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# Reactions of some anhydride-containing copolymers with γ-aminopropyltriethoxysilane

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**Abstract**

This work describes the synthesis and macromolecular reactions of maleic anhydride (MA)–methyl methacrylate (MMA) binary and MA–*trans*-stilbene (Stb)–*n*-butyl methacrylate (BMA) ternary reactive copolymers with γ-aminopropyltriethoxysilane (APTS) as a polyfunctional crosslinker. Copolymers with given compositions of MA–MMA (77.7 mol%) and MA (22.7 mol%)–Stb–BMA (54.2 mol%) are synthesised by radical binary and ternary copolymerisations with benzoyl peroxide as an initiator in toluene at 70°C and initial monomer ratios 1:4 and 1:1:1, respectively. It is shown that the network structure is formed in MA–MMA/APTS and MA–Stb–BMA/APTS in methyl ethyl ketone (MEK) solutions by intermolecular reactions between the anhydride unit and the amine group, as well as between the ethoxysilyl fragment and the free carboxyl group formed after the amidisation of the anhydride unit. Swelling parameters, such as the beginning time of xerogel-formation, initial rate of swelling and equilibrium swelling, are determined for the copolymer/APTS/MEK system with various polymer/crosslinker ratios. Formation of a hyperbranched network structure through the fragmentation of side-chain reactive groups in the studied systems is confirmed by FTIR, TGA and DSC methods.

*Keywords*: γ-aminopropyltriethoxysilane; Macromolecular reaction; Swelling

## 1. Introduction

Design and synthesis of novel macromolecular architectures based on hyperbranched polymers and new type of composites including crosslinked networks, hydrogels and solvent–gel systems are important fields of polymer science and macromolecular engineering [1–4]. From this position, highly reactive anhydride-containing macromolecules including alternating and random copolymers and terpolymers, cyclocopolymers, block and graft copolymers of maleic anhydride and its isostructural analogies can serve as starting materials for the realisation of the above-mentioned synthesis. Synthesis and macromolecular reactions of anhydride-containing polymers and copolymers with various amines, epoxides, alcohols, polyols, etc. were described and discussed [5,6].

Non-linear optical polymers with high glass transition temperature (178–228°C) were prepared by the polymer analogous reaction of maleic anhydride copolymers with aminoalkyl-functionalised azo- and stilbene chromophores [7]. A series of all solvent–gel organic–inorganic non-linear optical materials based on the melamines and an alkoxysilane dye was also investigated [8].

Silane-based coupling agents, most frequently γ-aminopropyltriethoxysilane (APTS), were used to improve the surface adhesion in various polymer composites [9], to surface modify polypropylene[10] and polyethylene films [11], and for the preparation of silica hybrid materials by situ solvent (THF)–gel process using maleic anhydride (12 mol%)–styrene random copolymer/tetraethoxysilane/APTS system [12]. The interactions of MA–styrene or MA–α-olefins alternating copolymers with APTS were studied by means of FTIR-ART spectroscopy [13]. Reaction of plasma-activated polyolefin films with maleic anhydride–vinyltriethoxysilane oligomer led to an increase in the hydophobicity of polypropylene surfaces as well as to a reduction in the swelling degree of films in cyclohexanone [10]. It was shown that the reaction of plasma-activated polypropylene with maleic anhydride–vinyltriethoxysilane oligomer proceeded through intermolecular esterification, intramolecular reaction of free carboxyl group with ethoxysilyl fragments and polycondensation of ethoxysilyl groups with the formation of crosslinked poly (organosiloxane) structures on the polymer surface [10]. Polyimide–silica hybrids were obtained using the non-aqueous solvent–gel process by polycondensation of phenyltriethoxysilane in a

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polyamic acid solution [14]. Self-catalysed hydrolysis of phenyl-substituted aloxysilane and modification on the polyimide structure were applied and resulted in highly compatible polyimide–silica hybrids. The prepared hybrid films with high silica content (45%) had high thermostability.

Recently we have reported that some anhydride-containing copolymers easily undergo crosslinking with APTS in non-aqueous solutions [15]. In the present work, the experimental results on the macromolecular reactions of maleic anhydride (MA unit of 22 mol%)–methyl methacrylate (MMA) random copolymer and MA (24.3 mol%)–*trans*-stilbene (Stb)–*n*-butyl methacrylate (BMA unit of 45.3 mol%) terpolymer with APTS as a polyfunctional crosslinker and the swelling process in the MA–MMA/APTS/MEK (solvent) and MA–Stb–BMA/APTS/MEK systems are described and discussed.

