

Synthesis and Characterization of New Hydrogels on the Basis of Water-Soluble Maleic Anhydride Copolymers with γ -Aminopropyltriethoxysilane

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ABSTRACT: This work describes the synthesis and macromolecular reactions of maleic anhydride (MA)–acrylic acid (AA) binary reactive copolymers with γ -aminopropyltriethoxysilane (APTS) as a polyfunctional crosslinker. Copolymers with a given composition of MA–AA (47.17–52.83 wt %) were synthesized by radical binary copolymerization with benzoyl peroxide as an initiator in *p*-dioxane at 70°C in nitrogen atmosphere and initial monomer ratio of 1 : 1. It is shown that the network structure is formed in MA–AA/APTS in water by intermolecular reaction between the anhydride unit and the amine group, as well as between the ethoxysilyl fragment and free carboxyl groups of the acrylic acid and maleic anhydride unit. Swelling parameters such as

beginning time of hydrogel formation, initial rate of swelling, swelling rate constant, equilibrium swelling, and equilibrium water content were determined for copolymer/APTS/water systems with various copolymer/crosslinker ratios. Formation of a hyperbranched network structure through the fragmentation of side-chain reactive groups in the studied systems was confirmed by FTIR, TGA, and DSC methods. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 90: 4009–4015, 2003

Key words: γ -aminopropyltriethoxysilane (APTS); maleic anhydride–acrylic acid (MA–AA) copolymer; crosslinking; hydrogels; swelling

INTRODUCTION

Design and synthesis of novel macromolecular architectures based on hyperbranched polymers and new types of composites including crosslinked networks, hydrogels, and solvent–gel systems are important fields of polymer science and macromolecular engineering.^{1,2} There are many different macromolecular structures that are possible for physical and chemical hydrogels. They include crosslinked or entangled networks of linear homopolymers, linear copolymers, and block or graft copolymers; polyion–multivalent ion, polyion–polyion, or H-bonded complexes; hydrophilic networks stabilized by hydrophobic domains; and interpenetrating networks or physical blends.³ From this position, highly reactive anhydride-containing macromolecules including alternating and random copolymers, cyclocopolymers, and block and graft copolymers of maleic anhydride (MA) and its isostructural analogies can serve as starting materials for the realization of the above-mentioned synthesis. Synthesis and macromolecular reactions of anhydride-

containing polymers and copolymers with various amines, epoxides, alcohols, polyols, and so forth were previously described and discussed.^{4,5}

Silane-based coupling agents, most frequently γ -aminopropyltriethoxysilane (APTS), were used to improve the surface adhesion in various polymer composites,⁶ to modify the surface of polypropylene⁷ and polyethylene films,⁸ and for the preparation of silica hybrid materials by *in situ* solvent (THF) gel process using a maleic anhydride (12 wt %) styrene random copolymer/tetraethoxysilane/APTS system.⁹ The interactions of MA–styrene or MA– α -olefins alternating copolymers with APTS were studied by means of FTIR–ART spectroscopy.¹⁰ Reaction of plasma-activated polyolefin films with MA–vinyltriethoxysilane oligomer led to an increase in the hydrophobicity of polypropylene surfaces as well as to a reduction in the swelling degree of films in cyclohexanone.⁷ It was shown that the reaction of plasma-activated polypropylene with MA–vinyltriethoxysilane oligomer proceeded through intermolecular esterification, intermolecular reaction of free carboxyl group with ethoxysilyl fragments, and polycondensation of the ethoxysilyl group with the formation of crosslinked poly(organosiloxane) structures on the polymer surface.⁷ Polyimide–silica hybrids were obtained using the non-aqueous solvent–gel process by polycondensation of phenyltriethoxysilane in a polyamic acid solution.¹¹ Self-catalyzed hydrolysis of phenyl-substituted alox-

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ysilane and modification on the polyimide structure were applied and resulted in highly compatible polyamide–silica hybrids. The prepared hybrid films with silica content (45 wt %) had high thermostability.

