

Network Structure/Mechanical Property Relationship in Multimethacrylates—Derivatives of Nadic Anhydride

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ABSTRACT: In this article the syntheses of dimethacrylate and trimethacrylate esters as well as the mechanical and thermal properties of their copolymers with methyl methacrylate and styrene are investigated. The esters were obtained from acidic derivatives of nadic anhydride and glycidyl methacrylate. The addition reaction of glycidyl methacrylate and the acidic compound was carried out in the presence of basic catalyst—tetraethylammonium bromide. The monomers and resins were UV cured in the presence of a suitable photoinitiator which was 2,2-dimethoxy-2-phenylacetophenone. The prepared polymers were subjected to different studies concerning evaluation of their mechanical properties, thermal stability, dynamic mechanical behavior (DMA) as well as the estimation of the content of unreacted double bonds in the

final product. The results proved their good thermal and mechanical properties. The degree of unsaturated bonds conversion was found to be growing with the amount of monovinyl monomer in the copolymer. Trimethacrylate-based copolymers are characterized by a greater content of double bonds present in the obtained material compared to that of dimethacrylate-based copolymers. As indicated by DMA the network structures of the copolymers seem to be more heterogeneous with the increasing weight fraction of trimethacrylate as well as dimethacrylate monomer. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 109: 2624–2635, 2008

Key words: mechanical properties; photopolymerization; degree of conversion; glass transition

INTRODUCTION

Industrial application of monomers and epoxyacrylate as well as epoxymethacrylate resins meant great progress in production of materials characterized by high temperature of deflection under load as well as high strength and chemical resistance. Because of good physical and mechanical properties, vinyl esters are used for preparation of casts as well as thermally and photochemically cured paints and lacquers resistant to corrosion. Such materials are successfully applied as masks and protective coatings in electronic and electrotechnique industries. They also find application as binders in glue and optical fiber production. Owing to their increased chemical resistance styrene solutions of vinyl esters (vinyl-ester resins) are a good substitute for unsaturated polyester resins^{1,2} particularly in production of laminates reinforced with glass fiber. Because of their nontoxicity and biocompatibility acrylic and methacrylic multiesters containing three and more (meth)acrylic groups are applied, among others, as dental materials.^{3–5}

Of numerous methods of monomers and vinyl-ester resins preparation, the addition of α,β -unsaturated mono- or dicarboxylic acids to compounds and epoxide resins is frequently used. These reactions without the catalyst proceed with low rate and small selectivity. The compounds of acidic and basic character as well as transition metal complexes are used as catalysts.^{6,7} In practice the addition of carboxylic groups with oxiranes is most frequently carried out in the presence of tertiary amines. Thus e.g., a series of epoxyacrylic resins was obtained using glycidyl ethers of various diols including bisphenol A as substrates.⁸

The alternative method of methacrylic monomer synthesis consists in addition of glycidyl methacrylate (GMA) to the compounds containing an active hydrogen atom e.g., carboxylic acids,⁹ phenols or amines.¹⁰ The article includes the description of synthesis of new di- and trimethacrylate monomers and presents physical, mechanical, and thermal properties of monomers and resins before and after curing.

EXPERIMENTAL

Materials

Glycidyl methacrylate (GMA, 97%, from Sigma-Aldrich Chemie GmbH), dicyclopentadiene (DCPD, 98%, from Merck KgaA Frankfurt), tetraethylammonium bromide (analytically pure, from Merck KgaA

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Frankfurt), maleic anhydride (99%, from POCh Gliwice), methacrylic acid (MAA, 99%, from Merck KgaA Frankfurt), hydroquinone (analytically pure, from Merck KgaA Frankfurt), 2,2-dimethoxy-2-phenylacetophenone (Irgacure 651, UV polymerization initiator, from Sigma-Aldrich Chemie GmbH), methyl methacrylate (MMA, analytically pure, from Ubichem) and styrene (ST, analytically pure, from POCh Gliwice) were used as received.

Synthesis of methacrylate esters

Nadic anhydride obtained by the diene addition of maleic anhydride and cyclopentadiene was used in the syntheses. The addition reaction was carried out using dicyclopentadiene which dedimerises in the reaction medium at about 170°C. The raw adduct was distilled twice under the reduced pressure. The acidic derivative of nadic anhydride was used for the synthesis of dimethacrylate ester (Meth-II). Bicyclo [2.2.1]-hept-5-ene-2,3-dicarboxylic acid crystallized from water was filtered and dried. The addition reaction of glycidyl methacrylate and bicyclo [2.2.1]-hept-5-ene-2,3-dicarboxylic acid was carried out in a three-necked round-bottomed 500-cm³ flask equipped with a heating jacket, stirrer, thermometer, and air cooler. Powdered acid was added in portions to glycidyl methacrylate containing 0.01 wt % hydroquinone and 0.15 wt % tetraethylammonium bromide and heated up to 80–85°C. The reagents were used at the ratio of 1 mol of dicarboxylic acid and 2 mol of glycidyl methacrylate. The reaction course extent was controlled by estimation of the PH level (PN-87/C-89082/11) of the reaction mixture which dropped from 249 mg KOH/g to 5–10 mg KOH/g as well as the evaluation of the epoxy value (PN-74/C-89085) which decreased from 0.43 epoxide gram-equivalents/100 g to 0.02–0.03 (Fig. 1). The pH level was determined after the addition of the total acid amount i.e., after about 0.5 h from the beginning of synthesis. Along with its decrease, the process temperature was increased to 105°C (average 5°C/h). The final PH level was achieved after 5–6 h.

Synthesis of trimethacrylate ester (Meth-III) was carried out in three stages. Stage I—the synthesis of glycidyl methacrylate and methacrylic acid adduct. The addition was carried out in a three-necked round-bottomed 500-cm³ flask equipped with a heating jacket, stirrer, thermometer and air cooler. The equimolar mixture of glycidyl methacrylate and methacrylic acid was heated up to 110°C in the presence of tetraethylammonium bromide (0.2 wt %) as a catalyst and hydroquinone (0.01 wt %) as an inhibitor of radical polymerization. Stage I ended when the PH level decreased to about 5 mg KOH/g.

