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Hyperbranched multimethacrylate resins of low viscosity and low oxygen inhibition for dental applications

Summary — This work presents the syntheses and characterization of new low viscosity and low oxygen inhibition hyperbranched multimethacrylate macromonomers capable of photopolymerization, for application in dental composites. Two types of multimethacrylate resins were synthesized. One based on bisphenol A core and polyether branches and the other one based on trimethylolpropane (TMP) and polyether structure containing urethane bonds, obtained with isocyanate or non-isocyanate method. The monomers were characterized by spectroscopic methods. The conversion of double bonds was investigated by FTIR. The physical properties of the multimethacrylate resins such as viscosity, density and polymerization shrinkage were determined. Based on the results obtained it has been shown that such resins are attractive materials to use in composites, especially dental ones.

Key words: hyperbranched polymers, dental composites, multimethacrylate resins, chemical structure, low viscosity.

SILNIE ROZGAŁĘZIONE ŻYWICE WIELOMETAKRYLOWE O MAŁEJ LEPKOŚCI I MAŁEJ INHIBICJI TLENOWEJ DO ZASTOSOWAŃ DENTYSTYCZNYCH

Streszczenie — Opisano sposób syntezy nowych silnie rozgałęzionych (hiperrozgałęzionych) wielometakrylowych makromonomerów zdolnych do fotopolimeryzacji. Charakteryzują się one zmniejszoną lepkością oraz ograniczoną inhibicją tlenową i są przeznaczone do zastosowań dentystycznych. Zsyntetyzowano dwa typy żywic: pierwszy zawierał cząsteczkę bisfenolu A jako rdzeń i ramiona polieterowe (Schemat A, produkty 4a—4c), drugi zaś — trimetylolopropan (TMP) i ramiona polieterowe z fragmentami uretanowymi (Schemat B, produkty 5c—7c oraz Schemat C, produkt 8b). Ugrupowania uretanowe zostały wprowadzone metodą bezizocyjanianową (5c—7c) bądź też tradycyjną z wykorzystaniem izocyjanianu (Schemat C, 8b). Budowę chemiczną makromonomerów scharakteryzowano metodami spektroskopowymi ^{1}H NMR (rys. 1—3, 5, 7) i FTIR (rys. 4 i 6). Metodą FTIR zbadano przebieg konwersji wiązań podwójnych w fotopolimeryzacji kilku żywic wielometakrylowych w funkcji czasu (rys. 8). Scharakteryzowano też ich gęstość i skurcz polimeryzacyjny (Tabela 1) oraz wybrane właściwości mechaniczne (wytrzymałość na zginanie i twardość powierzchniową, Tabela 2). Wyniki wskazują, że uzyskane żywice mogą stanowić alternatywę dla obecnie stosowanych kompozytów, w szczególności kompozytów dentystycznych.

Słowa kluczowe: polimery silnie rozgałęzione, żywice wielometakrylowe, kompozyty dentystyczne, budowa chemiczna, mała lepkość.

Dental resin composites based on 2,2-bis[4-(2-hydroxy-3-methacryloyloxypropoxy)phenyl]propane (Bis-GMA) are commonly used in dental restorations and in some bone cements [1, 2]. They show good physical properties and reasonable resistance to water, common liquids, and food [3]. However, they still have drawbacks during and after placement, mainly related to high viscosity of the resin, water absorption [4], the polymerization shrinkage and low conversion of methacrylic groups on the surface due to oxygen inhibition.

To reduce the drawbacks and to improve physical properties, a typical dental resin composite consists, in addition to the monomer system, of components such as cross linking agents, inorganic fillers and coupling agents that chemically bond the filler and the resin. The resin contains also an initiator system for free radical polymerization and stabilizers for maximizing the storage stability of the uncured resin and the chemical stability of the cured resin composite.

The high viscosity of Bis-GMA can lead to defects at the tooth/resin interface. These defects can act as points of stress concentration during mastication that, in turn, promote microcracks where saliva and other liquids diffuse. Generally, dimethacrylate agent such as triethyleneglycol-dimethacrylate (TEGDMA) or urethane diethy-

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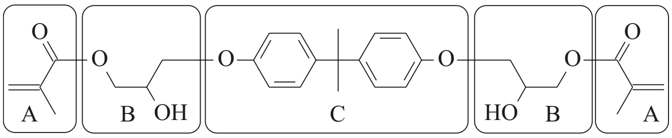
leneglycol methacrylate (UDEMA) is added with a purpose to reduce the initial viscosity of the polymer.

