Synthesis and Characterization of Phenyl Acrylates Cross-Linked to Hydroquinone Diacrylate

T. Narasimhaswamy, S. C. Sumathi, and B. S. R. Reddy*

Central Leather Research Institute, Adyar, Madras-600 020, India

Received April 29, 1991; Revised Manuscript Received February 11, 1992

ABSTRACT: Styrene (Sty), glycidyl methacrylate (GMA), phenyl methacrylate (PhMA), and 2,4,6-tribromo- (TBPA) and 4-acetylphenyl (APA) acrylates are copolymerized with hydroquinone diacrylate (HyDA; 4 mol %) by a free-radical aqueous suspension polymerization technique employing chlorobenzene as the monomer diluent at 80 °C. The resulting bead copolymers are characterized with various instrumental techniques. FT-IR and high-resolution solid-state ^{13}C NMR (CP-MAS) are used for identifying the monomeric units in the copolymers. The particle size distribution and the average particle size of the typical copolymer are determined with a Malvern particle size analyzer. Optical (OM) and scanning electron (SEM) microscopic techniques are employed to observe shape, size, and morphological features of the cross-linked bead copolymers. The swelling capacities of the copolymers are measured in various solvents. The possible applications of these resins in polymer support chemistry are discussed.

Introduction

The introduction of solid-phase peptide synthesis (SPPS) by Merrifield not only revolutionalized the chemical synthesis of peptides, for which it was meant, but also generated much interest in other areas of chemistry.[1–10] The Merrifield resin is basically a nonpolar, hydrophobic styrene cross-linked with divinylbenzene copolymer, with a reactive functional group.[1] Most of the polymers used in polymer-supported reactions are styrene- and divinylbenzene-based copolymers, because of their commercial availability and ease of functionalization.[11] In order to overcome some of the problems encountered with styrene-based resins, Sheppard introduced polar, hydrophilic acrylamide-based copolymers as basic supports in SPPS.[12] Although copolymers based on GMA (glycidyl methacrylate)–EDMA (ethylene dimethacrylate) have found applications in chromatography, in immobilization of enzymes, in biomolecules, in catalysis, etc.,[13–17] their use in SPPS is not known.

Generally polymer supports with a reactive functionality are prepared either by prefunctionalization or postfunctionalization techniques.[18] The former technique involves the synthesis of a functional monomer and successful copolymerization with a cross-linking agent, whereas the latter method concentrates on the synthesis of cross-linked copolymer followed by functionalization. The monomer instability and its copolymerization ability are noted problems encountered in the prefunctionalization techniques, whereas unwanted side reactions like further cross-linking are disadvantages in the case of postfunctionalization. Yet another technique of introducing a reactive functionality is to synthesize a prepolymer which consists of activated acrylates and to modify it with various reagents to get the desired polymer.[19–21]

Although the cross-linked polymers used as basic supports are prepared by bulk, solution, and emulsion polymerization techniques, suspension polymerization is a widely adopted method.[22,23] This technique facilitates the synthesis of the polymer in a spherical particulate form, thereby allowing its use in polymer-supported reactions where filtration with conventional apparatus is routine. The aim of the present investigation is to develop polymer supports based on phenyl acrylates for their use in SPPS and other related areas. The basic criteria required for an ideal support for SPPS are (i) the polymer support has to be morphologically microporous and should have compatibility with solvents such as chloroform, dimethylformamide, dioxane, and ethyl acetate, which are normally used in SPPS, (ii) the polymer should possess a reactive functional group for attachment of amino acids or it should contain functionalizable chemical units such as a phenyl ring, and (iii) the polymer support should possess chemical stability toward the reagents which are routinely employed in SPPS. This paper discusses the suspension copolymerization of phenyl acrylates with hydroquinone diacrylate and their characterization with different instrumental techniques.

Experimental Section

Materials. Phosphoric acid, anhydrous phosphorus pentoxide, 2-butanone, triethylamine, chloroform, chlorobenzene, methacrylic acid, benzoyl chloride, 2,4,6-tribromophenol, and 4-hydroxyacetophenone (Sisco-Chem) were used as received. Benzoyl peroxide (Fluka) was purified by recrystallization from a chloroform solution to methanol. Styrene (Sty) and glycidyl methacrylate (Fluka) were distilled under vacuum before use. Poly(vinyl alcohol) (MW 180 000; 88% hydrolyzed) was used as received.

Synthesis of the Monomers. Phenyl methacrylate (PhMA) was prepared by reacting methacrylic acid with phenol using poly(phosphoric acid) as the dehydrating agent by a reported procedure.[24] Acryloyl chloride was prepared by following the procedure of Stampel et al.[25] 2,4,6-Tribromophenyl acrylate (TBPA) and 4-acetylphenyl acrylate (APA) were synthesized by adding the acryloyl chloride (0.125 mol) to the corresponding phenols (0.125 mol) in the presence of triethylamine (TEA; 0.125 mol) at 0 °C in chloroform. The unreacted phenols were removed by washing with 5% sodium hydroxide solution. The solvent from the resulting solutions was removed by rotary evaporation. The crude solids thus obtained were purified by recrystallization. TBPA: mp = 75–76 °C. APA: mp = 72–74 °C.

IR and ^{1}H and ^{13}C NMR spectral data of the monomers are consistent with their structures.

The same procedure was adopted for synthesizing hydroquinone diacrylate. Thus, in a three-neck round-bottomed flask, equipped with a stirrer, dropping funnel, and thermometer, hydroquinone (0.125 mol) in 150 mL of chloroform with triethylamine (0.125 mol) was placed. Acryloyl chloride (0.25 mol) in 75 mL of chloroform was slowly added while maintaining the temperature at 0–5 °C using a freezing mixture. The reaction mixture was washed with distilled water and 5% aqueous sodium hydroxide to remove the unreacted hydroquinone. Finally, the solvent was removed with rotary evaporation, and the solid thus obtained was recrystallized from hexane: mp = 87–88 °C. IR (cm^{-1}): 3020, 2990, 1740, 1650, 1640, 1560, 1300, 1145, 840. ^{1}H

Table I
Suspension Copolymerization of Styrene, Glycidyl Methacrylate, and Phenyl Acrylates with Hydroquinone Diacrylate

copolymer	monomer (g)	cross-linking agent (g)	diluent[a] (g)	initiator[b] (g)	water (g)	stabilizer[c] (g)
Sty-HyDA	30	0.60	27	0.62	250	1.50
GMA-HyDA	30	0.80	35	0.62	250	1.50
PhMA-HyDA	30	0.90	39	0.62	250	1.50
TBPA-HyDA	30	2.20	128	0.66	250	1.62
APA-HyDA	30	1.10	139	0.63	250	1.50

[a] Chlorobenzene is used as the diluent. [b] Benzoyl peroxide is employed as an initiator. [c] Poly(vinyl alcohol) with 0.1 g each of $Ca_3(PO_4)_2$ and $CaSO_4$.

