

Synthesis and Characterization of Hydrogels Formed from Glycidyl Methacrylate (GMA) with Anhydride Derivatives

Hatice Kaplan Can^{1*}, Betül Kırıcı Denizli^{1,2}, Ali Güner¹ and Zakir M.O. Rzaev³

¹Hacettepe University, Faculty of Science, Department of Chemistry, Ankara, Turkey

²Arçelik A.Ş. Cooking Appliances Plant, Bolu, Turkey

³Hacettepe University, Faculty of Engineering, Department of Chemical Engineering, Ankara, Turkey.

Article Info

Article history:

Received
February 5, 2009

Received in revised form
March 25, 2009

Accepted
March 28, 2009

Available online
June 28, 2009

Key Words

Hydrogel, Swelling, FTIR, water soluble polymers, glycidyl methacrylate, poly(maleic anhydride-*alt*-*tert*-butyl vinyl ether), poly(maleic anhydride-*alt*-acrylic acid).

Abstract

The present investigation describes the synthesis and macromolecular reactions of maleic anhydride (MA)–acrylic acid (AA) and maleic anhydride (MA) - *tert*-butyl vinyl ether (t-VBE) binary reactive copolymers with glycidyl methacrylate (GMA) as a polyfunctional crosslinker. Copolymers with given composition of poly(maleic anhydride-*alt*-acrylic acid) (%47.17-%52.83) and poly(maleic anhydride-*alt*-*tert*-butyl vinyl ether) (% 45.18-%54.82) synthesized by radical binary copolymerization with benzoyl peroxide (BPO) and α,α' -azobisisobutyronitrile (AIBN) as initiator in *p*-dioxane and methyl ethyl ketone at 70°C in nitrogen atmosphere and initial monomer ratio 1:1, respectively. It is shown that the network structures are formed in copolymer/glycidyl methacrylate (GMA) in water and NaOH by intermolecular reaction between the anhydride units, as well as between hydroxyl fragment and free carboxyl groups of the acrylic acid and maleic anhydride unit, respectively. Swelling parameters such as beginning time of the hydrogel-formation, initial rate of the swelling, swelling rate constant, equilibrium swelling and equilibrium water content are determined copolymer/GMA/water system with various copolymer/crosslinker system. Formation of a hyperbranched network structure through the fragmentation of side-chain reactive groups in studied systems is confirmed by FTIR and DSC methods.

INTRODUCTION

In recent years, considerable efforts have been made to design and synthesize functional polymeric hydrogels useful for applications in medicine, as packing for various kinds of chromatography as well as-stationary phases for size exclusion/liquid chromatography, and for preparation of catalytic activity membranes, [1-5] for gas separations,

hyperfiltration, homo and electro dialysis, and genetic engineering [6-8]. Alternating copolymers of alkyl vinyl ethers with maleic anhydride (MA) have received significant attention due to their unique properties and a wide range of applications as adhesives, photocrosslinkable and photosetting resin compositions, photographic films, electrophotographic recording and glass fiber coatings, reversible shear thinning gels, detergents, viscosity improvers, flocculants and cellular plastics (only *tert*-butyl derivative), as well as controlled-release coatings, medicinal tablet coatings, animal antidiarrhea capsules, etc. [9-13]

* Correspondence to: Hatice Kaplan Can,

Hacettepe University, Faculty of Science, Department of Chemistry, Beytepe, 06800, Ankara, Turkey

Tel: +90312 297 6081; Fax: +90312 299 2163

E-mail: hkaplan@hacettepe.edu.tr

The complex-radical copolymerization of maleic anhydride with various functional comonomers is an effective method for the synthesis of functional macromolecules with given composition, structure and properties [9]. Reactive anhydride units in these copolymers can be used as a new site for the preparation of grafting and hyperbranched macromolecular architectures [10]. Synthesis and macromolecular reactions of maleic anhydride (MA)–Methyl methacrylate (MMA) and MA- *trans*-stilbene (Stb)-*n*-Butyl methacrylate (BMA) reactive copolymer and terpolymers with γ -aminopropyl triethoxysilane (APTS) as a polyfunctional crosslinker was studied [14,15].

Effect of H-complex in radical terpolymerization of vinyl acetate-maleic anhydride-acrylic acid and copolymerization maleic anhydride-acrylic acid were studied [16]. Synthetic polycarboxylic acids polymers were found to produce broad spectrum of immunological effects. They induce the interferon; modify the reticuloendothelial system and display immunoadjuvant, antiviral and antitumor activity [17]. The synthetic carboxylic acid polymers were first investigated as poly(acrylic acid), polymethacrylic acid, poly(ethylene-co-maleic anhydride), and oxidized polysaccharides [17]. Among these polymers hydrolyzed form of divinyl ether maleic anhydride copolymer (DIVEMA) and it also called as pyran copolymer which contains carboxylic acid groups exhibits high antitumor activity together with toxic side effects [17]. Numerous studies have been done to obtain dextran hydrogels by several different approaches. Edman et al. synthesized dextran hydrogels by chemical incorporation of glycidyl acrylate in aqueous phase, followed by free radical polymerization of the dextran derivatives in the presence of N'-N' methylenebisacrylamide as an additional crosslinker [18]. Van Dijk-Wolthuis et al. introduced vinyl group into dextran in a full control manner of the degree of conjugation by transesterification of GMA with

dextran hydrogels in DMSO at ambient temperature [19]. Vervoort et al. synthesized insulin hydrogels from polymerization of Methacrylate-insulin obtained by transesterification of the polysaccharide with GMA [20].

The objective of the present investigation is to prepare hydrogels from macromolecular reactions of maleic anhydride (MA)–acrylic acid (AA) and maleic anhydride (MA) - *tert*-butyl vinyl ether (*t*-VBE) binary reactive copolymers [16-21] with glycidyl methacrylate (GMA) as a polyfunctional crosslinker. GMA is employed for a functional crosslinker agent. This crosslinker agent is chosen because of its dual functionality - an acrylic group and an epoxy group in the same molecule. Formation of a network structure through the fragmentation of side-chain reactive groups in studied systems is confirmed by FTIR and DSC methods.