In addition, to optimization of the whole resin composition, a large effort is taken to modify the Bis-GMA structure. To summarize the literature concerning Bis-GMA we divided its structure into three units — structures A, B, and C [Formula (I)].



(I)

The modifications of substructure B containing a free hydroxyl group are most popular. The hydroxyl group can be etherificated in the presence of sodium hydride and alkyl iodide. According to this method, Jeon *et al.* introduced alkyl substituents of various lengths (methyl — pentyl) to the structure of Bis-GMA [5]. Due to the lack of hydrogen bonds, the obtained derivatives showed reduced viscosities of 3.65 Pa · s for the methyl group to 0.21 Pa · s for pentyl one (Bis-GMA — 574 Pa · s). All derivatives showed increased conversion of double bonds in the range of 70 % (Bis-GMA — 64.5 %) which resulted in improved mechanical properties. They also showed reduced water uptake of 0.87 to 0.72 % (Bis-GMA — 3.11 %). Other Bis-GMA derivatives containing various alkyl, alkoxy or siloxane substituents at 1, 2 and 3 positions of 1,3-propanediol unit B [6—8] showed slightly lower conversions of double bonds as well as higher viscosities and similar water uptake to those mentioned above.

Another important modification of Bis-GMA structure is the introduction of fluorine atoms. They can be positioned in B and C substructures. Such modification leads to materials of low surface energy, high hydrophobicity, low water uptake (down to 0.05 %) and biocompatibility. However, their low mechanical properties exclude their application in commercial dental materials [9].

The introduction of urethane linkages into Bis-GMA structure reduces the effect of oxygen inhibition [10]. Substructure B modified with various aliphatic chains linked *via* urethane bonds gave Bis-GMA of improved conversion of double bonds, reduced viscosity and low water uptake, however, the polymerization shrinkage was higher than in the original material. Improvement in mechanical properties of Bis-GMA, such as compression resistance, tensile strength and creep resistance can be achieved by replacing of the unit C with a structure containing multiple aromatic rings [11].

Hyperbranched polymers (HBPs) — highly branched, three-dimensional molecules — have gained widespread attention in the last decades [12—15]. They are characterized by several unique features such as high number of reactive sites, relatively low viscosity, high solubility and biocompatibility, which are known for dendrimers. Most of the recent works have concentrated on hyperbranched polymers based on polyglycidol [16] and 2,2-bis(hydroxymethyl)propionic acid [17].

This work presents the syntheses of hyperbranched, multimethacrylate macromonomers and determination of their spectral and physical properties.

EXPERIMENTAL

Materials

2,2-Bis[4-(2-hydroxy-3-methacryloyloxypropoxy) phenyl]propane, aminoethanol, methacrylic anhydride, methacrylic chloride, dimethyl carbonate, glycidol, potassium, 2,2-bis-(4-hydroxyphenyl)propane (bisphenol A), triethylamine, 4-*N*,*N*-dimethylaminepyridin, camphorchinone (bornanedion, 1,7,7-trimethylbicyclo[2.2.1] heptane-2,3-dion), 2-diethylamineethylmethacrylate, Irgacure 184, 651, and 907 were purchased from Sigma-Aldrich (Poznań, Poland) and used as received. Tetrahydrofuran was distilled prior to use over potassium benzophenone ketyl. DMF (POCh Gliwice, Poland) was dried over molecular sieves 4Å. Glycerol carbonate [18] and polyglycidols **5a**-**8a** (see Scheme A, B, C) [19, 20] were synthesized according to procedures previously published by us.

Methods of characterization

^{1}H NMR spectra were recorded using a Varian VXR 400 MHz spectrometer, with tetramethylsilane as an internal standard. FTIR spectra were recorded using a Biorad FTIR Spectrometer FTS165.

The molecular weights were measured with GPC LabAlliance apparatus equipped using Jordi Gel DVB Mixed Bed 250 × 10 mm column and a refractive index detector RI 2000-F. Chloroform was used as an eluent at 35 °C and poly(ethylene glycol) for the calibration.

The density of the monomers was determined using a pycnometer at 20 °C.

The density of the polymers was determined at 20 °C by hydrostatic balance using 10 × 10 × 10 mm cubic samples.

