

Cardanyl Acrylate/Methacrylate Based Cross-Linked Copolymers as Novel Supports: Synthesis and Characterization

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SYNOPSIS

Cardanyl acrylate/methacrylate on suspension polymerization with methyl methacrylate, styrene, and acrylonitrile yielded copolymer beads. The beads were almost uniform in size and cross-linked in nature. The copolymers synthesized were characterized by infrared, thermogravimetric analysis, scanning electron and optical microscopy, and swelling studies.

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INTRODUCTION

Following the well-known work of solid-state peptide synthesis of Merrifield,¹ studies on cross-linked polymers based on vinyl monomers have increased.^{2,3} Polymer supports based on activated acrylates have recently been shown to be useful in supported organic synthesis, metal ion separation etc.⁴⁻⁸ This prompted us to prepare copolymers of poly(cardanyl acrylate) (PCA) with vinyl monomers such as methyl methacrylate (MMA), styrene (St), and acrylonitrile (AN). In an earlier report, we showed that cardanyl acrylate (CA) forms uniform size beads on suspension polymerization to give PCA, which had basically hydrophobic surface characteristics indicating its usefulness as a material for supported reactions.⁹ This article reports the synthesis and characterization of copolymers of PCA and poly(cardanyl methacrylate) (PCMA) with MMA, St, and AN.

EXPERIMENTAL

Cardanol (37330-39-5) was obtained by double vacuum distillation of cashew nut shell liquid (CNSL,

8007-24-7) and the fraction distilled at 230–235°C at 3–4 mmHg was collected and used. Technical grade CNSL of IS specification (IS:840:1964) was purchased from Kerala State Cashew Development Corporation, Quilon, India. Monomers, MMA (BDH, Poole England), St (Fluka, Switzerland), and AN (E. Merk, Germany) were purified by earlier methods.¹⁰ Benzoyl peroxide (Aldrich, USA) was purified by recrystallization from methanol. Acryloyl chloride and methacryloyl chloride were prepared by the procedure of Stempel et al.¹¹ The monomers CA, **1** and cardanyl methacrylate (CMA), **2** were synthesized by the reported method.^{9,12} Benzoin ethyl ether (BEE) and poly(vinyl alcohol) (PVA) were products of Aldrich and were used as received and the solvents purified by distillation.

In a typical experiment, 50 mL of 2% PVA solution was used as the suspension medium. The monomer mixture (containing 0.005 mol of each monomer) and benzoyl peroxide (0.8 wt % with respect to monomer) initiator were dissolved in chlorobenzene (2.5 mL diluent) and the mixture was flushed with dry nitrogen and was added to the suspension medium while stirring. The stirring was continued for 3 h in a thermostat at 80°C. The polymer beads obtained were filtered, washed with hot water, methanol, acetone, and finally Soxhlet extracted using a suitable solvent to remove diluent and monomer and dried in a vacuum at 45°C. Alternatively, the polymer beads were also obtained by polymerization with UV irradiation using BEE as initiator in a suspension containing 2 wt % PVA.

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Measurements

Infrared (IR) spectra were recorded on a Perkin-Elmer model 882 spectrophotometer using a KBr pellet. Optical photographs of the copolymer beads were taken using a Nikon HFX phase contrast microscope. The unsieved samples were spread on a glass slide and photographs were taken at different magnifications under polarized light. Scanning electron micrographs of the copolymer beads were taken on a Jeol-JSM 35 C instrument. The surface of the sample was coated by sputtering with gold to get good electrical conductivity. Thermogravimetric analysis (TGA) was carried out in a nitrogen atmosphere using a Du Pont Model 2000 Thermal Analyst in conjunction with a 951 Thermogravimetric Analyzer.

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 that was closed with a rubber septum to prevent solvent evaporation. It was kept at room temperature for 3 h to allow the solvent to imbibe into the bead. Then the sample was centrifuged for 5 min. After removing the excess solvent, the filter tube was weighed. By using this procedure, the swelling of the copolymer beads in chloroform, toluene, ethyl acetate, and dimethylformamide (DMF) was carried out. The amount of the solvent imbibed into the copolymer beads was expressed as the weight of the solvent absorbed per weight of the dry resin.