EXPERIMENTAL PART

Materials

Initial monomer Acrylic acid (AA) supplied by Fluka was distilled before use. AA, bp 141.6°C, mp 13.5°C, $d_4^{20} = 1.0510$, $n_D^{20} = 1.4215$. Maleic Anhydride (MA) (Fluka) was purified before use by recrystallization from anhydrous benzene and sublimation in *vacuum*, m.p. 52.8°C and sublimation temperature 199°C. *t*-BVE (Aldrich) was distilled under reduced pressure before use: bp 75.6°C, $n_D^{20} = 1.3979$, $d_4^{20} = 0.7618$. ¹H NMR spectra: CH=, 1H quartet 6.51-6.46 ppm, CH₂=, 2H two quartets 4.16-4.12 ppm and 3.91-3.89 ppm, respectively and (CH₃)₃C-, 9H doublet 0.93 and 0.92 ppm. GMA (2,3-epoxypropyl methacrylate) supplied by Merck was distilled before use: $d_4^{20} = 1.080$, $n_D^{20} = 1.4495$, bp 75°C.

Benzoyl peroxide was purified by recrystallizing twice from chloroform solution by methanol when

was dried under vacuum, m.p. 106°C. α,α' -azobisisobutyronitrile (AIBN) (Fluka) was recrystallized twice from methanol: mp 102.5°C. Other reagents including organic solvents were purified by ordinary methods.

Synthesis of Binary Copolymers

Copolymerization of MA with AA was carried out in degassed Pyrex glass tubes *p*-dioxane in the presence of BPO (0.1%) as an initiator at 70°C under nitrogen atmosphere. After the given amount of monomers, initiators 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 tube was sealed and put into thermostat with glycerin bath. In order to determine the copolymer yield in the reaction mixture, hydroquinone as an inhibitor was added, and then mixture was poured into a large amount of methanol to precipitate copolymer. The powder-like product obtained was separated by filtration, and then purified by multiple washing in the anhydrous methanol and *n*-hexane. Copolymerization of *t*-BVE with MA was carried out in MEK under the nitrogen atmosphere with α,α' -azobisisobutyronitrile (AIBN) as a radical initiator at 65°C to conversions of 10-12%. The copolymer produced were recovered by addition of a 10-fold excess of methanol for *t*-BVE-MA copolymer and purified twice by reprecipitation from MEK solution into methanol or cold petroleum ether and by washing *n*-hexane and benzene. Purified copolymers were then dried in *vacuum* at 40°C to a constant weight.

Crosslinking Reactions

The process of the formation of network structures of synthesized copolymers was carried out with glycidyl methacrylate (GMA) as a crosslinker in poly(maleic anhydride-*alt*-acrylic acid) water and poly(maleic anhydride-*alt*-*tert*-butyl vinyl ether) in water and NaOH at 50°C during 45 minutes for the

gel formation, respectively. Obtained hydrogels confirmed by FTIR structural analysis as well as DSC analyses of the network polymers formed. Crosslinking reactions were carried out using the polymer/crosslinker molar ratio: poly(maleic anhydride-*alt*-acrylic acid)/GMA and poly(maleic anhydride-*alt*-*tert*-butyl vinyl ether)/GMA 5:1. For each sample the hydrogels characteristics were also determined.

Measurements

Fourier transformation infrared (FTIR) spectra of polymer powders films or coating were recorded FTIR Mattson 1000 spectrometer in the 4000-400 cm^{-1} range, where 30 scans were taken at 4 cm^{-1} resolution.

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

Intrinsic viscosities of synthesized copolymers were determined in *p*-dioxane and THF at $25 \pm 0.1^\circ\text{C}$ and in the concentration range of 0.1-1.0 g/dL using Ubbelohde viscometer.

$$[\eta] = \eta_{sp}/[c (1 + 0.333\eta_{sp})] \quad (1)$$

Swelling Studies

The swelling of hydrogels systems have been obtained in long cylindrical shapes cut into pieces 0.5 cm long. Polymer gels prepared in water for a week to remove uncrosslinked polymers dried to constant weight in vacuum at 40°C before the swelling experiment. Hydrogels were left for swelling in water at 25°C to determined swelling; then they were removed from the bath, dried, weighted and placed in the same bath. The swelling degree of hydrogels systems was determined gravimetrically by the following equation.

$$S (\%) = [(M_t - M_0) / M_0] \times 100 \quad (2)$$

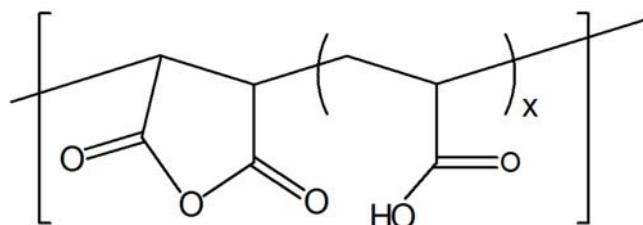
Where M_0 is the dry/initial weight of polymer gel, M_t the weight of swollen gel at given time (t) in water.

RESULTS AND DISCUSSION

Macromolecular Reactions of Binary Copolymers with Glycidyl Methacrylate (GMA)

For the studies of crosslinking and swelling process, anhydride containing poly(maleic anhydride-*alt*-acrylic acid) alternating copolymer with 47.17% MA-units and poly(maleic anhydride-*alt*-*tert*-butyl vinyl ether) alternating copolymer with 45.18% MA-units are used crosslinkable polymers. Hydrolyzed form of functional polymers which contains carboxylic acid groups exhibits high antitumor activity together with toxic side effects [23]. This functionality of the polymers has brought great attention to our study. Glycidyl methacrylate containing carbonyl and epoxy reactive groups are used as a polyfunctional crosslinker. The copolymers synthesized by the use of 1:1 molar ratios of initial monomers, respectively, had following characteristics [16,21,22].