NMR: δ 7.24 (4 H), 6.70–6.30 (4 H), 6.15–5.90 (2 H). ^{13}C NMR: δ 164.19 (C=O), 147.98 (^1C & ^4C), 132.47 (=CH_2), 127.77 (=CH), 122.27 (^2C, ^3C, ^5C, and ^6C).

Copolymerization. Suspension copolymerizations of various monomers, viz., styrene, glycidyl methacrylate, phenyl methacrylate, 2,4,6-tribromophenyl acrylate, and 4-acetylphenyl acrylate with hydroquinone diacrylate (4 mol %) were carried out at 80 °C. In a typical experiment, 250 mL of distilled water containing 1.5 g of poly(vinyl alcohol) and 0.1 g each of calcium sulfate and phosphate as suspension stabilizers was placed in a four-necked reaction kettle equipped with a water condenser, Teflon-blade stirrer, nitrogen inlet, and dropping funnel. A total of 30 g of 4-acetylphenyl acrylate, 1.1 g of hydroquinone diacrylate, and 0.63 g of benzoyl peroxide were dissolved in 140 mL of chlorobenzene, and the solution was flushed with nitrogen gas for 5 min. Then, the chlorobenzene solution was added from a dropping funnel into the reaction kettle while stirring the aqueous solution at 300 rpm. A slow stream of nitrogen was bubbled into the reaction mixture. The reaction mixture was maintained at 80 °C using a thermostated water bath, and the reaction was allowed to continue for 10 h. After that the solvent-embedded beads were washed with hot distilled water, acetone, chloroform, dioxane, and ethyl acetate sequentially three times. The beads were filtered through a sintered-glass funnel by applying suction. Finally the copolymer beads were dried in vacuo at 40 °C for 10 h. A similar procedure was adopted for preparing the other copolymer beads.

Instruments. FT-IR spectra of the copolymer samples were recorded on a Nicolet 20 DXB using KBr pellets. The solution NMR spectra of the monomers and homopolymers were run on a Bruker 90CXP operating at 22.63 MHz (^{13}C) in $CDCl_3$ solvent with TMS as an internal standard. The protons were decoupled from ^{13}C nuclei by broad-band irradiation. The ^{13}C CP-MAS NMR spectra of the cross-linked copolymers were recorded on a Bruker 300 MSL-CP-MAS instrument operating at 75.47 MHz at the Indian Institute of Science, Bangalore, India. The spectra were run with fine powders of glassy beads at room temperature. The samples were spun with a Kel-F rotor at 3.35–3.69 kHz, and the spectral width employed was 25 kHz. The cross-polarization time was 22 ms, and the number of scans was in the range of 200–600.

Optical photographs of the copolymer beads were taken on a Nikon phase contrast microscope. The unsieved samples were spread on a glass slide, and the photographs were taken at 100-fold magnification. Scanning electron micrographs of the copolymer beads were taken on a Jeol JSM 35CF instrument at the Central Electrochemical Research Institute, Karaikudi, India. Specimens were prepared by placing the dry powder on a round cover glass which was mounted with double-faced adhesive tape on a stud and then coated with a thin layer of gold under vacuum to observe the shape, size, and morphology of the beaded copolymers. Particle size distributions of the copolymer samples were studied with a Malvern particle size analyzer. The samples were suspended in water with the help of electrolytes.

Swelling studies of the cross-linked copolymers were conducted by a centrifuge method.[26] A sample of the resin (1 g) was introduced into a glass disk of porosity No. 3. The sample with the glass tube was weighed, and then 15 mL of solvent was added to the tube, closed with a rubber cap to prevent solvent evaporation. The tube was kept at room temperature for 1 h to allow the samples to swell. Then the sample was centrifuged at 500 rpm for 5 min using a Remi laboratory centrifuge. After removing excess solvent, the filter tube was weighed. By employing this procedure, the swelling of the resins in chloroform, dimethylformamide, dioxane, and ethyl acetate was carried out. The amounts of the solvent imbibed by the copolymer beads were expressed as g/g.

Results and Discussion

Copolymer supports based on styrene, glycidyl methacrylate, phenyl methacrylate, 2,4,6-tribromophenyl acrylate, and 4-acetylphenyl acrylate with hydroquinone diacrylate are successfully synthesized by using an aqueous suspension copolymerization technique at 80 °C (Table I). The resulting polymer beads are characterized with various techniques such as FT-IR, ^{13}C CP-MAS, particle size analysis, optical and scanning electron microscopy, and swelling studies. Most of the polymer supports reported in the literature involve the use of commercial divinylbenzene as a cross-linking agent and are mixtures of isomers. Studies of Walczynski et al. reveal the different reactivities of the various components present in the divinylbenzene.[27] In the present study hydroquinone diacrylate has been selected as a cross-linking agent in view of its chemical purity and structural similarity with phenyl acrylates.