Calculation of Kinetic Parameters from Thermal Data

The kinetic parameters for the thermal decomposition of the copolymers were done by using the Freeman and Carroll procedure. This method is based on the expression

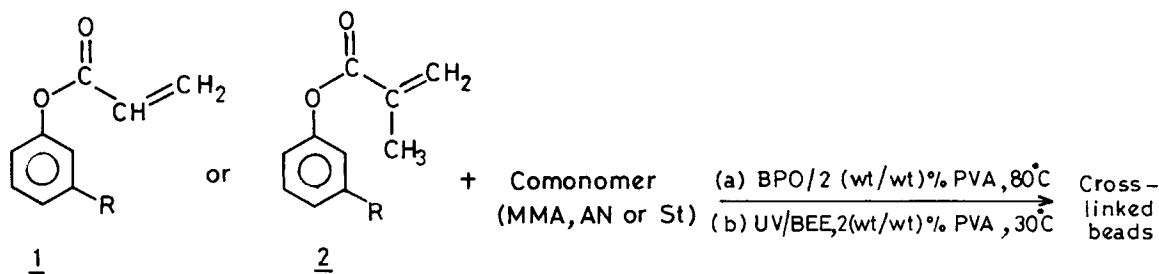
$$\Delta \log(dw/dt) = x \Delta \log W_r - (\Delta E^*/2.3R) \Delta(1/T)$$

where dw/dt is the rate of the reaction, x is the order of reaction, ΔE^* is the energy of activation, R is the gas constant, T is the absolute temperature, and $W_r = W_c - W$ (proportional to the amount of reactant), W being the weight loss at the point where dw/dt is taken, and W_c being the total weight loss associated with a given reaction.

To evaluate the constants in the equation, $\Delta \log dw/dt$ may be plotted against $\Delta \log W_r$ if $\Delta(1/T)$ is kept constant. The order of the reaction, x , is determined from the slope and the energy of activation from the intercept of $\log W_r = 0$.

RESULTS AND DISCUSSION

Copolymer beads based on CA and CMA were prepared in aqueous suspension medium at $80 \pm 1^\circ\text{C}$ (Scheme 1). Suspension was maintained by magnetic stirring and with the help of PVA as a suspension stabilizer. The resulting beaded copolymers were dried in vacuum and were sieved with mechanical sieves. The copolymer-beaded supports were characterized with IR spectroscopy,¹³ optical



Suspension polymerisation



Scheme 1 Copolymerization of monomers 1 or 2 with other vinyl monomers.

Table I Suspension Polymerization of Cardanyl Acrylate (CA) and Cardanyl Methacrylate (CMA) with MMA, St, and AN

Copolymer	No.	Monomer 1 : 1 Molar (g)	Cross-Linking Agent (g)	Diluent ^a (g)	Initiator ^b (mg)	Water ^c (g)
CA : MMA	3	2.27	0	2.5	20	50
CA : St	4	2.29	0	2.56	20	50
CA : AN	5	2.03	0	2.48	22	50
CMA : MMA	6	2.34	0	2.52	20	50
CMA : St	7	2.36	0.5	2.5	20	50
CMA : AN	8	2.10	0	2.54	23	50

^a Chlorobenzene was used as the diluent.

^b Benzoyl peroxide was used as the free radical initiator.

^c Poly vinyl alcohol, 2% solution, was used.

microscopy, scanning electron microscopy (SEM), thermogravimetry, and solvent imbibition studies.

Generally, simple acrylic monomers undergoing free radical polymerization reaction yield soluble polymers/copolymers in the absence of cross-linking agents.¹³ In contrast, polymers of **1** and **2** obtained by suspension polymerization were cross-linked and were insoluble in most of the common solvents. The copolymers of **1** and **2** with vinyl monomers such as MMA, St, and AN were insoluble and did not yield any soluble fraction on extraction. This possibly indicates that the beads formed are already self-cross-linked and do not need any cross-linking agent. Further evidence on the formation of cross-link was provided by IR study (see IR Spectroscopy section). Table I provides the conditions of formation of the cross-linked polymers. Polymer beads were also obtained by UV irradiation in the presence of BEE as initiator, other conditions remaining the same except the temperature in this case was kept at 30°C. The beads obtained by both methods were of comparable properties.

Characterization, Solubility, and IR Study

The copolymer beads were characterized by solubility studies and found to be insoluble in organic solvents indicating the cross-linked nature.

