JOURNAL OF Applied Polymer SCIENCE

Synthesis and Characterization of Low Viscosity Dimethacrylic Resin Based on Isosorbide

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ABSTRACT: In this article, synthesis and properties of novel dimethacrylic resin (ISETDMA) based on human friendly, biobased isosorbide was described. Its potential as a possible diluting monomer for medical applications, mainly dental restorative systems was assessed. The resin was obtained in two-step synthesis including ethoxylation of isosorbide and subsequent methacrylation with methacryloyl chloride. ^{1}HNMR, FTIR, and electrospray ionization mass spectroscopy (ESI-MS) techniques were used to identify products. ISETDMA as well as composition with 2,2-bis[4-(2-hydroxy-3-methacryloyloxypropoxy)phenyl]propane were polymerized using UV initiator IRGACURE 651. Double bond conversion, polymerization shrinkage, water sorption, and sol fraction of resulting polymers were determined. Selected mechanical (flexural strength and modulus, Brinell hardness) and thermomechanical (dynamic mechanical analysis) properties were also investigated. Triethylene glycol dimethacrylate and 2,2-bis(4-(2-methacryloxyethyl-1-oxy)phenyl)propane based homopolymers and copolymers were prepared as reference for comparison of particular properties. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2013

KEYWORDS: biomaterials; crosslinking; mechanical properties; monomers; oligomers; telechelics

Received 28 November 2012; accepted 19 April 2013; Published online 00 Month 2013

DOI: 10.1002/app.39435

INTRODUCTION

Multifunctional vinyl monomers, mainly dimethacrylates have become successful in a great variety of applications such as coatings, adhesives, electronics and optical communication devices.[1,2] Photo-induced polymerization of dimethacrylic monomers results in a highly crosslinked, chemically and thermally resistant polymers having tailor-made properties. High monomer conversion as well as nontoxicity and biocompatibility of dimethacrylate-based polymers allow them to be used in biomedical applications such as dental restoratives or bone implants.[3–8]

Most of the composites widely used in restorative dental procedures contain bisphenol A based 2,2-bis[4-(2-hydroxy-3-methacryloyloxypropoxy)phenyl]propane (BISGMA) and low viscosity monomers, used as diluents such as triethylene glycol dimethacrylate (TEGDMA).[9,10] Although being very popular, BISGMA resin introduced in 1962 by Bowen (Figure 1) has high viscosity which limits its applicability.[11] The use of low viscosity comonomer like TEGDMA helps to overcome this problem but adversely affect the properties of matrix by increasing the water sorption and polymerization shrinkage.[12] Many attempts were made to synthesize less viscous analogues of BISGMA in order to reduce amount of diluting comonomer. Different new low viscosity bulky dimethacrylic monomers as well as novel urethane dimethacrylates might be considered as an alternative.[13–20] The recent literature also shows examples of highly reactive monomethacrylic monomers being utilized as diluents for BISGMA-based compositions. Despite their good handling properties, they exhibit relatively low double bond conversion.[21] The medical research indicates that widely used TEGDMA is health uncertain and may even induce apoptosis of human dental pulp. This effect occurs immediately after the contact of the composition with human tissue just before curing as well as after a long-term release of unreacted monomers.[22–24]

Due to this, other monomers with comparable properties of resulting polymers are needed. Isosorbide-based dimethacrylic resin was considered as a possible diluting comonomer for dental and bone tissue repair applications and in this work the synthesis and characteristics were presented. Isosorbide is a bioderived and biodegradable compound qualified by Food and Drug Administration as "generally recognized as safe."[25] It is produced by the double dehydratation of sorbitol obtained in two step process from starch. Isosorbide—a V-shaped

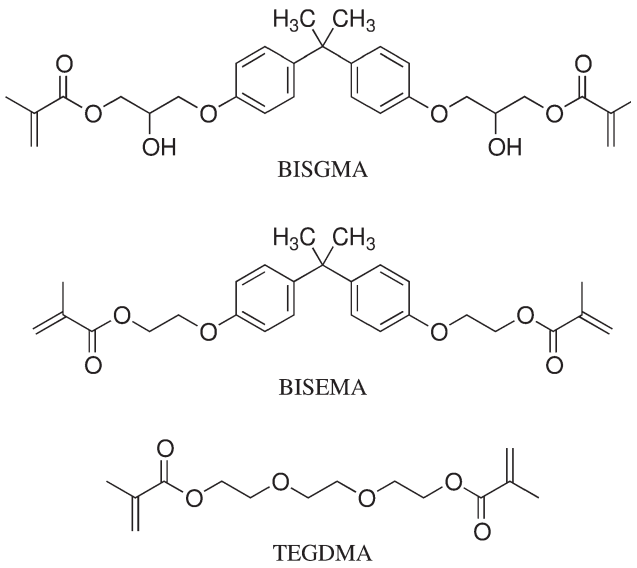

Figure 1. Chemical structures of three commercial dimethacrylates.

bicyclic diol is composed of two fused tetrahydrofuran rings. This structure provides high stiffness of its molecule and good chemical resistance.[26–28] Many isosorbide derivatives have already found an application in pharmaceutical industry and in cosmetics.[29] Recent literature describes synthesis of nontoxic aliphatic polyesters based on isosorbide which might be used as possible degradable biomaterials.[30] We have described in our previous work the synthesis and properties of isosorbide based BISGMA analogue as a possible monomer for biomedical applications.[31,32] Those features make this "green" compound an interesting substrate in the synthesis of dimethacrylic monomers.