Stage II—the reaction of nadic anhydride with glycidyl methacrylate and methacrylic acid adduct. A

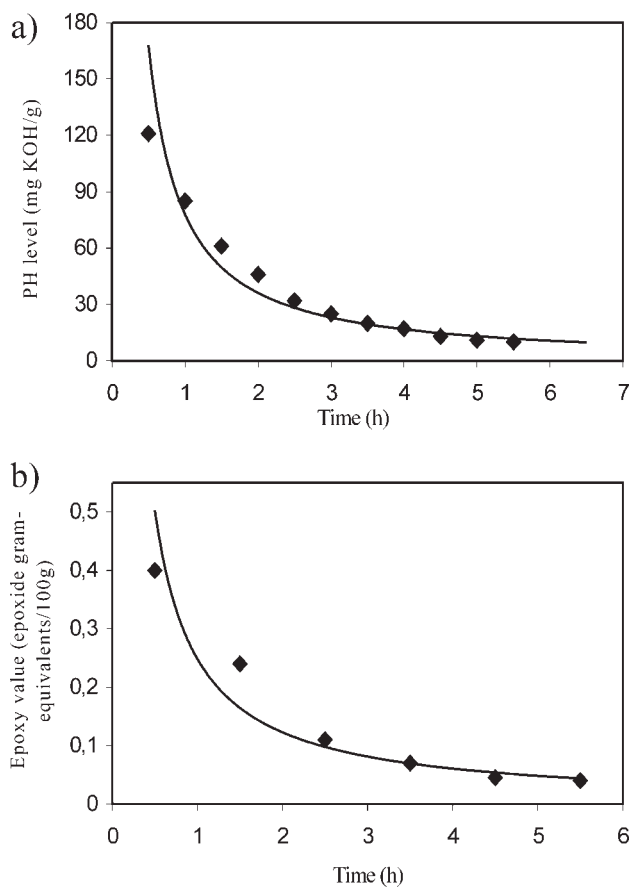


Figure 1 PH level decrease (a) and epoxy value decrease (b) during the Meth-II dimethacrylate ester synthesis.

stoichiometric amount of nadic anhydride was added to a round-bottomed 500-cm³ flask containing GMA and MAA adduct. The mixture was then heated at 105°C for 2.5 h. Stage II ended when the PH level dropped from 286 mg KOH/g to 150 mg KOH/g.

Stage III—the reaction of glycidyl methacrylate with acidic ester prepared in stage II. In the final stage glycidyl methacrylate in the amount corresponding to the determined PH level was added to the flask. New amounts of the catalyst (0.1 wt %) and inhibitor of radical polymerization (0.005 wt %) were added to the reaction mixture. The addition was carried out at 105–110°C for about 4 h. The process was reckoned as completed when the PH level dropped below 10 mg KOH/g.

In both syntheses tetraethylammonium bromide was used as the catalyst of the addition reaction of carboxylic groups to oxiranes. This choice was made because of higher yield of the obtained products when quaternary ammonium salts were used compared to amines or transition metal complexes.¹¹ Figures 2 and 3 present the equations of the described reactions.

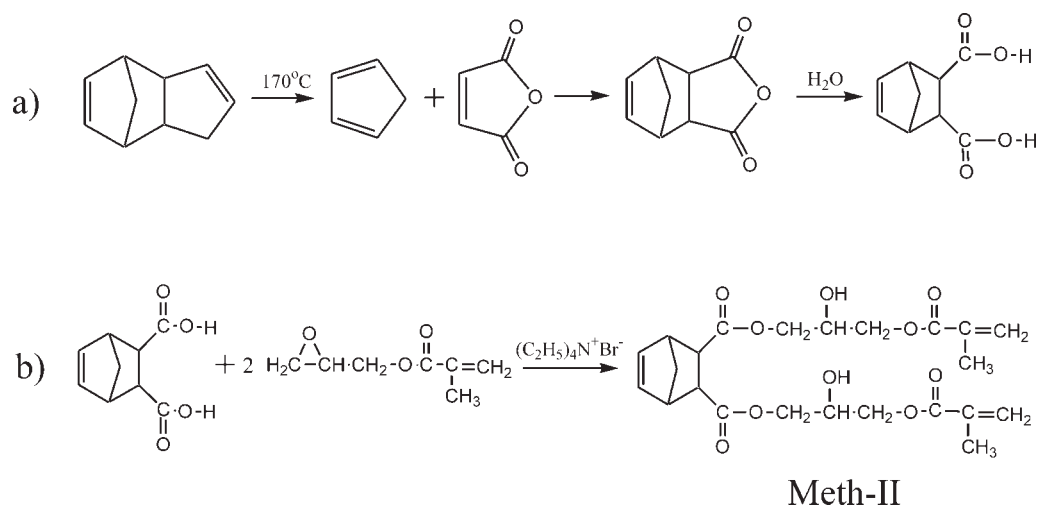


Figure 2 Equations of synthesis reaction of: (a) bicyclo[2.2.1]-hept-5-ene-2,3-dicarboxylic acid; (b) dimethacrylate ester (Meth-II).

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-

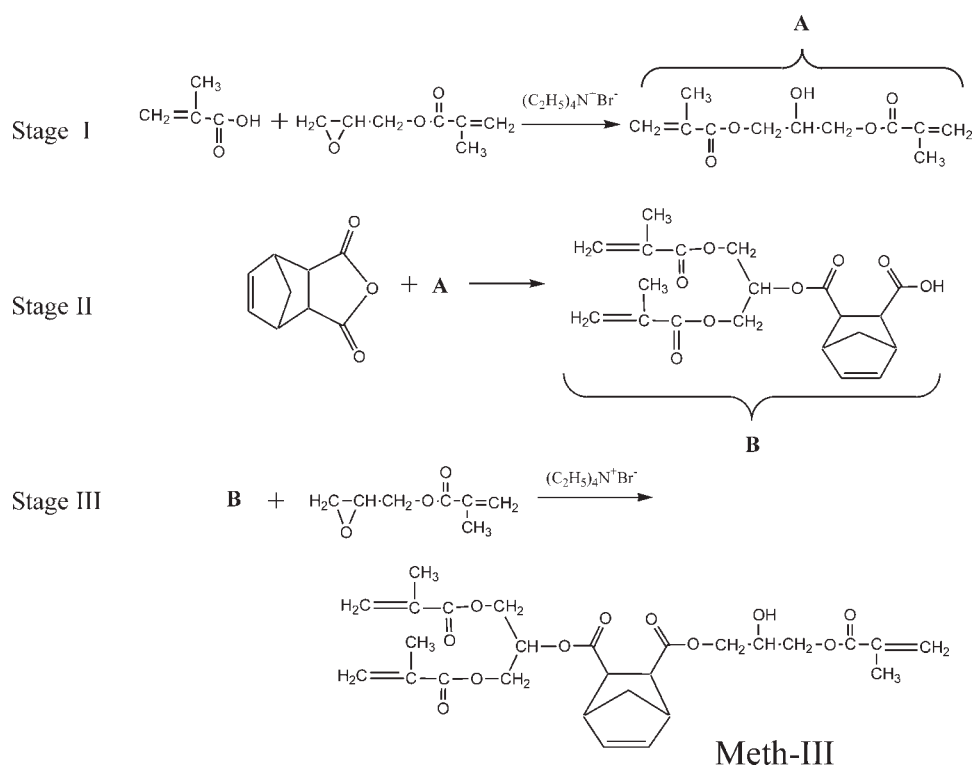


Figure 3 Equations of synthesis reaction of trimethacrylate ester (Meth-III).

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 $\text{mPa}\cdot\text{s}$.

Differential scanning calorimetry (DSC) measurements were performed on a Netzsch 204 apparatus at $10^\circ\text{C}/\text{min}$.