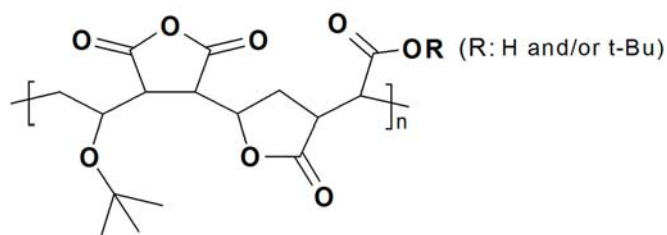
Poly[maleic anhydride-*alt*-(acrylic acid)]



where $x=1.12$ (AA unit=52.83), yield 80%, glass transition temperature $T_g = 111^\circ\text{C}$ and $T_m = 143^\circ\text{C}$ (by DSC analysis), intrinsic viscosity $[\eta] 1.25 \text{ dLg}^{-1}$ in *p*-dioxane at 25°C , monomer unit ratio in copolymer ($m_1:m_2$)= 1:1.12.

FTIR spectra (film), cm^{-1} : νOH 3060 (broad, in -COOH), νCH_3 2950 (as) and 2880 (s), νCH_2 2930 (as) and 2870 (s), νCOOH 2545 (broad), $\nu\text{C}=\text{O}$ 1836 (as) and 1766 (s) (C=O in anhydride unit), $\nu\text{C}=\text{O}$ 1730 (C=O in ester group), $\nu\text{C}=\text{O}$ 1585 (as) (in COO^-), δCH_2 1478 and 1443 (doublet), δCH_3 1385 and 1357 (doublet), $\delta\text{C}-\text{O}$ 1240-1170 (ester and carboxyl), $\nu\text{C}-\text{O}-\text{C}$ 1035 (in anhydride unit), δOH 943 (out-of-plane OH bending), δCH 886 and 871 (doublet), δCH_3 842 (rock), δCH_2 720 (rock), δCH 645 (in main chain from anhydride unit), and $\delta\text{O}-\text{C}=\text{O}$ 560 (s) (bend of COOH); 645 (in main chain from anhydride unit), and $\delta\text{O}-\text{C}=\text{O}$ 578 (s) (bend of ester group). In the FTIR spectra of hydrolyzed terpolymers there are disappeared characteristic bands for anhydride units, and appeared new bands in field of 1970, 1585 and 1630 cm^{-1} relating to -COOH groups, as well as increased in intensity of 3060 and 2545 cm^{-1} broad band. Same copolymers and terpolymers are cooled by liquid N_2 for recrystallization.

Poly[maleic anhydride-*alt*-(*tert*-butyl vinyl ether)]

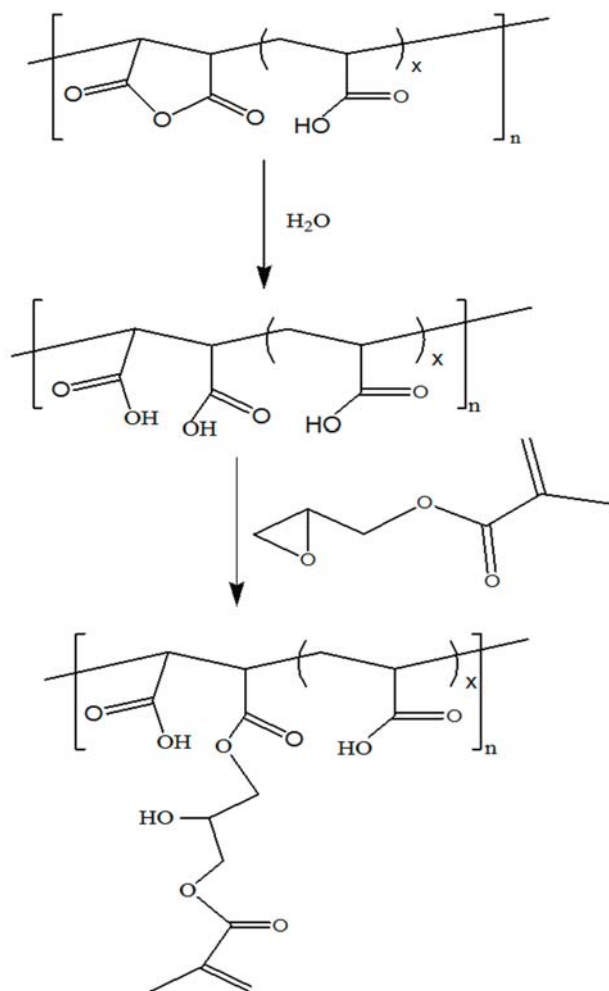


tert-butyl vinyl ether (t-BVE) unit =%54.82, yield 75%, glass transition temperature $T_g = 184^\circ\text{C}$, and $T_m 205^\circ\text{C}$ (by DSC analysis), intrinsic viscosity $[\eta] 0.18 \text{ dL/g}$ in MEK at 25°C , monomer unit ratio in copolymer ($m_1:m_2$)= 1:1.2.