## 2. Experimental part

### 2.1. Materials

Initial monomers such as methyl methacrylate (MMA) and *n*-butyl methacrylate (BMA) supplied by Fluka, were distilled before use. They had the following characteristics: MMA, b.p. 99.5°C, $d_4^{20} = 0.943$ and $n_D^{20} = 1.414$; BMA, b.p. 162.5°C, $d_4^{20} = 0.892$ and $n_D^{20} = 1.420$. Maleic anhydride (MA, Fluka product) was purified before use by recrystallisation from anhydrous benzene and by sublimation in vacuo, m.p. 52.8°C and sublimation temperature 199°C. Commercial *trans*-stilbene (Stb) was purified before use by two recrystallisations from concentrated benzene solution, m.p. 124°C.

Benzoyl peroxide initiator (BP) as a Fluka product was purified by recrystallising twice from chloroform solution with methanol. It was dried under vacuum, m.p. 106°C.

γ-Aminopropyltriethoxysilane (APTS, Fluka product), using as a crosslinker, $NH_2–CH_2CH_2CH_2–Si(OC_2H_5)_3$, was purified before use by distillation under vacuum and had the following average characteristics: b.p. 217°C (110°C/25.5 mm) $d_4^{20} = 0.9420$ and $n_D^{20} = 1.4210$.

### 2.2. Synthesis of binary and ternary copolymers

Synthesis of MA–MMA binary copolymer was carried out in degassed Pyrex glass tubes in toluene with BP (0.2%) as an initiator at 70°C under nitrogen atmosphere. After the given amount of monomers, initiator and solvent mixture had been placed into the glass tube and then degassed by three-fold freezing with subsequent melting under vacuum, the reaction system was blown off by purified nitrogen and the tube was sealed and put into a thermostat with glycerine bath. In order to determine the copolymers yield in the reaction mixture, hydroquinone as an inhibitor was added, then this mixture was poured into a large amount of methanol to precipitate the copolymers. The powder-like product obtained was separated by filtration, then purified by multiple washing in the methanol and diethyl ether, and filtration. The copolymers were dried under vacuum at 40°C to constant weight. The reaction conditions: [MA] = 0.5 mol/l, [MMA] or [BMA] = 2.0 mol/l, monomer ratio [MA]:[MMA] (or [BMA]) = 4 : 1, $[\text{benzene}]/[M]_{\text{total}} = 3.5$, $[BP] = 2.1 \times 10^{-3}$ mol/l, reaction temperature 70 ± 0.1°C, reaction time 3 h.

The MA–MMA random copolymer synthesised by a given concentration and molar ratio of the initial monomers had the following characteristics: yield 82.6%, glass transition temperature $T_g = 140$°C (by DSC), $T_m = 192$°C (by DSC), intrinsic viscosity $[\eta] = 0.91$ dl/g in dioxane at 25°C, acid number (AN) = 251 mg KOH/g, monomer unit ratio in copolymer $(m_1 : m_2) = 1 : 3.48$.

For the synthesis of MA–Stb–BMA ternary copolymer, terpolymerisation reaction was carried out in degassed glass tubes or dilatometer methyl ethyl ketone (MEK) with BP as an initiator (0.2%) at 70°C under nitrogen atmosphere. After allowing the reaction to proceed for a given time, the reactive mixture was poured into a large amount of methanol or *n*-hexane (solution/precipitator = 1:5) to precipitate the terpolymer and was separated by filtration. Then, terpolymer was purified by washing several times in methanol and diethyl ether and was redeposited by centrifugation. Terpolymers synthesised was powdered in liquid nitrogen and the powder-like product obtained was dried under vacuum at 40°C to constant weight.

The reaction conditions: $[M_i] = 0.5$ mol/l, monomer ratio of [MA]:[Stb]:[BMA] = 1:1:1, $[\text{MEK}]/[M]_{\text{total}} = 3.5$, $[BP] = 2.1 \times 10^{-3}$mol/l, reaction temperature 70 ± 0.1°C, reaction time 3 h.

The MA–Stb–BMA terpolymer synthesised by a given concentration and molar ratio of the initial monomers had the following characteristics: yield 76.5%, glass transition temperature $T_g = 78$°C (by DSC), $T_m = 185$°C (by DSC), intrinsic viscosity $[\eta] = 0.21$ dl/g in MEK at 25°C, acid number (AN) = 160 mg KOH/g.