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 – $250/300^\circ\text{C}$ at a constant heating rate of $4^\circ\text{C}/\text{min}$. 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 $10^\circ\text{C}/\text{min}$ 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°C to $200/300^\circ\text{C}$ with an initial soak time of 5 min at a heating rate of $2^\circ\text{C}/\text{min}$. 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

Methacrylate esters were dissolved in methyl methacrylate and styrene making the solutions of the concentrations: 25, 50, and 75% of monovinyl monomer. The obtained compositions were irradiated by an

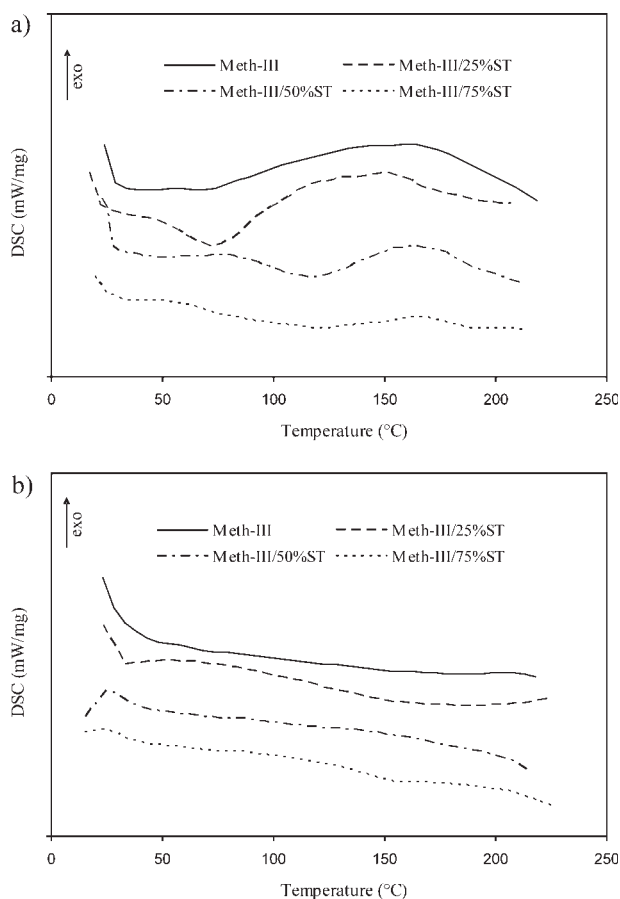


Figure 4 DSC curves of the Meth-III/ST polymers: (a) before and (b) after postcuring.

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 procedure was also applied to prepare homopolymers, which were thermally postcured at 120 – 160°C for 6 h like all copolymers. Conditioning temperature was established from the DSC analysis (position of exothermic peak maximum related to additional curing of polymers was decisive). The exemplary DSC scans for Meth-III/ST preparations are presented in Figure 4. From Figure 4(a) one can see that the exothermic peak maxima come out at around 160°C . This temperature was taken as the conditioning temperature for the Meth-III polymers. In the second DSC analysis [Fig. 4(b)] there is no indication of additional curing. The same effect can be achieved by long-term postcuring at 160°C . As can be seen from Figure 4, the glass transitions temperatures (T_g) could not be discerned by DSC, due to the breadth of the transition region. So the T_g values of the polymer networks were determined using a dynamic mechanical analyzer. The Meth-II polymers were conditioned at 120 – 140°C , since that was the temperature range of their exothermic peak maxima.

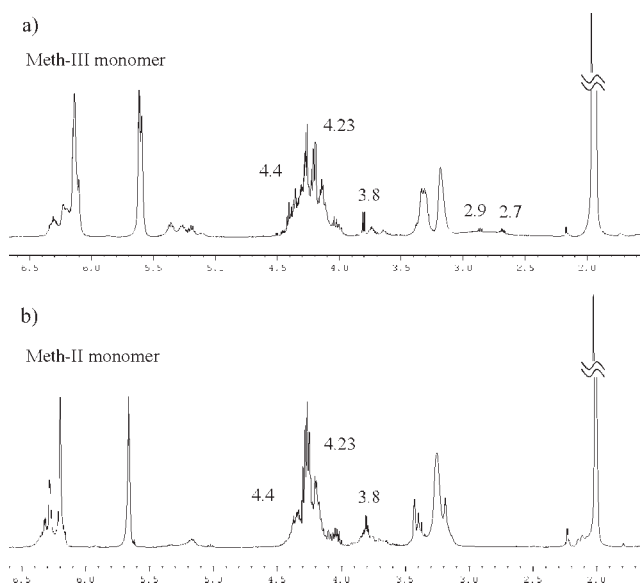


Figure 5 NMR spectra of methacrylate esters: (a), Meth-III; (b), Meth-II.

RESULTS AND DISCUSSION

NMR characteristics of similar synthesis products can come up with difficulties due to a large number of isomers formed in side reactions as well as the presence of unreacted substrates. In spite of this, the spectra analysis after the addition indicates disappearance of peaks for protons at the epoxide ring (2.7×10^{-6} , 2.9×10^{-6} , and 3.3×10^{-6}) and appearance of signal of ethylene protons in the vicinity of ester groups (4.23×10^{-6}). Similar to amines, quaternary ammonium salts are characterized by rather small selectivity. Both primary and secondary hydroxyl groups can be formed in the addition reaction of carboxylic groups to epoxide ones. As can be seen from Figure 5 this is confirmed by the presence of 4.40×10^{-6} bands for protons of $=\text{CHOH}$ groups and 3.80×10^{-6} bands for protons of $-\text{CH}_2\text{OH}$ groups. 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 compared to the number of acid groups determined during the synthesis (Fig. 1).

CHN analysis of the obtained methacrylate esters and substrates used in syntheses is as follows. The theoretical composition of nadic anhydride: %C: 65.85; %H: 4.88; %O: 29.27; the determined composition: %C: 65.36; %H: 4.74; %O: 29.90.

The theoretical composition of bicyclo[2.2.1]-hept-5-ene-2,3-dicarboxylic acid: %C: 59.34; %H: 5.50; %O: 35.16; the determined composition: %C: 58.98; %H: 5.40; %O: 35.62.

The theoretical composition of dimethacrylate ester (Meth-II): %C: 59.23; %H: 6.44; %O: 34.33; the

TABLE I
Physical Properties of Methacrylate Esters

| Properties | Adducts | |
|---|-----------|----------|
| | Meth-II | Meth-III |
| Viscosity at 25°C (mPa*s) | 125,380 | 17,620 |
| Density (g/cm ³) | 1.23 | 1.20 |
| Acid value (mg KOH/g) | 5–8 | 6–10 |
| Epoxy value (gram-equivalent ep./100 g) | 0.02–0.03 | 0.015 |
| Refractive index | 1.5044 | 1.4983 |

determined composition: %C: 58.83; %H: 6.52; %O: 34.65.