FTIR spectra (KBr pellet), cm^{-1} : 3610, 3200 and 2178 (OH stretching in COOH), 2980 (ν_{as} CH in CH_3), 2942 (ν_{as} CH in CH_2), 2920 (ν_{s} CH in CH_2), 2875 (ν_{as} CH in CH_3), 2860 (ν_{s} CH in CH_2), 1863 (ν_{as} C=O) and 1783 (ν_{s} C=O) for anhydride unit,

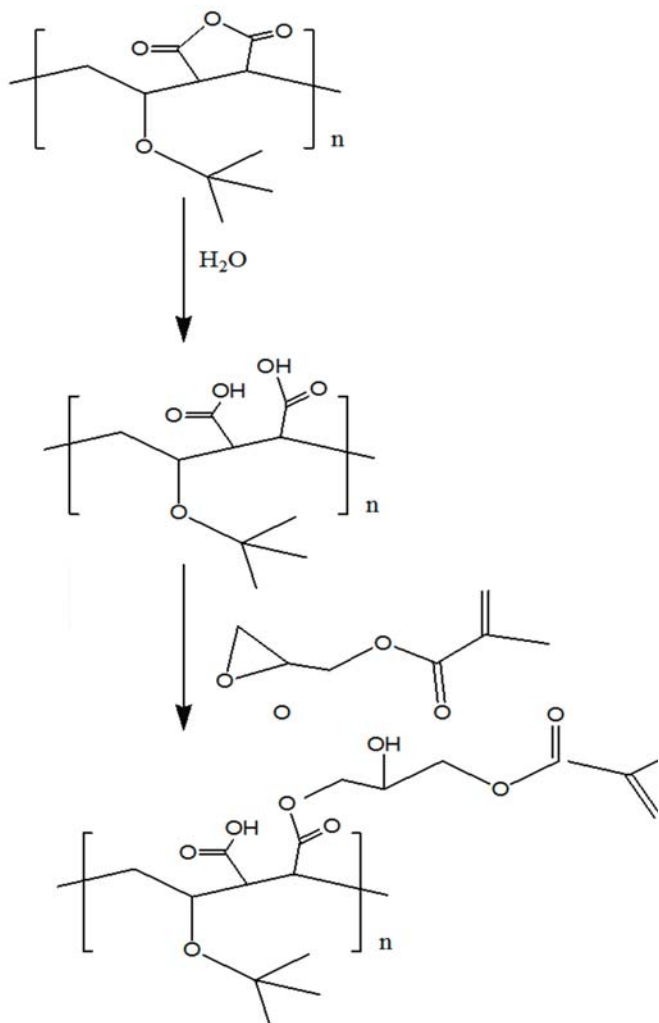
1743 (C=O) for γ -lactone or ester unit, 1634 (C=O) for shifted conjugated C=O stretching band, 1470 (scissor vibrations of CH₂), 1430 (δ_{as} CH₃ asymmetric deformation), 1395 and 1370 (δ_{as} CH₃ of *t*-butyl group), 1220-1180 (stretching of anhydride C-O-C), 1210-1200 (δ CH₃), 1255-1240 (δ CH₃ of *t*-butyl group), 1100 (broad stretching of C-O-C in lactone fragment), 920 (CH₃ rocking in *t*-butyl group), 620-595 (δ CH in CH-CH anhydride and lactone units). ¹H NMR (400 MHz) spectra in CHCl₃-d₁ (δ , ppm): 0.43 (9H, CH₃ from *t*-butyl group), 1.34 (2H, CH₂ from *t*-BVE unit), 1.67 (2H, CH₂ from γ -lactone unit), 2.75 (1H, CH-CO from MA unit), 2.93 (1H, CH-CO from γ -lactone), 3.20 (1H, CH-O from *t*-BVE unit), 3.30 (1H weak singlet, CH-O from γ -lactone unit) [24,25].

From the structural peculiarities of these polymers/crosslinker systems and classical principle of macromolecular reactions it can be assumed that the hyperbranched network structure network structure in these systems will be formed by the intermolecular reactions between the anhydride unit and epoxy group as well as free carboxyl fragments. The general scheme of crosslinking reactions with glycidyl methacrylate of anhydride containing copolymers can be represented in the following form (Scheme 1 and 2) [25,26]. It is shown that the gel-formation process in poly(MA-*alt*-AA) copolymer and poly(MA-*alt*-*t*-BVE) copolymer / GMA systems starts after heating at 50°C and intensive mixing of these polymer/crosslinker solutions in the water during a certain period of time. The beginning time of gel-formation in the studied system depends on the type of polymer, polymer/crosslinker ratio, temperature and other factors. After starting gel-formation, the dramatically increase of viscosity in polymer/crosslinker solutions and the formation of hydrogels are observed.



Scheme 1. Hydrolysis and crosslinking reaction of the poly(MA-*alt*-AA) with the glycidyl methacrylate (GMA).

For the elucidation of some peculiarities of gel-formation process in poly(MA-*alt*-AA) copolymer and poly(MA-*alt*-*t*-BVE) copolymer/GMA 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 coefficient (k , n) and equilibrium water content (EWC) are determined by using known methods which are described in experimental part. 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 [27].



Scheme 2. Hydrolysis and crosslinking reaction of the poly(MA-*alt*-*t*-BVE) with the glycidyl methacrylate (GMA).

The kinetic curves of swelling in the studied poly(MA-*alt*-AA)/GMA copolymer and poly(MA-*alt*-*t*-BVE) copolymer/GMA are illustrated in Figure 1. Swelling capacities of poly(MA-*alt*-AA) copolymer and poly(MA-*alt*-*t*-BVE) copolymer / GMA gels are increased by time, but after a certain period, they show constant swelling and the swelling process is transformed to the equilibrium state. Two binary polymer samples have alternating structures and maleic anhydride contents are closer to each other. Percent swelling value of the hydrogels systems are very close. But the swelling characters are different from each other because of the hydrophobic *tert*-butyl vinyl ether group of the poly(maleic anhydride-*alt*-*tert*-butyl vinyl ether). Swelling curves of hydrogels were used for the calculation of nature of diffusion of water into hydrogels [28]

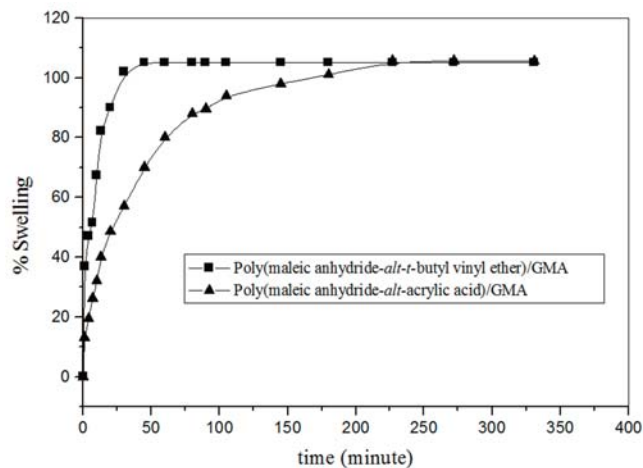


Figure 1. Swelling % - time curves of the poly(MA-*alt*-AA)/GMA and poly(MA-*alt*-*t*-BVE)/GMA hydrogels systems at constant temperature.