In this article, the synthesis of a dimethacrylic resin based on isosorbide ethoxylate (ISET) was described. The resin obtained was characterized by ^{1}HNMR, FTIR spectroscopy, as well as electrospray ionization mass spectrometry (ESI-MS). Its viscosity was evaluated and compared with that of TEGDMA. In addition, the novel resin was also compared with bisphenol A based monomer - 2,2-bis[4-(2-methacryloxyethyl-1-oxy)phenyl]-propane (BISEMA) because of its structural similarity (stiff aromatic core). Isosorbide-based resin and reference monomers (TEGDMA and BISEMA) were polymerized using UV irradiation source. Double bond conversion was measured by UV differential scanning calorimetry (UV-DSC) method. Flexural properties along with Birnell hardness were determined as well. Dynamic mechanical analysis (DMA) technique was used to investigate viscoelastic properties and glass transition temperatures. In addition, water sorption and sol fraction of resulting polymers were determined. Copolymers of BISGMA and three investigated monomers were prepared and characterized in the same manner as homopolymers.

EXPERIMENTAL

Materials

ISET was provided by ROKOPOLE polyol division of PCC ROKITA SA (Brzeg Dolny, Poland). Its hydroxyl number (LOH) determined using Titrator Mettler-Toledo AB204-S (Greifensee, Schweiz) was 386 mg KOH/g. 4 moles of ethylene oxide were used per mole of isosorbide and product characterized via FTIR and NMR spectroscopy. 2,2-bis(4-hydroxyphenyl)propane (97%, BPA, Bisphenol A), ethylene carbonate (>99%), tetrabutylammonium bromide (TBAB, >99%), triethylamine (99%, TEA) and sodium bicarbonate (>99%) all purchased from Acros Organics, New Jersey. Methacryloyl chloride (97%, MACl, distilled prior to use), 4-dimethylaminopyridine (>99% DMAP), isosorbide (IS, 98%), 2,2-bis[4-(2-hydroxy-3-methacryloyloxypropoxy)phenyl]propane (BISGMA), triethylene glycol dimethacrylate (95%, TEGDMA), Dowex Marathon MSC hydrogen form (activated and dried prior to use), and 4-methoxyphenol (99%, HQME) all purchased from Sigma Aldrich Sigma-Aldrich, Saint Louis. 2,2-Dimethoxy-2-phenyloacetophenone (Irgacure 651) purchased from Ciba, Basel, Switzerland. Dichloromethane (pure) and magnesium sulphate (pure, anhydrous) purchased from POCH, Gliwice, Poland. Hydrochloric acid (36%) purchased from Stanlab, Lublin, Poland. If not indicated, reagents were used as received.

Synthesis of Monomers

Synthesis of 2,2-bis[4-(2-methacryloxyethyl-1-oxy)phenyl]propane (BISEMA). BISEMA was obtained in a two-step synthesis. In the first step, 20 g (0.088 mole) mole of BPA was heated at 150°C together with 16.96 g (0.192 mole) of ethylene carbonate and 5.41 g (0.0176·mole) of TBAB as a catalyst in a three-neck round bottom flask equipped with magnetic stirrer, reflux condenser and thermometer. Reaction was carried out for 5 h under nitrogen atmosphere. Resulting product was washed several times with hot water and subsequently dissolved in dichloromethane. Solution obtained was next washed several times with diluted aqueous NaOH solution and saturated aqueous NaCl solution. Organic phase was dried over anhydrous $MgSO_4$, and finally, solvent was evaporated to give white solid (85% yield). Structure and purity of product obtained were confirmed by ^{1}HNMR and FTIR spectroscopy.

Mp 111°C; IR (KBr): ν = 3600–3120 (O—H), ν = 3000–2800 (C—H), ν = 1637 (C=C), ν = 1509 (C=Carom), ν = 1250–1180 (C—O); ^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.13/6.82 (8H, arom —CH), 4.05 (4H, —CH_2—OH), 3.93 (4H, —O—CH_2—), 2.34 (2H, —OH), 1.63 (6H, —CH_3).

In the second step 20 g (0.064 mole) of ethoxylated BPA was dissolved in 250 mL dichloromethane in a three-neck round bottom flask equipped with reflux condenser, thermometer and magnetic stirrer. Next 14.17 g (0.140 mole) of TEA as a hydrogen chloride scavenger was added. Solution was cooled down to 0°C, and subsequently, 12.96 g (0.132 mole) of MACl was added dropwise in such rate that the temperature did not exceed 5°C.

Afterward, 6.11 g (0.05 mole) of DMAP as catalyst was added and the reaction continued overnight. Resulting mixture was filtrated through a sintered funnel and washed several times with ice-cold water, diluted aqueous solutions of HCl and sodium bicarbonate, finally, with saturated aqueous solution of NaCl and dried over anhydrous $MgSO_4$. Solution was additionally purified

with Dowex Marathon ion exchange resin, and eventually, solvent was removed on a rotary evaporator to give colorless viscous liquid (80% yield). Product obtained was stabilized with 250 ppm of HQME and its structure confirmed by ^{1}HNMR and FTIR spectroscopy.