The viscosity of the branched macromonomers was measured using a Mettler RM180 rheomat at 25 °C with shear rate 64.6 1/s.

The polymerization shrinkage was calculated from the equation

$$\Delta V = (1 - \rho_m/\rho_p) \cdot 100\ \% \tag{1}$$

where: ρ_m — *density of monomer*, ρ_p — *density of polymer*.

The conversion (p) of double bonds in time was determined using Megalux (75 W) lamp in an air for 30 μm thick samples and calculated from the equation

$$p = 1 - [(A^1_{C=C}/A^1_{C=O})/(A^0_{C=C}/A^0_{C=O})] \tag{2}$$

where: $A_{C=C}$ — *absorbance at 1638 cm^{-1}*, $A_{C=O}$ — *absorbance at 1722 cm^{-1}*.

The flexural strength was measured with use of MTS Q Test apparatus for samples of 25 × 2 × 2 mm size and a crosshead speed 0.75 mm/min. The flexural strength determination was performed using a 3-point bending method according to the standard ASTM D-790. In this work the flexural strength was reported as the load at yield measured at 5% deformation of the outer surface for the samples that did not break or at break.

The hardness was determined by König pendulum and reported as numbers of pendulum swings.

The light-induced polymerizations for the preparation of samples for mechanical tests described above were performed using a Megalux (75 W) lamp or medium-pressure mercury lamp PLK type 5 (80 W) supplied by the Electrotechnical Institute (Warsaw, Poland).

Syntheses

2,2–Bis[4-(2,3-dihydroxypropoxy)phenyl]propane (2)

In a 150 mL three-neck flask equipped with a thermometer, magnetic stirrer and a nitrogen inlet, 18.3 g (0.15 mol) of glycerol carbonate, 10 g (44 mmol) of bisphenol A and 0.055 g (4.5 mmol) of potassium carbonate were placed. The reaction mixture was stirred in an atmosphere of nitrogen at 160 °C for 12 h. The FTIR spectrum was recorded to confirm disappearance of the cyclic carbonate band at 1786 cm^{-1}. Then, the reaction mixture was cooled down to 80 °C and treated with 50 mL of water. The water phase was removed and water treatment was repeated twice to remove any existing glycerol. The product was dissolved in THF and dried with $MgSO_4$. Removal of the solvent yielded 15 g (91 %) of 2,2–bis[4-(2,3-dihydroxypropoxy)phenyl]propane as a light yellow oil.

^{1}H NMR (DMSO-d_6, 400 MHz): δ (ppm) = 7.10—7.06 (m, 4H, H_{ar}), 6.82—6.78 (m, 4H, H_{ar}), 4.91 (d, 2H, CHOH, J = 4.8 Hz), 4.64 (t, 2H, CH_2OH, J = 5.6 Hz), 3.92 (dd, 2H, CH_2OH, J_1 = 9.5 Hz, J_2 = 4.1 Hz), 3.79 (dd, 2H, CH_2OH, J_1 = 9.5 Hz, J_2 = 6.0 Hz), 3.77—3.71 (m, 2H, CH_2CHCH_2), 3.41 (dd, 4H, CH_2O, J_1 = J_2 = 5.2 Hz), 1.56 (s, 6H, CH_3);

FTIR (KBr): ν (cm^{-1}) = 3401 (OH), 829 (C-C_{Ar}), 557 (C-C_{Ar}).

General procedure of the preparation of hyperbranched oligomers with hydroxyl groups (3a-c)

The oligomers containing on average 8, 10 or 12 hydroxyl groups were prepared by a modified procedure previously reported by Sunder *et al.* [21]. Namely, 30 g (80 mmol) of 2,2-bis[4-(2,3-dihydroxypropoxy)phenyl] propane (**2**) was placed in a 150 mL three-neck flask equipped with a thermometer, magnetic stirrer, nitrogen inlet and a condenser, followed by 1.25 g (32 mmol) of potassium. The mixture was stirred at 60 °C under nitrogen for 1 h until potassium dissolved in the reaction mixture. The temperature was increased to 95—100 °C. The 5 M solution of 24.7 g (0.32 mol) (**3a**), 37.1 g (0.48 mol) (**3b**) or 49.6 g (0.64 mol) (**3c**) of glycidol (96 %) in dry THF was then introduced with the rate of 3 mL/h by an infusion pump (Ascor Ap22). After all glycidol was added, the reaction mixture was heated for an additional 0.5 h. The remains of THF were removed under vacuum leaving the oligomer as a pale yellow viscous oil. The yield varied from 96 to 97 %.