IR Spectroscopy

The IR spectra of CA **1** and CMA **2** are shown in Figure 1. The IR spectrum of CA, **1** (a) and CMA **2** (b) showed characteristic absorptions for —C=C— stretching vibrations for acrylate and MA moieties at 1658/1640 cm^{-1} , respectively.¹⁴ The peaks at 1750/1740 cm^{-1} correspond to acrylic and methacrylic ester carbonyl group absorption. The

characteristic peak at 3020 cm^{-1} of the monomers **1** and **2** was due to the —CH=CH— stretching of the unsaturated groups present in the side chain of the monomers. The IR spectrum [Fig. 2(a) of the copolymer] **3** (CA : MMA) exhibits the characteristic peaks for ester group at 1750 cm^{-1} for CA and 1738 cm^{-1} for MMA. The double peak for the carbonyl group present in the spectrum indicate the incorporation of MMA in the copolymer. Similar results were obtained in the copolymer of CMA : MMA (**6**) and confirmed the formation of copolymer beads [Fig. 3(a)].

In the case of copolymers of CA, CMA with St [Figs. 2(b), 3(b)] the copolymer showed characteristic absorption for ester groups at 1750 and 1740 cm^{-1} , respectively. The intensity of absorption due to the aromatic structure 3000 and 1600 cm^{-1} in-

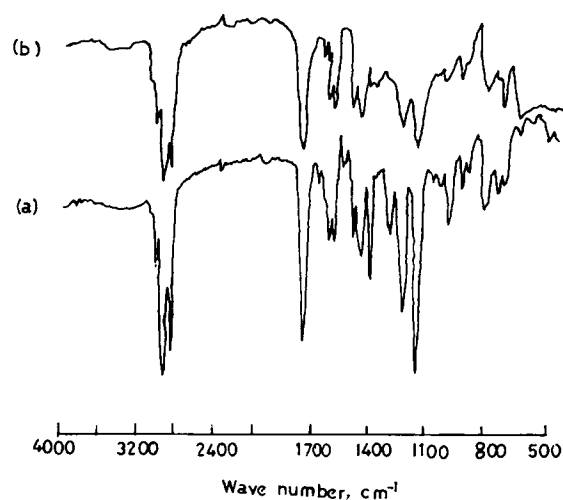


Figure 1 IR spectra of (a) cardanyl acrylate and (b) cardanyl methacrylate.