In the APTS–deuterated ethanol–H₂O system, the rate of release of ethanol from the ethoxy groups, a reaction that occurs during the condensation process, has been followed by use of ¹H-NMR spectroscopy at different temperatures.¹² By changing the hydrophilic–hydrophobic character of the precipitated silica, highly dispersed silica fibers were investigated.¹³ The immobilization of ethylenesulfide on silica gel surface was carried out by the sol–gel process.¹⁴ Recently we reported that some anhydride-containing copolymers easily undergo crosslinking with APTS in nonaqueous solutions.¹⁵ Synthesis and macromolecular reactions of MA–methyl methacrylate (MMA) and MA–*trans*-stilbene (Stb)–*n*-butyl methacrylate (BMA) reactive copolymer and terpolymers with APTS as a polyfunctional crosslinker were investigated.¹⁶ The effect of H-complex in radical terpolymerization of vinyl acetate–MA–acrylic acid (AA) and copolymerization of MA–AA were studied.¹⁷

In the present work, the experimental results on the macromolecular reactions of MA unit (47.17%)–AA (52.83%) alternating copolymer with APTS as a polyfunctional crosslinker and the swelling process in MA–AA/APTS/water systems are described and discussed.

EXPERIMENTAL

Materials

Initial monomer acrylic acid (AA: b.p. 141.6°C, m.p. 13.5°C, $d_4^{20} = 1.0510$, $n_D^{20} = 1.4215$), supplied by Fluka (Buchs, Switzerland), was distilled before use. Maleic anhydride (MA: m.p. 52.8°C; sublimation temperature 199°C; Fluka) was purified before use by recrystallization from anhydrous benzene and sublimation *in vacuo*. Benzoyl peroxide (BPO: m.p. 106°C) was purified by recrystallizing twice from chloroform solution by methanol after being dried under vacuum. Other reagents including organic solvents were purified by ordinary methods.

γ -Aminopropyltriethoxysilane [APTS, NH₂–CH₂–CH₂–CH₂–Si(OC₂H₅)₃; Fluka], used as a crosslinker, was purified before use by distillation under vacuum and had the following average characteristics: b.p. 217°C (110°C/25.5 mm), $d_4^{20} = 0.9420$, $n_D^{20} = 1.4210$.

Synthesis of binary copolymers

Copolymerization of MA with AA was carried out in degassed Pyrex glass tubes in *p*-dioxane in the presence of BPO (0.1%) as an initiator at 70°C under nitrogen atmosphere. Poly(MA–*alt*-AA) copolymer was

synthesized by the use of 1 : 1 mol ratios of initial monomers, respectively, and had the following characteristics: yield 75%; glass-transition temperature (T_g) 111°C; melting temperature (T_m) 153°C (by DSC analysis); intrinsic viscosity $[\eta]_{in}$ in *p*-dioxane at 25°C, 1.25 dL g⁻¹; acid number (AN) = 878 mg KOH/g; and monomer unit ratio in copolymer ($m_1 : m_2$) = 1 : 1.12.

After given amounts of monomers, initiators, and solvent mixture had been placed into the glass tube and then degassed by threefold freezing with subsequent melting under vacuum, the reaction system was blown off by purified nitrogen and the tube was sealed and placed in a thermostat with glycerin bath. To determine the copolymer yield in the reaction mixture, hydroquinone as an inhibitor was added, after which the mixture was poured into a large amount of methanol to precipitate the copolymer. The powder-like product obtained was separated by filtration and then purified by multiple washings in anhydrous methanol and *n*-hexane. The synthesized copolymer was dried under vacuum.

Synthesis of amino-silanized polymer networks

The crosslinking reactions of poly(MA–*alt*-AA) synthesis was carried out with APTS as a crosslinker in water at 40°C, 30–40 s before gel formation of the hydrogel. Then from the MA–AA/APTS solution with various ratios of polymer/crosslinker, the process of network structure formation was carried out under various thermotreatment conditions at 140°C (15, 30, and 45 min) and confirmed by FTIR structural analysis and both DSC and thermogravimetric (TGA) analyses of the network polymers formed. Crosslinking reactions were carried out using the polymer/crosslinker molar ratios: MA–AA : APTS: 11.1 : 1, 5.5 : 1, 2.75 : 1, and 1.85 : 1. Characteristics of each hydrogel sample were also determined.