### 2.3. Synthesis of amino-silanised polymer networks

The crosslinking reactions of MA–MMA copolymer and MA–Stb–BMA terpolymer synthesised were carried out with γ-aminopropyltriethoxysilane (APTS) as a crosslinker in the non-aqueous MEK solution at 40°C for 30–40 s before the formation of xerogel. Then, from MA–MMA/ARTS and MA–Stb–BMA/ARTS solutions with various ratios of polymer/crosslinker, thin polymer coatings were formed on the glass or KBr disk surface. The process of formation of network structures on the surface was carried out in the various thermotreatment conditions (at 80°C for 15 min and at 110°C for 30 min) and confirmed by FTIR structural analysis as well as by DSC and thermogravimetric (TGA) analyses of the network polymers formed. Crosslinking reactions were carried out using the following polymer/crosslinker molar ratios: MA–MMA (or MA–Stb–BMA):ARTS = 5:1, 10:1 and 20:1. For each sample of the polymer xerogels, the swelling characteristics were also determined.

### 2.4. Measurements

Fourier transformation infrared (FTIR) spectra of polymer powders, films or coatings were recorded with FTIR Nicolet 510 spectrometer in the 4000–400 $\mathrm{cm}^{-1}$ range, where 30 scans were taken at 4 $\mathrm{cm}^{-1}$ resolution. For the composition analysis of terpolymer, specifically contents of Stb and BMA units, absorption bands of 764 (mono-substituted benzene ring) or 711 $\mathrm{cm}^{-1}$ (aromatic ring), and 1733 $\mathrm{cm}^{-1}$ (C=O ester group) were used as analytical bands. For the MA unit, an absorption band of 1852 $\mathrm{cm}^{-1}$ of C=O group was also used. The absorption bands of 1180 and 1354 $\mathrm{cm}^{-1}$, the intensity of which almost does not change for the various compositions of terpolymers, are used as standard bands.

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

Differential scanning calorimetry (DSC) analysis of copolymers and terpolymers was carried out under nitrogen atmosphere at a heating rate of 10°C/min using a DuPont 910 calorimeter.

The acid number (AN) of the anhydride-containing copolymers and terpolymers were determined by non-aqueous titration method using the following equation:

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

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

Intrinsic viscosities of copolymers and terpolymers synthesised were determined in toluene or MEK at $20 \pm 0.1$ or $25 \pm 0.1$°C and in the concentration range of 0.1–1.0 g/dl using an Ubbelohde viscosimeter.

The swelling of MA–BMA copolymer and MA–Stb–BMA terpolymer samples have been obtained in long cylindrical shapes cut into pieces 0.5 cm long. Polymer gels prepared in MEK or *p*-dioxane solvent were first immersed in purified MEK for a week to remove uncrosslinked polymers dried to constant weight in vacuum at 40°C before the swelling experiment. Powdered polymer gels were left for swelling in MEK at 25°C to determine the swelling; then they were removed from the silicon bath, dried, weighted and placed in the same bath. The swelling degree of crosslinked polymer/APTS crosslinker systems was determined gravimetrically by the following equation:

$$S(\%) = [(M_t - M_0)/M_0]100$$

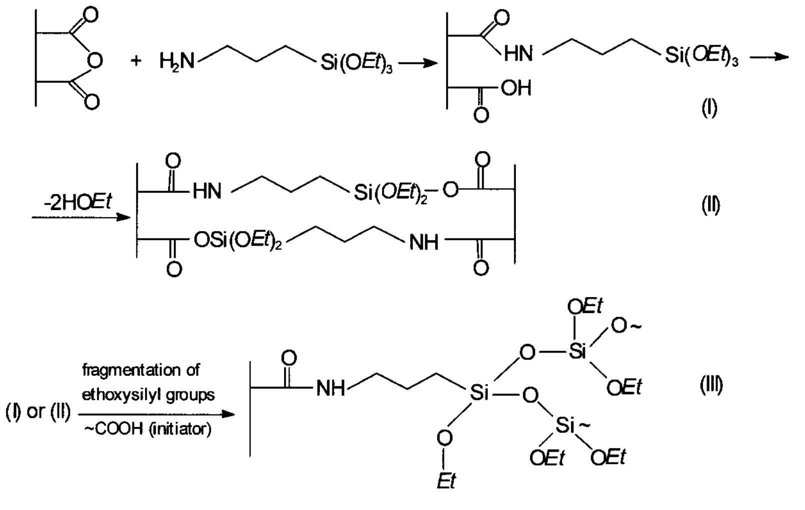
where $M_0$ is the dry/initial weight of polymer gel, $M_t$ the weight of swollen gel at given time ($t$) in MEK or *p*-dioxane.