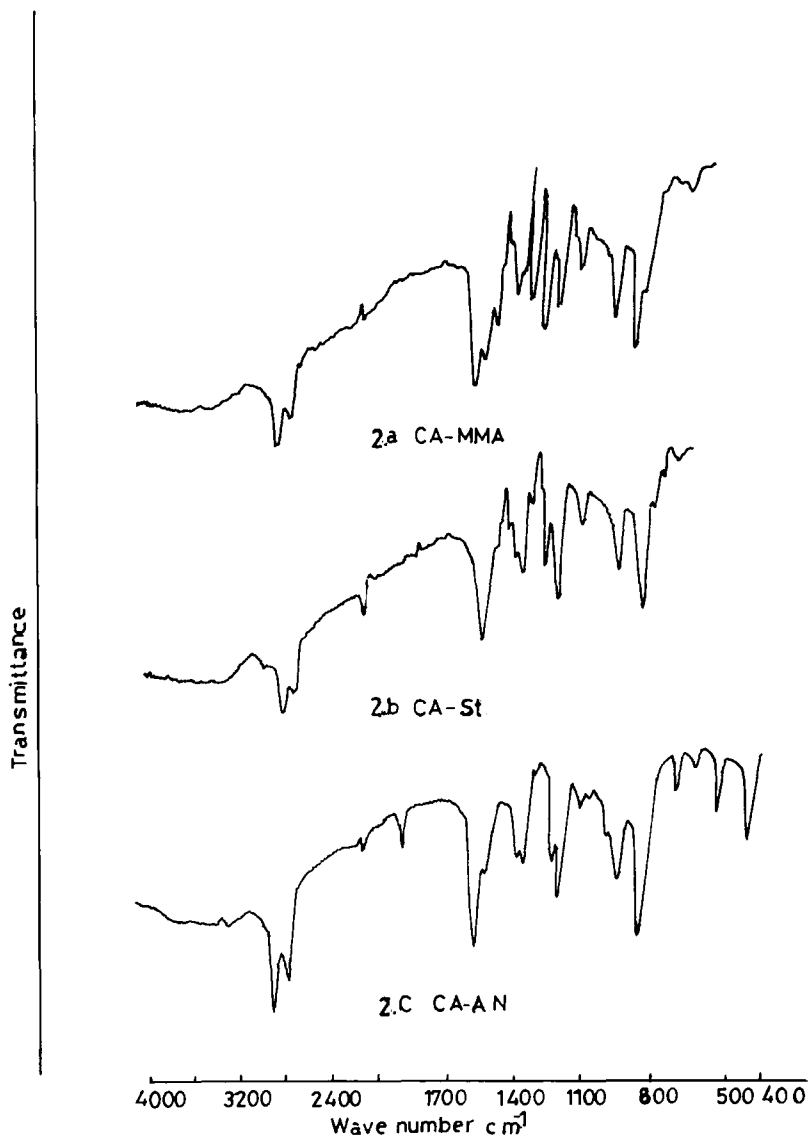


Figure 2 IR spectra of copolymers of cardanyl acrylate with methyl methacrylate (CA-MMA), styrene (CA-St), and acrylonitrile (CA-AN).

creased and the incorporation of St in the copolymer was indicated.

The IR spectrum of the copolymer beads [Figs. 2(c), 3(c)] of CA, CMA with AN exhibits the characteristic absorption of CN group at 2250 cm^{-1} which explains the incorporation of AN in the copolymer. The absorption for acrylic (1750 cm^{-1}) and methacrylic (1740 cm^{-1}) groups shows the presence of CA and CMA in the copolymer.

The significant feature of the IR of all copolymer beads is the absence of the characteristic absorption for the olefinic double bonds of the side chain of the monomer —HC=CH— at 3020 cm^{-1} suggesting

that the side chain double bonds got involved in the cross-link formation. It appears therefore that in suspension polymerization, the participation of the side chain of the **2** and **3** in the polymerization is inferred because cross-linked beads were obtained. The characteristic IR bands of the copolymers are summarized in Table II.

Optical Microscopy

The optical micrograph of the polymer beads are shown in Figure 4. Based on visual appearance, the beads were classified as transparent.¹⁴ It can be seen

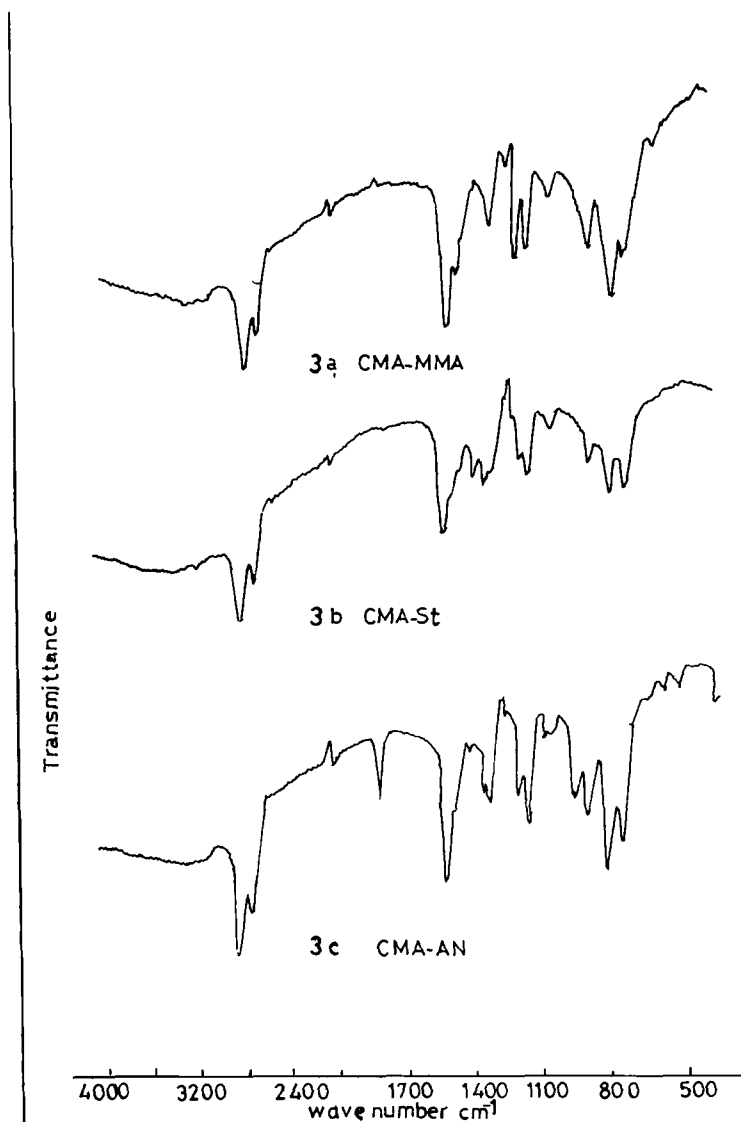


Figure 3 IR spectra of copolymers of cardanyl methacrylate with methyl methacrylate (CMA-MMA), styrene (CMA-St), and acrylonitrile (CMA-AN).