^{1}H NMR (DMSO-d_6) (400 MHz) — **3a:** δ (ppm) = 7.13—7.09 (m, 4H, H_{Ar}), 6.86—6.82 (m, 4H, H_{Ar}), 5.2—4.4 (m, 8H, OH), 4.2—3.2 (m, 30H, CH and CH_2), 1.55 (s, 6 H, CH_3); **3b:** δ (ppm) = 7.10—7.05 (m, 4H, H_{Ar}), 6.96—6.92 (m, 4H, H_{Ar}), 5.2—4.4 (m, 10H, OH), 4.2—3.1 (m, 40H, CH and CH_2), 1.55 (s, 6H, CH_3); **3c:** δ (ppm) = 7.15—7.09 (m, 4H, H_{Ar}), 6.87—6.81 (m, 4H, H_{Ar}), 5.2—4.4 (m, 12H, OH), 4.2—3.2 (m, 50H, CH and CH_2), 1.55 (s, 6 H, CH_3);

FTIR (KBr): **3a-c**, ν (cm^{-1}) = 3400 (OH), 830 (C-C_{Ar}), 560 (C-C_{Ar}).

General procedure of the preparation of methacrylic macromonomers (4a-c)

In a 150 mL three-neck flask equipped, with a thermometer, magnetic stirrer, dropping funnel and a nitrogen inlet, the oligomers **3a-3c** containing an average 25 mmol of hydroxyl groups — 3.03 g (**3a**), 2.79 g (**3b**) or 2.63 g (**3c**) — were dissolved in 50 mL of dry DMF and 3.03g (30 mmol) of triethylamine was added. The reaction mixture was cooled down to 15 °C and 2.87 g (27.5 mmol) of methacryloyl chloride was added dropwise during 4 h. The reaction mixture was stirred under nitrogen for 2 h at room temperature and for 48 h in the atmosphere of dry air. The precipitate of triethylamine hydrochloride was filtrated off, then the solution was poured into 100 mL of water. The product was extracted with dichloromethane and washed with sodium bicarbonate and water, 5 mg of phenothiazin was added and the organic phase dried with $MgSO_4$. The solvent was removed prior to use. Yields varied from 86 to 91 %.

^{1}H NMR (DMSO-d_6) (400 MHz) — **4a**: δ (ppm) = 7.13—7.08 (m, 4H, H_{Ar}), 6.86—6.80 (m, 4H, H_{Ar}), 6.00 (bs, 8H, =CH_2), 5.68 (bs, 16H, =CH_2), 4.42—3.20 (m, 30H, CH and CH_2), 1.85 (bs, 24H, CH_3), 1.57 (s, 6H, CH_3); **4b:** δ (ppm) = 7.15—7.08 (m, 4H, H_{Ar}), 6.87—6.83 (m, 4H, H_{Ar}), 6.03 (bs, 10H, =CH_2), 5.69 (bs, 10H, =CH_2), 4.40—3.20 (m, 40H, CH and CH_2), 1.87 (bs, 30H, CH_3), 1.55 (s, 6H, CH_3); **4c:** δ (ppm) = 7.13—7.10 (m, 4H, H_{Ar}), 6.88—6.79 (m, 4H, H_{Ar}), 6.01 (bs, 12H, =CH_2), 5.66 (bs, 12H, =CH_2), 4.40—3.20 (m, 50H, CH and CH_2), 1.86 (s, 36H, CH_3), 1.56 (s, 6H, CH_3);

FTIR (KBr): **4a-c**, ν (cm^{-1}) = 1727 (C=O), 1638 (C=C), 829 (C-C_{Ar}), 557 (C-C_{Ar}).

General procedure of the preparation of hyperbranched polymers with urethane groups (5b-7b)

In a 50 mL round bottom flask equipped with a magnetic stirrer, a thermometer and a reflux condenser, 11.5 mmol of cyclic carbonate groups of polyglycidols **5a** (10 g), **6a** (13.1 g) or **7a** (6.53 g) were placed (see Materials), followed by 0.74 g (12.1 mmol) of 2-aminoethanol. The reaction mixture was heated at 90 °C overnight. The reaction progress was monitored by FTIR and continued until the cyclic carbonate absorption band at 1800 cm^{-1} disappeared completely. The product **5b** was precipitated from methanol/THF mixture and the products **6b** and **7b** from THF/hexane mixture; they were obtained as a pale yellow oils with following yields: **5b** — 68 %; **6b** — 82 %; **7b** — 74 %.

