

Network Structure/Mechanical Property Relationship in Crosslinked Dimethacrylates of Different Chain Lengths

Maciej Podgórski

Faculty of Chemistry, MCS University, pl. Marii Curie-Skłodowskiej 5, 20-031 Lublin, Poland

Received 28 May 2008; accepted 6 December 2008

DOI 10.1002/app.29843

Published online 24 February 2009 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: In this article, the syntheses of three novel dimethacrylates of different chain lengths as well as the mechanical and thermal properties of their copolymers with methyl methacrylate and styrene were studied. The monomers were prepared by the reaction of glycidyl methacrylate with dicarboxylic acid esters obtained from maleic anhydride and ethylene, 1,4-butylene and 1,6-hexylene glycols. The addition reaction of glycidyl methacrylate and the acidic compound was carried out in the presence of basic catalyst, tetraethylammonium bromide. The monomers were UV-copolymerized with methyl methacrylate and styrene in the presence of a photoinitiator which was 2,2-dimethoxy-2-phenylacetophenone. The prepared polymers were subjected to different studies concerning evaluation of their flexural properties, thermal stability, dynamic mechanical behavior as well as qualitative estimation of the content of unreacted double bonds. The dependence of glass transition temperatures (T_g) as well as degree of inhomogeneity on the crosslinking density has

been examined in different copolymer systems. Evidence that the dependence of the T_g on the crosslinking density is not straightforward is presented. Dynamic mechanical measurements have demonstrated that the heterogeneity of the crosslinked polymers depends strongly on the crosslinking density of the system and the nature of methacrylate monomers used. Depending on the monomer size as well as its functionality, the resultant polymer may have features such as crosslinks or residual unsaturations that influence and define the properties of the materials. It is proved that the new dimethacrylates change their functionality in copolymerization with different monovinyl monomers. Also, the degree of unsaturated bonds conversion was found to be growing with the amount of monovinyl in the copolymer. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 112: 2942–2952, 2009

Key words: mechanical properties; photopolymerization; dimethacrylates; glass transition

INTRODUCTION

Photoinitiated polymerization of multifunctional (meth)acrylates is a rapidly expanding technology resulting from its main advantages: the process is solvent-free, energy efficient, occurs under ambient conditions, and enables production of materials having tailor-made properties.^{1–5} Because of good mechanical properties as well as chemical resistance, crosslinked polymers have found use in a wide variety of applications. They are successfully applied as casts and thermally and photochemically cured paints and lacquers resistant to corrosion, masks, and protective coatings in electronic and electrotechnique industries, binders in glue and optical fiber production, optical discs and optical communication devices. Because of their nontoxicity and biocompatibility multivinyl monomers are applied, among others, as components in contact lenses production and dental restorative materials.^{4–8}

(Meth)acrylate-based resins are a subject of thorough investigations as they are by far the most widely used UV-curable systems, because of their great reactivity. A large variety of high performance compounds are now commercially available. Most of the research devoted to studying the relationship between network structure and mechanical properties of crosslinked polymers have been performed on the commonly known (meth)acrylates. It is of particular importance to carry out such experiments especially for new materials, which have not been reported yet. These studies will help to better understand the correlations between basic network parameters and mechanical as well as thermal properties of crosslinked polymers.

In previous studies, we have investigated the influence of network structure on the mechanical and thermal properties of crosslinked polymers prepared from new di- and trimethacrylate multiesters, derivatives of maleic and nadic anhydrides.^{9–11} We have discussed, among others, the copolymer and crosslinking effects in new copolymer systems,^{10,11} the contribution of primary cyclizations in overall crosslinking reactions and the influence these cyclizations exert on material properties⁹ and also the double bond conversion degree in

Correspondence to: M. Podgórski (m.podgorski@op.pl).

Research methods

^1H NMR spectra of raw methacrylate monomers were recorded at 20°C on an FT NMR Bruker Avance (Germany) spectrometer operating at the ^1H resonance frequency of 300 MHz. Chemical shifts were referenced to tetramethyl silane serving as an internal standard.

FTIR spectra were recorded by using an FTIR spectrophotometer (Perkin–Elmer 1725X). A small drop of each sample containing photoinitiator, 2,2'-dimethoxy-2-phenylacetophenone (Irgacure 651) was analyzed after being placed on a KBr crystal. UV irradiated and postcured polymeric samples were powdered and analyzed in the form of KBr pellets.

Elementary analysis of the obtained methacrylate esters and substrates used in the syntheses was carried out using the Perkin–Elmer CHN 2400 apparatus.

Viscosities of the methacrylate monomers were measured at different temperatures by means of a rotating spindle rheometer (Brookfield, model DV-III) using appropriate spindles and standard solutions. Viscosity was measured at various spindle speeds (5–150 rpm) and only readings obtained around 50% torque were recorded and expressed as mPa s.

Differential scanning calorimetry (DSC) measurements were performed on a NETZSCH 204 apparatus at 10°C/min. The calorimeter was calibrated with indium (ΔH fusion 28.6 J/g, melting point 156.6°C) before use. An empty aluminum pan was used as a reference.

The effect of temperature on viscoelastic properties of the obtained polymers in the area of linear dependence between stress and strain was determined using a DMA Q800 apparatus produced by TA (USA) calibrated according to the producer's recommendation. Thermomechanical properties of the cured polymers were evaluated from storage modulus (E'), mechanical loss (E'') and $\tan \delta$ curves obtained at constant frequency (10 Hz). Also, from the $\tan \delta$ curves the full-width-at-half-maximum (FWHM) values were determined. Measurements for all samples were made in the temperature range 0–200/250°C at a constant heating rate of 4°C/min. Rectangular profiles of the sizes: $a = 4 \pm 0.2$ mm, $b = 10 \pm 0.2$ mm, and $c \geq 35$ mm were used in the measurements.

Flexural properties were determined in a three-point loading configuration using a Zwick Roell Strength Machine (model Z010). Specimen dimensions were $(10 \pm 0.2$ mm) \times $(4 \pm 0.2$ mm) \times (64+ mm). Measurements were carried out at room temperature with a crosshead speed of 5 mm/min. At least five specimens were tested for every datum point (PN-82/C-89051).

Hardness according to Brinell was determined by means of a hardness tester HPK (PN-84/C-89030).

Thermogravimetric experiments were carried out on a MOM derivatograph (Paulik and Erdey, Budapest) under the following operational conditions: sample weight 100 mg, heating rate 10°C/min in air atmosphere, reference material $\alpha\text{-Al}_2\text{O}_3$.