Measurements

FTIR spectra of polymer powder films or coatings were recorded by FTIR Mattson 1000 (Great Britain) spectrometer in the 4000–400 cm⁻¹ range, where 30 scans were taken at 4 cm⁻¹ resolution. For the copolymer composition, maleic anhydride (1630 cm⁻¹) and acrylic acid (1580 cm⁻¹) analytical bands were used.

TGA and differential thermal analysis (DTA) was carried out with a derivatograph DuPont TA 951 (DuPont, Boston, MA) in nitrogen atmosphere at a heating rate of 10°C/min.

DSC analysis of copolymers was carried out under nitrogen atmosphere at a heating rate of 10°C/min using a DuPont 910 calorimeter. The AN values of the anhydride-containing copolymers were determined by an aqueous titration method using the following equation:

$$\text{AN (mg KOH/g)} = \frac{56.1(V_1N_1 - V_2N_2)}{m}$$

where V_1 is the total content of KOH before addition (mL), N_1 is the normality of KOH (0.0909N KOH), V_2 is the content of HCl required to titrate the abundant KOH (mL), N_2 is the normality of HCl (0.096N HCl), and m is the content of polymer sample (g).

The intrinsic viscosity of the synthesized copolymer was determined in *p*-dioxane at $25 \pm 0.1^\circ\text{C}$ and in the concentration range of 0.1–1.0 g/dL using a Ubbelohde viscometer (Cannon-Ubbelohde, State College, PA).

The swelling of MA-AA copolymer samples occurred in long cylindrical shapes cut into pieces 0.5 cm long. Polymer gels prepared in water for 1 week to remove uncrosslinked polymers were dried to constant weight in vacuum at 40°C before the swelling experiment. Powdered polymer gels were kept for swelling in water at 25°C to determine the degree of swelling; they were then removed from the silicon

TABLE I
Preparation Conditions of Polymer/Crosslinker System
[Poly(MA-*alt*-AA)/APTS] in Water at $40 \pm 0.1^\circ\text{C}$

Polymer crosslinker system	Initial polymer and APTS mixture		
	[P] (mol L ⁻¹)	[APTS] (mol L ⁻¹)	Molar ratio (P/APTS)
Poly(MA- <i>alt</i> -AA)/APTS	11.8	1.06	11.1 : 1
	11.8	2.13	5.54 : 1
	11.8	4.26	2.75 : 1
	11.8	6.38	1.85 : 1

bath, dried, weighed, and placed in the same bath. The swelling degree of crosslinked polymer/APTS crosslinker systems was determined gravimetrically by the following equation:

$$S (\%) = \frac{M_t - M_0}{M_0} \times 100$$

where M_0 is the dry/initial weight of the polymer gel and M_t is the weight of swollen gel at a given time (t) in water.