$$F = M_t / M_\infty = kt^n \tag{3}$$

Where M_t and M_∞ denote the amount of solvent diffused into the gel at the time t and the infinite time (at equilibrium), respectively, k is a constant related to the structure of the network, and the exponent, n , is a number 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 diffusion is non-Fickian. 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 1. It is seen from the table that the values of the diffusion exponent range between and are found to be nearly 0.50. Hence the diffusion of water into poly(MA-*alt*-AA)/GMA and poly(MA-*alt*-*t*-BVE)/GMA hydrogels was taken Fickian character. For extensive swelling of poly(MA-*alt*-AA)/GMA and poly(MA-*alt*-*t*-BVE)/GMA hydrogels the following equation can be written as: [29-30].

$$t/S = A + Bt \tag{4}$$

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 r_i ; and k_s is the swelling rate constant. This relation represents second order kinetics (Figure 2). The

obtained results are given in Table 1. The values of theoretical equilibrium swelling of the hydrogels are in good agreement with the results of equilibrium swelling of poly(MA-*alt*-AA)/GMA and poly(MA-*alt*-t-BVE)/GMA hydrogels (Figure 1). It is well known that the swelling phenomena are directly related to the structure of crosslinked polymer and/or density of gel. Equilibrium water content (EWC) has been calculated from the following equation [31]:

$$\text{EWC} = [(W_{\text{eq}} - W_{\text{dry}}) / W_{\text{eq}}] \times 100 \quad (5)$$

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 1. EWC and swelling behavior of hydrogel mainly depend on the nature of network the network structure, i.e., hydrophilicity, crosslink density, and the average molecular weight between two consecutive crosslinks.

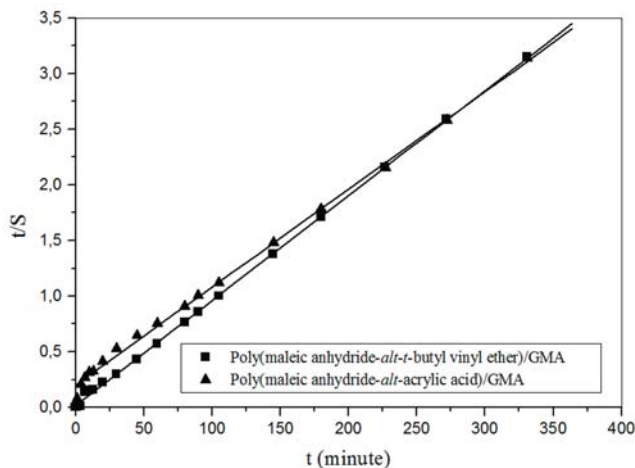


Figure 2. t/S vs. t graph plotted for poly(MA-*alt*-AA)/GMA and poly(MA-*alt*-t-BVE)/GMA hydrogels systems at constant temperature.

Table 1. Swelling parameters (G_t , beginning time of gel-formation; % S_{eq} equilibrium swelling; r_i , initial swelling rate; k_A swelling rate constant, n , k Fick coefficient; S_{max} , maximum swelling equilibrium; % EWC, equilibrium water content) of the poly(MA-*alt*-AA)/GMA and poly(MA-*alt*-t-BVE)/GMA hydrogels systems.

[Copolymer / GMA] Molar Ratio (5:1)	Swelling Parameters				Fick Coefficients			
	G_t (min)	S_{eq} %	r_i^a	k_A^b	S_{max}	% EWC	k	n
Poly(MA- <i>alt</i> -t BVE)	40	105.1	0.0153	$5.83 \cdot 10^{-5}$	113.8	51.25	0.0628	0.424
Poly(MA- <i>alt</i> -AA)	40	105.5	0.2024	$3.82 \cdot 10^{-4}$	105.9	51.34	0.1142	0.469

*a: $(g_{\text{water}}/g_{\text{gel}})/\text{min}$; b: $(g_{\text{gel}}/g_{\text{water}})/\text{min}$

FTIR Studies of the Crosslinking Reaction with Glycidyl Methacrylate (GMA)

FTIR studies of intra- and intermolecular reactions between the functional groups of the poly(MA-*alt*-AA) and poly(MA-*alt*-t-BVE) copolymers and their hydrogels with glycidyl methacrylate (GMA) have been performed. The analysis of the FTIR spectrum allows us the following changes of macromolecules as a consequence of the intermolecular reactions between the functional groups of the copolymers and GMA [16];

(1) disappearance of the anhydride unit bands at 1730 cm^{-1} ($\nu_{\text{C=O}}$) Spectra c, in Figure 4 and 5. Due to the crosslinking reaction from the carboxylic groups of the poly(MA-*alt*-t-BVE) and poly(MA-*alt*-AA). This effect is more appreciable (spectrum c) in Figure 4 and 5. Related to the full transformation of the anhydride unit to carboxylic and esteric form in the case of gel formation system; these changes observed can be explained by the initial transesterification reaction of the anhydride unit as shown in the scheme 1 and 2 [25,26].

(2) the intensity of band at 1731 cm^{-1} enlarges because of the intra -H bonding between maleic anhydride -C=O groups (Spectrum c, Figure 4). And also second acid peak can be seen from the Spectrum c in Figure 5 at 1575 cm^{-1} .