Thermal resistance under loading was evaluated using an HDT 3 VICAT apparatus produced by CEAST S.p.A (Italy). Specimens of $(4 \pm 0.2$ mm) \times $(10 \pm 0.2$ mm) \times (70+ mm) were submerged in an oil bath, and the oil bath heated from 20 to 200°C with an initial soak time of 5 min at a heating rate of 2°C/min. The heat distortion temperature was detected by a linear variable displacement transducer as the temperature at which a 2% deflection under a load of 1.8 MPa occurred. The reported HDT was an average of three measurements.

Curing procedure

All dimethacrylate esters were dissolved in methyl methacrylate and styrene making the solutions of the concentrations: 25, 50, and 75% of monovinyl monomer. Unfortunately, four of nine styrene solutions stratified into two phases. Because of the limited miscibility only 25 and two 50 wt % styrene compositions were copolymerized and examined.

The obtained compositions were irradiated by an ultraviolet light (340–360 nm) in the presence of a photoinitiator (Irgacure-651) used in the amount of 1 wt %. Curing was carried out at 25°C for 0.5 h. This same procedure was applied to prepare homopolymers, which subsequently underwent thermal postcuring at 140°C for 6 h like all copolymers. Thermal postcuring was monitored by means of a DSC. The exemplary DSC scans for the MA-BG/MMA preparations are presented in Figure 2. From Figure 2(a), one can see the exothermic peak maxima related to additional curing of polymer. The effect of postcuring becomes less significant with the increasing content of monovinyl monomer. In the second DSC analysis [Fig. 2(b)], there is no indication of further curing. The same effect can be achieved by long-term postcuring at 140°C. As can be seen from Figure 2, the glass transitions temperatures (T_g) could not be discerned by DSC, due to the breadth of the transition region (only one curve exhibits inflection typical of vitrification). Therefore, the T_g values of the polymer networks were determined using a dynamic mechanical analyzer.

RESULTS AND DISCUSSION

Molecular structures of new dimethacrylates have been confirmed by NMR analysis (Fig. 3). The ring-opening reaction of epoxides usually leads to

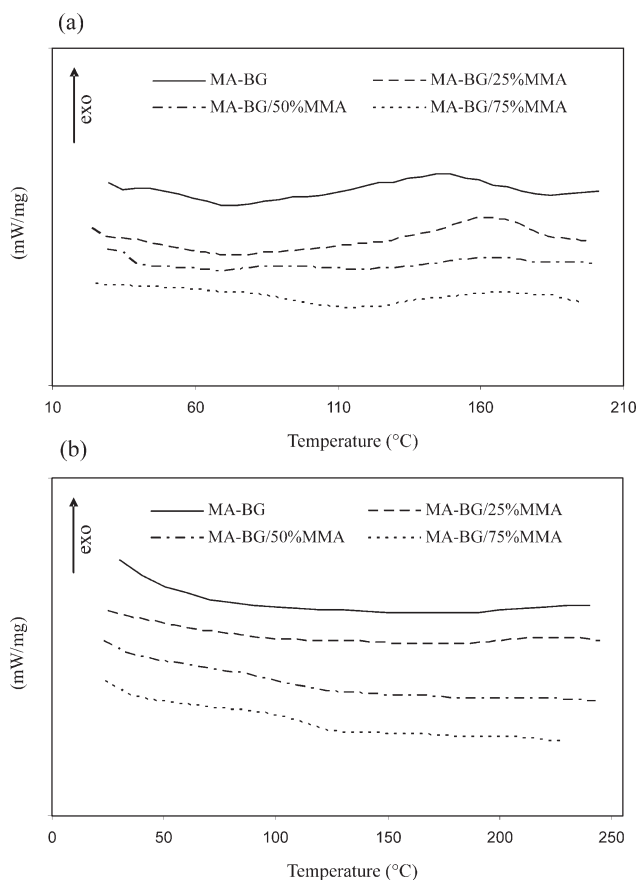


Figure 2 DSC curves of the MA-BG/MMA polymers: (a) before and (b) after postcuring.

mixture of isomers. Depending upon the selectivity of the catalyst and the reaction temperature, in the addition acid-epoxide both primary and secondary hydroxyl groups are formed at different ratios. Tetraethylammonium bromide like tertiary amines is characterized by rather small selectivity. It produces isomers with primary hydroxyl groups in the amount of 15–22%.¹³ In the present study, this is confirmed by the presence of bands for protons of =CHOH groups (4.40 ppm) and protons of —CH₂OH groups (3.80 ppm). Other side reactions like alcohol etherification with epoxide groups or esterification with acid groups are less likely to occur as indicated by a proportional loss of epoxide groups when compared with the number of acid groups determined in similar syntheses.¹⁰

CHN analysis of the obtained dimethacrylate esters is as follows.

The theoretical composition of dimethacrylate ester MA-EG: %C: 53.14; %H: 5.54; %O: 41.32; the determined composition: %C: 53.28; %H: 5.71; %O: 41.01.

The theoretical composition of dimethacrylate ester MA-BG: %C: 54.73; %H: 5.96; %O: 39.31; the determined composition: %C: 54.76; %H: 5.66; %O: 39.58.

The theoretical composition of dimethacrylate ester MA-HG: %C: 56.16; %H: 6.35; %O: 37.49; the determined composition: %C: 55.53; %H: 6.33; %O: 38.14.

Basic properties of methacrylate monomers in the noncrosslinked state, that is, refractive index, viscosity, and density are presented in the article (Table I, Fig. 4).