IR (KBr): ν = 3210–3000 (=C—H), ν = 3000–2800 (C—H), ν = 1720 (C=O), ν = 1637 (C=C), ν = 1610–1509 (C=Carom), ν = 1206–1100 (C—O); ^{1}H NMR (300 MHz, $CDCl_3$, δ): 7.12–6.48 (8H, arom —CH), 6.13/5.57 (4H, $=CH_2$), 4.48/4.19 (8H, $—OCH_2—$), 1.94 (6H, $—CH_3$), 1.63 (6H, $—CH_3$).

Synthesis of Ethoxylated Isosorbide Dimethacrylic Resin (ISETDMA). Three-neck round bottom flask equipped with thermometer, magnetic stirrer and reflux condenser was charged with 20 g of ethoxylated isosorbide (LOH = 386 mg KOH/g, η = 0.845 Pa·s at 25°C), 15.38 g (0.152 mole) of TEA as hydrochloric acid scavenger and 200 mL of CH_2Cl_2. The solution was cooled down to 0°C and subsequently 15.31 g (0.147 mole) of MACl was added dropwise in such rate that the temperature did not exceed 5°C. Next, 6.11 g (0.05 mole) of DMAP as catalyst was added and the reaction continued overnight. Resulting mixture was filtrated through a sintered funnel and washed several times with ice-cold water, diluted aqueous solutions of HCl and sodium bicarbonate, finally, with saturated aqueous solution of NaCl and dried over anhydrous $MgSO_4$. Solution was additionally purified with Dowex Marathon ion exchange resin and eventually solvent was removed on a rotary evaporator to give yellowish viscous liquid (89% yield). Product obtained was stabilized with 250 ppm of HQME. Scheme of the reaction is presented in Figure 2b. ^{1}HNMR, FTIR as well as ESI-MS spectra were recorded in order to confirm structure and described in the following chapter.

Characterization of Monomers

NMR spectra were recorded at 25°C with UNITY/INOVA (Varian, Palo Alto) spectrometer operating at 300 MHz (^{1}H NMR). $CDCl_3$ and tetramethylsilane were used as a solvent and internal standard, respectively. The IR spectra were recorded with BIO-RAD FTS 175L (Hercules) spectrophotometer at room temperature after applying a thin film on a KBr disk. Mass spectra were recorded with ESI Mass Spectrometer ABSciex System 4000 QTRAP® at positive mode of ionization (Framingham) operating at room temperature. Viscosities of synthesized monomers and ethoxylated isosorbide were measured at 25°C by means of Brookfield rheometer (FUNGILAB VISCO STAR Plus L, Illkirch-Cedex, France) using appropriate spindles (L-3 and L-4) according to PN-EN ISO 2555:2011. The density of monomers and polymers were determined using the liquid pycnometer at 25°C according to PN-EN ISO 1183-1:2006.

Polymerization

Compositions of BISGMA with TEGDMA ISETDMA and BISEMA in a ratio of 60 : 40 [w/w] were prepared in a glass vessel by stirring at 40°C for 24 h. Resulting mixtures as well as single monomers were afterwards mixed with 1% [w/w] of Irgacure 651 UV initiator and poured into rectangular-shape Teflon® moulds in amount assuring desired thickness of resulting specimens (4 mm). Photopolymerization was carried out under a mercury lamp (FAMED-1, model L-6/58, 375 W, Łódź, Poland) set 15 cm above the mould for 30 min. for each sample side (sample were removed from moulds in order to irradiate the lower surface). The obtained polymers were subsequently postcured at 130°C for 2 h. Afterward, the inhibition layer of the specimen was removed by polishing with fine sandpaper 1000 grid.

Determination of the Degree of Double Bonds Conversion

Approximately 7 mg samples of compositions prepared as described in Polymerization were cured in aluminium pans in a nitrogen atmosphere. The isothermal photopolymerization study by means of UV-DSC was performed using a METTLER-TOLEDO, DSC822e calorimeter (Greifensee, Schweiz) at a temperature of 40°C which is close to human oral temperature. It was equipped with a Hamamatsu Lighting Cure LC8 (Hg–Xe lamp, Hamamatsu, Japan) with two beams, one for the sample and the other for the reference. Two scans were performed on each sample in order to subtract the thermal effect of the UV irradiation on the sample from the photocuring experiment. Each procedure comprised of 4 min of temperature conditioning, 10 min of irradiation, and finally, 4 min more without UV light. The light intensity at the sample pan position was measured by the carbon black method as 80 mW·cm^{-2}. Degree of double bonds conversion (DC) was calculated according to the following equation:

$$\mathrm{DC}\,(\%) = \frac{\Delta H_x}{\Delta H_0 n} \times 100\% \qquad (1)$$

where ΔH_x is the curing enthalpy of the sample, ΔH_o is the theoretical molar polymerization enthalpy of methacrylic double bond (57 kJ/mol) and n is the number of moles of methacrylic groups present in the sample.[33] Measurements were repeated three times for each monomer and composition.

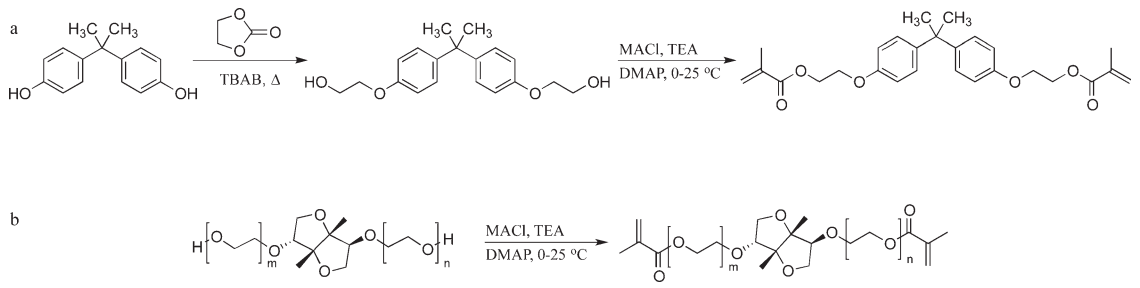

Figure 2. Synthesis of a) BISEMA and b) ISETDMA resins.