IR Spectroscopy. In the present work, we have used FT-IR for identification of the monomeric units in the copolymer. Figure 1a shows the FT-IR spectrum of the Sty-*co*-HyDA polymer. The incorporation of styrene units in the copolymer is confirmed by observing the absorption frequencies at 3024, 2920, and 2864 cm^{-1} which are due to aromatic –CH and backbone methylene stretching vibrations. The band at 1600 cm^{-1} is for the C=C of the aromatic ring. The –CH deformation vibrations are seen at 756 and 700 cm^{-1}. The FT-IR spectrum of the PhMA-HyDA copolymer is shown in Figure 1b. The appearance of a group of bands at 3024, 2968, 2928, and 2832 cm^{-1} is due to aromatic, methyl, and methylene stretching vibrations, respectively. The characteristic carbonyl of phenyl ester appears at 1747 cm^{-1} as a sharp band. The aromatic skeletal C=C stretching vibration is seen at 1591 cm^{-1}. The appearance of a 1193-cm^{-1} absorption is due to the CO stretching of ester groups. In the case of glycidyl methacrylate and 2,4,6-tribromophenyl and 4-acetylphenyl acrylates, the characteristic ester carbonyl stretching vibrations are observed at 1730, 1769, and 1756 cm^{-1}, respectively.

^{13}C CP-MAS NMR. Since the pioneering work of Schaefer on the ^{13}C CP-MAS, this technique has found wide applications in studying the polymers in solid state.[28–35] The variable-temperature CP-MAS technique produces well-resolved signals even in insoluble amorphous copolymers, which are comparable with the signals of a liquid spectrum.[36] In recent years CP-MAS is also used for characterizing the cross-linked polymer beads.[37–39] Ford et al. employed this technique for studying Sty–DVB cross-linked resins and calculated the pendant unreacted double bonds by measuring the peak areas.[39]

In the present investigation, ^{13}C CP-MAS NMR is used for identifying the monomeric units in the cross-linked

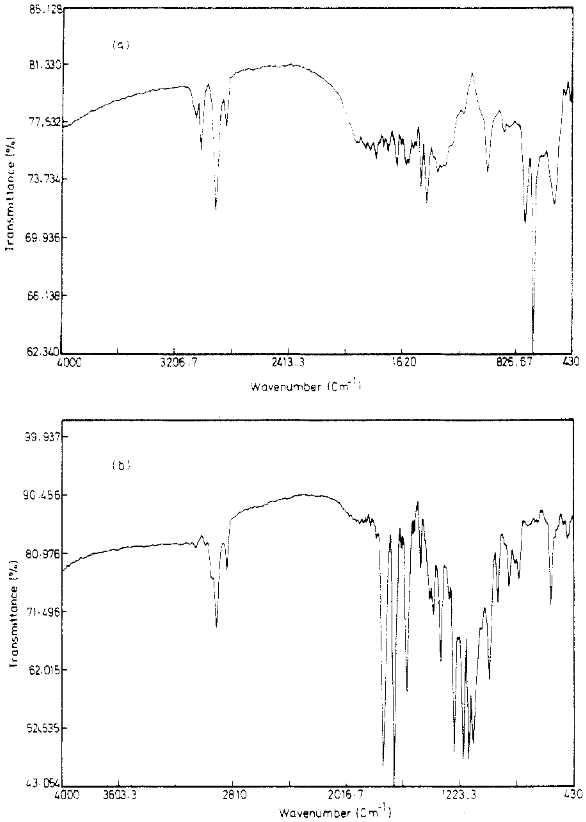


Figure 1. (a) FT-IR spectrum of the Sty–HyDA copolymer. (b) FT-IR spectrum of the PhMA–HyDA copolymer.

copolymers. The high-resolution solid-state ^{13}C NMR spectra of the cross-linked copolymers with their soluble homopolymer analogs are discussed. The ^{13}C CP-MAS spectra of the PhMA–HyDA copolymer and the homopolymer of phenyl methacrylate are shown in Figure 2. The α-methyl group of PhMA appears in the solid state as a broad peak at 16.44 ppm, whereas in the homopolymer it gave three sharp lines at 16.00–19.93 ppm, respectively. The backbone methylene group shows sharp intense lines in both the homo- and copolymers at 45.61 and 44.08 ppm, respectively. This follows a small broad peak due to the backbone quatenary carbon in the systems at both 53.80 and 54.00 ppm. Due to the presence of the ester group adjacent to the phenyl ring, the aromatic carbons appear as four lines in the PhMA homopolymer. The –O^{1}C is seen at 150.42 ppm followed by sharp intense lines at 129.20, 125.66, and 120.79 ppm which are due to ^{2}C & ^{6}C, ^{4}C, ^{3}C, and ^{5}C respectively. However, in the cross-linked copolymer the ^{1}C is observed at 149.42 ppm as a sharp intense line, ^{2}C & ^{6}C at 127.61 ppm, and ^{4}C as a small shoulder peak at 124.90 ppm. The line due to ^{3}C & ^{5}C is seen at 119.58 ppm as a sharp intense line.

The proton-decoupled ^{13}C NMR spectra of poly(APA) and its copolymer with HyDA in the solid state are shown in Figure 3. The methyl carbon of the acetyl group shows a sharp intense line at 26.36 ppm in solution, whereas in a cross-linked system it appears as a sharp intense peak at 24.86 ppm. This follows a small line at 41.70 ppm in the homopolymer which is due to the backbone methylene and in the copolymer at 39.85 ppm as a broad peak. The –O^{1}C of the homopolymer gives a small line at 153.59 ppm, whereas in the solid it appears at 152.49 ppm as a sharp intense line. The ^{2}C & ^{6}C of the phenyl ring in the homopolymer appears at 129.30 ppm. The ^{3}C & ^{5}C of the aromatic ring in poly(APA) gives a sharp intense line at 121.45 ppm, and in the copolymer it appears at 120.66 ppm as a sharp line. Due to the presence of –COCH$_3$ in APA, the ^{4}C gives a sharp line at 133.59 ppm in the homopolymer, but in the copolymer it appears as a sharp line at 133.18 ppm. The carbonyl of the aceto group is seen at 196.39 ppm in the copolymer and at 196.29 ppm as a sharp line in the homopolymer. However, the phenyl ester carbonyl is observed at 172.24 ppm as a broad line in the cross-linked copolymer.