As can be seen from the data in Table I and Figure 4, the monomers are characterized by considerably different viscosities. This is obviously caused by a different weight fraction of hydroxyl groups present

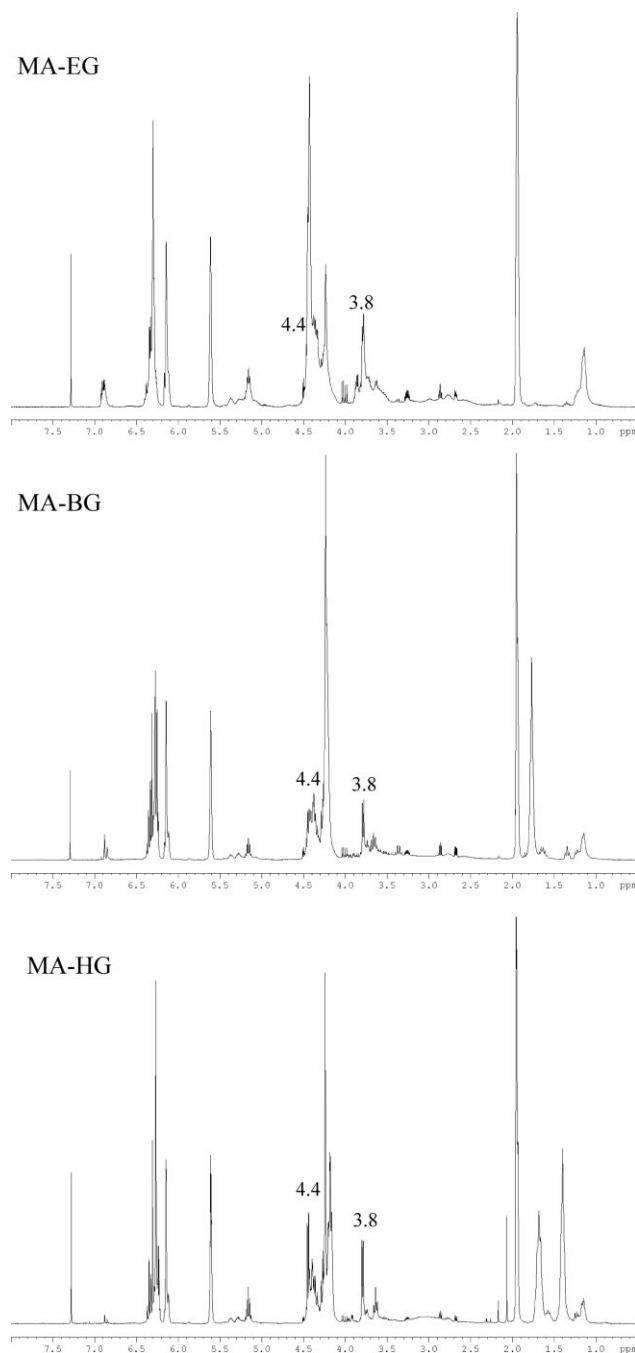


Figure 3 ¹H NMR spectra of dimethacrylates.

TABLE 1
Physical Properties of Dimethacrylates

Properties	Dimethacrylates		
	MA-EG	MA-BG	MA-HG
Viscosity at 25°C (mPa · s)	251,188	49,374	17,139
Density (g/cm ³)	1.255	1.231	1.208
PH level (mg KOH/g)	≤8	5–10	5–10
Epoxy value (gram-equivalent ep./100 g)	0.02–0.04	0.02–0.04	0.02–0.04
Refractive index	1.5000	1.4985	1.4959

in the molecules of each methacrylate. The presence of hydroxyl groups usually results in inter- and/or intramolecular hydrogen bonding. Of these two types of hydrogen bonding, the former leads to the increase in viscosity, whereas the latter causes decrease in viscosity. Therefore, the differences in viscosities observed for the dimethacrylates studied can be attributed to the mode of hydrogen bonding. A fairly long chain that separates hydroxyl groups in the methacrylate monomers makes intramolecular hydrogen bonding hardly probable. As presented in Table I and Figure 4, the viscosity decreases as the length of the hydrocarbon chain is increased. The quasi-network hydrogen bonded structure that is expected to form in dihydroxyl containing molecules should be of higher density in dimethacrylates with a greater weight fraction of hydroxyl groups. This would lead to the increase in viscosity. On the other hand, increasing hydrocarbon chain length reduces the extent of intermolecular hydrogen bonding and hence leads to the decrease in viscosity.

DMA of the obtained polymers

The dynamic mechanical behavior (DMA) results along with other strength and thermal properties are

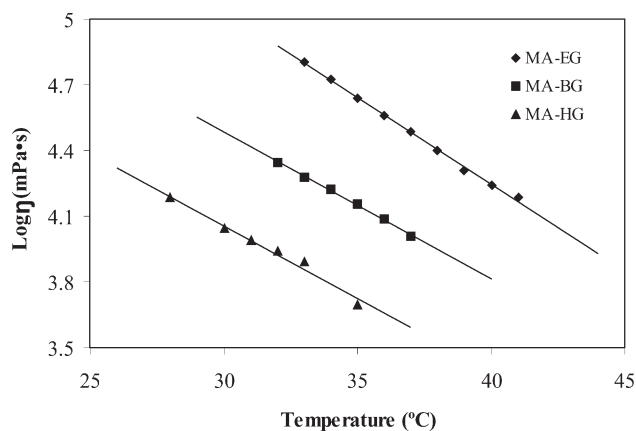


Figure 4 Viscosities of the methacrylate esters in the function of temperature.

TABLE 2
Thermal and Mechanical Properties of the Obtained Polymers

Properties	MA-EG						MA-BG						MA-HG					
	HP	25% ST	25% MMA	50% MMA	75% MMA	75% MMA	HP	25% ST	25% MMA	50% MMA	75% MMA	75% MMA	HP	25% ST	25% MMA	50% MMA	75% MMA	
Initial decomposition temperature (10% mass loss) (°C)	300	325	295	280	280	275	295	320	305	280	270	265	300	330	270	265	260	
HDT (°C)	69	120	83	93	102	102	52	115	133	75	92	100	50	84	63	80	94	
Hardness according to Brinell (MPa)	188	170	183	173	159	159	149	152	149	152	152	156	116	127	132	142	142	
Flexural modulus at bending (GPa)	5.04	4.22	4.54	4.09	3.78	3.78	3.68	3.55	3.53	3.87	3.59	3.56	2.96	3.36	3.54	3.52	3.52	
Storage modulus (MPa) (T = 25°C)	4641	4146	4481	4360	4140	4140	3880	3438	3362	3925	3690	3736	3683	3126	3928	3915	3894	
FWHM (°C)	67	77	45	40	37	37	67	82	68	53	41	37	68	74	46	38	35	
Glass transition temperature (T _g) (°C)	122	172	129	141	151	151	110	173	188	128	141	148	105	142	117	130	143	

HP, respective homopolymers.