that the beads are spherical in nature and uniform in size. However, it was observed that more small size particles are formed if the speed of stirring during polymerization is increased above 2500 rpm. The transparent nature of the beads obtained in the present experimental conditions demonstrate that the diluent employed in the synthesis of polymer beads is a good solvent.¹⁴

Scanning Electron Microscopy (SEM)

SE micrographs of the typical polymer beads are shown in Figure 5. The bead size, shape, and surface can be observed from these micrographs. The mi-

crographs show that almost all particles are perfectly spherical and almost uniform in their sizes and that the surface is even and smooth. The even and smooth surface of the particles also demonstrates that the monomer diluent is a good solvent for the resulting beads.¹⁵

TGA

The TG curves for the cross-linked copolymer beads of CA 1 and CMA 2 with the other three monomers are shown in Figures 6 and 7, respectively. The decomposition temperature (DT) and the energy of activation involved in the degradation process were

Table II Characteristic IR Absorptions for Monomers CA, CMA, and Copolymers Prepared

Sample	Absorption at cm^{-1}				
	CH_2, CH Str Vibration	$-\text{CH}=\text{CH}-$	Acrylic/Methacrylic Ester Group	Acrylic/Methacrylic Double Bond	$-\text{CN}$ Group
CA, 1	2926, 2855	3020	1750	1658	
CMA, 2	2935, 2859	3020	1743	1640	
CA : MMA, 3	2930, 2855	Absent	1758, 1735	Absent	
CA : St, 4	2937, 2858	Absent	1755	Absent	
CA : AN, 5	2945, 2855	Absent	1755	Absent	2255
CMA : MMA, 6	2935, 2851	Absent	1743, 1735	Absent	
CMA : St, 7	2928, 2857	Absent	1742	Absent	
CMA : AN, 8	2935, 2853	Absent	1745	Absent	2252

determined by the Freeman et al. method.^{16,17} The initial decomposition temperature, that is, at 10% decomposition (T_i) of the copolymer **3**, CA-MMA was noted at 300°C, whereas final decomposition temperature (90%) T_f was 470°C. The 40, 50, 60, and 70% weight losses that occurred are tabulated in Table III. The activation energy is 24.3 kcal/mol. The CMA : MMA **6** also shows similar results. St copolymers of CA and CMA also showed thermal stability and activation energies on the same order. But the TG curves of acrylonitrile copolymer **6c** and **7c** showed enhanced thermal stability compared to the other copolymer systems. The T_i of copolymers **5** and **8** were 340 and 350°C, respectively, compared to that (300°C) of the other systems and the T_f of **5** and **8** were 490 and 480°C, respectively (90% decomposition). The degradation of all copolymer systems occurred in a single stage. The

comparison of activation energies shows that the thermal stability of AN copolymers is higher than that of others. This is in conformity with values reported by earlier workers for AN systems.¹⁸

Swelling Studies

One of the applications that could be used for the cross-linked beads of copolymers of CA and CMA is in the area of polymer supports.⁴⁻⁸ 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, cross-link ratio and the chemical nature of the polymer support employed. It is well known that microporous resins possess porosity only in a swollen condition and this

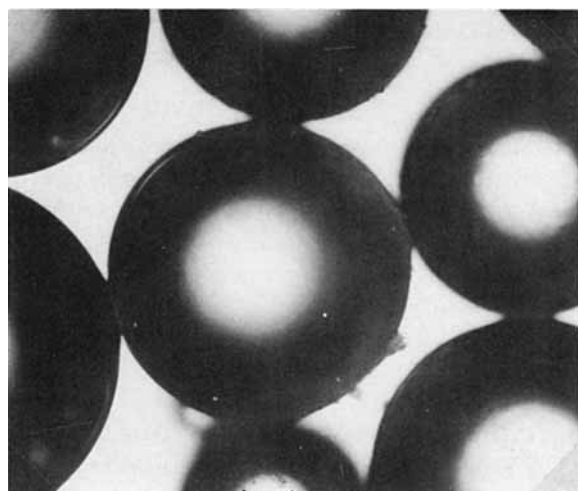


Figure 4 Optical photograph of typical cross-linked CA/CMA based copolymer beads. Magnification $\times 40$.