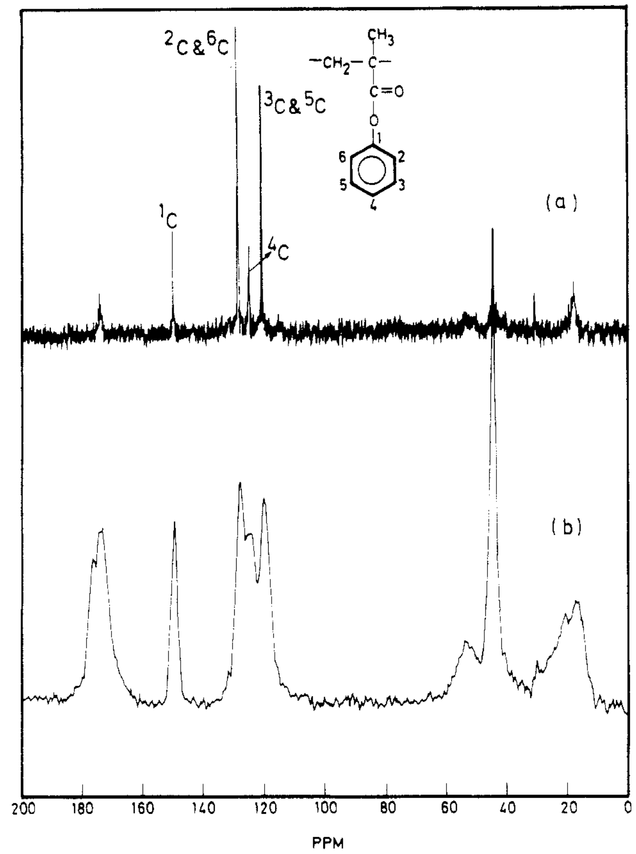


Figure 2. (a) ^{13}C {^{1}H} NMR spectrum of poly(PhMA). (b) ^{13}C CP-MAS NMR spectrum of the PhMA-*co*-HyDA polymer.

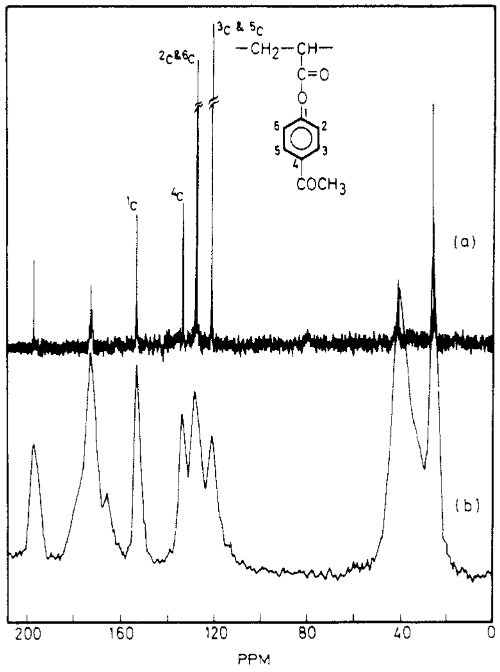


Figure 3. (a) ^{13}C {^{1}H} NMR spectrum of poly(APA). (b) ^{13}C CP-MAS NMR spectrum of the APA-*co*-HyDA polymer.

Particle Size Analysis. The particle size distribution curve of the GMA-*co*-HyDA polymer is shown in Figure 4. Among the parameters which influence the particle

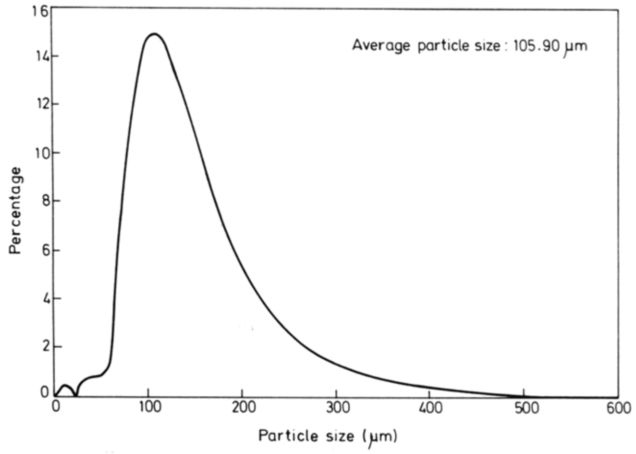


Figure 4. Particle size distribution curve of the GMA–HyDA copolymer.

size in suspension polymerization are nature and amount of stabilizer, geometry of the vessel, type of stirrer, and stirring rate.[40–44] Balakrishnan and Ford[45] studied the influence of various parameters on the particle size formation in suspension copolymerization of Sty–DVB resins. In the present study the copolymer beads are synthesized using a Teflon-blad stirrer and employing 500 rpm as the stirring rate. Comparison of these results with our earlier study revealed that, by keeping all other parameters constant and by decreasing the stirring rate, bigger size particles are formed.[46–48] The curve (Figure 4) shows that the distribution is relatively broad. The average (median) particle size of the copolymer beads is 105.9 μm.

Optical Microscopy. In the present study both translucent and opaque cross-linked beads are observed. The optical micrograph of the GMA–HyDA copolymer beads is shown in Figure 5a. The particles are perfectly spherical and are translucent. The translucency shows that the diluent (chlorobenzene) employed in the course of polymerization is a good solvent for the copolymer formed. In the case of the TBPA–HyDA copolymer (Figure 5b), the particles appear as opaque. The particles are relatively spherical with some amount of distortion, due to the diluent employed in the polymerization being a poor solvent (chlorobenzene) for the copolymer formed. These resins are known as precipitated resins.[49] The visual appearance of the beads is explained based on the cluster formation of microgels.[50]