## 3. Results and discussion

### 3.1. Macromolecular reactions of binary and ternary copolymers with γ-aminopropyltriethoxysilane

For the studies of crosslinking and swelling process, anhydride containing MA–MMA random copolymer with 22.5 mol% of MA-units and MA–Stb–BMA terpolymer with a monomer unit composition of $m_1 : m_2 : m_3 = 22.97 : 23.15 : 53.94$ are used as crosslinkable polymers. APTS containing amine and triethoxysilyl reactive groups is 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 (forming after amidisation of anhydride units) fragments. The general scheme of crosslinking reactions of anhydride containing copolymer or terpolymer can be presented in the following form:



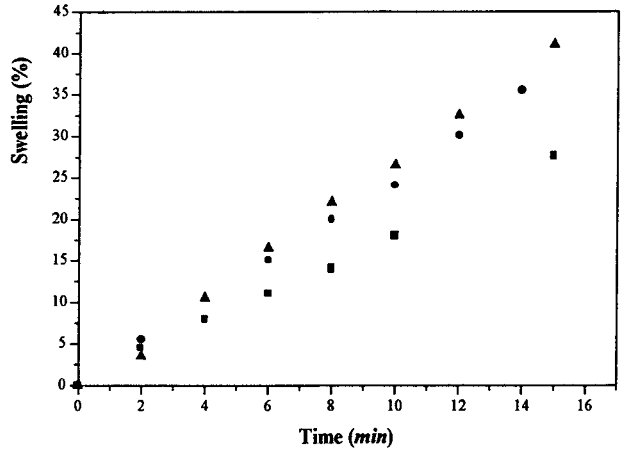


Fig. 1. Swelling (%)–time (min) plots for MA–MMA copolymer/APTS systems in the initial stationary state of swelling at different copolymer/crosslinker molar ratios: 5:1 (–△–), 10:1 (–●–) and 20:1 (–□–).

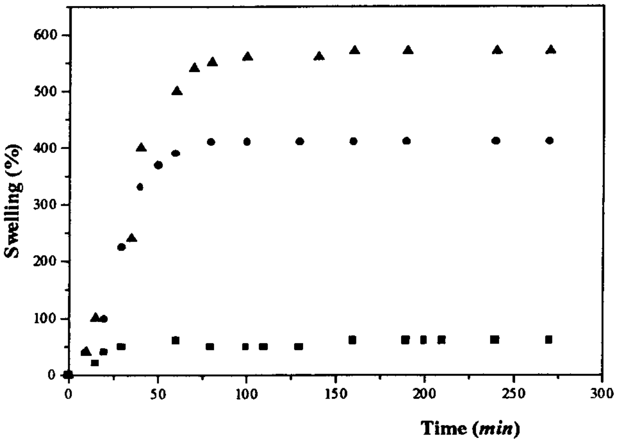


Fig. 2. Kinetic curves of swelling for the MA-MMA random copolymer/APTS system in MEK solution at 40 ± 0.1°C in various concentrations of APTS. [MA–MMA] = constant = 1.5 mol/l; [APTS] = 0.3 (–△–), 0.15 (–●–) and 0.075 mol/l (–□–).

It is shown that the gel-formation process in MA–MMA copolymer/APTS and MA–Stb–BMA terpolymer/APTS crosslinker systems starts after heating at 40°C and intensive mixing of these polymer/crosslinker solutions in MEK during a certain period of time. The beginning time of gel-formation in the studied systems depends on the type of polymer, polymer/crosslinker ratio, temperature and other factors. After starting gel-formation, the dramatical increase of viscosity in polymer/crosslinker solutions and the formation of xerogels are observed.

For the elucidation of some peculiarities of gel-formation process in MA–MMA copolymer/APTS and MA–Stb–BMA terpolymer/APTS crosslinker systems, swelling parameters such as beginning time of xerogel-formation ($G_t$), initial rate of xerogel-formation ($R_s$) and equilibrium swelling ($S_{eq}$) are determined by using known methods which are described in Section 2.

The values of $R_s$ are determined from the slopes of the swelling–time plots (Fig. 1, for MA–MMA/APTS copolymer system) and using the data of Table 1 (for MA–Stb–BMA terpolymer/APTS) in the initial stationary state of swelling when these plots have a linear character.

The kinetic curves of swelling in the studied MA–MMA copolymer/APTS system using various molar ratios of copolymer/crosslinker are illustrated in Fig. 2. Experimental data of swelling–time plots for MA–Stb–BMA terpolymer/APTS system using different concentrations of APTS are presented in Table 1 and Figs. 3 and 4. It is clearly seen that the swelling capabilities of both xerogels are increased by time, but after a certain time these systems show constant swelling behaviour, and the swelling process is transformed to the equilibrium state. The increase of APTS concentration in the limited range provided an increase of swelling behaviour.