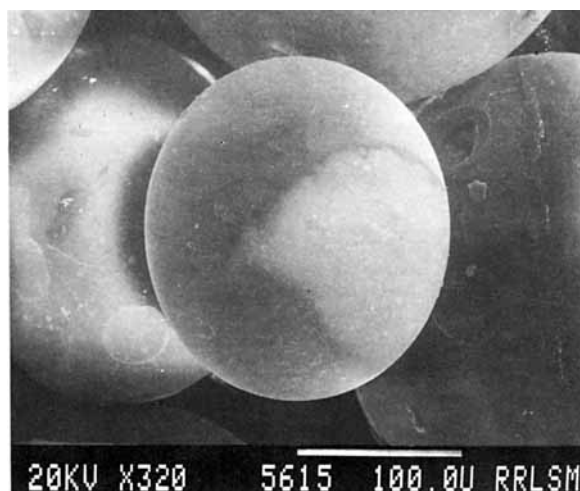


Figure 5 SEM photograph of typical cross-linked CA/CMA based copolymer beads.

TGA

Comment 10 °C/min in N₂

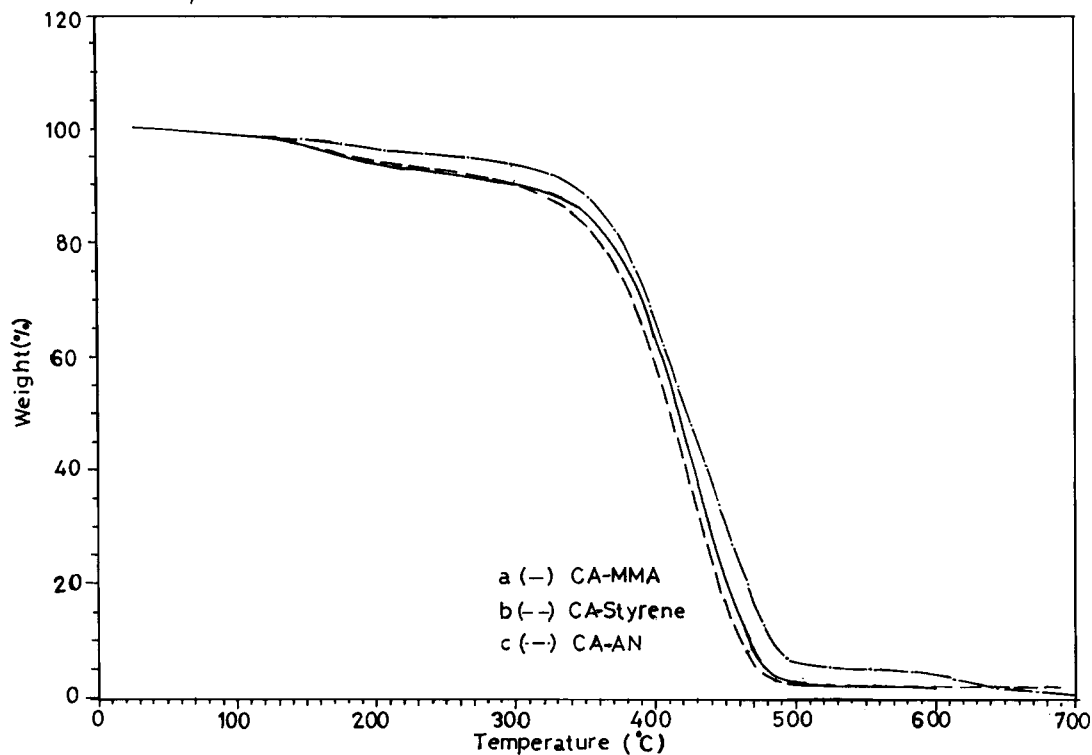


Figure 6 TGA curves for copolymers of CA with MMA, St, and AN.