5b: ^1H NMR (DMSO-d_6) (400 MHz): δ (ppm) = 7.04 (bs, $N\underline{H}_{(E)}$), 6.94 (bs, $N\underline{H}_{(Z)}$), 5.0—4.0 (bs, $O\underline{H}$), 3.8—2.8 (m, $C\underline{H}O$, $C\underline{H}_2O$, $C\underline{H}_2NH$), 1.22 (br, $C\underline{H}_2$), 0.78 (s, $C\underline{H}_3$); FTIR (KBr) ν (cm^{-1}) = 3400 (OH), 1722(C=O), 1100 (COC).

6b: ^1H NMR (DMSO-d_6) (400 MHz): δ (ppm) = 7.00 (bs, $N\underline{H}_{(E)}$), 6.93 (bs, $N\underline{H}_{(Z)}$), 5.0—4.0 (bs, $O\underline{H}$), 3.8—2.8 (m, $C\underline{H}O$, $C\underline{H}_2O$, $C\underline{H}_2NH$), 2.0 (s, $OC(O)C\underline{H}_3$), 1.22 (br, $C\underline{H}_2$), 0.78 (s, $C\underline{H}_3$); FTIR (KBr): ν (cm^{-1}) = 3400 (OH), 1740 (C=O), 1100 (COC).

7b: ^1H NMR (DMSO-d_6) (400 MHz): δ (ppm) = 7.38 (m, $C\underline{H}_{Ar}$), 7.00 (bs, $N\underline{H}_{(E)}$), 6.93 (bs, $N\underline{H}_{(Z)}$), 5.2-4.6 (bs, $O\underline{H}$), 4.6 (s, $C\underline{H}_2Ph$), 3.8—3.0 (m, $C\underline{H}O$, $C\underline{H}_2O$, $C\underline{H}_2NH$), 1.22 (bs, $C\underline{H}_2$), 0.78 (s, $C\underline{H}_3$); FTIR (KBr): ν (cm^{-1})= 3400 (OH), 1722 (C=O), 1100 (COC), 720 ($C\text{-}C_{Ar}$), 675 ($C\text{-}C_{Ar}$).

General procedure of the preparation of methacrylic-urethane macromonomers (5c-7c)

In a 50 mL three-neck flask, equipped with a thermometer, magnetic stirrer, dropping funnel and a nitrogen inlet, 5g of the polymer **5b-7b** and 0.07 g (0.58 mmol) of 4-dimethylaminopyridine were dissolved in 20 mL of dry DMF. To the solution methacryloyl anhydride [**5b:** 6.62 g (43 mmol); **6b:** 1.94 g (1.26 mmol); **7b:** 2.98 g (19.4 mmol)] was added and the reaction mixture was stirred under nitrogen for 4 h at room temperature and then for 20 h in the atmosphere of dry air. Next, 2.03 mg (0.015 mmol) of $CuCl_2$ was added and the solvent removed in vacuum. The residue was dissolved in dichloromethane and washed with sodium bicarbonate and water. 2.83 mg of phenothiazin was added and the organic phase dried with $MgSO_4$. The solvent was removed prior to use. Yields varied from 85 to 90 %.

5c: ^1H NMR (DMSO-d_6) (400 MHz): δ (ppm) = 7.02—6.96 (bs, $N\underline{H}$), 6.02 (s, $=C\underline{H}_2$), 5.65 (s, $=C\underline{H}_2$), 4.0—3.1 (m, $C\underline{H}O$, $C\underline{H}_2O$, $C\underline{H}_2NH$), 1.82 (s, $C\underline{H}_3$), 1.22 (bs, $C\underline{H}_2$), 0.78 (s, $C\underline{H}_3$); FTIR (KBr): ν (cm^{-1}) = 3440 (OH), 1722(C=O), 1638 (C=C), 1100 (COC).

