

Synthesis and Properties of Dimethacrylates—Derivatives of Maleic and Fumaric Acids

Tadeusz Matynia, Maciej Podgórski

Faculty of Chemistry, MCS University, Lublin 20-031, Poland

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ABSTRACT: In this work, the synthesis as well as the mechanical and thermal properties of dimethacrylate copolymers are investigated. These copolymers were obtained from glycidyl methacrylate, maleic and/or fumaric acid adducts, methyl methacrylate, and/or styrene. The addition reaction of glycidyl methacrylate as well as maleic

and fumaric acids was carried out in the presence of basic catalyst. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 108: 2902–2907, 2008

Key words: photopolymerization; degree of polymerization; glass transition; monomers; resins

INTRODUCTION

With the development of electronics and electrotechniques, interest in thermo- and chemoresistant plastics increases. This group of polymers includes, among others, polyarenes, aromatic polyamides, aromatic polycarbonates, aromatic polysulphides, aromatic polysulphones, and polybenzimidazoles. The materials prepared by homopolymerization and copolymerization of multifunctional methacrylate monomers also exhibit interesting properties.

Monomers and hydroxyacrylate or methacrylate resins are obtained by esterification of epoxide compounds (or resins) with acrylate or methacrylate acid.^{1–3} Reactions of epoxide resins with methacrylate without a catalyst proceed with a small rate and selectivity. Compounds of acidic or basic character and transient metal complexes are used as catalysts.^{4,5} Addition of methacrylate acid to epoxide resins is more frequently carried out in the presence of tertiary amines. In this way, epoxyacrylate resin was obtained from glycidyl ester of maleopimaric acid.⁶ Functionality of the prepared resin was not consistent with the theory due to the fact that the initial raw material (resin of glycidyl ester type) was characterized by a small epoxide number. A series of epoxyacrylate resins were obtained in an analogous way using glycidyl ester of various diols including bisphenol A as substrates.⁷ Methacrylate monomers and ester-vinyl resins fit perfectly for curing with

UV and other kinds of radiation. After crosslinking, they are characterized by large chemoresistance and mechanical strength.

The alternative method of hydroxyacrylate monomer synthesis consists in addition of glycidyl methacrylate (GMA) to the compounds containing an active hydrogen atom, e.g., carboxylic acids, phenols, or amines.⁸ This article presents the description of synthesis of new dimethacrylate monomers as well as discussion of physical, mechanical, and thermal properties of monomers, and resins before and after curing.

EXPERIMENTAL

Materials

- Glycidyl methacrylate (GMA) 97%, from Sigma-Aldrich Chemie, GmbH, Germany,
- tetraethylammonium bromide, analytically pure, from Merck KgaA, Frankfurt,
- maleic acid (MA) 99%, from Merck KgaA, Frankfurt,
- fumaric acid (FA) 99%, from Merck KgaA, Frankfurt,
- hydroquinone, analytically pure, from Merck KgaA, Frankfurt,
- irgacure 651 (2,2-dimethoxy-2-phenylacetophenone), UV polymerization initiator, from Sigma-Aldrich Chemie GmbH, Germany,
- methyl methacrylate (MMA), analytically pure, from Ubichem, Hampshire, UK, and
- styrene (ST), analytically pure, from POCh, Gliwice.

Correspondence to: T. Matynia (Tmatynia@hermes.umcs.lublin.pl).

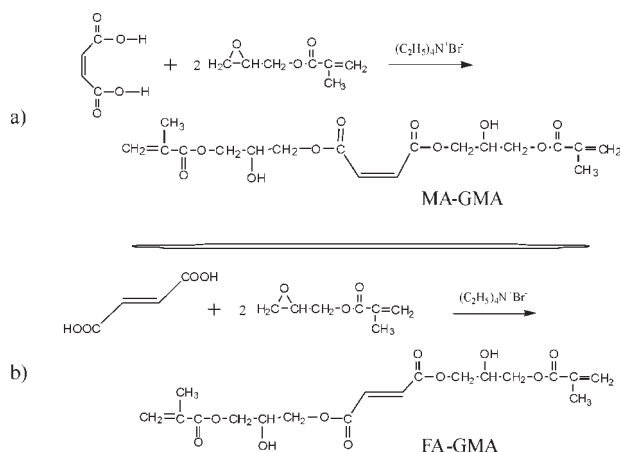


Figure 1 Equations of dimethacrylate esters synthesis reaction: (a) synthesis of glycidyl methacrylate and maleic acid adduct; (b) synthesis of glycidyl methacrylate and fumaric acid adduct.