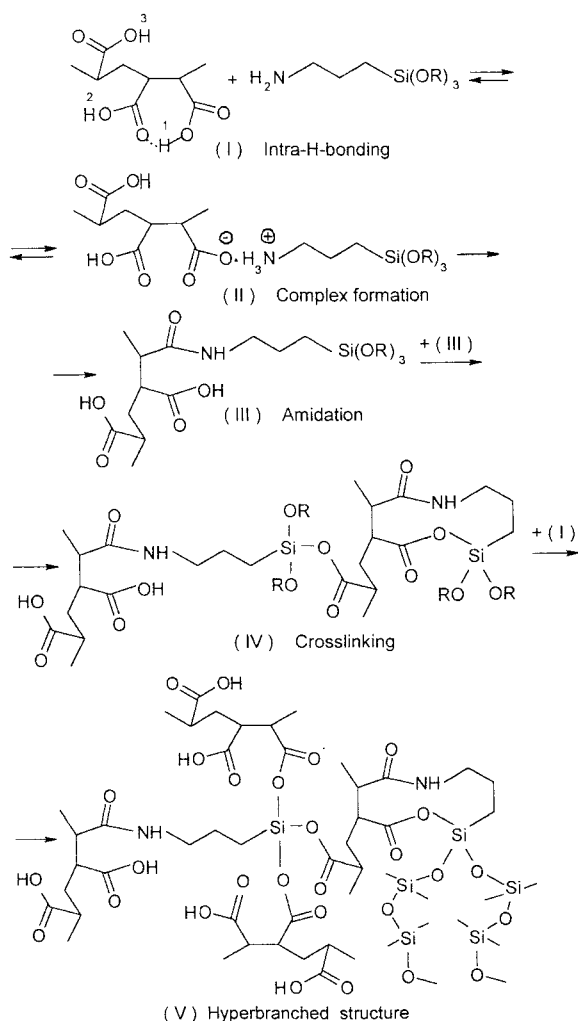
RESULTS AND DISCUSSION

Macromolecular reactions of binary poly(MA-*alt*-AA) with APTS

For the studies of crosslinking and swelling process, anhydride-containing poly(MA-*alt*-AA) alternating copolymer with 47.17 wt % MA units was used as a crosslinkable polymer. APTS containing amine and triethoxysilyl reactive groups was used as a polyfunctional crosslinker.

From the structural peculiarities of these polymers/crosslinker systems and classical principle of macromolecular reactions it can be assumed that the hyperbranched network structure in these systems will be formed by the intermolecular reactions between the anhydride unit and the amine group as well as between the ethoxysilyl and free carboxyl fragments. The general scheme of crosslinking reactions of anhydride-containing copolymer can be represented in the following form (**Scheme 1**).

It is shown that the gel-formation process in the poly(MA-*alt*-AA) copolymer/APTS systems starts after heating at 40°C and intensive mixing of these polymer/crosslinker solutions in water for a prescribed period of time. Table I represents the preparation conditions of polymer/crosslinker systems in water. The beginning time of gel formation in the studied system depends on the type of polymer, polymer/crosslinker ratio, temperature, and other factors. After gel formation started, there was a dramatic increase of viscosity in polymer/crosslinker solutions and the formation of hydrogels was also observed.



Scheme 1

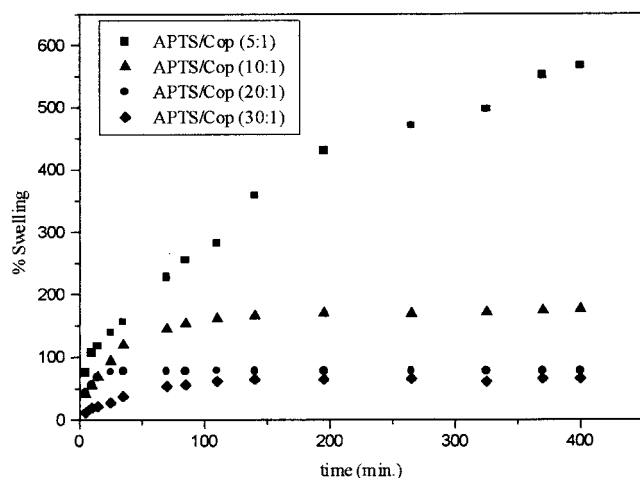


Figure 1 Kinetic curves of swelling of poly(MA-*alt*-AA)/APTS system using various ratios of copolymer/crosslinker.

To elucidate some peculiarities of the gel-formation process in poly(MA-*alt*-AA)/APTS crosslinker systems, swelling parameters such as beginning time of hydrogel formation (G_t), equilibrium swelling, initial swelling rate (r_i), rate constant (k_s), maximum swelling equilibrium S_{max} , Fick coefficients (k , n), and equilibrium water content (EWC) were determined by using known methods that are described in the Experimental section. A fundamental relationship exists between the swelling of a crosslinked polymer in a solvent and the nature of polymer and the solvent. Swelling of the three-dimensional network structure in a suitable solvent is the most important parameter for swelling measurements.^{18,19} The kinetic curves of swelling in the investigated poly(MA-*alt*-AA)/APTS system using various molar ratios of copolymer/crosslinker are illustrated in Figure 1. The swelling capacities of poly(MA-*alt*-AA)/APTS gels increase with time, but after a certain period, they show constant swelling and the swelling process is transformed to the equilibrium state.²⁰ The increase of APTS concentration in the gel system causes a decrease in swelling behavior. The swelling curves of hydrogels were used for the calcu-