Experimental results are presented in Table 1. As seen from these data, swelling parameters essentially change with increasing polymer/crosslinker ratio and the substitution of copolymer with terpolymer in the systems studied.

The results obtained only allow to reflect the possibility of the network structure formation in the MA–MMA copolymer/APTS and MA–Stb–BMA terpolymer/APTS xerogel systems.

The formation of the network structure is also confirmed by the FTIR studies of the structural changes inthe MA–MMA copolymer/APTS and MA–Stb–BMA terpolymer/

Table 1

Swelling parameters ($G_t$, beginning time of gel-formation; $R_s$, initial rate of gel-formation and $S_{eq}$, equilibrium swelling) of the various MA–MMA/APTS and MA–Stb–BMA/APTS systems in the methyl ethyl ketone solutions at 40 ± 0.1°C

| Polymer and crosslinker system | Initial polymer and APTS mixture | | | Swelling parameters of xerogels | | |
|---|---|---|---|---|---|---|
| | [P] (mol l$^{-1}$) | [APTS] (mol l$^{-1}$) | Molar ratio (P:APTS) | $G_t$ (min) | $R_s$ (% min$^{-1}$) | $S_{eq}$ (%) |
| MA–MMA copolymer and APTS | 1.5 | 0.30 | 5:1 | 30 | 1.85 | 52 |
| | 1.5 | 0.15 | 10:1 | 75 | 2.46 | 415 |
| | 1.5 | 0.075 | 20:1 | 145 | 2.57 | 565 |
| MA–Stb–BMA Teropolymer and APTS | 1.5 | 0.30 | 5:1 | 21 | 3.75 | 78 |
| | 1.5 | 0.15 | 10:1 | 62 | 7.84 | 560 |
| | 1.5 | 0.075 | 20:1 | 105 | 15.20 | 895 |

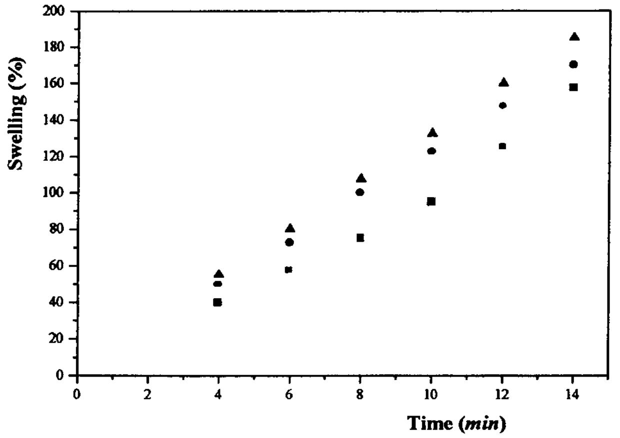


Fig. 3. Swelling (%)–time (min) plots for the MA–Stb–BMA terpolymer/APTS system in the initial stationary state of swelling at different polymer/crosslinker molar ratios: 5:1 (–△–), 10:1 (–●–) and 20:1 (–□–).

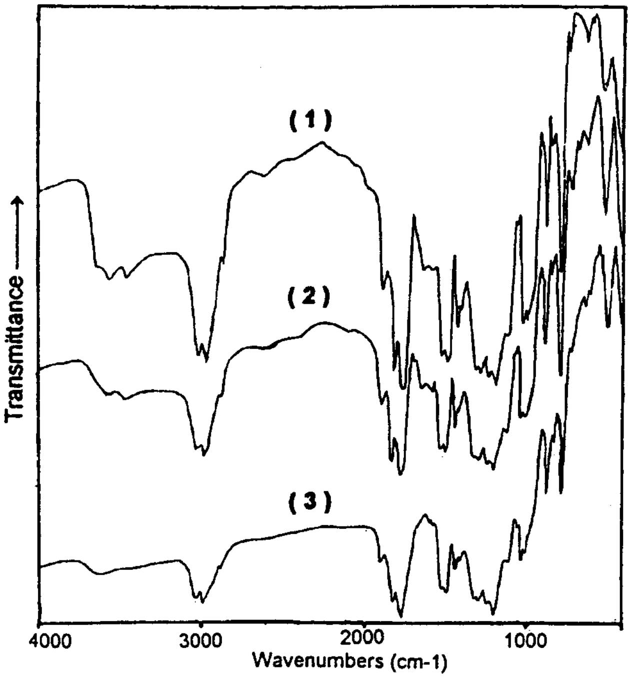


Fig. 5. FTIR spectra of MA–MMA copolymer/APTS (copolymer:APTS = 10:1) gel-coating before (3) and after thermotreatment at 80°C during 30 min (2) and at 110°C during 15 min (1).