Synthesis of dimethacrylates

Addition of GMA and MA was made in a three-necked round-bottomed 250-mL flask equipped with heating coat, stirrer, thermometer, and air cooler. The disintegrated MA was added batchwise to GMA (heated up to 105–110°C) containing 0.01 wt % hydroquinone and 0.15 wt % tetraethylammonium bromide. The reagents were used at the ratio of 1 mol of MA and 2 mol of GMA. The measure of reaction course degree was drop of the acid value (PN-87/C-89,082/11) of the reaction mixture from 280 mg KOH/g to the final value not exceeding 5 mg KOH/g as well as drop of the epoxide value (PN-74/C-89,085) from 0.5 epoxide gram-equivalents per 100 g to 0.02–0.03. Determination of the acid value was

made after addition of the total acid amount, i.e., after 1.5 h, from the synthesis start. The final acid value was achieved after 4–4.5 h. The same procedure was applied in the second synthesis for GMA and FA. In both syntheses, tetraethylammonium bromide was used as a catalyst of addition reaction of carboxylic groups to oxiranes. This choice was due to greater yield of the products obtained when there were used tertiary ammonium salts than amines or transient metal complexes.⁹ The equations of both reactions are presented in the Figure 1.

Characteristics of dimethacrylates

¹H NMR spectra of raw dimethacrylate monomers were made at 20°C using a spectrometer NMR Model BS 567A (Czechoslovakia) working in the resonance frequency of protons ¹H equal to 100 MHz. Chemical shifts were determined in relation to tetramethylsilane as an internal standard.

NMR analysis of products of similar syntheses can cause some difficulties because of a large number of isomers formed in side reactions. Tetraethylammonium bromide alike amines but contrary to transient metal complexes is characterized by small selectivity. In the addition reaction of carboxylic groups to the epoxide ones, both primary and secondary hydroxylic groups can be formed, which is confirmed by ¹H NMR spectra (Fig. 2). Other side reactions like etherification of alcohols with epoxide groups or esterification with acid groups are much less probable. The evidence is a proportional epoxide group loss when compared with acid groups determined in the synthesis.

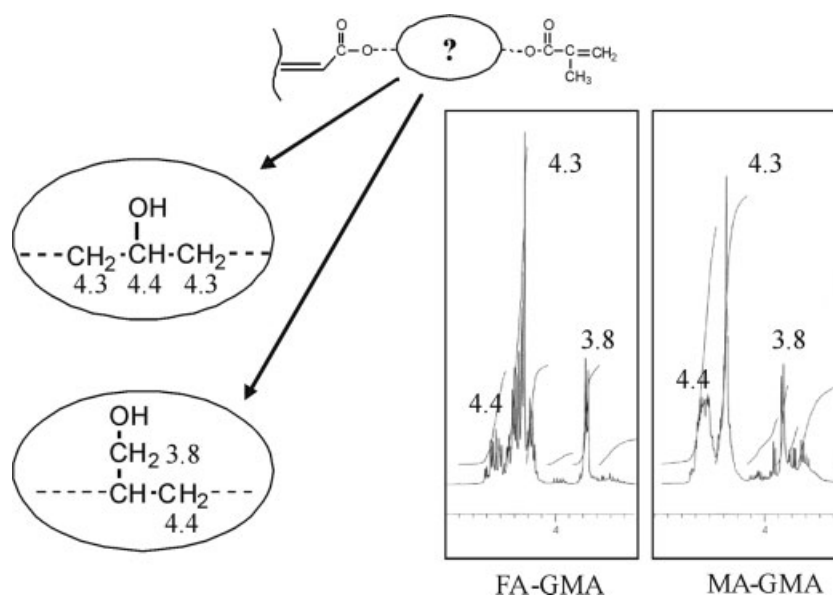


Figure 2 NMR analysis of dimethacrylates FA-GMA and MA-GMA.