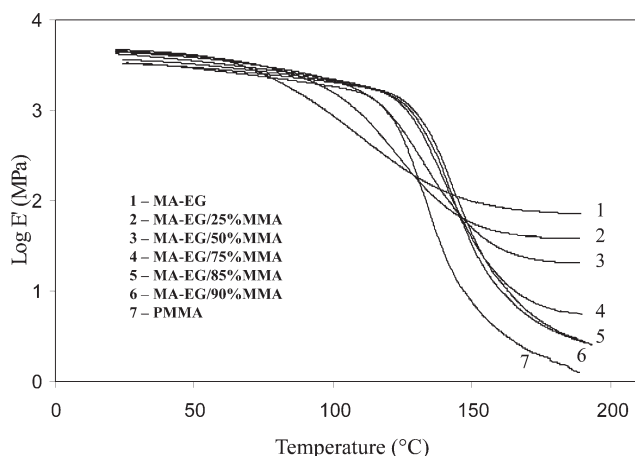


Figure 5 Storage modulus versus temperature for MA-EG/MMA compositions.

summarized in Table II. The representative DMA scans are depicted in Figures 5–8 and 12.

In Figures 5 and 6, the storage moduli in the function of temperature for the MA-EG/MMA and MA-BG/ST polymers are depicted. As can be seen from them, the modulus behavior is well captured within the whole temperature range. There is no indication of a continued reaction during the temperature scans. This means that the polymers are thermally stable and their networks could be heated without facilitating further crosslinking. The storage modulus undergoes a change from the glassy state to the rubbery state. This transition is clearly observed for all the studied samples. However, as can be seen from the width of the $\tan \delta$ curves (Figs. 7 and 8), it spreads over a wide temperature range. It is one of the features that differs crosslinked polymers from linear ones, which usually have very narrow transition regions. Because in crosslinked polymers the glass transition region is spread over a wide temperature range, it is difficult to provide a specific tem-

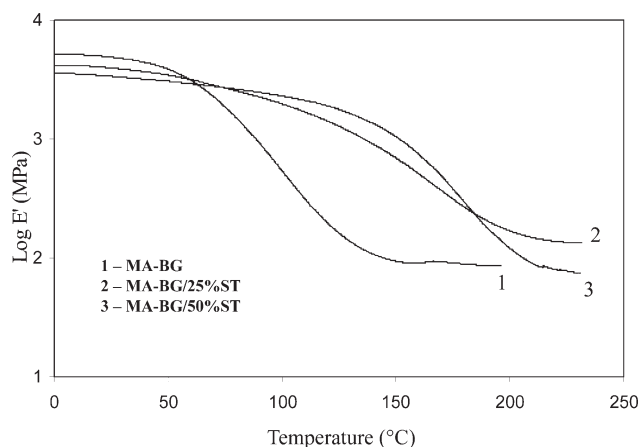


Figure 6 Storage modulus versus temperature for MA-BG/ST compositions.

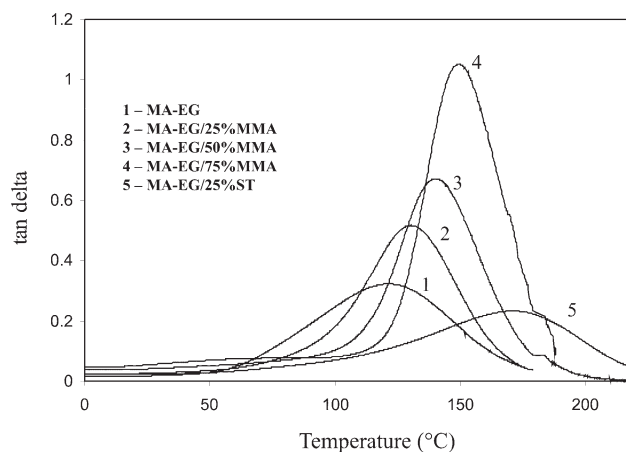


Figure 7 Tangent δ versus temperature for MA-EG polymers.

perature as their glass transition temperature. In this work, the glass transition temperature (T_g) was taken as the temperature at the peak of the $\tan \delta$ curve in the glass transition region.

Another important feature of crosslinked polymers is the plateau in the rubbery moduli region. These rubbery moduli are related to the crosslinking density of the materials. There have been several network theories,^{14,15} which have related the modulus in the rubbery region to the crosslinking densities of polymers. In this study, the plateau in the rubbery region is used as a measure of crosslinking density.

In Figure 9, the absolute temperature (taken in the rubbery region at $T_g + 50^\circ\text{C}$) divided by the rubbery modulus is plotted for all methacrylate polymers. This ratio, ζ , is inversely related to the crosslinking density of the polymer and directly proportional to the molecular weight between crosslinks in the polymer network.^{15,16} In this figure, it can be seen that as a weight ratio of the dimethacrylate is increased within a copolymer system, ζ decreases (i.e.,

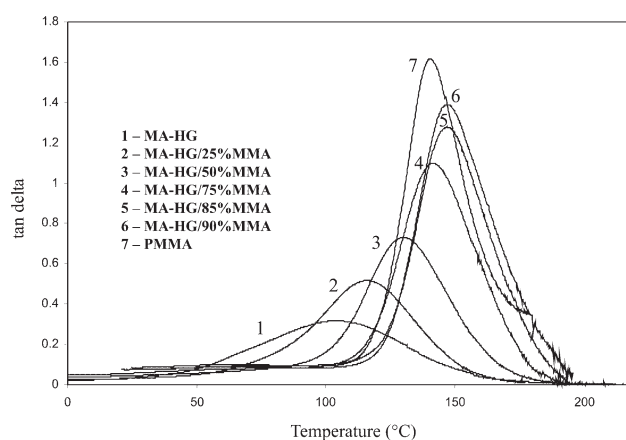


Figure 8 Tangent δ versus temperature for MA-HG/MMA polymers.