TGA

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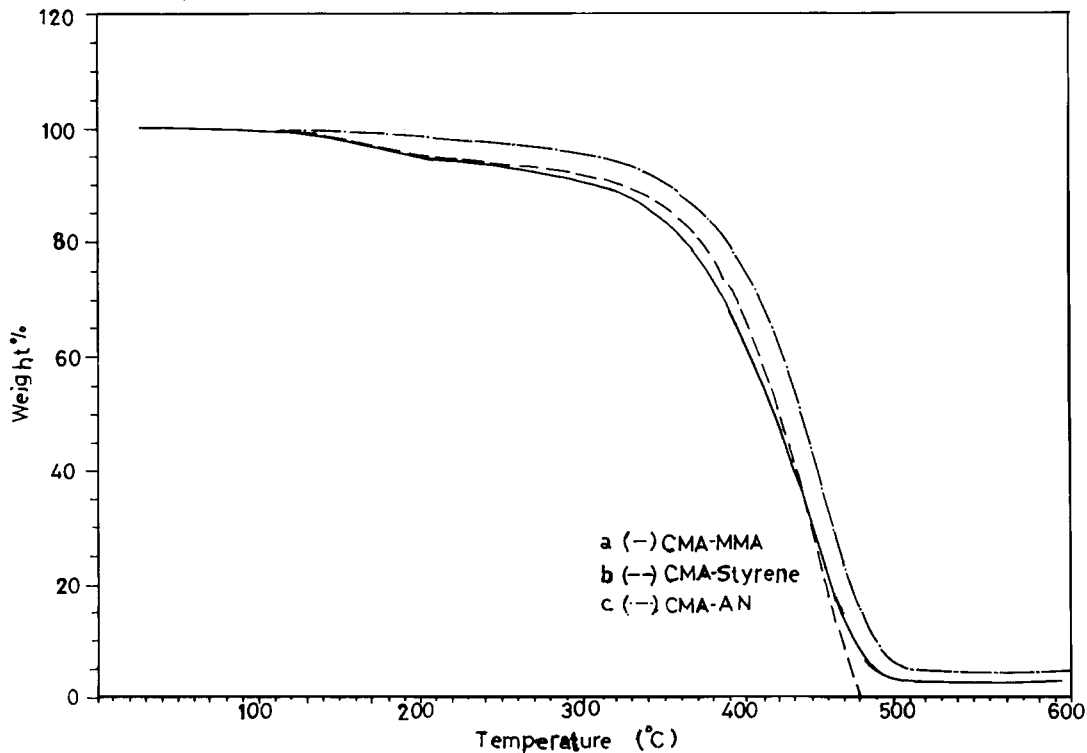


Figure 7 TGA curves for copolymers of CMA with MMA, St, and AN.

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

Copolymer	Decomposition Temperature (°C)					Stages of Decomposition	Temperature Range (°C)	Order Parameter (<i>n</i>) and Energy of Activation (<i>E_a</i>) ^a	
	10% <i>T_i</i>	30%	50%	60%	90% <i>T_f</i>			<i>n</i>	<i>E_a</i> (kcal)
CA : MMA, 3	300	390	410	425	440	Single	220–470	0.9	24.3
CA : St, 4	300	390	420	425	460	Single	220–490	0.8	24.7
CA : AN, 5	340	400	440	450	490	Single	230–580	0.8	26.2
CMA : MMA, 6	300	385	420	430	470	Single	220–500	1.1	25.9
CMA : St, 7	310	390	425	430	460	Single	220–460	0.8	25.8
CMA : AN, 8	350	410	435	445	480	Single	300–510	0.78	27.1

^a Freeman–Carrol method.¹⁶

is called gel porosity.¹⁹ Swelling studies are important for identifying a good solvent in order to select the suitable reaction medium for performing a reaction on polymer supports.²⁰ Moreover, the phenomenon of swelling implies the porous nature of the beads that in turn depends on the cross-link density and the chemical nature of the beads.¹⁹ To investigate the swelling behavior of these polymer beads, solvent imbibition studies were undertaken. The samples were allowed to swell for 1 h in chloroform, toluene, ethyl acetate, and DMF, which are common solvents used for the supported reactions.²¹ The excess solvent was removed by the centrifugal method²² and the results were expressed as the weight of the solvent absorbed per weight of the dry resin.

Table IV shows the swelling behavior of copolymers prepared in commonly used organic solvents such as chloroform, toluene, and DMF for supported reaction. Because the copolymers are cross-linked and a reasonable amount of swelling was observed, it was assumed the beads are porous in nature. The SEM picture (Fig. 5) showed a smooth surface, therefore, the beads might be microporous.