TABLE I
Properties of Dimethacrylate Esters Before Curing

Properties	Dimethacrylates	
	MA-GMA	FA-GMA
Viscosity at 25°C (mPa·s)	12305	9309
Density (g/cm ³)	1.24	1.23
Acid value (mg KOH/g)	2–4	3–5
Refractive index	1.4949	1.4968
Molecular mass (g/mol)	422	410

Another evidence confirming insignificant contribution of side reactions (except the reactions leading to formation of α and β isomers on carbons of epoxide groups) is the numerical agreement of average molecular masses with the theoretical value. They were determined by means of the osmometer KNAUER GmbH, Germany. The measurement was made with the accuracy of about 5%. The adduct of GMA and fumaric acid (FA-GMA) were 410 g/mol, and 422 g/mol for GMA and MA (MA-GMA). The theoretical molecular masses of both dimethacrylates were 400 g/mol. The determined values are within the error limit.

Elementary analysis of the obtained dimethacrylates was made using the analyzer PerkinElmer CHN 2400. The calculated composition is the same for both dimethacrylates: %C: 54; %H: 6; %O: 40. The composition determined for adduct of MA and GMA is %C: 53.76; %H: 6.25; %O: 39.99, and for adduct of FA and GMA is %C: 53.43; %H: 6.08; %O: 40.49.

Properties of dimethacrylates

Elementary properties of dimethacrylate monomers were determined in the noncrosslinked state, i.e., refractive index, viscosity, and density (Table I, Fig. 3).

The obtained dimethacrylates were dissolved in MMA and styrene making solutions of the concentrations: 25, 50, and 75% of crosslinking monomer. Of styrene solutions, 50 and 75% ones were stratified into two phases. Only 25% solutions were examined because of the limited miscibility.

Curing procedure

The obtained compositions were UV (340–360 nm) cured by exposure in the presence of 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 postcured at 120–160°C for 5 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). Crosslinked homopolymers and copolymers were subjected to mechanical and thermal studies.

Research methods

After crosslinking, bending strength (PN-79/C-89027), rupture stress (PN-81/C-89034), relative elongation at rupture (PN-81/C-89034), flexural modulus at bending (Young modulus) (PN-82/C-89051), deflection temperature (HDT), and hardness, according to Brinell (PN-84/C-89030), were determined. The dynamic mechanical analysis (DMA) was made and the conversion degree of unsaturated bonds was determined for homopolymers and all obtained copolymers. Before determination, there were prepared samples of photopolymerization power containing 1% photoinitiator—2,2'-dimethoxy-2-phenylacetophenone (Irgacure 651). Each sample was exposed to UV radiation of 340–360 nm length and degree of unsaturated bonds conversion was determined by means of the spectroscopy FTIR. To find conversion, degree intensities of peaks responsible for vibrations of C=C and C=O groups (internal standard) before and after polymerization were compared. In the case of copolymers with styrene intensity of the peak formed due to absorption of radiation by aromatic ring was taken into account (Fig. 4).

Mechanical studies were carried out using a strength machine, Zwick Roell Z010. According to Brinell, hardness was determined by means of a hardness tester HPK. Thermal stability was measured using a derivatograph MOM (Paulik and Erdey, Budapest) in the temperature range of 20–1000°C (sample heating rate, 10°C/min). Measurement of thermal resistance under loading was made using an apparatus HDT 3 VICAT produced by CEAST S.p.A, Italy.

RESULTS

Strength and thermal properties of homopolymers and copolymers are presented in Table II. Homopolymers prepared from isomeric dimethacrylates differ in both physicochemical and thermal properties. Homopolymer FA-GMA is characterized by much

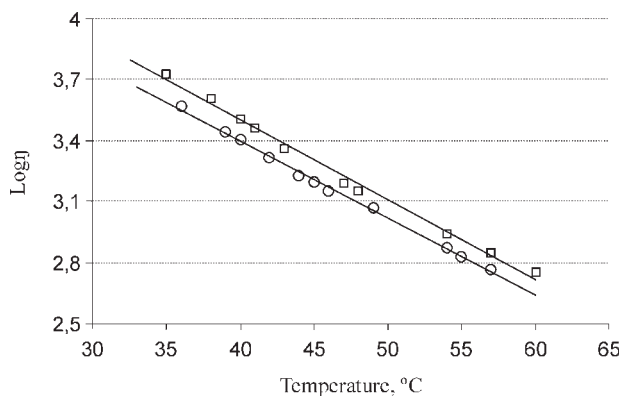


Figure 3 Viscosity of dimethacrylate esters in the function of temperature; (□), MA-GMA; (○), FA-GMA.