lation of the nature of diffusion (F) of water into hydrogels²¹:

$$F = M_t/M_\infty = kt^n \quad (1)$$

where M_t and M_∞ denote the amount of solvent diffused into the gel at time t and infinite time (at equilibrium), respectively; k is a constant related to the structure of the network; and the exponent n is a number used to determine the type of diffusion. For cylindrical shapes, $n = 0.45$ – 0.50 and corresponds to Fickian diffusion, whereas $0.50 < n < 1.0$ indicates that the diffusion is non-Fickian.²² The equation was applied to the stages of swelling and plots of $\ln F$ against $\ln t$ yielded straight lines from which exponent n and k were calculated from the slope and intercept of lines listed in Table II. It is seen from the table that the values of the diffusion exponent range between 0.424 and 0.562 and are found to be nearly 0.50. Hence the diffusion of water into poly(MA-*alt*-AA)/APTS hydrogels was taken to be both Fickian and non-Fickian in character. It can also be noticed from this table that at the higher crosslinked MA-AA/APTS gel structure, the greater the transport of water into the hydrogels, the more the diffusion becomes non-Fickian. This behavior is generally explained as a consequence of slow relaxation rate of the polymer matrix.

For extensive swelling of poly(MA-*alt*-AA)/APTS hydrogels, the following equation²³ can be written:

$$t/S = A + Bt \quad (2)$$

where $B = 1/S_{eq}$ is the reciprocal of the maximum or equilibrium swelling; $A = 1/(k_s S_{eq}^2)$ is the reciprocal of the initial swelling rate of the gel; and k_s is the swelling rate constant. This relation represents second-order kinetics (Fig. 2). The obtained results are given in Table II. The values of theoretical equilibrium swelling of the hydrogels are in good agreement with the results of equilibrium swelling of poly(MA-*alt*-AA)/APTS hydrogels (Fig. 1). It is well known that the swelling phenomena are directly related to the struc-

TABLE II
Swelling Parameters of Various Copolymer/APTS Systems^a

Molar ratio [Cop/APTS]	G_t (min)	% S_{eq}	Swelling parameters			Fick coefficient		% EWC
			r_i^b	k_A^c	S_{max}	k	n	
11 : 1	60	593	0.1477	1.52×10^{-5}	666.7	0.0628	0.424	85.6
5.5 : 1	60	171	0.1098	2.69×10^{-4}	183.8	0.1142	0.469	63.1
2.75 : 1	60	77.5	0.0218	7.52×10^{-3}	78.1	0.3444	0.310	43.5
1.85 : 1	60	67	0.362	2.25×10^{-4}	66.7	0.0699	0.562	39.6

^a G_t , beginning time of gel formation; % S_{eq} , equilibrium swelling; r_i , initial swelling rate; k_A , swelling rate constant; n and k , Fick coefficients; %EWC, equilibrium water content.

^b (g water/g gel)/min.

^c (g gel/g water)/min.

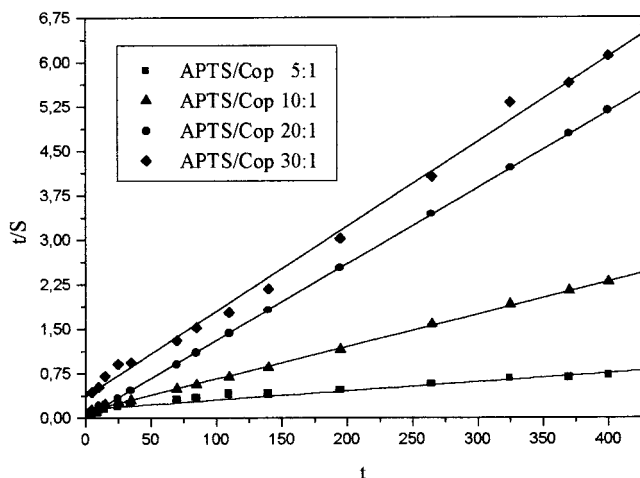


Figure 2 Swelling (%) versus time (min) plots for the poly(MA-*alt*-AA)/APTS at different polymer/APTS ratios.