The theoretical composition of trimethacrylate ester (Meth-III): %C: 60.67; %H: 6.37; %O: 32.96; the determined composition: %C: 60.80; %H: 6.59; %O: 32.61.

Basic properties of methacrylate monomers in the noncrosslinked state i.e., refractive index, viscosity and density are presented in the article (Table I, Fig. 6).

As can be seen from the data in Table I and Figure 6, the monomers are characterized by considerably different viscosities. This is obviously caused by a different number of hydroxyl groups present 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 Meth-II and Meth-III monomers can be attributed to the mode of hydrogen bonding. The Meth-II monomer exhibits higher viscosity as compared to the Meth-III monomer. This is probably due to the presence of the quasi-network hydrogen bonded structure of dimethacrylate monomer which possesses two hydroxyl groups per a monomer molecule. On the other hand, the presence

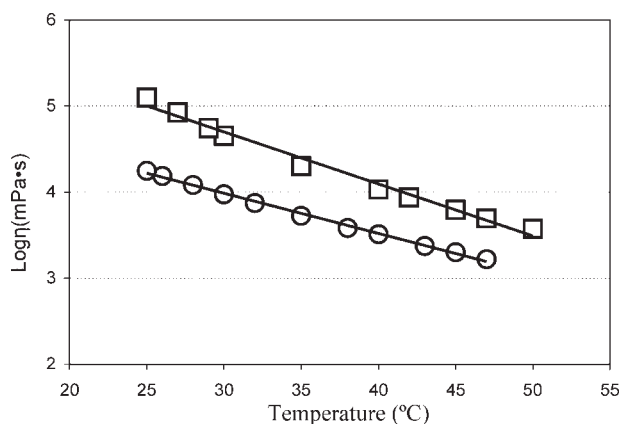


Figure 6 Viscosities of methacrylate esters in the function of temperature: (□), Meth-II; (○), Meth-III.

of only one hydroxyl group in the structure of the Meth-III monomer can be the reason for the reduced intermolecular hydrogen bonding. In consequence, the trimethacrylate monomer has significantly lower viscosity than the dimethacrylate one. Lower viscosity makes the Meth-III monomer much easier in processing and polymerization. This important feature is decisive in technological applications.

DMA of the obtained polymers

Postcured homopolymers and copolymers were subjected to mechanical and thermal studies. The DMA results along with other strength and thermal properties are summarized in Table II. The representative DMA scans are depicted in Figures 7, 8 and 10.

Using conventional initiators in crosslinking polymerizations leads to entrapping of free radicals in highly crosslinked regions.^{12–14} The presence of trapped radicals makes it very difficult to heat the network without facilitating further reaction and crosslinking. To study the mechanical behavior, a sample that will not change chemically over a range of temperatures is required. By using iniferters (i.e., living radical polymerizations) it is possible to avoid radical trapping and, therefore, synthesize a network that does not undergo further reaction upon heating. In this work, thermally stable samples were achieved by long-term thermal postcuring.

In Figure 7(a,b) the storage moduli in the function of temperature for the Meth-II/ST and Meth-III/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. The storage modulus undergoes a change from a glassy state to the rubbery state. This change is clearly observed for most of the polymers studied. However, in the case of the Meth-III homopolymer the rubbery modulus is the same order of magnitude as the glass modulus and the glass transition region is hardly discernible. This is a very unusual feature for an amorphous polymer, especially for an ester type methacrylate, and could be attributed to a very high crosslinking density of the network. For other polymers the glass transition region extends over 200°C for the Meth-II polymers and 250°C for the Meth-III.

From the width of the $\tan \delta$ curves [Fig. 8(a,b)] it can be observed that the glass transition region spreads over a very wide temperature range. Further, the temperature range is more extended in the case of Meth-III polymers. This extended transition region is a result of high degree of structural heterogeneity of the polymer samples studied. The broader the $\tan \delta$ peak implies a more heterogeneous polymer with a wide distribution of relaxation times.^{15–19}

TABLE II
Thermal and Mechanical Properties of the Obtained Polymers; (HP), Homopolymers

| Properties | Meth-II | | | | | | | | Meth-III | | | | | | |
|--|---------|------|------|------|------|------|------|------|------------------|------|------|------|------|------|------|
| | 25% | | 50% | | 75% | | MMA | | 25% | | 50% | | 75% | | |
| | HP | ST | HP | ST | HP | ST | HP | ST | HP | ST | HP | ST | HP | ST | |
| Initial decomposition temperature (10% mass loss) (°C) | 270 | 280 | 280 | 280 | 250 | 250 | 250 | 250 | 285 | 280 | 275 | 280 | 265 | 250 | 250 |
| HDT (°C) | 115 | 113 | 69 | 114 | 110 | 94 | 110 | 94 | 295 | 183 | 163 | 111 | 228 | 157 | 136 |
| Hardness according to Brinell (MPa) | 204 | 165 | 152 | 196 | 186 | 162 | 186 | 162 | 194 | 178 | 160 | 157 | 182 | 164 | 160 |
| Flexural modulus at bending (GPa) | 5.13 | 4.46 | 3.47 | 4.82 | 4.35 | 4.07 | 4.35 | 4.07 | 4.82 | 4.46 | 3.90 | 3.68 | 4.72 | 4.67 | 4.45 |
| Storage modulus (MPa) ($T = 25^\circ\text{C}$) | 4718 | 4009 | 3255 | 4380 | 4151 | 3864 | 4151 | 3864 | 4522 | 3851 | 3512 | 3298 | 4610 | 4516 | 4425 |
| FWHM (°C) | 96 | 40 | 31 | 56 | 43 | 38 | 43 | 38 | 163 | 92 | 47 | 37 | 94 | 66 | 45 |
| Glass transition temperature (T_g) (°C) | 163 | 162 | 110 | 157 | 160 | 149 | 160 | 149 | 155 ^a | 214 | 200 | 154 | 213 | 206 | 188 |

^a No obvious maximum on the $\tan \delta$ curve due to a very broad transition region.

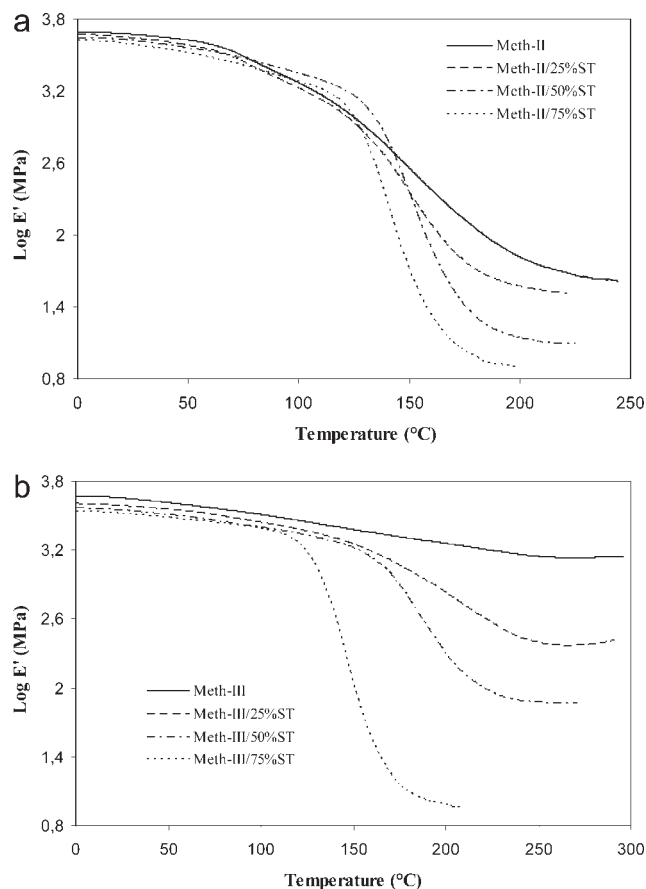


Figure 7 Storage modulus versus temperature curves: (a) Meth-II/ST compositions; (b) Meth-III/ST compositions.