Scanning Electron Microscopy. In this paper SEM has been used for observing the shape, size, and morphological features of the typical copolymer beads. The low-magnification micrograph of the GMA–HyDA copolymer is shown in Figure 6a. It is observed from the micrograph that all the particles are perfectly spherical with a smooth surface which is also seen in OM. Klein et al. also observed the same surface in styrene-cross-linked divinylbenzene copolymers.[51] The SEM plate also shows that the bigger size particles are more in number. The smooth surface of the copolymer beads explains that the resins are microporous or of a gel type which is also confirmed by BET surface area measurements. The microporous resin of the Sty–DVB resin also showed similar features in SEM.[51] A low-magnification scanning electron micrograph of the Sty–HyDA copolymer beads is shown in Figure 6b,c. The single particle is spherical in shape with an uneven surface. The OM of these beads also shows opacity with deformed sphericity. The uneven surface is due to the porogen which is a poore solvent (chlorobenzene) for the polymer, and it is already observed that the precipitated resins show an uneven surface.[52,53] The higher magnification SEM plate of Sty–HyDA shows some interesting features. The aggregation of spherical particles formed during suspension polymerization is noticed. Jacobelli et al. studied the formation of a macroporous structure with a nonsolvent as a porogenic agent.[54] They found three structures: (a) elementary nuclei of spherical particles of 100–200 Å, (b) microspheres of about 500–1000 Å, and (c) the microspheres forming aggregates of 2500–10 000 Å. Guyot discussed the precipitation polymerization of vinyl chloride with the formation of fused agglomerated particles of 2–10 μm, at 90% conversion.[55] The scanning electron micrograph of precipitated poly(vinyl chloride) very much resembles the SEM of the Sty–HyDA copolymer, thereby showing that the interaction of the diluent (chlorobenzene) with polymer results in phase separation.[56–58] The SEM of Sty–HyDA also explains that final stage aggregation of particles is in the process of formation of beads. The other acrylate copolymer systems reported in the literature such as GMA–EDMA and HEMA–EDMA are macroporous in nature because of the use of high amounts of (<10%) cross-linking agents with poor solvents as diluents in suspension polymerization.

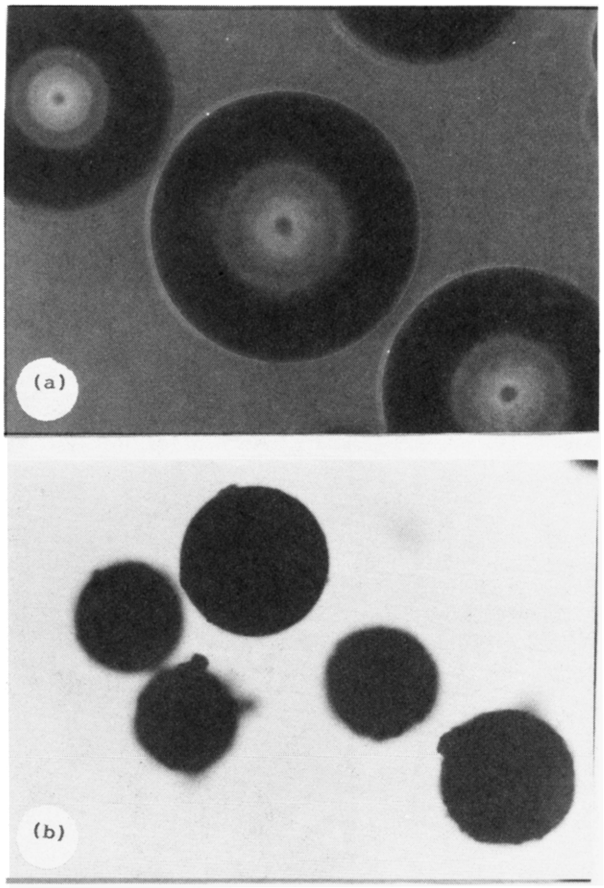


Figure 5. (a) Optical micrograph of the GMA–HyDA copolymer beads. (b) Optical micrograph of the TBPA–HyDA copolymer beads.

Swelling Studies. Solvent imbibition or swelling studies are important for identifying the good solvent for the polymer support for performing chemical reactions. Factors which influence the swelling are (i) the cross-link ratio, (ii) the morphology of the resin, and (iii) the chemical nature of the resin and the solvent used. Pepper et al. demonstrated the effect of the degree of cross-linking on the swelling of ion-exchange resins.[26] They observed a lower swelling as the amount of the cross-link ratio increased. Depending upon the reaction conditions employed in the course of polymerization, the morphological features of the beads change. The microporous resins

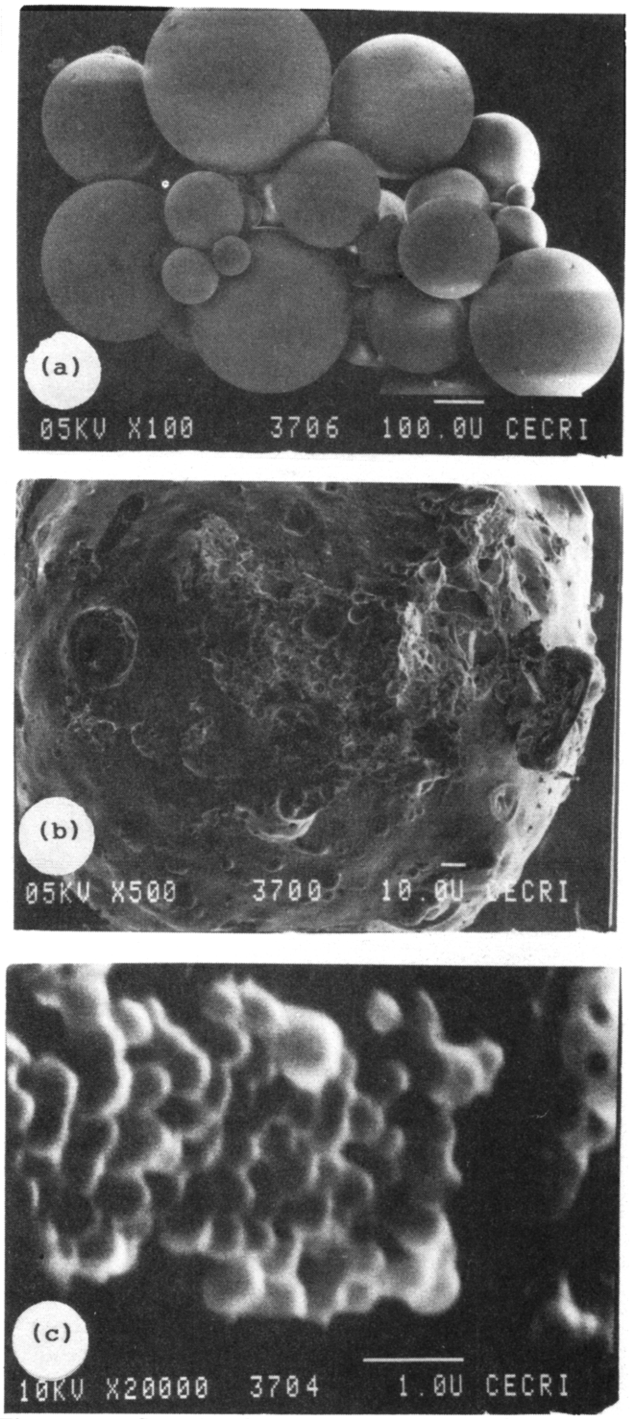


Figure 6. (a) Scanning electron micrograph of the GMA–HyDA copolymer. (b) Scanning electron micrograph of the TBPA–HyDA copolymer. (c) Scanning electron micrograph of the Sty–HyDA copolymer.