ture of crosslinked polymer and/or the density of gel. Percentage equilibrium water content (%EWC) was calculated from the following equation²³:

$$\text{EWC} = \frac{W_{\text{eq}} - W_{\text{dry}}}{W_{\text{eq}}} \times 100 \quad (3)$$

where W_{eq} is the water content diffused into the gel at equilibrium state and W_{dry} is the weight of initially dried gel; determined EWC values are presented in Table III. Along with the increase of the APTS concentration in the gel system, the EWC is decreased for hydrogel systems. Both the EWC and the swelling behavior of a hydrogel mainly depend on the nature of the network structure, that is, hydrophilicity, crosslink density, and the average molecular weight between two consecutive crosslinks.

FTIR studies of intra- and intermolecular reactions between the functional groups of the polymers and APTS

Analysis of the FTIR spectra allows determination of the following changes of macromolecules as a consequence of the intermolecular reactions between the functional groups of the polymers and APTS:

1. Increase of the anhydride unit band at 1716 cm^{-1} ($\nu_{\text{C=O}}$) [Fig. 3, spectrum (a)].
2. Disappearance of the 3425 cm^{-1} peak of $-\text{COOH}$ because of intra-H bonding between MA $-\text{C=O}$ groups.
3. Appearance of a new peak at 3030 cm^{-1} attributed to complex formation (1,1 and 1,2 complexes) between amine groups of APTS and $-\text{COOH}$ of MA groups.
4. The intensity of bands appreciably increases by thermotreatment, as shown in Figure 3 (spectra). With respect to the full transformation of the anhydride unit to the amide form in the case of gel-coating system containing a relatively high concentration of APTS, these observed changes can be explained by the initial amidization reaction of the anhydride unit as shown in **Scheme 1**.
5. The appearance of new N—H bands at $1580\text{--}1640 \text{ cm}^{-1}$ (for the amide group) in the form of a doublet attributed to the known interaction between symmetrical stretching and bending vibrations in the $-\text{O=C-NH-}$ group; the intensity of these bands increases by thermotreatment (Fig. 4). A new band at 1640 cm^{-1} is related to the antisymmetrical stretching vibration of the amide band; it is a known fact that even in the case of interaction between MA copolymers and the same drugs with a free amine group, reaction proceeds by amidization of the anhydride group, and the FTIR analysis indicates the formation of the amide band.
6. The presence of the bands at 1610 and 1485 cm^{-1} attributed to the stretching vibrations of the $-\text{C=O}$ groups and the carboxylate ion groups ($-\text{C=O}$ in $-\text{COOH}$, $-\text{COO}^-$, NH_3^+ , and $-\text{COOSi}(\text{OEt})_n$ fragments). Reaction of the anhydride cycle with the primary and carbonyl group in the salt form ($-\text{COOH} \cdot \text{NH}_2^-$) is a known fact; furthermore the deformation bands between 1400 and 1635 cm^{-1} represent impacts of the formed silicon carboxylate fragments in the network structure and the Si—O—Si stretching bands appear in the field of $1029\text{--}1120$ and 850 cm^{-1} , which also confirmed the formation of a crosslinked network in the studied systems