Because the glass transition region is spread over a wide temperature range, it is difficult to provide a specific temperature as the glass transition temperature of the material. 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 that should be noted while observing the modulus behavior is the plateau in the rubbery region. The values of storage modulus drop uniformly with the temperature increase until they reach the plateau. These are equilibrium storage moduli which do not change their values up to the beginning of thermal decomposition of the polymer. These rubbery moduli values are related to the crosslinking density of the materials. There have been several network theories,^{20,21} 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(a,b) the absolute temperature (taken in the rubbery region at $T_g + 50^\circ\text{C}$) divided by the rubbery modulus is plotted for both types of methacrylate polymers. This ratio, ζ , is inversely related to the crosslinking density of the polymer and directly pro-

portional to the molecular weight between crosslinks in the polymer network.^{21,22} In this figure, one can see that as a weight ratio of the crosslinking monomer is increased within a copolymer system, ζ decreases (i.e., molecular weight between crosslinks decreases and the crosslinking density increases). This increase in crosslinking density is expected because an increase in the crosslinking monomer concentration will contribute to the formation of an increased number of “effective” crosslinks. It can be also observed that with the increasing concentration of the crosslinking monomer, the changes in crosslinking density become less significant. A similar trend can be seen in the changes of glass transition temperatures (Table II). The differences in glass transition temperature values diminish with the increasing concentration of crosslinking monomer. This behavior may be explained by two different effects that contribute to the dependence of glass transition temperature (as well as other properties) on the composition of the crosslinking agent. These effects are the “copolymerization effect” and the “crosslinking effect.”^{23,24} The “copolymerization effect” is a result of merely changing the fractions and types of the monomers that are copolymerized. The “crosslinking effect” is the effect of the constraints caused by the crosslinks on the properties of the copolymer.

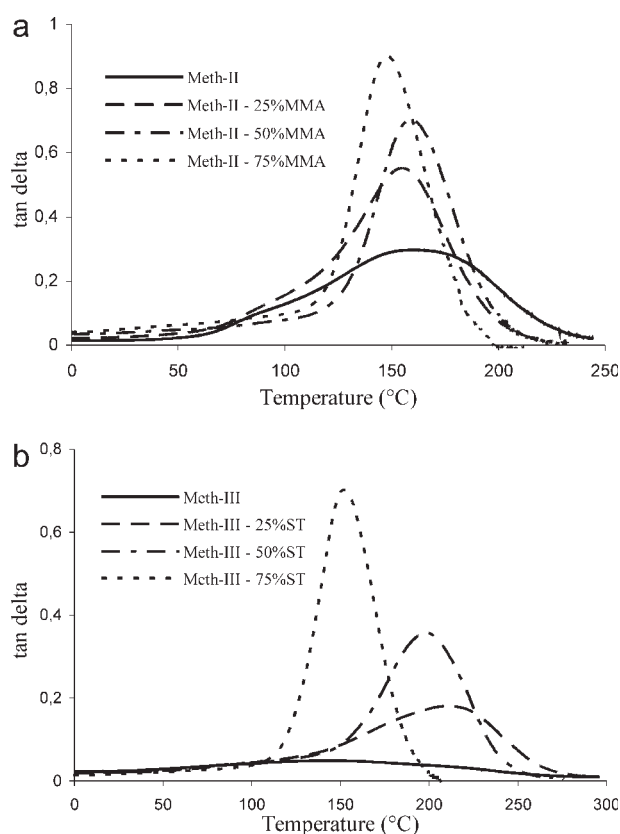


Figure 8 Tangent δ versus temperature curves: (a) Meth-II/MMA compositions; (b) Meth-III/ST compositions.

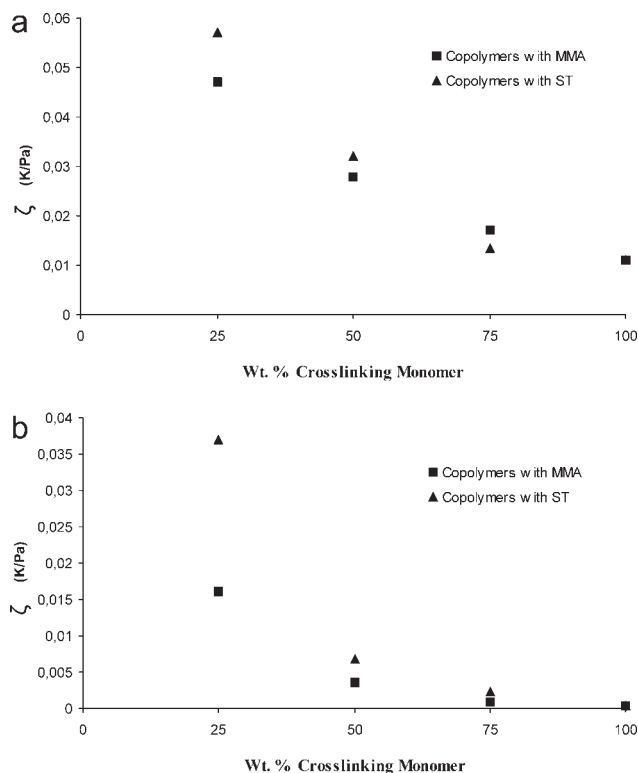


Figure 9 The inverse ratio of the modulus in the rubbery region to the temperature at $T_g + 50^\circ\text{C}$ (ζ) plotted as a function of the wt % of crosslinking monomer: (a) Meth-II polymers; (b) Meth-III polymers.

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 (an increase in the composition of the crosslinking agent significantly increases the crosslinking density) whereas the copolymerization effect seems to become more dominant at higher concentrations of the crosslinker (a decrease in the growth of the T_g versus the composition trend is observed). This effect is even more pronounced in the case of the Meth-III polymers as a total reversal in the growth of the T_g is observed.