APTS systems. The thin polymer coatings on the surface of the KBr pill are prepared from the MEK solution of polymers/APTS mixtures and undergo thermotreatment at 80°C for 30 min and at 110°C for 15 min. Then, the FTIR spectra of the surface coatings formed (before and after themotreatments) are recorded. Results obtained for the MA–MMA copolymer/APTS are illustrated in Figs. 5 and 6. The intense bands at 1845, 1770 and 1729 cm$^{-1}$ in the spectra of the starting MA–MMA copolymer (spectra 1, Fig. 6) and MA–MMA copolymer/APTS gel-coating systems (spectra 1–3, Fig. 5 and spectra 2–5, Fig. 6) are assigned to the carbonyl groups of the anhydride unit and the ester fragment of the macromolecules, respectively.

The analysis of the FTIR spectra allows us to reveal the following structural changes of macromolecules as a consequence of the intermolecular reactions between the functional groups of polymers and APTS: (1) essential increase (Fig. 5, spectra 1–3) and then full disappearance of the anhydride unit band at 1845 and 1770 cm$^{-1}$ ($\nu_{C=O}$) (Fig. 6, spectra 5); (2) appearance of new N–H bands at 1560 cm$^{-1}$ (for amide group) in the form of a doublet with 1571 and 1542 cm$^{-1}$ due to the known interaction between symmetrical stretching and bending vibrations in O=C–NH group [16]; the intensity of these bands appreciably increases by thermotreatment; this effect is more appreciable for spectra 5 (Fig. 6) related 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 changes observed can be explained by the initial amidisation reaction of the anhydride unit as shown in the scheme; (3) a new band at 1645 cm$^{-1}$ is related to the antisymmetrical stretching vibration of the amide bond; it is a known fact [17] that even in the case of the interaction between MA copolymers and some drugs with a free amine group, reaction proceeds via the amidisation of the anhydride group, and the FTIR analysis indicates the formation of a new amide band at 1645–1650 cm$^{-1}$; (4) presence of the bands at 1610–1595, 1485 and 1324 cm$^{-1}$ arising from the stretching vibrations of the C=O groups and the carboxylate ion groups (C=O in –COOH, $-COO^{-}$. $^{+}NH_3$– and $-COOSi(O\mathit{Et})_n$ fragments); it is a known fact that the reaction of the anhydride cycle with primary aliphatic amine provides the formation of monoamide and carbonyl group in the salt form ($-COOH \cdot NH_2-$) [18]; furthermore, the enhanced deformation bands between 1635–1400 cm$^{-1}$ represent impacts of the formed silicon carboxylate fragments in the network structure) and (4) Si–O–Si stretching bands appear in the field of 1120 and 1029 cm$^{-1}$ which also

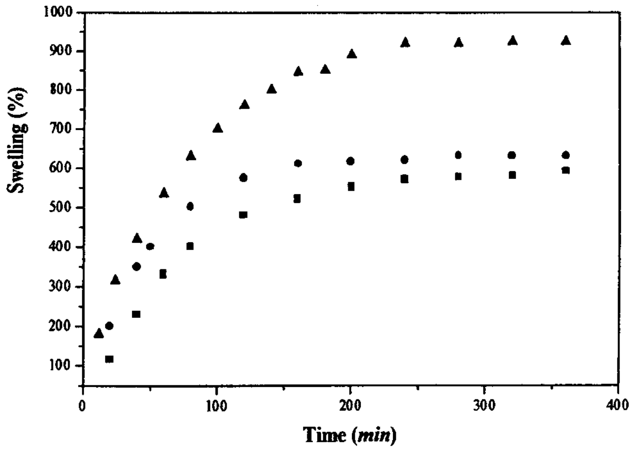


Fig. 4. Kinetic curves of swelling for the MA–Stb–BMA terpolymer/APTS system in MEK solution at 40 ± 0.1°C in the different concentrations of APTS. [MA–Stb–BMA] = constant = 1.5 mol/l; [APTS] = 0.3 (–△–), 0.15 (–●–) and 0.075 mol/l (–□–).