Characterization of Polymers

Mechanical Properties. The effect of temperature on viscoelastic properties of the obtained polymers in the limits of linear dependence between stress and strain was determined using a GABO Qualimeter Eplexor 150 N DMA (Ahlden, Germany) device equipped with a testing needle of $\phi = 1$ mm, working in compression mode. Thermomechanical properties of the cured resins were evaluated based on storage modulus (E'), loss modulus (E") and tangent δ curves obtained at constant frequency (10 Hz). Measurements for all 4 mm thick samples (three repetitions for each material) were made in the temperature range 25–250°C at a constant heating rate of 4°C/min. The flexural strength and the flexural modulus were determined in accordance with ISO 178:2003 in a three-point bending test, using a universal testing machine INSTRON (Norwood), model TT-CM equipped with 5 kN crosshead. Specimen dimensions were: 10 ± 0.2 mm × 4 ± 0.2 mm × 83 mm. Measurements were carried out at room temperature with a crosshead speed of 10 mm/min. The ball indentation hardness (Brinell hardness) was determined in accordance with ISO 2039-1:2004 using VEB Werkstoffprüfmaschinen 300/250 (Leipzig, Germany) apparatus. Test specimens, with a 4 mm height and a 12 mm diameter, were prepared in the same way as mentioned above. Every measurement was repeated five times for each investigated material.

Determination of the Polymerization Shrinkage. The polymerization shrinkage (PS) was determined by measuring densities of monomers and monomers mixtures and comparing them with densities of resulting polymers. The following equation was used for calculations:

$$\mathrm{PS}\,(\%) = \frac{d_p - d_m}{d_m} \times 100\,\% \qquad (2)$$

where d_p is the density of polymer and d_m is the density of monomer/monomers mixture.

Measurement of the Water Sorption and Sol Fraction. In order to determine the water sorption of polymerized materials five disk-like samples (15 mm × 1 mm) of each material were prepared according to EN-ISO 4049:2009. Immediately after polymerization, the specimens were placed in a preconditioning oven at 37°C. The specimens were repeatedly weighed until constant mass (m_0) was obtained. They were then individually placed in sealed glass vessels containing 10 mL of distilled water at 37°C. After 7 days, vessels were removed from the oven and left