(3) appearance of new 3425 cm^{-1} peak of -COOH because of intra -H bonding between maleic

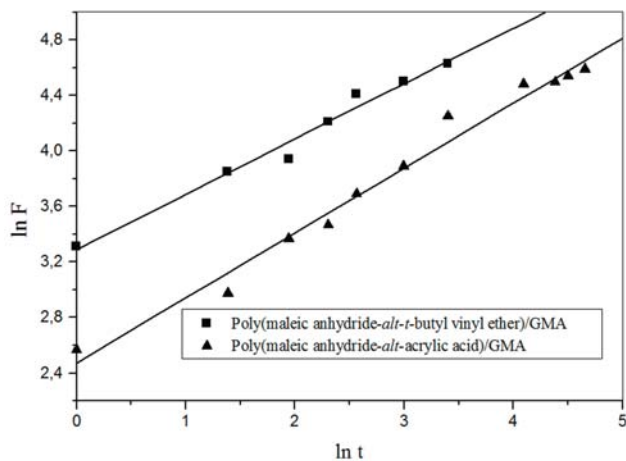


Figure 3. $\ln F$ vs. $\ln t$ graph plotted for poly(MA-*alt*-AA)/GMA and poly(MA-*alt*-*t*-BVE)/GMA hydrogels systems at constant temperature.

anhydride -C=O groups with the glycidyl methacrylate groups epoxy groups, Spectra c, in Figure 4 and 5.

(4) decrement and weakening of these bands due to the crosslinking; (cm^{-1}) 1743 (C=O) for γ -lactone or ester unit, 1634 (C=O) for shifted conjugated C=O stretching band, 1470 (scissor vibrations of CH_2),

1430 ($\delta_{\text{as}}\text{CH}_3$ asymmetric deformation), 1395 and 1370 ($\delta_{\text{as}}\text{CH}_3$ of *t*-butyl group), 1220-1180 (stretching of anhydride C-O-C), 1210-1200 (δCH_3), 1255-1240 (δCH_3 of *t*-butyl group), 1100 (broad stretching of C-O-C in lactone fragment), Spectra c, in Figure 4.

(5) Increment of the bands at 1220-1180 (stretching of anhydride C-O-C) and 2950 cm^{-1} due to the presence of glycidyl methacrylate groups CH groups (Figure 4 and 5).

(6) disappearance of the anhydride unit band at 1700 cm^{-1} ($\nu_{\text{C=O}}$) Spectra c, in Figure 5. Due to the crosslinking reaction from the carboxylic group of the poly(MA-*alt*-AA). This effect is more appreciable (spectrum c) in Figure 5. Related to the full transformation of the anhydride unit to acid and ester form in the case of gel formation system; these observed changes can be explained by the initial transesterification reaction of the anhydride unit as shown in the scheme 2 [25,26].

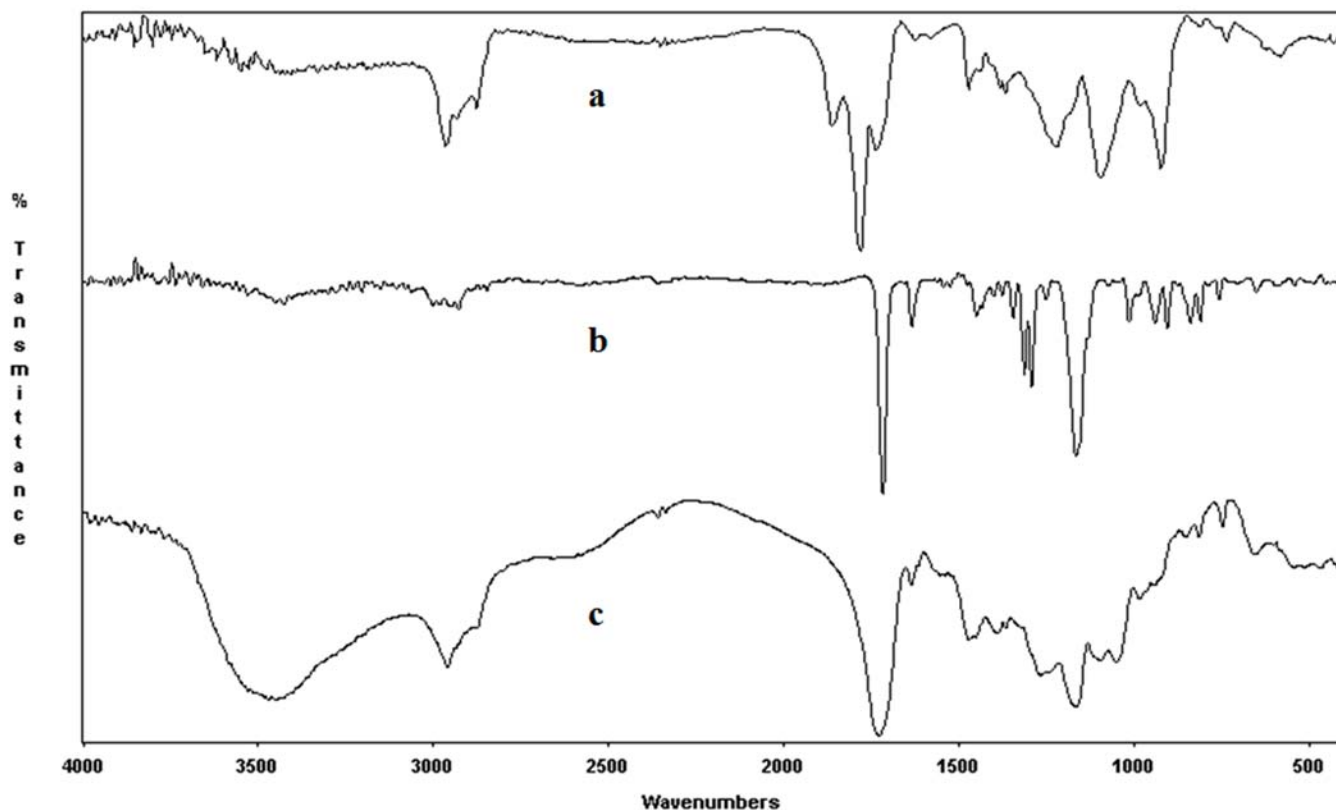


Figure 4. FTIR spectra of the poly(MA-*alt*-*t*-BVE) copolymer (a), GMA (b), and poly(MA-*alt*-*t*-BVE)/GMA (c).