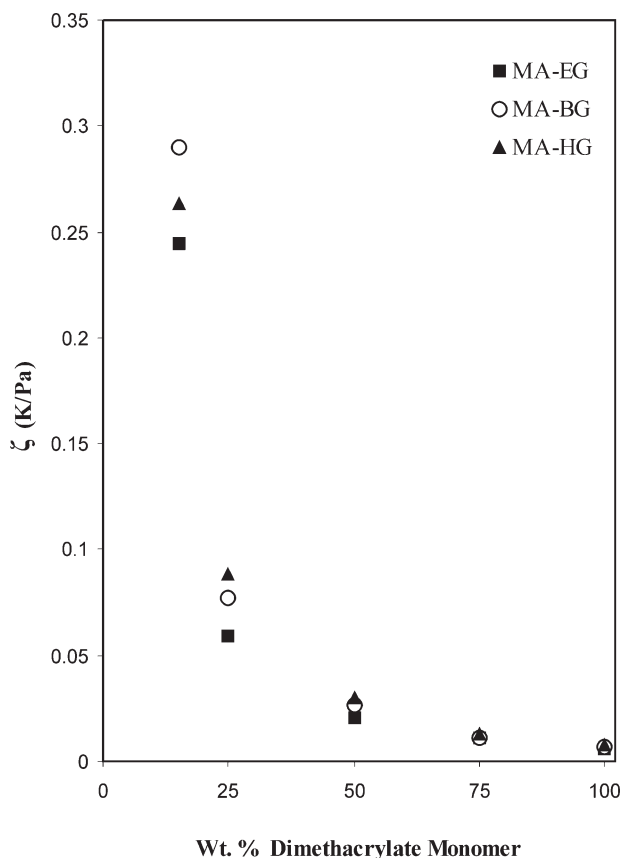


Figure 9 The inverse ratio of the modulus in the rubbery region to the temperature plotted as a function of the wt % of dimethacrylate monomer for MMA polymers.

molecular weight between crosslinks decreases and the crosslinking density increases). It can be also observed that with the increasing concentration of the crosslinker, the changes in crosslinking density become less significant. Interestingly, as follows from the data in Table II, increasing the concentration of methyl methacrylate causes an increase in the T_g of the copolymer. In other words, the T_g values increase despite the decreasing crosslinking density. One might consider this behavior as unexpected because an increase in the crosslinking density is accompanied by a decrease in mobility of the copolymer. Usually, as the mobility is decreased, the T_g of the material increases. Searching for an explanation, additional copolymers of the concentration of 85 and 90 wt % of methyl methacrylate were prepared and put to the dynamic mechanical examination. As can be seen in Figure 10, the methyl methacrylate copolymers show maxima in the T_g versus the comonomer composition plots. This anomalous behavior may be explained by two different effects that contribute to the dependence of glass transition temperature on the composition of the crosslinker. These effects were widely discussed in the previous paper¹⁰ and they are the “copolymer-

ization effect” and the “crosslinking effect.”^{17,18} The “copolymerization effect” is a result of merely changing the fractions and types of the monomers that are copolymerized, whereas the “crosslinking effect” is the effect of the constraints caused by the crosslinks on the properties of the copolymer. Typically, an increase in crosslinking results in an increase in the T_g as the mobility of the copolymer becomes increasingly restricted. Based on the type of crosslinking monomers, the crosslinking effect dominates at lower concentration of the crosslinker (increasing the composition of the crosslinker significantly increases the crosslinking density). However, it can be observed that after 25 wt % crosslinking monomer, there is only a marginal decrease in the value of ζ (Fig. 9). It means that the number of effective crosslinks added when the concentration of the crosslinker is increased beyond 25 wt % is not significant. This observation, when applied to the T_g trend shown in Figure 10, would imply that the crosslinking effect, which dominates at low concentrations of crosslinker becomes less dominant at the higher concentration of the crosslinker. Further, it is the copolymerization effect that seems to dominate at higher concentrations of the crosslinker (a total reversal in the growth of the T_g is observed).

Depending upon the crosslinking ability of a crosslinker the maxima in the T_g versus comonomer composition plots may come out at low or high crosslinker concentration. The better the crosslinker the broader the range of comonomer composition in which crosslinking effect is dominant. If a good crosslinker is used the values of T_g may increase even until 75 wt % of its concentration. Such behavior was observed in previous works, where novel trimethacrylate multiesters were investigated.^{10,11} The dimethacrylates discussed in this study behave as weak crosslinkers in copolymerization with MMA (crosslinking effect prevails only at very low

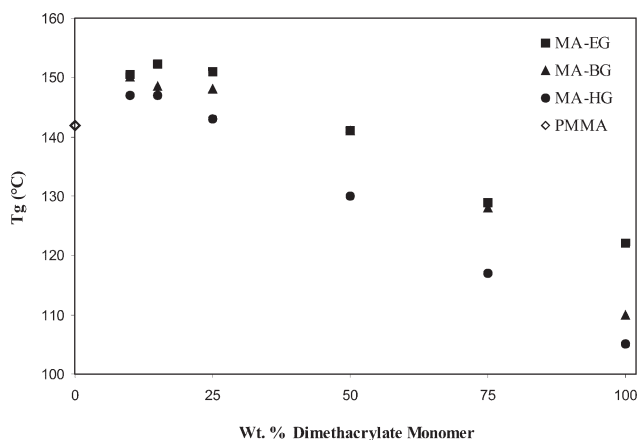


Figure 10 T_g dependence on the wt % of crosslinking agent in MMA copolymers.

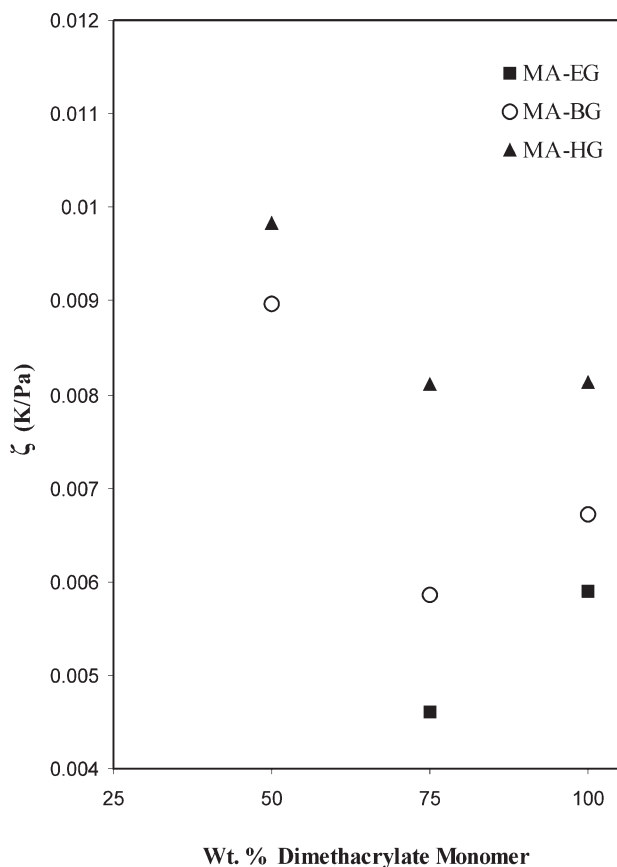


Figure 11 The inverse ratio of the modulus in the rubbery region to the temperature plotted as a function of the wt % of dimethacrylate monomer for ST polymers.

crosslinker concentrations). However, their behavior in copolymerization with ST is quite different.

