵ It is known from the literature that microporous resins possess porosity only in a swollen condition because of "swelling," also known as gel porosity.³ Since the resins under study are microporous in nature, the swelling studies are important for identifying the good solvent in order to select the suitable reaction medium for performing reactions on polymer supports.³⁶ To investigate the swelling behavior of these copolymer supports, solvent imbibition studies were undertaken. The samples were allowed to swell for 1 h in dichloromethane, dimethylformamide, dioxan, and ethyl acetate, which are common solvents for solid-phase peptide synthesis.³⁷ The excess solvent was removed by the centrifugal method,³⁸ and the results were expressed as the weight of the solvent absorbed per weight of the dry resin. The swelling of the resins in dichloromethane is comparatively higher than that in the other solvents studied in this work, thereby showing the hydrophobicity of the supports. Among the copolymers studied, the PhMA-DVB-based resins have a comparatively higher swollen capacity in all the solvents (Table III).

SUMMARY

Novel cross-linked copolymers based on phenyl acrylates and divinyl benzene were synthesized suc-

cessfully by employing an aqueous suspension copolymerization technique. The beaded copolymers thus obtained were characterized using different instrumental techniques such as FTIR and high-resolution solid-state ¹³C-NMR for identifying the incorporation of the acrylate unit in the copolymer. The optical and scanning electron microscopic techniques were used for studying the size, shape, and morphology of the beaded copolymers. The average particle size of the copolymer beads was determined by a particle-size analyzer, and the values obtained for GMA-DVB and PhMA-DVB copolymer systems show the successful reproducibility of the suspension polymerization technique. Thermogravimetric studies showed that the TBPA-DVB copolymer is more stable thermally than other copolymer systems. The swelling index indicates that the copolymer supports studied in the present investigation are basically hydrophobic in nature.

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