Table II
Swelling Studies in Solvents
(Weight of the Copolymer Gel in Grams)

copolymer[a]	$CHCl_3$	DMF	dioxane	EtoAc
Sty–HyDA	19.30	7.72	2.81	3.44
GMA–HyDA	7.23	5.87	5.11	2.45
PhMA–HyDA	11.75	7.85	7.43	5.57
TBPA–HyDA	9.59	5.57	4.02	3.46
APA–HyDA	12.50	4.90	10.06	3.37

[a] 1 g of the copolymer.

involve low amounts of cross-linking agents (<10%) with a good solvent as diluent, whereas the macroporous and macroreticular resins consist of more cross-linking agent with either a good solvent or poor solvent as the porogen.[59,60] Another type of resin known as isoporous resin shows similar qualities of macroporous or macroreticular characteristics but swells even in poor solvents.[63] The role of the support in SPPS is very well recognized, and some of the problems encountered with Merrifield's resin are explained on the basis of the chemical nature of the support. Sheppard in 1971 elegantly demonstrated the influence of the chemical nature of the support in SPPS by introducing acrylamide-based copolymers which are polar and hydrophilic in contrast to the Sty–DVB hydrophobic resins.[64]

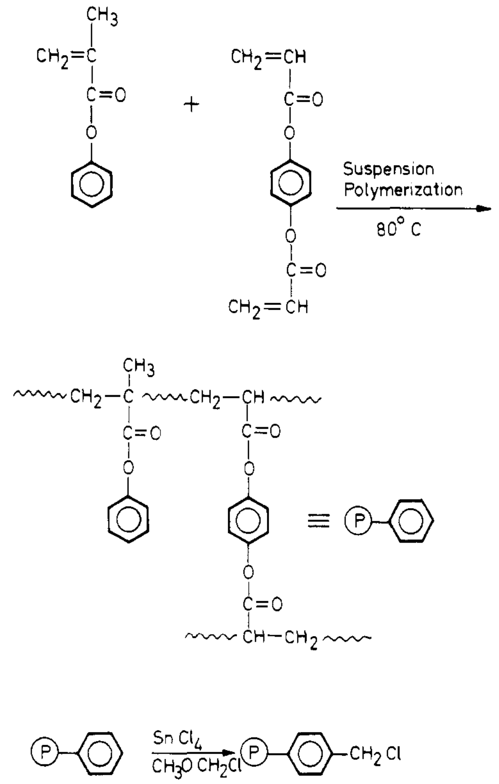
Optical and scanning electron micrographic studies showed that the resins studied in the present investigation are microporous in nature. This is also confirmed by measuring the surface area under dry conditions using the BET method, and the values are found to be less than 1 m^2/g. It is already established that the microporous resins under dry conditions do not possess large surface areas. In order to observe the swelling behavior of these resins in organic solvents, solvent imbibition studies are undertaken. The samples are allowed to swell in solvents like chloroform, dimethylformamide, ethyl acetate, and dioxane for 1 h, the excess solvents are removed by centrifugation, and the results obtained are shown in Table II. The swelling studies indicate that the resins are basically hydrophobic in nature. All the resins exhibit high swelling in chloroform compared to other solvents. Among the resins investigated the copolymer of PhMA–HyDA exhibited a high swelling capacity in all the solvents employed in this study.

The presence of an aromatic ring in the Sty–HyDA copolymer enables the introduction of a chloromethyl group which can be modified with a wide range of reagents to synthesize a variety of functionalized supports. The oxirane group in the GMA copolymer is a highly versatile functional group that can be modifed with a number of reagents, as established in the literature.[17] In the case of PhMA–HyDA copolymers the phenyl ring which is susceptible to electrophilic substitution reactions gives a wide scope for its use as a basic polymer support (Scheme I). This resin can be functionalized by a prefunctionalization technique by the incorporation of a reactive monomer such as 4-(hydroxymethyl)phenyl methacrylate, and the resulting resin can be used in SPPS (Scheme II). $-CH_2OH$ may be used for attaching the protected amino acids using dicyclohexylcarbodiimide as a condensing agent. Copolymers based on TBPA–HyDA are classified as activated acrylate because of the presence of the bromine atoms, and the tribromophenoxy group can be removed by treatment with nucleophilic reagents.[47] The copolymer of APA–HyDA is a reactive polymer due to the presence of $-COCH_3$ which can be suitably modified by treatment with compounds like hydroxylamine hydrochloride, thiosemicarbazide, isoicotinic acid hydrazide, etc. The oxidation of $-COCH_3$ with Br_2 in NaOH generates the carboxylic functionality for its use as support for the immobilization of enzyme or in polymeric reagents.