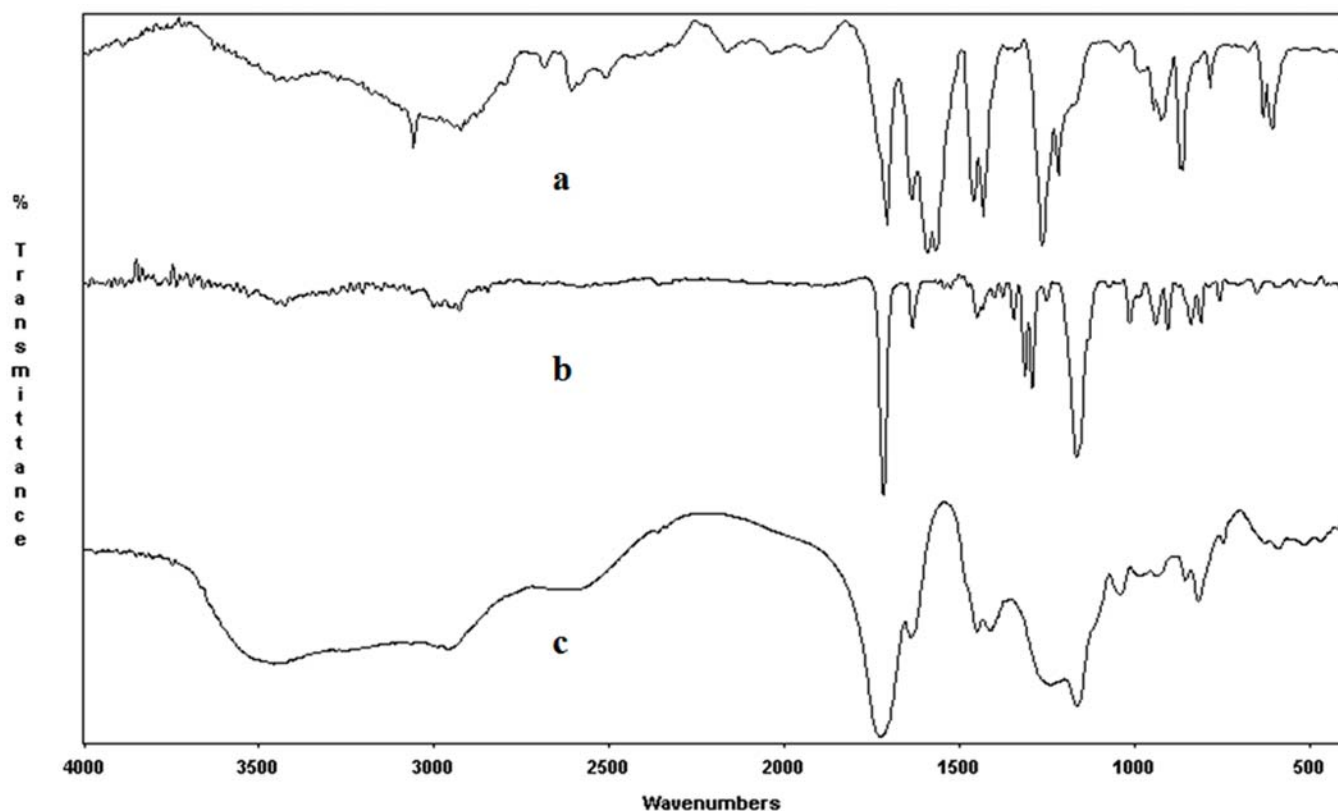


Figure 5. FTIR spectra of the poly(MA-*alt*-AA) copolymer (a), GMA (b), and poly(MA-*alt*-AA)/GMA (c).

(7) appearance of a new peak at 3030 cm^{-1} because of complex-formation (1,1 and 1,2 complex) between epoxy groups and $-\text{COOH}$ of MA groups (Figure 4 and 5).

(8) the intensity of bands at 1650 cm^{-1} appreciably increases by gelation, this effect is more appreciable (spectrum c) in Figure 4 and 5.

(9) appearance of new 1100 cm^{-1} (stretching of C-O-C in GMA) band in the form of a singlet due to the known interaction between symmetrical stretching and bending vibrations in the $-\text{O}=\text{C}-$ epoxy group; Spectra c, in Figure 4 and 5. A new band at 1640 cm^{-1} is related to the antisymmetrical stretching vibration of the GMA functional group; it is a known fact that even in the case of interaction between MA copolymers and some drugs with an epoxy group, the reaction proceeds via crosslinking of the hydrolyzed anhydride group, and the FTIR analysis indicates the formation of this reaction [32].

(10) the presence of the bands at $1650, 1575\text{ cm}^{-1}$ arising from the stretching vibrations of the $-\text{C}=\text{O}$ groups and the carboxylate ion groups ($-\text{C}=\text{O}$ in $-\text{COOH}$, $-\text{COO}^-$ fragments); the reaction of the anhydride cycle with primary and carbonyl group the enhanced deformation bands between $1700\text{--}1575\text{ cm}^{-1}$ represent impacts of the formed hydrogel carboxyl fragments in the network structure and C-O-C at stretching bands appear in the field of $1000\text{--}1100\text{ cm}^{-1}$ which is also confirmed by the formation of crosslinked network in the studied systems through the carboxylic acid and functional epoxy group initiating with free carboxyl groups as shown in the scheme 1 and 2 [25,26].