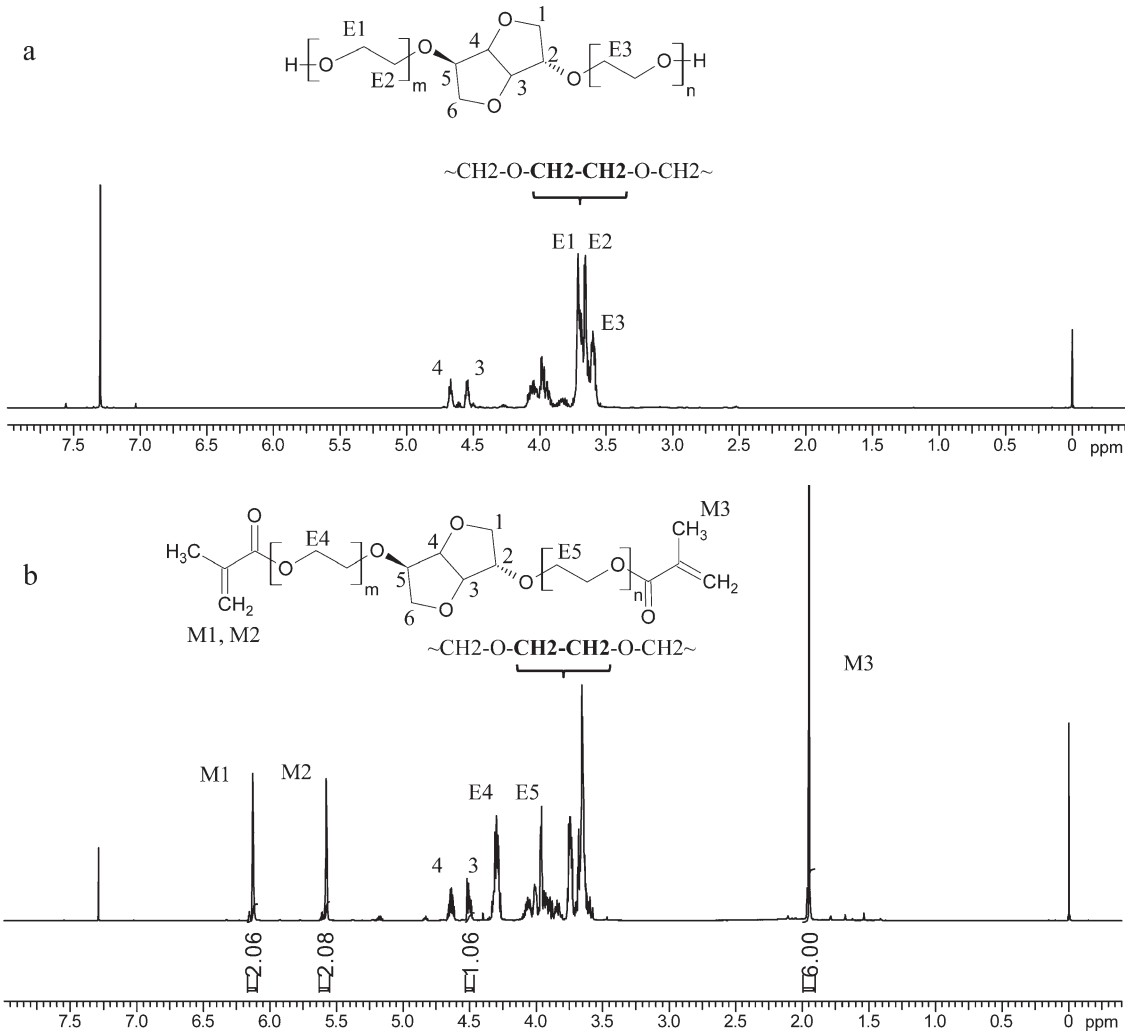

Figure 3. ^{1}HNMR spectra of ISET (a) and ISETDMA (b).[34]

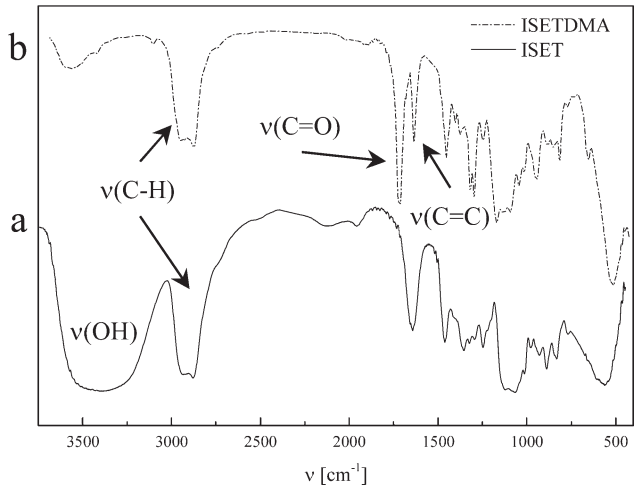

Figure 4. FTIR spectra of ISET (a) and ISETDMA (b).

at room temperature for 1 h. The specimens were gently wiped with a soft absorbent paper and weighed (m_7). Afterwards, the specimens were placed in the desiccator that contained anhydrous calcium chloride and dried at 37°C until the final constant mass was obtained (m_x). Water sorption (WS) and sol fraction (S) were calculated using the following formulas:

$$\mathrm{WS}\left(\tfrac{\mu g}{mm^3}\right) = \frac{m_7 - m_0}{V} \quad (3)$$

$$S\left(\tfrac{\mu g}{mm^3}\right) = \frac{m_0 - m_x}{V} \quad (4)$$

Where m_0 is the weight before immersing, m_7 is weight after 7 days, m_x is the weight after drying (all in μg) and V (in mm^3) is an initial volume of the sample.

RESULTS AND DISCUSSION

In this work, dimethacrylic resin based on ISET was obtained with a good yield of 89 %. Complex ^{1}HNMR spectra of both substrate (a) and product (b) are shown in Figure 3. Groups of signals E1 (3.54–3.62 ppm), E2 (3.63–3.67 ppm) E3 (3.67–3.75 ppm) in the spectrum (a) might be assigned to methylene protons of the oxyethylene fragments, while signals 3 (4.54 ppm) and 4 (4.66 ppm) are characteristic to the methine protons of the isosorbide core.

Proton spectrum of ISETDMA (b) is more clear and shows signals belonging to methylene protons M1 (6.13 ppm) and M2 (5.58 ppm) of the vinyl group as well as protons M3 (1.95 ppm) of the methyl group. Due to methacrylation the signal of methylene protons of the outermost oxyethylene fragments was shifted to 4.30 ppm due to the deshielding effect of ester group. Thorough analysis of spectrum (b) reveals two signals of isosorbide methine protons 2 (5.18 ppm) and 4 (4.83 ppm) indicating that ethoxylate consisted of some molecules with present exo hydroxyl group of the isosorbide ring. Nevertheless, equal intensities of signals M1/M2 and 3/4 clearly prove that the dimethacrylic resin was obtained.

Analysis of FTIR spectra presented in Figure 4 confirms the structure of ISETDMA. The stretching deformations wide band in spectrum at 3025–3725 cm^{-1} (O—H) (a) of the ISET is absent on the spectrum (b) what indicates that all hydroxyl groups underwent methacrylation. Strong stretching deformations band at 1711 cm^{-1} of carbonyl group (C═O) and bending deformation at 1637 cm^{-1} of vinyl group (C═C) on spectrum (b) are related to the methacrylic group.