The swelling of the resins in chloroform is comparatively higher than that in the other solvents for St and MMA copolymers with **1** and **2**. This possibly suggests a hydrophobic character for the beads. In DMF, AN copolymer beads show a higher swelling than other solvents. So, DMF might be the suitable solvent for the AN copolymer.

CONCLUSION

Novel cross-linked copolymers based on CA/CMA with MMA, St, and AN were synthesized successfully in the absence of any cross-linking agent by employing the aqueous suspension polymerization technique. The beaded copolymers thus obtained were characterized using different instrumental techniques, such as IR, for studying the incorporation of the various monomers in the copolymer. The optical and scanning microscopic techniques were used for studying the size, shape, and morphology of the beaded copolymers. TGA shows that the AN containing copolymer registers higher thermal stability in comparison to others. The swelling studies

Table IV Swelling Behavior of Copolymers

Polymer	Weight of Polymer Beads (g)	Chloroform (g)	Toluene (g)	Ethylacetate (g)	Dimethylformamide (g)
CA : MMA, 3	1	2.43	1.20	1.85	1.1
CA : St, 4	1	2.51	1.31	1.92	1.05
CA : AN, 5	1	1.7	1.02	1.3	1.85
CMA : MMA, 6	1	2.39	1.32	1.41	1.10
CMA : St, 7	1	2.72	1.41	1.52	1.02
CMA : AN, 8	1	1.42	1.39	1.50	1.93

indicate that the copolymer supports studied in the present investigation are basically hydrophobic in nature.

REFERENCES

1. R. B. Merrifield, *J. Am. Chem. Soc.*, **85**, 2149 (1963).
2. P. Hodge and D. C. Sherrington, Eds., *Polymer Supported Reactions in Organic Synthesis*, Wiley, Chichester, 1980.
3. A. Akelah and D. C. Sherrington, *Chem. Rev.*, **81**, 551 (1981).
4. R. Arshady, *Makromol. Chem. Rapid. Commun.*, **4**, 273 (1983).
5. R. Arshady, *Makromol. Chem.*, **185**, 2387 (1984).
6. R. Arshady, *J. Chromatogr.*, **586**, 187 (1991).
7. T. Narasimhaswamy and B. S. R. Reddy, *J. Appl. Polym. Sci.*, **43**, 1645 (1991).
8. T. Narasimhaswamy, S. C. Sumathi, B. S. R. Reddy, and G. D. Devasagayam, *Polym. Int.*, **27** (1992).
9. George John and C. K. S. Pillai, *Makromol. Chem. Rapid. Commun.*, **13**, 255 (1992).
10. E. A. Collins, Jan Bare, and Fred W. Billmeyer, *Experiments in Polymer Science*, Wiley Interscience, New York, 1973.
11. G. H. Stempel, R. P. Cross, and R. P. Marella, *J. Am. Chem. Soc.*, **72**, 2899 (1950).
12. W. R. Sovenyson and T. W. Campbell, *Preparative Methods of Polymer Chemistry*, Interscience Publishers, New York, 1961.
13. J. I. Crowley and H. Rapoport, *Acc. Chem. Res.*, **9**, 135 (1976).
14. George John, *Chemical Modification of Natural Monomers and Polymers*, Ph.D. Thesis submitted to Kerala University, 1992.
15. A. Guyot and M. Bartholin, *Prog. Polym. Sci.*, **8**, 277 (1982).
16. E. S. Freeman and B. Carroll, *J. Phys. Chem.*, **62**, 394 (1958).
17. D. A. Anderson and E. S. Freeman, *J. Polym. Sci.*, **54**, 253 (1961).
18. E. T. Conley, Ed., *Thermal Stability of Polymers, Vol. I, Monographs in Macromolecular Chemistry*, Marcel Dekker Inc., New York, 1970.
19. G. R. Marshall and R. B. Merrifield, in *Biochemical Aspects of Reaction on Solid Supports*, G. B. Stark, Ed., Academic Press, New York, 1977.
20. J. M. J. Frechet and M. J. Farral, in *Chemistry and Properties of Crosslinked Polymers*, S. S. Labana, Ed., Academic Press, New York, 1977.
21. R. B. Merrifield, *Br. Polym. J.*, **16**, 73 (1984).
22. K. W. Pepper, D. Reichenberg, and D. K. Hale, *J. Chem. Soc.*, **1952**, 3129 (1952).

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