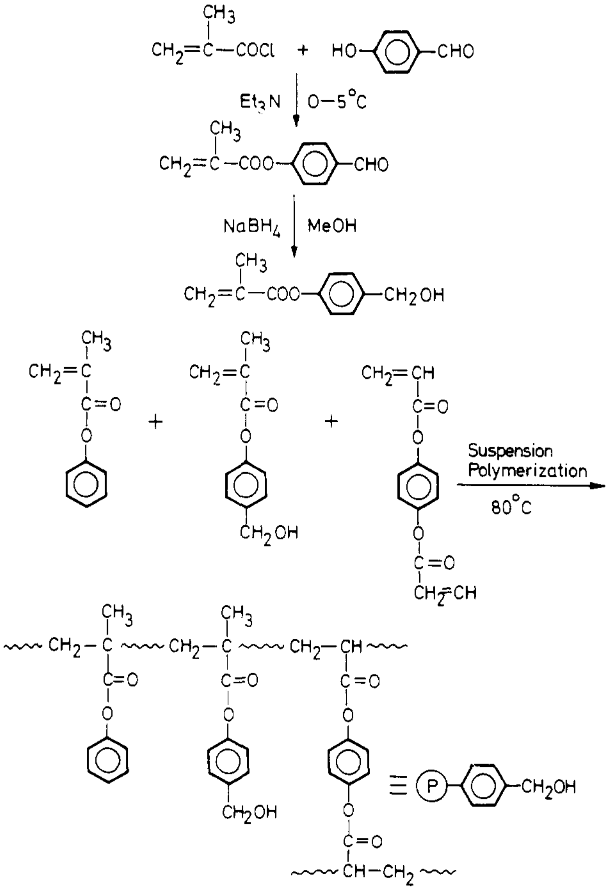
Conclusion

A series of novel copolymeric supports based on phenyl acrylates and hydroquinone diacrylate (4 mol %) are successfully synthesized by a well-defined aqueous suspension polymerization technique. The resulting copolymer beads are characterized with various instrumental techniques. FT-IR and solid-state ^{13}C CP-MAS NMR spectroscopies are used for identifying the incorporation of polymeric units. Particle size analysis is used for

Scheme I



Scheme II



studying the distribution pattern of the beads and its average (median) particle size. Optical and scanning electron microscopic techniques are adopted for observing the appearance, size, shape, and morphological features of the resins. OM showed the formation of both translucent and opaque resins depending upon the interactions of the diluent (chlorobenzene) with the polymer. The SEM results showed that all the copolymer supports are microporous, and this is further confirmed by BET surface area measurement. The swelling studies revealed that all the copolymers are basically hydrophobic in nature. When compared to other systems the PhMA-HyDA copolymer showed a wide range of solvent compatability.

On the basis of the results, we have selected the PhMA-HyDA copolymer system as a basic support for SPPS since it satisfies the criteria for an ideal support. This resin is morphologically microporous and showed good compatability with the solvents employed for swelling, in contrast to other resins under study. Because of the phenyl ring, it can be easily functionalized by the postfunctionalization technique. The choice of PhMA as a comonomer in the PhMA-HyDA system is made because of its chemical resistivity with reagents normally used in SPPS. Our earlier studies on the reaction of the PhMA-DVB resin with monoethanolamine at 100 °C for 10 h revealed that only 5% of the phenol was released from the resin.[47] The choice of hydroquinone diacrylate as a cross-linking agent (4 mol %) is made because of its chemical purity (in contrast to DVB), structural similarity (like the GMA-EDMA system) with phenyl acrylates, and chemical resistivity.

Acknowledgment. We are thankful to Mr. V. V. Muralidhara Rao of this institute for helpful discussions. Our thanks are also due to Prof. C. L. Khetrapal and his group in IISc, Bangalore, India, for providing ^{13}C CP-MAS NMR spectra and Prof. T. Ramanujam and Mr. Lalitha Prasad, IIT, Madras, India, for providing particle size analysis data. We are grateful to Dr. G. Thyagarajan, Director, CLRI, for his kind permission to publish this work. T.N. thanks CSIR, New Delhi, India, for awarding him a Research Associateship.

References and Notes

(1) Merrifield, R. B. *J. Am. Chem. Soc.* **1963**, *85*, 2149.
(2) Gutte, B.; Merrifield, R. B. *J. Biol. Chem.* **1971**, *246*, 1922.
(3) Mathur, N. K.; Williams, R. E. *J. Macromol. Sci., Rev. Macromol. Chem.* **1976**, *C15*, 117.
(4) Hodge, P.; Sherrington, D. C. *Polymer Supported Reactions in Organic Synthesis*; John Wiley: Chichester, U.K., 1980.
(5) Sherrington, D. C. *Br. Polym. J.* **1984**, *16*, 164.
(6) Geckeler, K.; Pillai, V. N. R.; Mutter, M. *Adv. Polym. Sci.* **1981**, *39*, 65.
(7) Kraus, M. A.; Patchornik, A. *J. Polym. Sci., Macromol. Rev.* **1980**, *15*, 55.
(8) Hodge, P. *Chem. Br.* **1978**, *14*, 237.
(9) Guyot, A. In *Syntheses and Separations Using Functional Polymers*; Sherrington, D. C., Hodge, P., Eds.; John Wiley: Chichester, U.K., 1988.
(10) Pillai, V. N. R.; Mutter, M. *Top. Curr. Chem.* **1982**, *106*, 119.
(11) Frechet, J. M. J.; Farrall, M. J. *The Chemistry and Properties of Crosslinked Polymers*; Labana, S. S., Ed.; Academic Press: New York, 1977.
(12) Arshady, R.; Atherton, E.; Clive, D. L. J.; Sheppard, R. C. *J. Chem. Soc., Perkin. Trans.* **1981**, 529.
(13) Kalal, J. *J. Polym. Sci., Polym. Symp.* **1978**, *62*, 251.
(14) Hradil, J.; Svec, F.; Frechet, J. M. J. *Polymer* **1987**, *28*, 1593.
(15) Dorbnik, J.; Saudek, V.; Svec, F.; Kalal, J.; Vojitisek, V. O.; Barta, M. *Biotechnol. Bioeng.* **1978**, *21*, 1317.
(16) Hradil, J.; Svec, F. *Angew. Makromol. Chem.* **1985**, *130*, 81.
(17) Kalal, J.; Svec, F.; Marousek, V. *J. Polym. Sci., Polym. Symp.* **1974**, *47*, 155.
(18) Mathur, N. K.; Narang, C. K.; Williams, R. E. *Polymers as Aids in Organic Chemistry*; Academic Press: New York, 1980.
(19) Arshady, R. *Makromol. Chem.* **1988**, *189*, 1295.
(20) Arshady, R. *Makromol. Chem.* **1984**, *185*, 2387.
(21) Arshady, R. *Makromol. Chem., Rapid. Commun.* **1983**, *4*, 273.
(22) Mark, H.; Wohenstein, W. P. *J. Polym. Sci.* **1946**, *1*, 127.
(23) Arshady, R.; Ledwith, A. *React. Polym.* **1983**, *1*, 159.
(24) Bader, A. R.; Kontowicz, A. *J. Am. Chem. Soc.* **1953**, *75*, 5416.
(25) Stampel, G. H.; Cross, R. P.; Maliella, R. P. *J. Am. Chem. Soc.* **1950**, *72*, 2899.