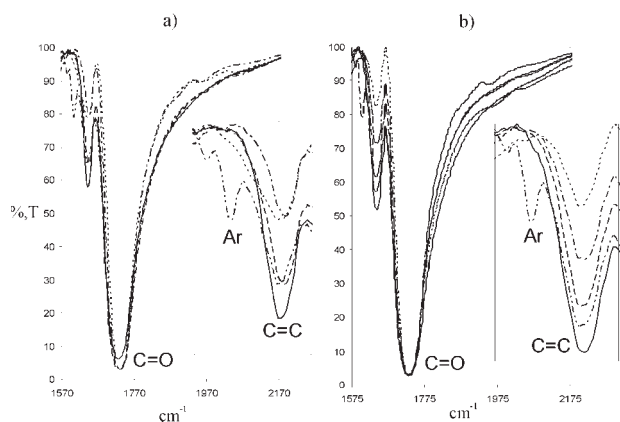


Figure 4 FTIR analysis of the obtained polymers: (a) polymers FA-GMA; (b) polymers MA-GMA; — Homopolymer; - - - Copolymer: 25% MMA; - · - · Copolymer: 50% MMA; ····· Copolymer: 75% MMA; - - - - Copolymer: 25% ST.

greater resistance to temperature when compared with that of homopolymer MA-GMA (initial decomposition temperature higher by 15°C, heat deflection temperature higher by over 100°C, and glass transition temperature higher by 34°C). However, homopolymer MA-GMA exhibits better physicomechanical properties (larger hardness and resistance to bending, larger Young elasticity modulus). Among copolymers, those with styrene show greater resistance to temperature. They are characterized by such physicomechanical properties as hardness or resistance to bending, which are similar to those of copolymers with MMA. Properties of copolymers with MMA change proportionally to the change of copolymer composition. With the increase of MMA con-

tent in the copolymer, hardness, flexural modulus, and initial decomposition temperature decreases, and in the case of FA-GMA copolymers, decreasing glass transition temperatures as well as heat deflection temperatures are found.

DMA of prepared copolymers and homopolymers

Effect of temperature on viscoelastic properties of obtained polymers in the linear area of dependence between stress and strain was determined using an apparatus DMA Q800 produced by TA (USA), calibrated according to the producer's recommendations. Glass transition temperature (α relaxation) for the prepared polymers was determined from the dependence of the loss modulus on temperature. Viscoelastic properties of crosslinked compositions were estimated from the changes of storage modulus (E') at bending as well as from the changes of mechanical loss (E'') at constant frequency (10 Hz) depending on temperature. Measurements for all samples were made in the temperature range 0–300°C with the constant heating rate 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 then. DMA curves are presented in Figures 5–8.

At room temperature, homopolymers are characterized by the largest values of storage modulus, which decreases uniformly to 520 MPa for homopolymer FA-GMA and 140 MPa for homopolymer MA-GMA with the increasing temperature. These are equilibrium storage moduli, which do not change their values till the beginning of polymer thermal decomposition.

TABLE II
Thermomechanical Properties of Cured Dimethacrylate Esters and Their Solutions

Properties	MA-GMA					FA-GMA				
	HP	25% ST	25% MMA	50% MMA	75% MMA	HP	25% ST	25% MMA	50% MMA	75% MMA
Initial decomposition temperature (10% mass loss) (°C)	280	300	270	265	260	295	310	280	280	265
Deflection temperature HDT (°C)	107.6	123.2	111.2	111.7	111.2	212.8	210.8	155.3	129.1	116.7
Hardness according to Brinell method (MPa)	193	180	181	170	156	183	175	177	173	163
Flexural modulus at bending (GPa)	4.35	4.01	4.21	3.87	3.56	4.26	3.97	4.15	3.70	3.53
Maximal force at bending (N)	234	244	247	226	162	232	206	232	187	177
Extension at maximal force (%)	6.44	5.87	5.70	6.52	4.33	4.37	3.97	5.60	5.09	4.67
Storage modulus (MPa) ($T = 25^\circ\text{C}$)	4714	4077	4628	4474	4143	4466	4045	4379	4308	4126
Tangent of phase shift angle ($\tan \delta_{\max}$)	0.207	0.272	0.314	0.469	0.926	0.083	0.098	0.193	0.357	0.808
Glass transition temperature (°C)	132	133	137	136	136	166	192	163	154	144