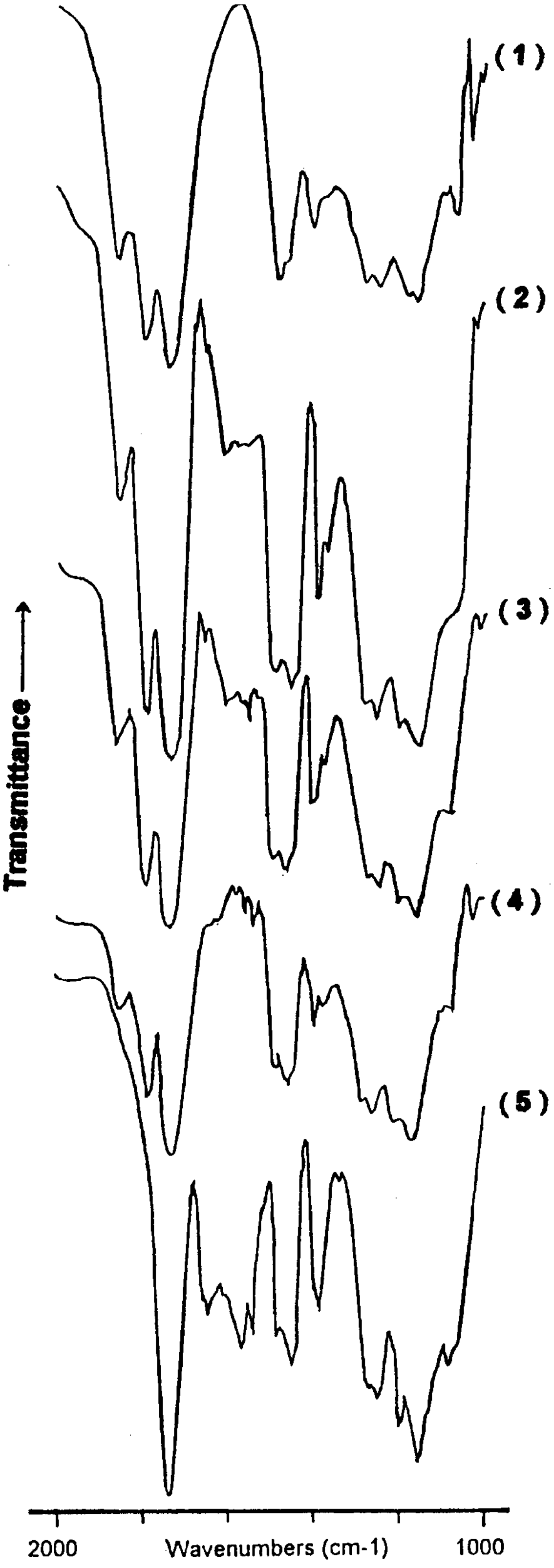


Fig. 6. Fragments of FTIR spectra of MA–MMA copolymer (1), MA–MMA copolymer/APTS (copolymer:APTS = 10:1) gel-coating before (2) and after thermotreatment at 80°C during 30 min (3) and at 110°C during 15 min (4); MA–MMA copolymer/APTS (copolymer:APTS = 5:1) gel-coating after thermotreatment at 110°C during 15 min (5).

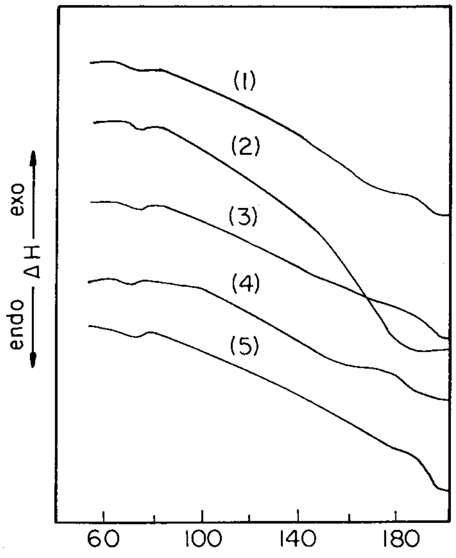


Fig. 7. DSC thermograms of MA–Stb–BMA terpolymers with different BMA unit contents: (1) 52.2, (2) 40.4 and 33.0 mol%, (3) and MA–Stb–BMA (40.4 mol%)/APTS systems with terpolymer:ARTS ratios of (4) 5:1 (initial system) and (5) thermotreated system, (6) 10:1 and (7) 20:1.