(26) Pepper, K. W.; Reinchenberg, D.; Hale, D. K. *J. Chem. Soc.* **1952**, 3129.
(27) Walczynski, B.; Kolazz, B. N.; Galina, H. *Polym. Commun.* **1985**, *26*, 276.
(28) Schaefer, J.; Stejskal, E. O.; Buchdahl, R. *Macromolecules* **1975**, *8*, 291.
(29) Schaefer, J.; Stejskal, E. O. *Topics in Carbon-13 NMR Spectroscopy*; Levy, C. G., Ed.; John Wiley: New York, 1979.
(30) Komoroski, R. A. *High Resolution NMR Spectroscopy of Synthetic Polymers in Bulk*; VCH Publishers: Deerfield Beach, FL, 1986.
(31) Voekel, R. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1468.
(32) Mehring, M. *Principles of High Resolution NMR in Solids*; Springer: Berlin, 1983.
(33) Garroway, A. N.; Moniz, W. B.; Resing, H. A. *ACS Symp. Ser.* **1979**, *103*, 67.
(34) Axelson, D. E.; Russel, K. E. *Prog. Polym. Sci.* **1985**, *11*, 221.
(35) Laupretre, F.; Monnerie, L.; Virlet, J. *Macromolecules* **1984**, *17*, 1397.
(36) Sterna, L. L.; Smith, H. C. *J. Magn. Reson.* **1988**, *79*, 528.
(37) Stover, H. D. H.; Frechet, J. M. J. *Macromolecules* **1991**, *24*, 883.
(38) Ford, W. T.; Periyasamy, M.; Mohanraj, S.; McEnroe, F. J. *J. Polym. Sci., Polym. Chem. Ed.* **1989**, *27*, 2345.
(39) Periyasamy, M.; Ford, W. T.; McEnroe, F. J. *J. Polym. Sci., Polym. Chem. Ed.* **1989**, *27*, 2357.
(40) Church, J. M.; Shinnar, R. *Ind. Eng. Chem.* **1961**, *53*, 479.
(41) Winslow, F. H.; Matreyek, W. *Ind. Eng. Chem.* **1951**, *43*, 1108.
(42) Dawkins, J. V. In *Comprehensive Polymer Science*; Allen, G., Ed.; Pergamon: New York, 1989; Vol. 4, p 231.
(43) Apostolidou, C.; Stamatoudis, M. *Collect. Czech. Chem. Commun.* **1990**, *55*, 2244.
(44) Hopff, H.; Lussi, H.; Gerspacher, P. *Makromol. Chem.* **1966**, *78*, 24.
(45) Balakrishnan, T.; Ford, W. T. *J. Appl. Polym. Sci.* **1982**, *27*, 133.
(46) Narasimhaswamy, T.; Reddy, B. S. R. *J. Appl. Polym. Sci.* **1991**, *43*, 1645.
(47) Narasimhaswamy, T.; Devasagayam, D.; Sumathi, S. C.; Reddy, B. S. R. *Polym. Int.* **1992**, *27*, 75.
(48) Narasimhaswamy, T.; Sumathi, S. C.; Reddy, B. S. R.; Rajadurai, S. *Polymer Science: Contemporary Themes*; Sivaram, S., Ed.; Tata McGraw-Hill: New Delhi, India, 1991; p 416.
(49) Kun, A.; Kunin, R. *J. Polym. Sci.* **1968**, *7*, 2689.
(50) Albright, R. L. *Catalysts Supports and Supported Catalysts*; Stiles, A. B., Ed.; Butterworth: Stoneham, MA, 1987.
(51) Klein, J.; Widdecke, H.; Bothe, N. *Makromol. Chem. Suppl.* **1984**, *6*, 211.
(52) Sederal, W. L.; Dejong, G. J. *J. Appl. Polym. Sci.* **1973**, *17*, 2835.
(53) Negre, M.; Bartholin, M.; Guyot, A. *Angew. Makromol. Chem.* **1982**, *106*, 67.
(54) Jacobelli, H.; Bartholin, M.; Guyot, A. *J. Appl. Polym. Sci.* **1979**, *23*, 927.
(55) Guyot, A. In *Comprehensive Polymer Science*; Allen, G., Ed.; Pergamon: New York, 1989; Vol. 4, p 261.
(56) Guyot, A. *Pure Appl. Chem.* **1988**, *60*, 365.
(57) Howard, G. J.; Midgley, C. A. *J. Appl. Polym. Sci.* **1981**, *26*, 3845.
(58) Coutino, F. M. B.; Cid, R. C. A. *Eur. Polym. J.* **1990**, *11*, 1185.
(59) Horak, Z.; Pelzbauer, Z.; Bleha, M.; Ilavsky, M.; Svec, F.; Kalal, J. *J. Appl. Polym. Sci.* **1981**, *26*, 411.
(60) Horak, D.; Svec, F.; Bleha, M.; Kalal, J. *Angew. Makromol. Chem.* **1981**, *95*, 109.
(61) Coupeck, J.; Krivakova, M.; Pakrony, S. *J. Polym. Sci., Polym. Symp.* **1973**, *42*, 185.
(62) Munzer, M.; Trommsdorff, E. In *Polymerization Processes*; Schildknecht, C. E.; Skiest, J., Eds.; Wiley-Interscience: New York, 1976.
(63) Davankov, V. A.; Tsyurupa, M. *Angew. Makromol. Chem.* **1980**, *91*, 127.
(64) Sheppard, R. C. *Peptides 1971*; Nesvadba, H., Ed.; North-Holland: Amsterdam, The Netherlands, 1973.