6c: ^1H NMR (DMSO-d_6) (400 MHz): δ (ppm) = 7.04—6.95 (bs, $N\underline{H}$), 6.02 (s, $=C\underline{H}_2$), 5.65 (s, $=C\underline{H}_2$), 4.01—3.12 (m, $C\underline{H}O$, $C\underline{H}_2O$, $C\underline{H}_2NH$), 2.0 (s, $OC(O)C\underline{H}_3$), 1.82 (s, $C\underline{H}_3$), 1.22 (bs, $C\underline{H}_2$), 0.78 (s, $C\underline{H}_3$); FTIR (KBr): ν (cm^{-1}) = 3400 (OH), 1740 (C=O), 1638 (C=C), 1100 (COC).

7c: ^1H NMR (DMSO-d_6) (400 MHz): δ (ppm) = 7.38 (m, $C\underline{H}_{Ar}$), 7.00—6.92 (bs, $N\underline{H}$), 6.00 (s, $=C\underline{H}_2$), 5.67 (s, $=C\underline{H}_2$), 4.62 (s, $C\underline{H}_2Ph$), 4.00—3.16 (m, $C\underline{H}O$, $C\underline{H}_2O$, $C\underline{H}_2NH$), 1.82 (s, $C\underline{H}_3$), 1.22 (bs, $C\underline{H}_2$), 0.78 (s, $C\underline{H}_3$); FTIR (KBr): ν (cm^{-1}) = 3400 (OH), 1722 (C=O), 1638 (C=C), 1100 (COC), 720 ($C\text{-}C_{Ar}$), 675 ($C\text{-}C_{Ar}$).

Procedure for the preparation of methacrylic-urethane macromonomer (8b)

In a three-neck round bottom flask, equipped with a magnetic stirrer, reflux condenser, thermometer and a nitrogen inlet, 5 g (17.6 mmol of hydroxyl groups) of polyglycidol **8a**, 2.73 g (17.6 mmol) of 2-isocyanateethylmethacrylate and 0.04 g (0.1 mmol) of tin 2-ethylhexanoate were dissolved in 20 mL of dry THF. The reaction mixture was heated at 50 °C for 6 h to the disappearance of the isocyanate absorption bands in the FTIR spectrum. The product was purified by precipitation from THF/hexane mixture and obtained as a viscous oil with 88 % yield.

8-b: ^1H NMR (DMSO-d_6) (400 MHz): δ (ppm) = 7.39 (m, $C\underline{H}_{Ar}$), 7.10—6.78 (bs, $N\underline{H}$), 6.00 (s, $=C\underline{H}_2$), 5.62 (s, $=C\underline{H}_2$), 4.55 (s, $C\underline{H}_2Ph$), 3.78—3.21 (m, $C\underline{H}O$, $C\underline{H}_2O$, $C\underline{H}_2NH$), 1.81 (s, $C\underline{H}_3$), 1.22 (bs, $C\underline{H}_2$), 0.78 (s, $C\underline{H}_3$); FTIR (KBr): ν (cm^{-1}) = 3400 (OH), 1722 (C=O), 1638 (C=C), 1100 (COC), 720 ($C\text{-}C_{Ar}$), 675 ($C\text{-}C_{Ar}$).