HP, homopolymers

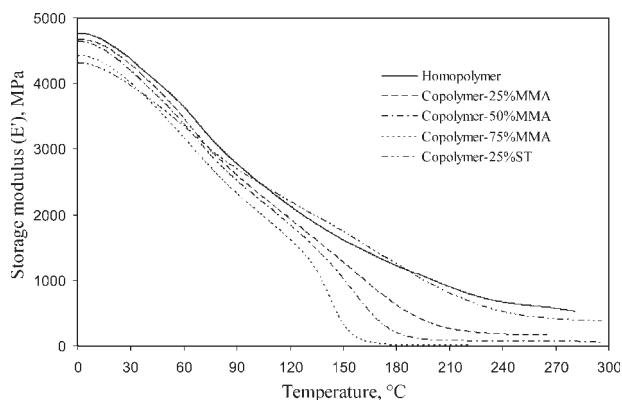


Figure 5 Storage modulus of homopolymer and copolymers FA-GMA.

From the analysis of curves of storage modulus, change in the temperature function is as follows (Figs. 5 and 6):

- The larger content of MMA in copolymer, the lower value of storage modulus in the glassy state, and the more rapid transition to the highly elastic state that proceeds at lower and lower temperatures (in the whole temperature range).
- Storage moduli of copolymers with styrene are characterized by lower values in the glassy state, higher in the middle temperature range, and in the highly elastic state when compared with the copolymers with MMA.

These differences are due to the structure of polymer lattices of prepared copolymers. Interactions of side groups in copolymers with MMA visible in the diagram of loss modulus dependence on temperature in the β relaxation form (Figs. 7 and 8) are the cause of uniform and relatively rapid drop of storage modulus in the temperature function up to the sudden increase of polymer main chains mobility,

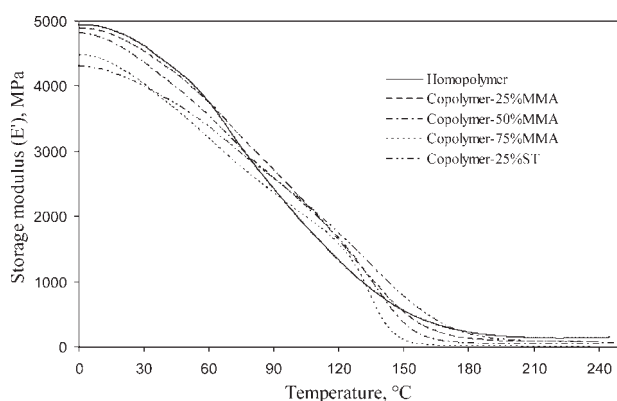


Figure 6 Storage modulus of homopolymer and copolymers MA-GMA.

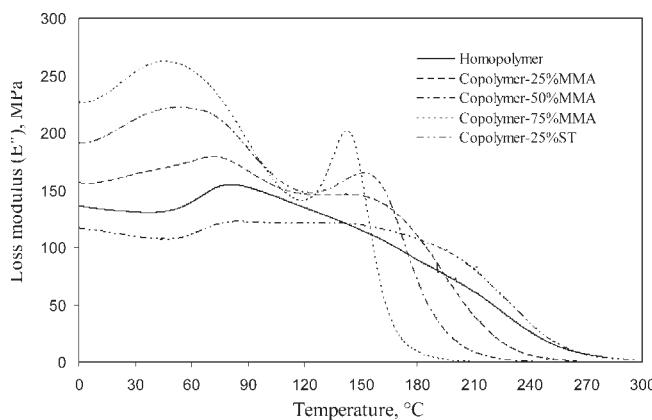


Figure 7 Loss modulus of homopolymer and copolymers FA-GMA.

which is observed as α relaxation and assumed as glass transition temperature. Increase in the amount of monofunctional monomer, MMA is favorable for the formation of longer units in the polymer lattice, and as far as properties are concerned, getting similar to those of poly(methyl methacrylate), where β relaxation is associated with interactions of side ester groups.¹⁰

With the increase of the amount of monofunctional monomer in the copolymer, the values of $\tan \delta_{\max}$ increase as well. The values $\tan \delta_{\max}$ for copolymers with styrene are smaller than those of copolymers with MMA of the same composition (Table II). This fact indicates their better thermal properties.