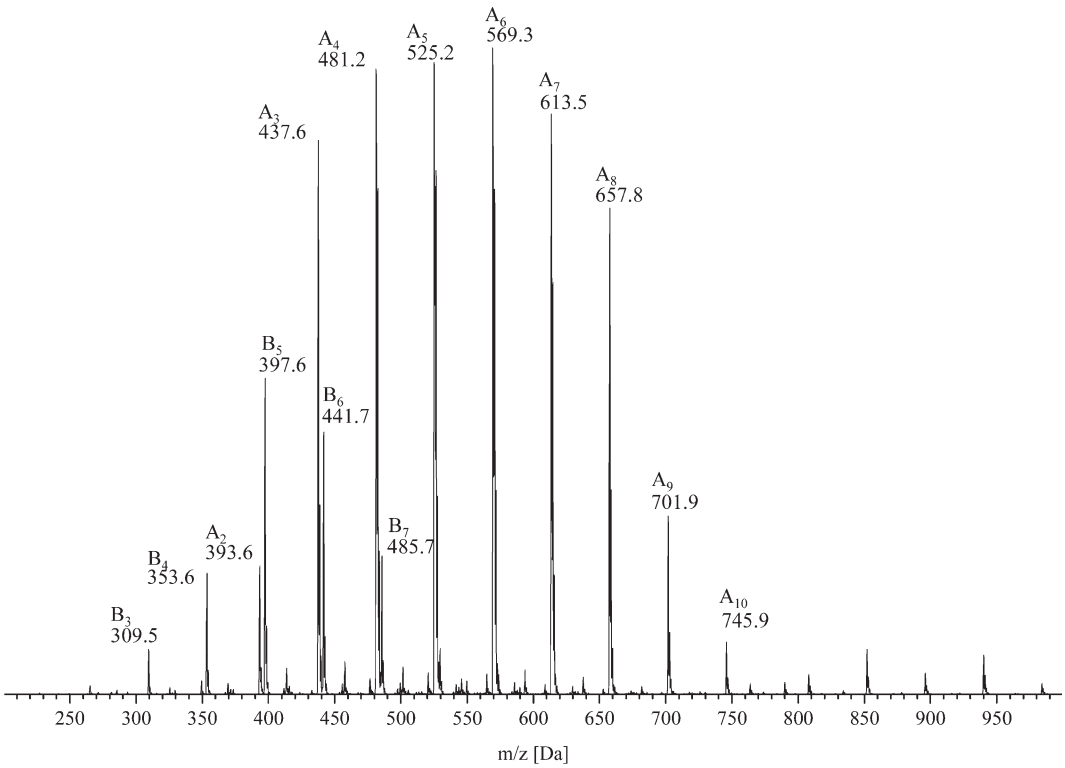

Figure 5. ESI-MS spectrum of ISETDMA.

The ethoxylation process always gives a complex mixture of homologues that differ in chain length and, in case of bifunctional substrate like isosorbide, also in length of both oxyethylene "arms." ESI-MS spectrum of ISETDMA shown in Figure 5 provides information about different species present in the resin. One may observe the main series A_n of signals representing sodium clusters of isosorbide-based methacrylates with highest intensities for species containing between three and eight oxyethylene units. Second marginal series B_n consist of signals in range from 309.5 Da to 485.7 Da, which might be assigned to oligoethylene glycol dimethacrylates. These side products are the consequence of ethoxylation process where initiation took place on water molecules that were present in the system as moisture.

Physical properties of investigated monomers are shown in Table I ISETDMA presents similar double bond concentration as BISEMA but lower than TEGDMA. Novel resin should therefore exhibit lower density of crosslinking after polymerization than the latter. ISETDMA shows low viscosity of 0.062 Pa·s, which is of the same order of magnitude as TEGDMA and much lower than BISEMA. Higher viscosity of the isosorbide based resin than that of TEGDMA is caused by the presence of molecules having long oxyethylene chains in their structures.

Double bond conversion is an important factor which influences final properties of dimethacrylates based polymers. Due to vitrification, cyclization, immobilization, and gelation phenomena conversion never reaches 100%. Nevertheless, the use of dimethacrylic monomers reduces possible leakage of unreacted monomer and in consequence lowers toxicity of resulting polymers. Results of UV-DSC investigation of double bond conversion presented in Table II show that ISETDMA exhibits DC of 70%, which is similar to TEGDMA and much higher than BISEMA. Higher viscosity as well as vitrifacation phenomena affected the final

Table I. Basic Physical Properties of TEGDMA, ISETDMA, and BISEMA monomers

	Monomer			
Properties	TEGDMA	ISETDMA	BISEMA	BISGMA
Concentration of double bonds (mmol/g)	6.99	4.69[a]	4.42	3.89
Viscosity at 25 °C (η) (Pa·s)	0.011	0.062	0.980	462.3[31]
Density at 25 °C (d) (g/cm^3)	1.09	1.16	1.12	1.16[31]

[a] Calculated with hydroxyl number of isosorbide ethoxylate.

Table II. Selected Properties of Cured Homo- and Copolymers

	Polymers					
Properties	A	B	C	D	E	F
Polymerization shrinkage (PS) (%)	11.4	9.5	6.8	8.0	6.0	5.8
Degree of double bonds conversion (DC) (%)	68.9	70.0	54.9	63.3	58.3	51.4
Glass transition temperature (T_g) (°C)	178	137	160	156	162	139
Brinell hardness (MPa)	127 ± 2	95 ± 1	161 ± 1	164 ± 2	144 ± 1	175 ± 1
Flexural modulus (GPa)	2.6 ± 0.19	2.9 ± 0.21	4.45 ± 0.25	4.35 ± 0.22	4.39 ± 0.23	5.57 ± 0.28
Flexural strength (MPa)	76.3 ± 4.7	80.2 ± 7.9	38.6 ± 3.2	81.4 ± 7.2	105.9 ± 11.8	50.1 ± 9.7
Water sorption (WS) (μg/mm^3)	53.6 ± 1.5	97.3 ± 0.5	5.6 ± 0.3	19.7 ± 1.0	26.0 ± 1.1	9.3 ± 0.3
Sol fraction (S) (μg/mm^3)	6.9 ± 0.4	7.9 ± 0.2	0.8 ± 0.2	2.7 ± 0.7	3.5 ± 0.7	0.5 ± 0.1

A – Poly(TEGDMA).
B – Poly(ISETDMA).
C – Poly(BISEMA).
D – Poly(BISGMA-*co*-TEGDMA).
E – Poly(BISGMA-*co*-ISETDMA).
F – Poly(BISGMA-*co*-BISEMA).