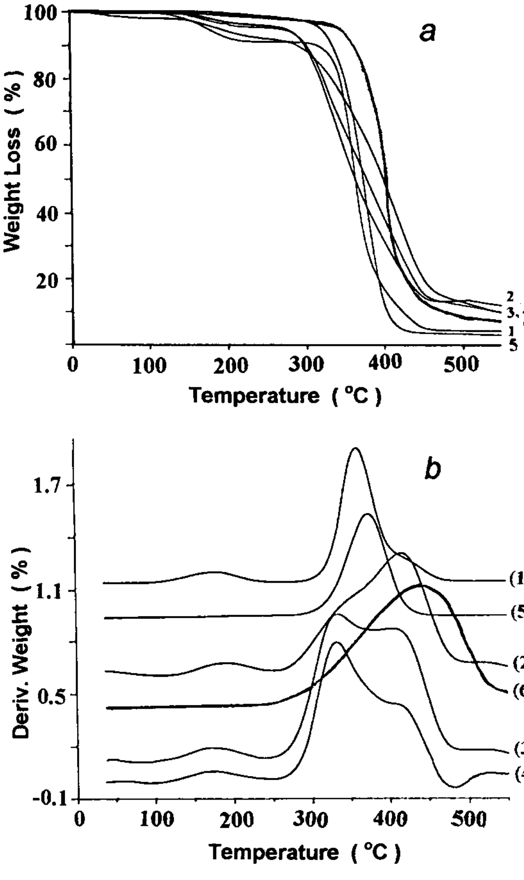


Fig. 8. (a) TGA and (b) DTA curves of MA–MMA copolymer (1) and MA–Stb–BMA terpolymer (5), and their networks: (2) MA–MMA/APTS (5:1), (3) MA–MMA/APTS (10:1), (4) MA–MMA/APTS (20:1) and (6) MA–Stb–BMA/APTS (5:1).

Table 2
Thermal characteristics of binary and ternary copolymers and their networks

| Copolymers, terpolymers and their networks | $T_g$ (°C) | $T_{dec}$ (°C) | Weight loss at different temperatures (%) | | | |
|---|---|---|---|---|---|---|
| | | | 150°C | 200°C | 250°C | 350°C |
| MA(22.0 mol%)–MMA random copolymer | 140 | 168/330 | 1.85 | 4.50 | 5.00 | 12.00 |
| MA(24.3 mol%)–Stb–BMA (45.3 mol%) terpolymer | 120 | 360 | 0.00 | 1.30 | 2.00 | 3.80 |
| MA–MMA/APTS (5:1) network | 185 | 430 | 0.00 | 2.13 | 2.80 | 35.00 |
| MA–MMA/APTS (10:1) | 176 | 325/420 | 1.20 | 1.85 | 2.08 | 32.50 |
| MA–MMA/APTS (20:1) | 158 | 328 | 1.50 | 3.83 | 4.08 | 29.30 |
| MA–Stb–BMA/APTS (5:1) | 160 | 445 | 0.00 | 1.20 | 1.75 | 9.20 |

confirmed the formation crosslinked network in the studied systems through the fragmentation of side-chain ethoxysilyl groups initiating with free carboxyl groups as shown in the scheme. Analogous changes in the FTIR spectra are observed for the MA–Stb–BMA copolymer/APTS gel-coating system.

### 3.2. Thermal behaviours of copolymers and their networks

The values of the decomposition temperature ($T_{dec}$) and the weight loss at different temperatures for the synthesised polymer systems are obtained from the TGA analysis and the values of glass-transition temperature ($T_g$) from the DSC analysis (Fig. 7). Some thermal characteristics of binary and ternary copolymers and their networks synthesised are presented in Fig. 8 and Table 2. As evidenced from these values (Table 2), more flexible BMA-units in ternary copolymers decrease $T_g$ values. Crosslinked binary and ternary copolymer networks containing amide and siloxane fragments have high thermostability. The intensity of $T_g$ endopeak increases increasing a content of flexible BMA-unit in terpolymer (Fig. 7). Similar change is observed for the melting point, $T_m$ of terpolymers which increases from 185.1 to 195.2°C for terpolymers with different BMA-unit contents. A broad exo-peak on the DSC thermogram (Fig. 7, curve 4) at 85–115°C can be related to crosslinking reactions proceeding in the isothermal conditions of DSC. $T_m$ endopeaks disappeared by transfer to the network structure and shifted to the thermodestruction region of crosslinked terpolymer.

In accordance with the present investigation and experimental results obtained it can be concluded that the anhydride-containing binary (MA–MMA) and ternary (MA–Stb–BMA) copolymers easily undergo crosslinking with polyfunctional APTS through anhydride unit–amine groups–ethoxysilyl groups intermolecular reactions with the formation of the hyperbranched network structure containing amide and siloxane crosslinked fragments. It is observed that the ternary MA–Stb–BMA copolymer has high crosslinking, swelling and thermal behaviours as compared to the binary MA–MMA copolymer.

Generally, this reaction can be applied to the wide range of anhydride-containing polymers such as random and alternating copolymers, terpolymers and cyclocopolymers of MA, which would allow us to design new macromolecular architectures with given hyperbranched network structure and synthesise novel types of supercomposite with unique properties, that will be the subject of our future studies.

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