RESULTS AND DISCUSSION

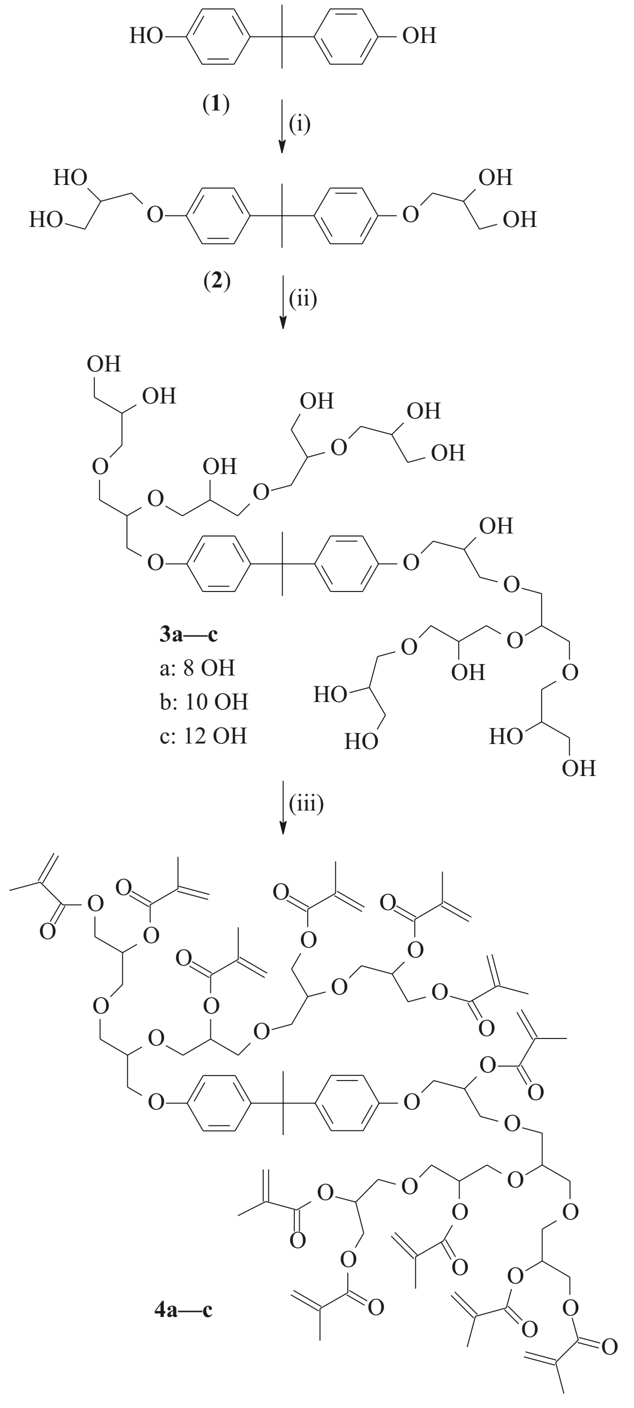
Syntheses of multimethacrylate macromonomers

Bisphenol A can be easily used as a core for the syntheses of hyperbranched polyethers. They can be next used for the preparation of multifunctional Bis-GMA analogues. Scheme A presents the way of their preparation. In the first step, bisphenol A was reacted with an excess of glycerol carbonate giving tetrol **2**. Next, a modified procedure of preparation of polyglycidol reported previously by Sunder was applied [20, 21]. The amount of glycidol was calculated to obtain the molecules containing on average 8, 10 or 12 hydroxyl groups. Finally, methacrylic groups were introduced in the reaction with methacryloyl chloride in dry DMF.

Figure 1 shows the ^1H NMR spectrum of tetrol **2** obtained from bisphenol A and glycerol carbonate. Compound **2** was used for the syntheses of polyethers **3a-c**. ^1H NMR spectra of these polyethers showed an increasing amount of CH protons of polyether structures as well as hydroxyl group protons with an increasing amount of glycidol. The spectra are collected in figure 2.

Polyethers **3a-c** were also characterized by GPC. Prior to the measurement, the hydroxyl groups in polymers were protected with trimethylchlorosilane which eliminated the influence of formation of hydrogen-bonded agglomerates on the GPC results. The molecular weight (M_n) values (1650—1880) fitted in the range of expected values.

The polyethers **3a-c** were then converted into methacrylic resins in the reaction with methacryloyl chloride.



Scheme A. The synthesis of bisphenol A based hyperbranched polyethers: (i) glycerol carbonate, K_2CO_3, 160 °C; (ii) glycidol, potassium, 90 °C; (iii) methacryloyl chloride, DMF, triethylamine, room temperature

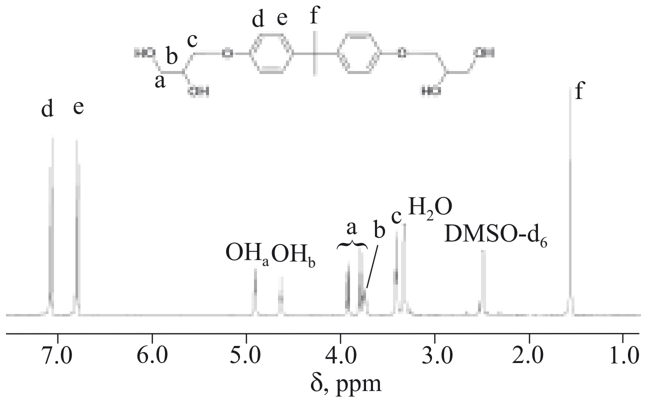


*Fig. 1. ^1H NMR (400 MHz, DMSO-d_6) spectrum of tetrol **2** used for preparation of hyperbranched polyethers*