Thermal Behaviors of Copolymer and Their Networks

The values of the glass-transition temperature (T_g), for synthesized copolymer and their various network are obtained from DSC analysis. As evidence from the T_g values at the constant ratio of crosslinker and copolymer of (crosslinker/copolymer: 1:5), T_g value

of poly(MA-*alt-t*-BVE) ($T_g = 193^\circ\text{C}$) network is higher than the poly(MA-*alt*-AA) ($T_g = 142^\circ\text{C}$) network. This can be explained by the rigid structure of the tertiary butyl groups of the poly(MA-*alt-t*-BVE) polymer. Crosslinking behavior in copolymers looks similar; because of the presence of functional groups which give the different network rheology have different T_g values. Crosslinked networks give high thermo-stability to the copolymer (Poly(MA-*alt*-AA) $T_g = 111^\circ\text{C}$ and poly(MA-*alt-t*-BVE) $T_g = 184^\circ\text{C}$). All the DSC thermograms have the broad exo-peak at $50\text{-}120^\circ\text{C}$ which can be related to crosslinking reactions proceeding in the isothermal conditions of DSC [16,21,26].

CONCLUSIONS

In accordance with this present investigation and experimental results obtained, it can be concluded that the anhydride containing binary poly(MA-*alt*-AA) and poly(MA-*alt-t*-BVE) easily undergo crosslinking reaction with functional GMA through anhydride unit epoxy groups intermolecular and intramolecular reactions with the formation of the network structure containing etheric and esteric crosslinked fragments. It is observed that binary poly(MA-*alt*-AA)/GMA and poly(MA-*alt-t*-BVE)/GMA (5:1) has high crosslinking, low swelling properties and high thermal stability (T_g) compared to the copolymers.

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

ACKNOWLEDGEMENTS

This study was carried out in Department of Chemistry of Hacettepe University and was supported by TÜBİTAK (The Scientific and Technological Research Council of Turkey) through Project MISAG-146 which is acknowledged.

REFERENCES

1. Finch, C.A. Chemistry and Technology of Water Soluble Polymers, Plenum Press, New York, 1981.
2. Spychai, T., Bartkowiak, A., Hunkeler, D. Int. J. Polym. Charact., 2, 1, 1995.
3. Spychai, T., Bartkowiak, A. Polym. Adv. Technol., 8, 1, 1997.
4. Spychai, T., Bartkowiak, A. Macromol. Symp., 110,191, 1996.
5. Bartkowiak, A., Jezierska, I., Spychai, T. Polym. Bull., 41, 191, 1998.
6. Turbak, A. Synthetic Membranes, ACS Symposium Series, Vol 153, American Chemical Society, Washington, DC, 1981.
7. Kesting, R.E. Synthetic Polymeric Membranes, Wiley, New York, 1985.
8. Cooper, A. Ultrafiltration Membranes and Applications, Plenum, New York, 1981.
9. Rzaev, Z.M.O. Prog. Polym. Sci., 25, 163, 2000.
10. Kaplan Can, H., Güner, A., Rzaev, Z.M.O. J. Mol. Liq. 111, 77, 2004.
11. Triverdi, B.C., Culbertson, B.M. Maleic Anhydride, Plenum Press, New York, 1982.
12. Rzaev, Z.M.O. Polymers and Copolymers of Maleic Anhydride, Elm, Baku, 1984.
13. Cowie, J.M.G. Alternating Copolymers, Plenum Press, New York, 1985, p.61.
14. Rzaev, Z.M.O., Güner, A. and Kaplan Can, H.; Asıcı, A. Polymer 42, 5599, 2001.
15. Rzaev, Z.M.O., Güner, A., Kibarar, G., Kaplan Can, H., Asıcı, A. Eur. Polym. J., 38, 1245, 2002.

16. Kaplan Can, H., Rzaev, Z.M.O., Güner, A. J. Appl. Polym. Sci., 90, 4009, 2003.
17. Ottenbrite, R.M. ACS Symposium series 186, American Chemical Society, Washington DC, 1982.
18. Edman, P., Ekman, B, Sjöholm, I. J. Pharm. Sci., 69, 838, 1980.
19. Van Dijk Wolthuis, W.N.E., Franssen, O., Talsma, H., Van Steenbergen, M.J., Van Den Bosch Kettenes, J.J., Hennink, W.E., Macromolecules, 28, 6317, 1995.
20. Vervoort, L., Van Den Mooter, G., Augustijns, P., Busson, R., Toppet, S., Kinget, R. Pharm. Res., 14, 1730, 1997.
21. Kırıcı Denizli, B., Kaplan Can, H., Rzaev, Z.M.O., Güner, A. J. Appl. Polym. Sci., 100, 2455, 2006.
22. Kavlak, S., Kaplan Can H., Güner A., Rzaev Z.M.O. J. Appl. Polym. Sci., 90, 1708, 2003.
23. Kaplan Can, H., Doğan L., Rzaev, Z.M.O., Hasegeli Üner, A., Güner A. J. Appl. Polym. Sci., 100, 3425, 2006.
24. Kırıcı B., Kaplan Can, H., Rzaev, Z.M.O., Güner A. NATO-ASI Chemical Modification and Blending of Synthetic and Natural Macromolecules, Book of Abstract, 6-16 October 2003, Tirrenia, Pisa, Italy.
25. Giammona, G., Tomarchio, V., Pitarresi, G., Cavallaro, G. Polymer, 38, 3315, 1997.
26. Reis, A.V., Cavacanti, O.A., Rubira, A.F., Muniz, E.C. Int. J. Pharm., 267, 13, 2003.
27. Mencer, H.J., Gomzi, Z. Eur. Polym. J. 30, 33, 1994.
28. Frisch, H.L. Polym. Eng. Sci., 20, 2, 1980.
29. Kaplan H., Güner A. J. Appl. Polym. Sci., 78, 994, 2000.
30. Kaplan Can, H. Kavlak, S., Kırıcı, B., Güner, A. Adv. Polym. Tech., 22, 252, 2003.
31. Kaplan Can, H., Kırıcı, B., Kavlak, S., Güner, A. Radiat. Phys. Chem., 68, 811, 2003.
32. Canto, L.V., Pessan, L.A., Poly. Test . 21, 35, 2002.