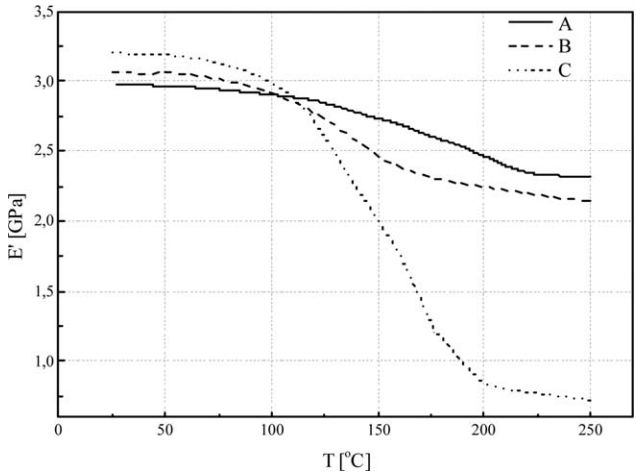

Figure 6. Storage modulus of investigated homopolymers as a function of temperature (symbols described in Table II).

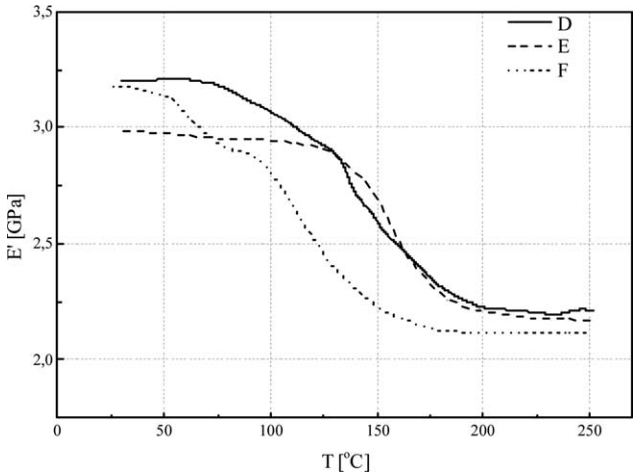

Figure 7. Storage modulus of investigated copolymers as a function of temperature (symbols described in Table II).

conversion of the latter, which is still above 50%. In case of compositions containing BISGMA, DC for investigated monomers increases in the following order: BISEMA<ISETDMA∼TEGDMA. Copolymers present lower DC than homopolymers mainly due to higher viscosity of monomer compositions.

Polymerization shrinkage, PS is an important property associated with double bond conversion and molecular structure of monomers. Considering biomedical applications, low PS value is most desired, since reduction of biomaterial's volume during polymerization creates internal stress that adversely affects surrounding tissues and can cause a severe pain or, in case of dental fillings create gaps prone to cavity. TEGDMA shows highest PS (11.4%) of all due to high conversion and relatively low molecular weight in comparison to other investigated monomers. ISETDMA presents lower shrinkage (9.5%) in spite of similar DC to TEGDMA. This behavior might be explained by the higher average molecular weight of the novel resin. The lowest PS of BISEMA homopolymer corresponds to its lower double bond conversion. Polymerization shrinkage of copolymers of BISGMA and other investigated monomers ranges from 5.8 to 8.0% and shows the same trend as homopolymers, however, presence of bulky aromatic methacrylate as well as slightly lower DC resulted in lower PS than found for homopolymers.

DMA was used to investigate thermal stability and behavior of tested materials under dynamic load. Figures 6 and 7 present compression storage modulus [E'] behavior as a function of temperature. All three homopolymers show good initial stiffness around 3 GPa. During heating the modulus drops down and there is no visible increase in stiffness what indicates that no postcuring took place and all polymer networks are stable. Poly(ISETDMA) presents similar behavior to poly(TEGDMA) due to stiff isosorbide structure, although the latter exhibits slightly better performance in higher temperatures. Poly(BISEMA) in spite of having the highest initial modulus shows fast decrease of stiffness above 100°C.

Low double bond conversion as well as structural heterogeneity of its network may explain such behavior. In case of copolymers, similar initial stiffness was observed and no postcuring was visible as well. Poly(BISGMA-*co*-ISETDMA) shows the lowest modulus but much better mechanical performance up to 120°C than other copolymers.

Analysis of Figures 8 and 9 reveals glass transition temperatures (T_g) taken at the highest point of tangent δ curve and provides information about homogeneity of investigated materials. Polymerization of dimethacrylates leads to heterogeneous polymer network in which highly crosslinked regions are suspended in less crosslinked matrix.[35] Due to this structural heterogeneity of polymer network, widening of tangent δ peak is observed. It is shown that ISETDMA creates the most heterogeneous network of all investigated monomers and its T_g (137°C) is shifted towards lower values, while poly(BISEMA) and poly(TEGDMA) tend to exhibit similar heterogeneity of their networks. In contrast to homopolymer, poly(BISGMA-*co*-ISETDMA) forms somewhat more homogenous network of all copolymers with the highest T_g of 162°C.