In Figure 11, the inverse ratio of the rubbery modulus to the temperature (ζ) is plotted for all styrene polymers. It can be clearly seen that the 25% styrene copolymers have higher density of crosslinks than the corresponding homopolymers. It seems improbable to achieve a polymer with a higher degree of crosslinking than homopolymerized dimethacrylate, simply by copolymerizing it with a monovinyl monomer. However, this apparent anomaly has a plausible explanation. In homopolymerization (or copolymerization with MMA) of dimethacrylates studied in this work, the maleic double bonds seem to remain intact. They are immune to the methacrylic radicals generated in the polymerizing medium. On the other hand, the copolymerization with styrene could lead to higher crosslinking because of styrene-maleate radical reaction. It can be concluded that the functionality of new dimethacrylates changes in different copolymer systems.

Examining the ζ information in Figures 9 and 11 more closely one can see that increasing the chain length that separates methacrylate double bonds causes a decrease in crosslinking density (as indi-

cated by the increase of ζ). With the decreasing crosslinking the molecular weight between crosslinks increases and the glass transitions temperatures decrease. The differences in crosslinking densities are seemingly significant in homopolymers. When comparing the T_g , it changes from 122°C for the MA-EG homopolymer, to 110°C for the MA-BG and to 105°C for the MA-HG, respectively.

Photopolymerization of multifunctional monomers leads to the evolution of a very heterogeneous structure because a diverse distribution of microenvironments (highly crosslinked regions as well as pools of unreacted monomer) is present in the polymer networks. This heterogeneity of the network manifests itself as a wide distribution of relaxation times because there exists a very broad distribution of mobilities in the matrix. In this work, the heterogeneity of the polymer network has been evaluated qualitatively by examining the width of the $\tan \delta$ peak.^{19–21} Physically, this width provides a measure of the range of mobilities that exist within the polymer.

It can be observed from the data in Table II that as the content of MMA and/or ST is increased in the copolymer, the peak width of the $\tan \delta$ (FWHM) decreases. This decrease suggests that the width of the distribution of relaxation times decreases by increasing the content of monovinyl monomer in the system. It can be seen that the styrene copolymers are more heterogeneous than the copolymers with methyl methacrylate. Besides, they have in majority higher values of FWHM than the homopolymers. As mentioned previously, this behavior seems to be caused by additional crosslinking through maleate double bonds. Increasing monomer functionality in crosslinking polymerizations usually leads to the increase in heterogeneity of the final material. The degree of structural heterogeneity of the copolymers increases with the increasing crosslinking monomer composition provided that the functionality of the crosslinker remains unchanged. Further, the degree of heterogeneity does not seem to depend on the type of dimethacrylate used. The corresponding copolymers (within the methyl methacrylate and styrene series) have very similar peak widths of the $\tan \delta$. A transition from MA-HG to MA-BG and from MA-BG to MA-EG as a crosslinking agent does not contribute much to the increase in the microgel formation. The multifunctional methacrylates contain in their structure hydroxyl groups whose presence may additionally contribute to the broadening of relaxation times distribution, and thus, enhance their structural heterogeneity.

The presence and interactions of side groups in the copolymers with MMA (visible in Fig. 12 in the form of β relaxation) seem to be the reason for their increased stiffness when compared with their

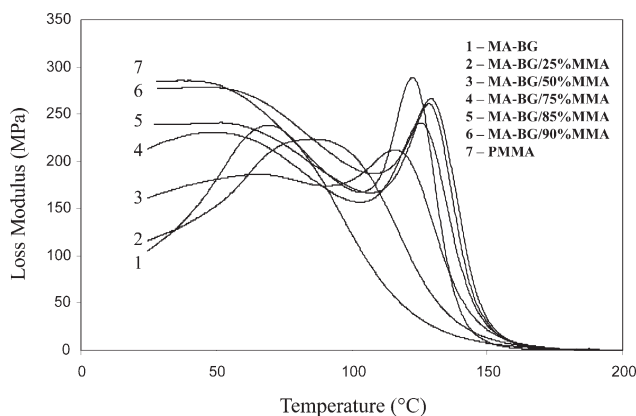


Figure 12 Loss modulus versus temperature for MA-BG/MMA compositions.

styrene analogues as indicated by the storage modulus values presented in Table II. Increase in the content of monovinyl monomer (MMA) is favorable for formation of longer units in the polymer network and thus becoming similar to poly(methyl methacrylate) properties where β relaxation is associated with the side motions of ester groups.²²

Flexural and thermal properties of cured methacrylates

As follows from the data in Table II, the copolymers with MMA are characterized by lower initial decomposition temperatures than the homopolymers and the copolymers with ST. Further, the increasing amounts of methyl methacrylate in copolymers are responsible for the decrease of the initial decomposition temperatures. The reasons for the observed tendencies are the same as those discussed in previous studies.^{10,11} This is understandable because methacrylates of similar chemical origin are investigated in both articles. The mechanism of thermal degradation that was proposed previously can also be used for explanation of the present results. With the increasing concentration of MMA, the number of ester groups in the polymer network increases, and longer poly(methyl methacrylate) chain units are formed due to a significant MMA molar excess. This is the reason that can be responsible for radical depolymerization and its shifting toward lower temperatures, whereas degradation at higher temperatures can be associated with initiation by random scission. Styrene copolymers show better thermal stability due to the presence of aromatic rings and lower content of ester bonds. Besides, as was already discussed, the higher degree of crosslinking in styrene copolymers caused by styrene-maleate copolymerization may additionally increase their decomposition temperatures.

Changes in the heat deflection temperatures show an apparent trend with composition. Comparing the values tabulated, it can be seen that this trend is analogous to the one observed for the glass transition temperature. In all series of copolymers, the HDT values drop with the increasing concentration of crosslinking monomer. Similar to the T_g , styrene copolymers have significantly higher HDT than their methyl methacrylate analogues. The reasons for the observed tendency appear to be the same as those discussed for the dependence of glass transition temperatures on the crosslinking agent composition. The contribution of the coexisting (and at times opposing) effects of copolymerization and crosslinking seems to be decisive. On the other hand, the increased functionality of the dimethacrylates in copolymerization with styrene has to have crucial importance for the thermal properties of styrene polymers.