The network structure that evolves during photopolymerizations of multifunctional monomers is quite complex. The cyclization reactions and the formation of microgels in the polymer are responsible for the evolution of a very heterogeneous structure. As mentioned previously, this heterogeneity manifests itself as a wide distribution of relaxation times because there exists a very broad distribution of mobilities in the polymer matrix. In this work, the heterogeneity of the polymer network has been evaluated qualitatively by examining the width of the $\tan \delta$ peak.^{18,19,25} 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 and Figure 8 that as the content of ST and/or MMA 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 (along with the glass transition temperature) by increasing the content of monovinyl monomer in the system. In other words, the degree of structural heterogeneity of the copolymers increases with the increasing crosslinking monomer composition. It can be seen that the Meth-III polymers are more heterogeneous than the Meth-II. Further, within the given (tri- or dimethacrylate) series of polymers, it appears that the MMA-based copolymers are more heterogeneous than their ST-based counterparts. Transition from dimethacrylate to trimethacrylate as a crosslinking agent contributes to an increase in the microgel formation, increased differences in the reactivity of various double bonds and increased formation of cycles and/or crosslinks. In consequence, all of these changes during the formation of these networks enhance their structural inhomogeneity.

The presence and interactions of side groups in the copolymers with MMA [visible in Fig. 10(a) in the form of β relaxation] seem to be the reason for

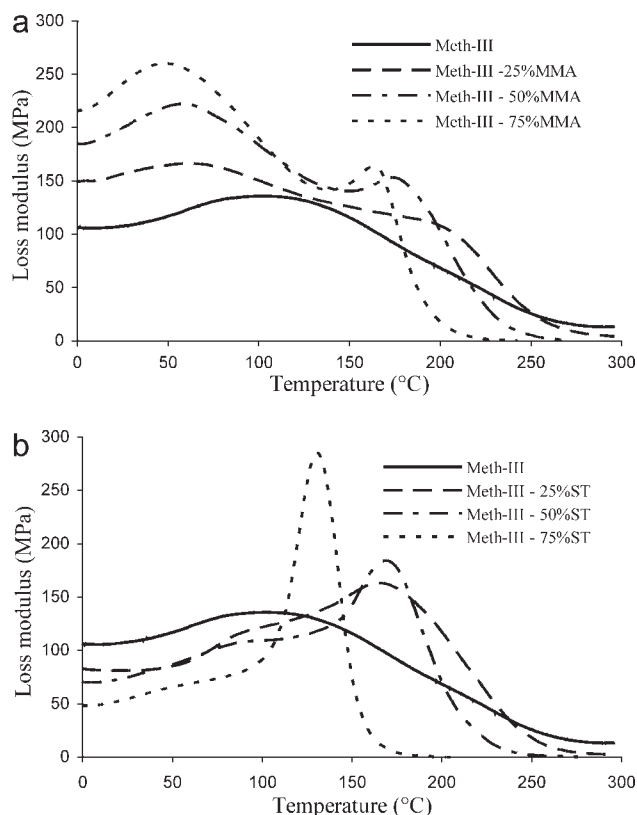


Figure 10 Loss modulus versus temperature curves: (a) Meth-III/MMA compositions; (b) Meth-III/ST compositions.

their increased stiffness compared to their styrene analogues. 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.²⁶ On the other hand, these side interactions may additionally contribute to the broadening of relaxation times distribution, and thus, enhance structural heterogeneity to some extent.

The multifunctional methacrylates contain in their structure hydroxypropyl groups whose presence is evident in the form of peak (copolymers with MMA) or shoulder (copolymers with ST) in the diagrams of loss modulus dependence on temperature [Fig. 10(b)]. Similar observations were made by other authors.^{17,27} Position of this peak/shoulder can depend on a number of hydroxypropyl groups or the presence of other groups and their interactions.

Flexural and thermal properties of cured methacrylates

The polymers prepared from the Meth-III methacrylate monomer differ considerably in their properties from those prepared from the dimethacrylate monomer—Meth-II.

As follows from the data in Table II, the increasing amounts of styrene in copolymers seem to increase the initial decomposition temperatures whereas the increasing amounts of methyl methacrylate are responsible for decreasing of the initial decomposition temperatures. However, thermal stability of the Meth-III styrene copolymers does not seem to be affected by variations in the styrene content. Their initial decomposition temperatures oscillate between 280 and 275°C. A comprehensive analysis of the products of degradation has to be carried out to evaluate probable steps in the degradation mechanism. However, the mechanism of degradation of poly(methyl methacrylate) can be partially adopted for explanation of the results. With the increasing concentration of MMA, the number of ester groups in the polymer network increases. Besides, 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.

Changes in the HDT show an apparent trend with composition. In both series of copolymers the HDT values drop with the increasing concentration of styrene and methyl methacrylate as well. In the case of

the Meth-II copolymers all but one composition (25% styrene/75% dimethacrylate) show lower heat deflection temperatures when compared to the Meth-II homopolymer. Addition of styrene in the amount of 25 wt % seems to be the reason for the improved HDT of the copolymer. As can be seen from Figure 9(a) the Meth-II homopolymer and the Meth-II/25% ST copolymer have very similar rubbery moduli and almost identical ζ parameters. The implication is that they are characterized by comparable crosslinking densities. Despite the lower content of a crosslinker in the copolymer, similar crosslinking density is caused by a higher degree of double bond conversion. Besides, styrene copolymer has more homogenous network structure as indicated by its FWHM value of 40°C as opposed to 96°C of the homopolymer. Relatively high crosslinking density coupled with a fairly homogenous network structure seems to be the reason for better thermal resistance of the 25% ST copolymer.

Of all the Meth-III polymers, the homopolymer exhibits the highest HDT value of 295°C. With the growing content of monovinyl monomer in the composition, the HDT values drop to 111°C for ST-75% and 136°C for MMA-75%. This tendency can be explained by considerable changes in the crosslinking density which decreases with the increasing content of monovinyl monomer. Along with the decreased crosslinking, longer chain units are formed that enhance the polymers elasticity and in consequence, lower their HDT values.

Regarding the results tabulated, it can be seen that Brinell's hardness decreases as the percent methyl methacrylate and/or styrene is increased. This is not unusual since increasing the weight percentage of monovinyl monomer causes an increase in the molecular weight between crosslinks (an increase in ζ parameters is observed). Thus, as the molecular weight between crosslinks increased, the hardness decreased. Larger hardness of the Meth-II polymers compared with their Meth-III counterparts could be attributed to the nature of the methacrylates used.

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 both types of methacrylate polymers and is understandable since reduced crosslinking densities usually lower flexural moduli of the materials.