TABLE III
Thermal Characteristics of Copolymer and Its Networks

Copolymer and networks	T_g (°C)	T_{dec} (°C)	Weight loss at different temperatures (°C)						
			150	200	250	300	350	400	450
Poly(MA- <i>alt</i> -AA)	111	290	2.5	20.0	22.5	27.5	32.5	37.5	42.5
Poly(MA- <i>alt</i> -AA)/APTS (11.1 : 1)	187	421	0.0	5.0	25.0	35.0	45.0	47.5	57.5
Poly(MA- <i>alt</i> -AA)/APTS (5.54 : 1)	188	423	0.0	7.5	17.5	30.0	35.0	40.0	55.0
Poly(MA- <i>alt</i> -AA)/APTS (2.75 : 1)	188	492	0.0	10.0	20.0	27.5	30.0	35.0	40.0
Poly(MA- <i>alt</i> -AA)/APTS (1.85 : 1)	190	497	1.0	11.5	17.5	22.5	25.0	27.5	37.5

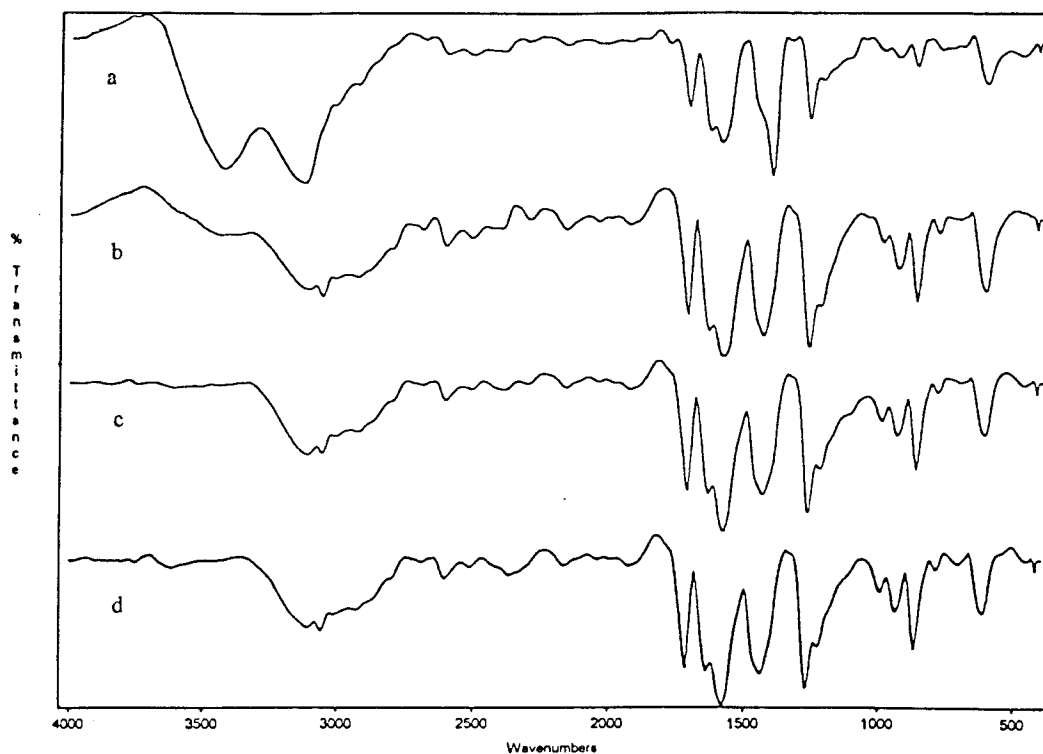


Figure 3 FTIR spectra of (a) poly(MA-*alt*-AA) and poly(MA-*alt*-AA)/APTS (10 : 1) gel system thermotreatment at 140°C for (b) 15 min, (c) 30 min, and (d) 45 min.