Regarding the results tabulated, it can be seen that Brinell's hardness decreases for the MA-EG polymers as the percent methyl methacrylate and/or styrene is increased, remains approximately unchanged for all the MA-BG compositions, and increases with the percent methyl methacrylate and/or styrene in the case of the MA-HG preparation. The differences in hardness are particularly large when comparing the homopolymers, and they diminish with the increasing concentration of monovinyl monomer. This tendency gives a clear evidence of how important to the property is the plasticizing effect of the hydrocarbon chain length. Of the three dimethacrylates, the best plasticizer is the one with the longest hydrocarbon chain, that is, the MA-HG monomer. In its case, the plasticizing effect causes a decrease in hardness despite the increasing crosslinking density. On the other hand, the short two-carbon chain of the MA-EG monomer exerts the weakest plasticizing effect (increasing its concentration leads to the increase in hardness of the copolymer). Examining the MA-BG preparation, it seems that the plasticizing effect of the hydrocarbon chain is compensated by the increasing crosslinking density (the hardness does not change significantly with copolymer composition). It can be concluded that the plasticizing ability of the new dimethacrylates is dependent upon their molecular structure, specifically the length of their hydrocarbon chain.

The effect of a plasticizer influences also flexural moduli of the new materials. From the data in Table II, it can be seen that with the increasing concentration of ST and/or MMA in the copolymer, the values of flexural modulus decrease. This is a common feature for all types of methacrylate polymers and is understandable because reduced crosslinking densities usually lower the flexural moduli of the materials. However, the plasticizing effect of the

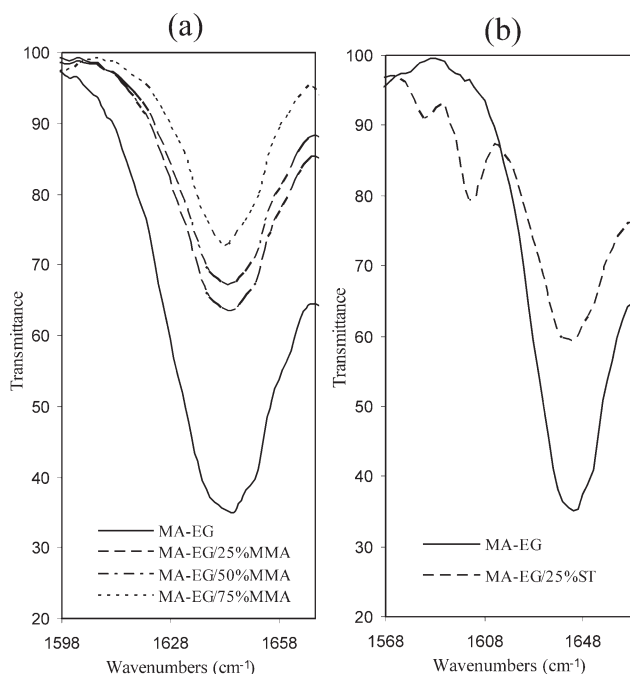


Figure 13 FTIR spectra of the MA-EG polymers: (a) copolymers with MMA; (b) copolymer with ST.

hydrocarbon chain becomes evident when comparing flexural moduli of the homopolymers. Increasing the chain length causes a rapid drop of flexural modulus. As a consequence, the MA-HG homopolymer, in which the plasticizing effect is the strongest, has the lowest value of flexural modulus of all the obtained polymers.

Conversion of unsaturated bonds

The FTIR spectra of all the obtained polymers are presented in Figures 13–15.

Conversion of double bonds in multifunctional methacrylates is rarely complete because of immobilization, gelation, vitrification, or steric isolation. In real systems, that is, in chemically or lightly cured dimethacrylates, the conversion of double bonds ranges from 55 to 75%.²³

The dimethacrylate monomers used in this study can be considered as relatively high molecular weight crosslinking agents, in which methacrylate double bonds are separated by a long multiester chain. It is commonly known that during the polymerization of dimethacrylates with long flexible chains, vitrification does not occur and the final conversion of double bonds may reach 100%.²⁴ In polymerization of new dimethacrylates, the cyclization reactions, which are known to be responsible for entrapping pendant double bonds, should be hampered by the presence of the separating multiester chain. Thus, the degree of double bond conversion

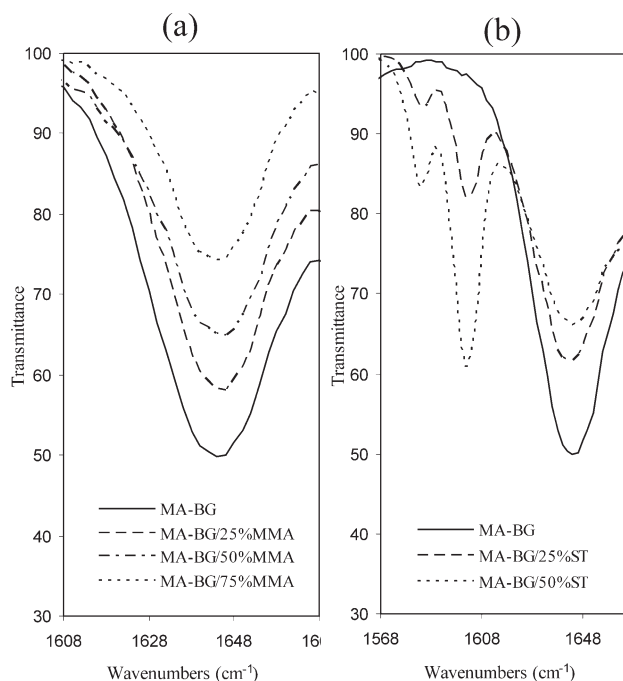


Figure 14 FTIR spectra of the MA-BG polymers: (a) copolymers with MMA; (b) copolymers with ST.

may be expected to reach higher values than those cited above.