Comparing the results tabulated, it can also be seen that the values of flexural modulus extend over a broader range in the case of the Meth-II polymers. Discussing the Meth-II preparation, it is apparent that the homopolymer has the highest flexural modulus value of all the obtained polymers. On the contrary, the 75% ST and 75% MMA dimethacrylate compositions have the lowest values of flexural moduli. In the Meth-III polymers, the homopolymer

modulus is lower (when compared to the modulus of the Meth-II homopolymer) but the moduli of the 75% ST and MMA copolymers are higher than those of the Meth-II analogues. These tendencies can be explained by the combined effects of the polymer composition and the density of crosslinks. It seems that at higher concentration of the methacrylate the compositional effect becomes more dominant as indicated by high values of the flexural modulus found for the Meth-II polymers with a significant crosslinker concentration. However, when the weight percentage of monovinyl monomer is increased beyond 50% ST and 25% MMA, this tendency becomes reversed. Being a better crosslinker, the trimethacrylate monomer produces more densely crosslinked networks than the dimethacrylate one, especially when smaller amounts of crosslinker are used. High crosslinking densities affect significantly flexural properties in copolymers with a large content of monovinyl monomer.

Conversion of unsaturated bonds

To find the conversion degree, intensities of peaks responsible for stretching vibrations of C=C (1637 cm^{-1}) and C=O (1720 cm^{-1}) groups before and after polymerization were compared. In the case of the copolymers with styrene, the peak at 1608 cm^{-1} assigned to the aromatic C=C bond was used as an internal standard. The FTIR spectra for all polymers are presented in Figures 11 and 12.

The conversion degree dependence on the crosslinking monomer content is shown in Figures 13 and 14. The lowest degrees of unsaturated bonds conversion were found for homopolymers. The degree of conversion increases with the increasing content of monovinyl monomer. The copolymers with MMA are usually characterized by higher conversion degree than those with ST. However, two of six pairs of copolymers i.e., the 50 and 75% Meth-II preparations exhibit inversed conversion dependence (Fig. 13). With the growing content of the monovinyl monomer, the differences in the conversion degree diminish noticeably within each pair of copolymers. For the 50 and 75% Meth-II and 75% Meth-III compositions the differences in conversion spread over a narrow range from 92 to 95%. The differences are negligibly small and one could treat these copolymers as equally cured. Therefore, the inversion in conversion dependence observed for two Meth-II styrene compositions may be subjected to experimental error rather than actual discrepancy. Further, there was found a higher conversion degree of Meth-II polymers compared to that of Meth-III.

These tendencies are due to different molecular structures of the crosslinking monomers as well as their functionality. A higher degree of functionality

(greater number of double bonds per monomer molecule) leads to higher reaction rates and higher density of crosslinks as proved by DMA. In dense networks the degree of conversion is reduced and a large portion of double bonds remains unreacted.

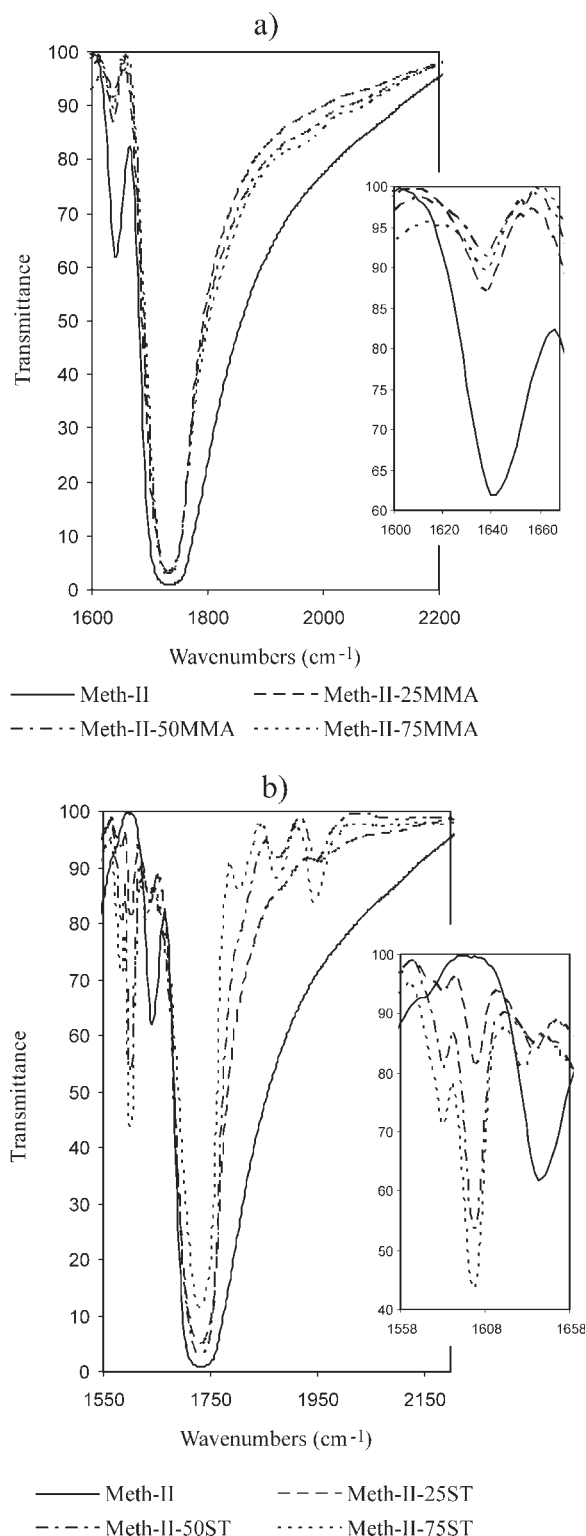


Figure 11 FTIR spectra of the Meth-II polymers: (a) copolymers with MMA; (b) copolymers with ST.

As the composition of the crosslinker (di- or trimethacrylate) is increased, the maximum double bond conversion that the sample may attain decreases

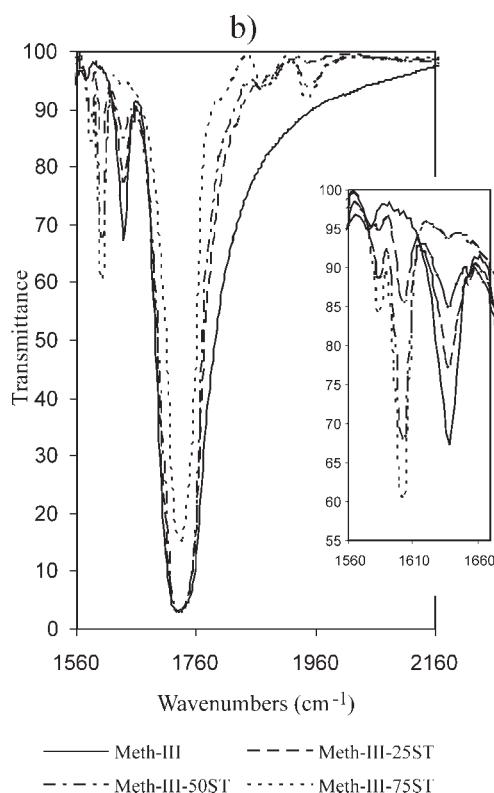
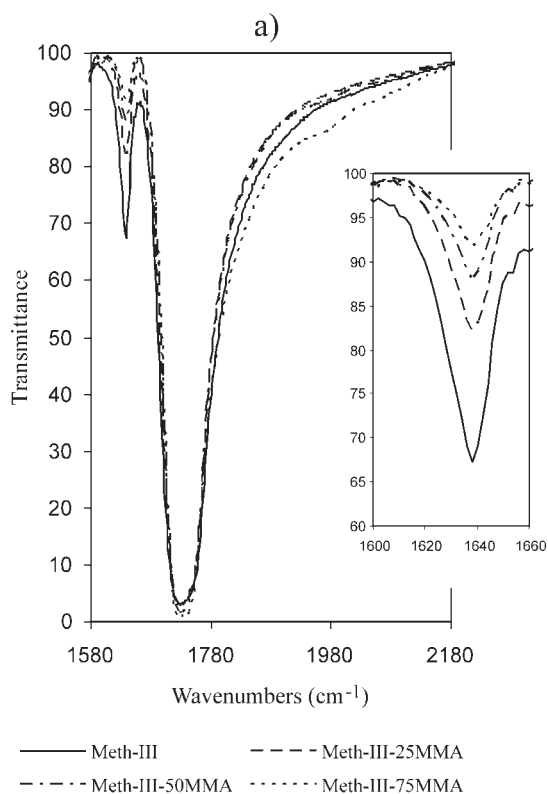