Following the dependence of loss modulus on temperature, 25% of styrene increases the glass transition temperature significantly when compared with the analogous copolymers with MMA.

The obtained dimethacrylate monomers contain hydroxypropyl groups in their structure, 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 tempera-

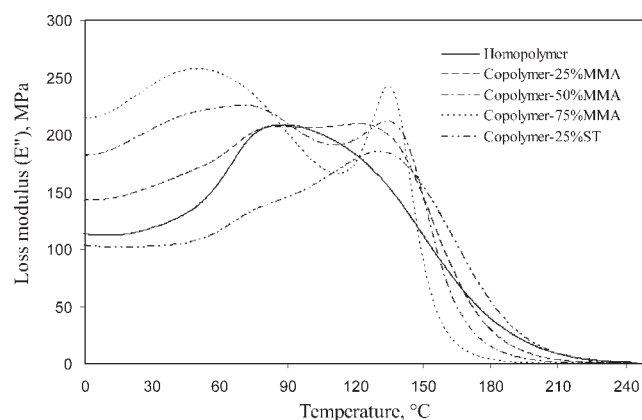


Figure 8 Loss modulus of homopolymer and copolymers MA-GMA.

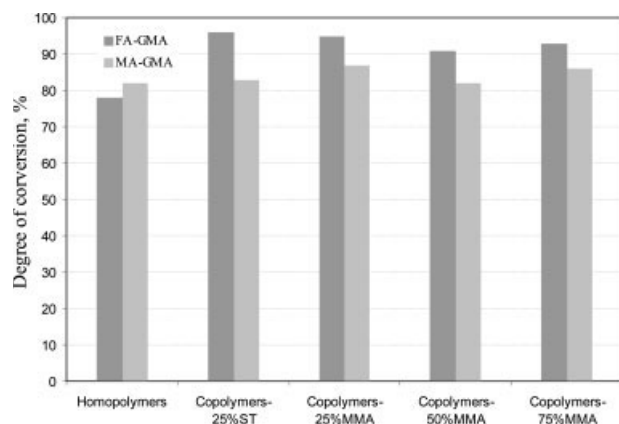


Figure 9 Conversion degrees of obtained polymers.

ture (Figs. 7 and 8). Similar observations were made by other authors.^{11,12} Position of this peak/shoulder can depend on a number of hydroxypropyl groups or the presence of other groups as well as interactions between them.

Determination of unsaturated bonds conversion degree

FTIR spectra for all copolymers and homopolymers are presented in Figure 4. Dependence of conversion degree on crosslinking monomer contents is presented in Figure 9. Conversion degrees of the obtained polymers are in the range 80–95%. These data refer to conversion of unsaturated bonds of methacrylate residues. The bonds C=C of fumaric or maleic core are not polymerized under the investigation conditions, the evidence of which are negative results of the tests of dimethyl maleate and dimethyl fumarate photocopolymerization with MMA and ST made by us. The lowest degree of unsaturated bonds conversion was found for homopolymers. Copolymers FA-GMA is characterized by the higher conversion degree than copolymers MA-GMA. This tendency is probably due to different molecular structures of the crosslinking monomers. Trans-isomerism in monomer FA-GMA as opposed to cis-isomerism of MA-GMA monomer is the reason for greater space separation of methacrylic double bonds. This makes the cyclization reactions, which are known to be respon-

sible for entrapping pendant double bonds, less probable. In consequence, the resulting final degrees of double bond conversions of FA-GMA copolymers are somewhat higher.

CONCLUSIONS

Application of multifunctional carboxylic acids in the addition reaction with GMA can be an effective and productive method of preparation of multifunctional monomers and methacrylate resins. This is an alternative way of methacrylates synthesis when compared with the addition reaction of monocarboxylic (acrylic and methacrylic) acids and polyfunctional epoxides reported in literature. Different state of matter of reagents does not limit the synthesis. However, high boiling point of acids and low temperature of the process (not higher than 115°C) combined with large exothermic effect accompanying the addition reaction make batching necessary. Such a procedure allows to avoid overheating of reaction mixture, and as a result loss of reaction control. High degree of substrates conversion into products, over 98% indicates effectiveness of the discussed syntheses. The proposed method allows to prepare dimethacrylates of various thermal properties (HDT from 100 to over 200°C) characterized by good physico-mechanical properties.

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