Flexural properties shown in Table II again reveal the influence of isosorbide structure on stiffness of investigated polymers. One may presume that presence of oligooxyethylene fragments in ISETDMA should lead to rather elastic network exhibiting

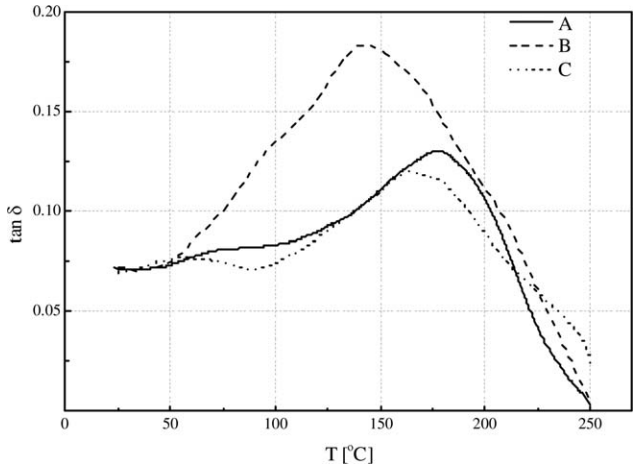

Figure 8. Tangent delta of investigated homopolymers as a function of temperature (symbols described in Table II).

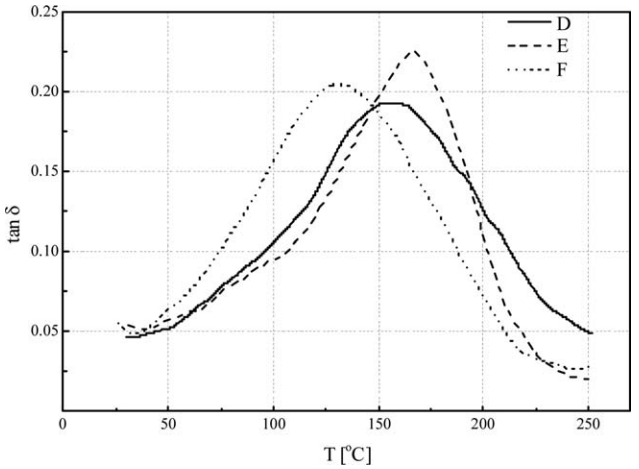

Figure 9. Tangent delta of investigated copolymers as a function of temperature (symbols described in Table II).

low modulus. Results show however that poly(ISETDMA) is as stiff as poly(TEGDMA) with flexural modulus of 2.9 GPa. Very rigid structure of BISEMA provides its homopolymer the highest stiffness of 4.45 GPa. The same tendency may be seen in the series of copolymers where materials based on aliphatic dimethacrylates show comparable modulus, slightly above 4 GPa while for poly(BISGMA-*co*-BISEMA) it is 1.5 GPa higher. Among investigated monomers BISEMA creates the most brittle materials in contrast to ISETDMA, which was shown to produce the most homogenous copolymer with BISGMA.

The results of Brinell hardness measurements are also presented in Table II. This mechanical property is related to the crosslinking ability of monomers. Novel resin due to its structural diversity results in the least rigid network with hardness of 95 MPa, while BISEMA with its two aromatic rings creates very dense and rigid structure despite lower double bond conversion. The same dependence might be observed for the copolymers where poly(BISGMA-*co*-BISEMA) exhibits the highest hardness of 175 MPa and that of copolymer of ISETDMA is the lowest.

Water sorption shows the affinity of polymer network to water. It is known that loose networks are more susceptible to water penetration.[36] This is why poly(ISETDMA) absorbs nearly two times more water than reference homopolymer of TEGDMA. Very low WS of poly(BISEMA) was expected due to its highly crosslinked and hydrophobic aromatic structure. Copolymers of TEGDMA and ISETDMA with BISGMA present lower WS, while poly (BISGMA-*co*-BISEMA) absorbs more water than poly(BISEMA) as a result of hydroxyl groups introduced into the polymer network by BISGMA. Sol fraction indicates the presence of water-soluble components entrapped in the polymer network especially unreacted monomer. Both, homopolymers and copolymers of TEGDMA and ISETDMA show similar low sol fraction. Polymers based on BISEMA despite their lower conversion release only traces of soluble species mainly due to their hydrophobic nature.

CONCLUSIONS

In this work, low viscosity dimethacrylic resin based on bioderived cycloaliphatic diol—isosorbide was obtained in a two-step synthesis. Presence of the fused tetrahydrofuran rings system in the polymer network provides good thermal performance and excellent mechanical properties, comparable to those of the materials where commercial TEGDMA was used as a diluting monomer. High degree of double bond conversion as well as moderate water sorption and low sol fraction may increase biocompatibility of ISETDMA based polymers. Novel dimethacrylic resin might be considered as a potential "green" diluting monomer for biomedical applications.

ACKNOWLEDGMENTS

The authors would like to greatly acknowledge the support of the PCC ROKITA S.A. polyol division in the ethoxylation process. Support from DoktoRIS—Scholarship Program for Innovative Silesia is mostly acknowledged.

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