Figure 12 FTIR spectra of the Meth-III polymers: (a) copolymers with MMA; (b) copolymers with ST.

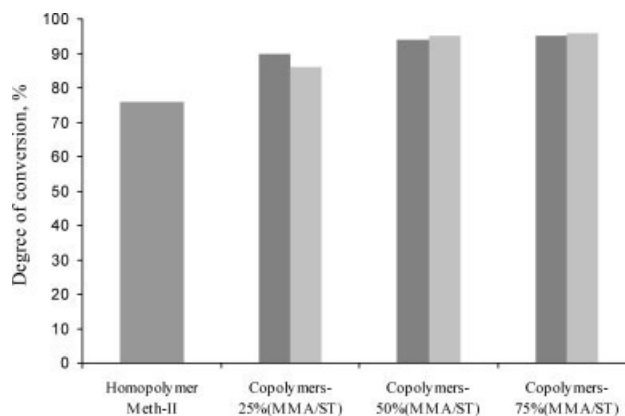


Figure 13 Conversion degrees of the Meth-II polymers; (■)—copolymers with MMA; (■)—copolymers with ST.

because of diffusional limitations to the polymerization process.^{12,28–30} The multifunctional methacrylate monomers used in this study have quite compact and rigid structures. The double bonds lie in close vicinity to each other. During polymerization of these monomers, the cyclization is more pronounced and the network inhomogeneity higher. Therefore, the properties of these materials are influenced not only by the effects of crosslinking and copolymerization but residual unsaturation as well. At higher concentrations of a crosslinking monomer the “copolymerization effect” and that of limited double bond conversion cannot be separated. As a result, it is not clear which mechanism dominates at higher concentrations of a crosslinker.

As mentioned above, the methyl methacrylate copolymers have in majority higher conversions than the copolymers with styrene. Depending upon the substituent groups on the double bond, styrene and methyl methacrylate differ considerably in reactivity in free radical polymerizations. Despite styrene being more reactive than methyl methacrylate, it gives less reactive free radicals due to multiplicity of resonance forms and hence, increased stability. In consequence, the styrene/crosslinking monomer systems are char-

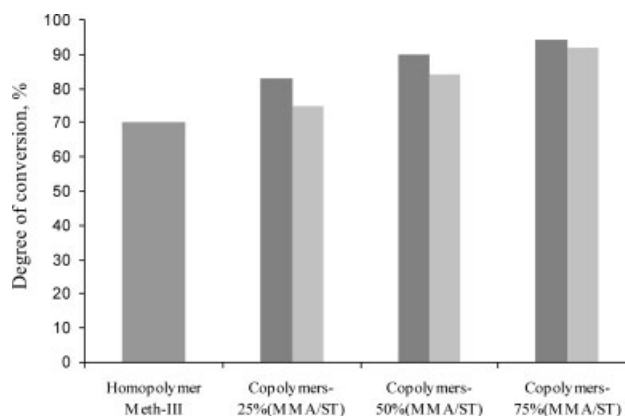


Figure 14 Conversion degrees of the Meth-III polymers; (■)—copolymers with MMA; (■)—copolymers with ST.

acterized by slower reaction rates, and thus, may be expected to reach lower double bond conversions.

CONCLUSIONS

The article presents the syntheses of di- and trimethacrylate monomers as well as the properties of the obtained homopolymers and copolymers with methyl methacrylate and styrene. The use of polycarboxylic acids in the addition reaction with glycidyl methacrylate can be an effective and productive method in preparation of multifunctional monomers and methacrylate resins. This is an alternative way of methacrylates synthesis compared with the addition reaction of monocarboxylic (acrylic and methacrylic) acids and polyfunctional epoxides known in literature. Synthesis of new polyfunctional methacrylate esters is based on known and frequently applied addition reactions where it is not necessary to remove by-products formed e.g., in esterification reactions. Owing to this, the syntheses are less time consuming and do not require complicated apparatus. The high degree of conversion of substrates into products, which exceeds 98%, indicates their great effectiveness. The limitation is low temperature of the process (not higher than 115°C), which besides a large exothermic effect accompanying the addition reaction, makes batching of reagents and gradual increase of temperature during the synthesis necessary. Such a procedure allows to avoid overheating of reaction mixture, and as a result loss of reaction control.

The polymers prepared from the new methacrylate esters were submitted to extensive studies of their mechanical and thermal properties.

The dependence of glass transition temperatures as well as degree of inhomogeneity on the crosslinking density has been examined in different copolymer systems. The crosslinking density was varied by varying the composition as well as type of the crosslinking agent. Interesting behavior has been observed when examining the Meth-III copolymers. Copolymers of the Meth-II dimethacrylate monomer exhibit typical T_g behavior as a function of wt. fraction of crosslinking agent. T_g of the polymer increases with the increasing crosslinking agent composition. However, in the case of the Meth-III polymers, an increase in T_g is observed until the 75% crosslinker concentration is reached. Then, there is a significant drop in T_g of the homopolymer. This behavior was attributed to the coexisted effects of copolymerization and residual unsaturation.

Based on the dynamic mechanical analysis and estimation of the degrees of double bond conversion, there were shown correlations between the network parameters (i.e., crosslinking density, degree of heterogeneity and residual unsaturations) and the

resulting mechanical and thermal properties. Dynamic mechanical measurements have demonstrated that the increasing crosslinking density, despite making the polymer network more heterogeneous, increases hardness, flexural moduli as well as heat distortion temperatures of the materials.

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 and type as well as its functionality, the resultant polymer may have features such as crosslinks and/or cycles and residual unsaturation that influence and define the properties of the materials. Therefore, in choosing the composition and type of the crosslinking monomer for a specific application, it is essential to consider these correlations between structure and properties of the material.

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