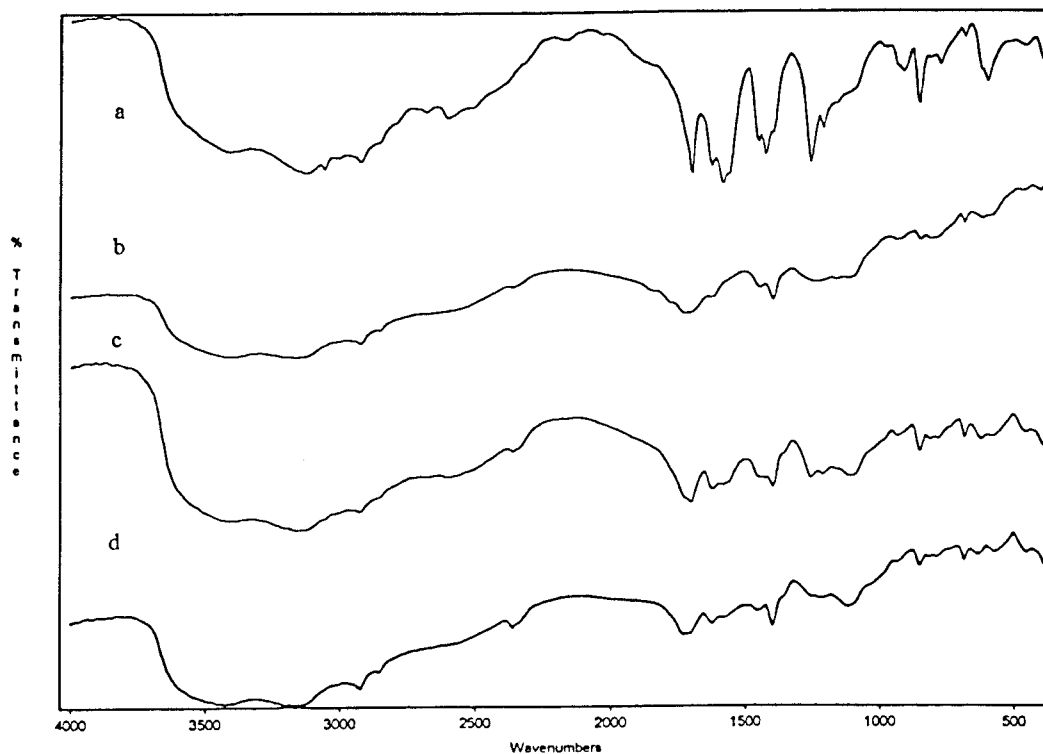


Figure 4 FTIR spectra of poly(MA-*alt*-AA)/APTS gel systems with different molar ratios of copolymer/APTS: (a) 5 : 1, (b) 10 : 1, (c) 20 : 1, and (d) 30 : 1.

through the fragmentation of side-chain ethoxysilyl groups initiating with free carboxyl groups as shown in **Scheme 1**.

Thermal behaviors of copolymer and their networks

The values of the glass-transition temperature (T_g), the weight loss at different temperatures, and decomposition temperature (T_{dec}) for synthesized copolymer and its various networks were obtained from DSC and TGA analysis. Some thermal characteristics of binary copolymers and their networks are represented in Table III. As evidence from these values at the lower concentration of APTS, T_g values of networks decreased. Amide and siloxane-containing crosslinked networks give the networks high thermostability to the copolymer [poly(MA-*alt*-AA) $T_g = 111^\circ\text{C}$]. All the DSC thermograms having a broad exo-peak at 50–120°C can be related to crosslinking reactions proceeding in the isothermal conditions of DSC. T_m endo-peaks disappeared by transfer to the network structure and shifted to the thermodestruction region of the crosslinked copolymers.

CONCLUSIONS

In accordance with the present investigation and experimental results obtained it can be concluded that the anhydride-containing binary poly(MA-*alt*-AA) easily undergoes a crosslinking reaction with polyfunctional APTS through intermolecular reactions of anhydride unit amine groups and ethoxysilyl groups with the formation of the hyperbranched network structure containing amide and siloxane crosslinked fragments. It is observed that poly(MA-*alt*-AA)/APTS (1.85 : 1) has high crosslinking, low swelling properties, and high thermal stability compared to those of the lower APTS composition.

Generally, this reaction can be applied to the wide range of anhydride-containing polymers such as random or alternating copolymers, terpolymers, and cy-

clopolymers of MA, which would allow us to design new macromolecular architectures with given hyperbranched network structure and synthesize novel types of supercomposites with unique properties. These will be the focus of our future studies.

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