Usually, to find the conversion degree, intensities of peaks responsible for stretching vibrations of the C=C (1637 cm^{-1}) group before and after polymerization are compared. Depending upon the

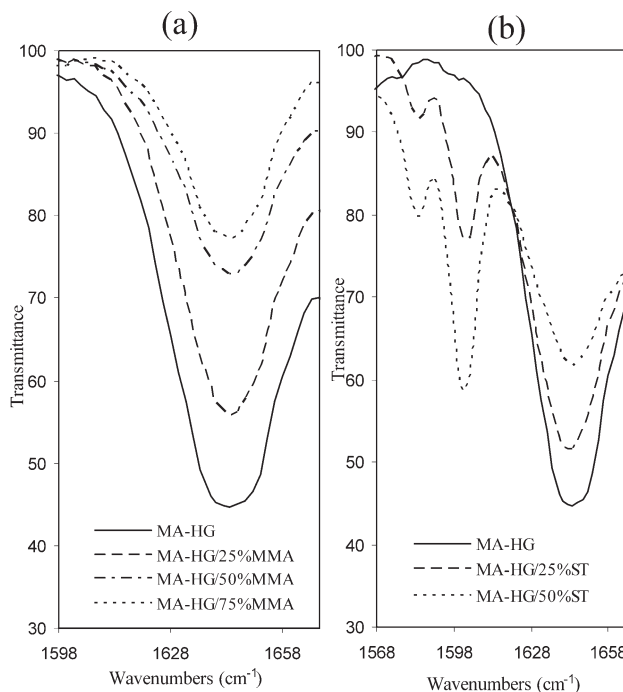


Figure 15 FTIR spectra of the MA-HG polymers: (a) copolymers with MMA; (b) copolymers with ST.

monomer type and comonomer composition, different peaks are used as internal standards. However, it is very difficult to make such evaluations for the dimethacrylates studied because they have qualitatively different double bonds (methacrylate as well as maleate). As already discussed, the maleate double bonds are presumably inactive in copolymerization with MMA and participate in copolymerization with ST. Therefore, the contribution of both types of double bonds to the FTIR spectra after polymerization would be different in different copolymer systems. Examining Figures 13–15, it is evident that the absorption bands for the C=C group of the polymerized and postcured samples are significant regardless of the copolymer type. In MMA copolymers, it seems to be caused mainly by the presence of maleate double bonds, whereas in ST copolymers it may be caused by the presence of unreacted maleate as well as methacrylate double bonds. Based on the FTIR analysis, the evaluation of the double bond conversion degree could not be done quantitatively.

Examining Figures 13–15 further, it can be seen that homopolymers have the lowest degrees of unsaturated bonds conversion. The degree of conversion increases with the increasing content of monovinyl monomer. As the composition of the crosslinker is increased, the maximum double bond conversion that the sample may attain decreases because of diffusional limitations to the polymerization process.^{5,25–27} A higher degree of functionality (a greater number of double bonds per a monomer molecule) leads to higher reaction rates and higher density of crosslinks. In dense networks, the degree of conversion is reduced and a large portion of double bonds remains unreacted. Therefore, the properties of the new materials are influenced not only by the effects of crosslinking and copolymerization but residual unsaturation as well.

CONCLUSIONS

The obtained copolymers exhibit untypical T_g behavior as a function of weight fraction of crosslinking agent. An increase in T_g is observed only for low concentration of the crosslinker. Continued increase of the dimethacrylate concentration results in a decrease in the glass transition temperature of the copolymers. This decrease is attributed to the “copolymerization effect.” However, at higher concentrations of crosslinker, the “copolymerization effect” and that of residual unsaturation cannot be

separated. As a result, it is not clear what mechanism dominates at higher concentrations of the crosslinker.

Interesting behavior has been observed when examining the flexural properties of new materials. Increasing the length of the hydrocarbon chain increases the plasticizing ability of a dimethacrylate. It leads to a total reversal in flexural properties when replacing the MA-EG dimethacrylate with the MA-HG one.

Furthermore, as proved by the obtained results, the new dimethacrylates could behave as di- or tetrafunctional monomers dependent upon the comonomer type and reactivity.

References

- Blanding, J. M.; Osborn, C. L.; Watson, S. L. *J Radiat Curing* 1978, 5, 13.
- Decker, C.; Moussa, K. *Macromolecules* 1989, 22, 4455.
- Kloosterboer, J. G.; Lippits, G. M. *J Radiat Curing* 1984, 11, 1.
- Anseth, K. S.; Newman, S. M.; Bowman, C. N. *Adv Polym Sci* 1995, 122, 177.
- Kloosterboer, J. G. *Adv Polym Sci* 1988, 84, 1.
- Bland, H. M.; Peppas, N. A. *Biomaterials* 1996, 17, 1109.
- Kim, J. G.; Chung, C. M. *Biomaterials* 2003, 24, 3845.
- Chung, C. M.; Kim, J. G.; Kim, M. S.; Kim, K. M.; Kim, K. N. *Dent Mater* 2002, 18, 174.
- Matynia, T.; Podgórski, M. *J Appl Polym Sci* 2008, 108, 2902.
- Podgórski, M.; Matynia, T. *J Appl Polym Sci* 2008, 109, 2624.
- Podgórski, M.; Matynia, T. *Przem Chem* 2008, 87, 874.
- Matynia, T.; Podgórski, M. *Przem Chem* 2005, 84, 927.
- Bukowska, A.; Bukowski, W.; Galina, H. *Wiad Chem* 1997, 51, 217.
- Treloar, L. R. G. *The Physics of Rubber Elasticity*; Oxford University Press: London, 1958.
- Charlesworth, J. M. *Polym Eng Sci* 1988, 28, 230.
- Elliott, J. E.; Nie, J.; Bowman, C. N. *Polymer* 2002, 44, 327.
- Fox, T. G.; Loshaek, S. *J Polym Sci* 1955, 15, 371.
- Bicerano, J.; Sammler, R. L.; Carriere, C. J.; Seitz, J. T. *J Polym Sci Part B: Polym Phys* 1996, 34, 2247.
- Simon, G. P.; Allen, P. E. M.; Williams, D. R. G.; Cook, W. D. *Polymer* 1991, 32, 2577.
- Allen, P. E. M.; Williams, D. R. G.; Clayton, A. B. *Eur Polym J* 1994, 30, 427.
- Kannurpatti, A. R.; Anseth, J. W.; Bowman, C. N. *Polymer* 1998, 39, 2507.
- Jones, D. S. *Int J Pharm* 1999, 179, 167.
- Watts, D. C. *Medical and Dental Materials*; VCH: New York, 1992; p 209.
- Anseth, K. S.; Kline, L. M.; Walker, T. A.; Anderson, K. J.; Bowman, C. N. *Macromolecules* 1995, 28, 2491.
- Cook, W. D. *Polymer* 1992, 33, 2152.
- Anseth, K. S.; Wang, C. M.; Bowman, C. N. *Polymer* 1994, 35, 3243.
- Andrzejewska, E. *Prog Polym Sci* 2001, 26, 605.