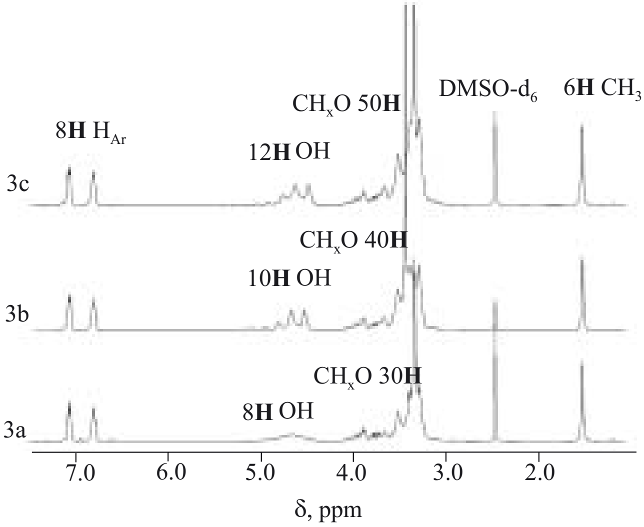


*Fig. 2. ^1H NMR (400 MHz, DMSO-d_6) spectra of polyethers **3a-c***

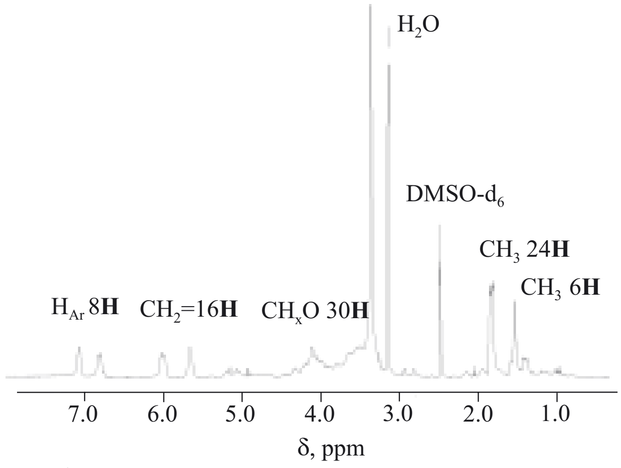


*Fig. 3. ^1H NMR (400 MHz, DMSO-d_6) spectrum of polymethacrylate resin **4a***

Figure 3 shows the ^1H NMR spectrum of the final product **4a**. The methacrylate group signals are represented by two broad signals at 6.0 and 5.6 ppm of methylene group and a singlet at 1.8 ppm of methyl group. The bisphenol A unit is represented by aromatic protons at 7.2 and 6.8 ppm and methyl group at 1.6 ppm. The polyether structures show signals in the range of 4.2 to 3.2 ppm. The final product does not contain free hydroxyl groups which can be seen in the FTIR spectrum in Figure 4. There are also characteristic signals of C=C methacrylate groups at 1640 cm^{-1} present in the spectrum.

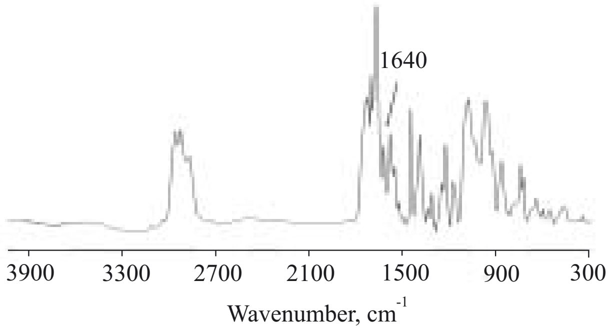


Fig. 4. FTIR spectrum of polymethacrylate resin ***4a***

The presence of urethane bonds can reduce the oxygen inhibition during the polymerization of acrylates [22]. The presence of cyclic carbonates in the hyperbranched polyethers structures make them attractive starting materials for the modification with aminoalcohols. This method leads to formation of urethane linkages without use of isocyanates. In the reaction of cyclic carbonate with 2-aminoethanol, in addition to the urethane bond two hydroxyl groups are produced. They can be subsequently converted into (meth)acrylic esters leading to structures of a high number of polymerizable groups.

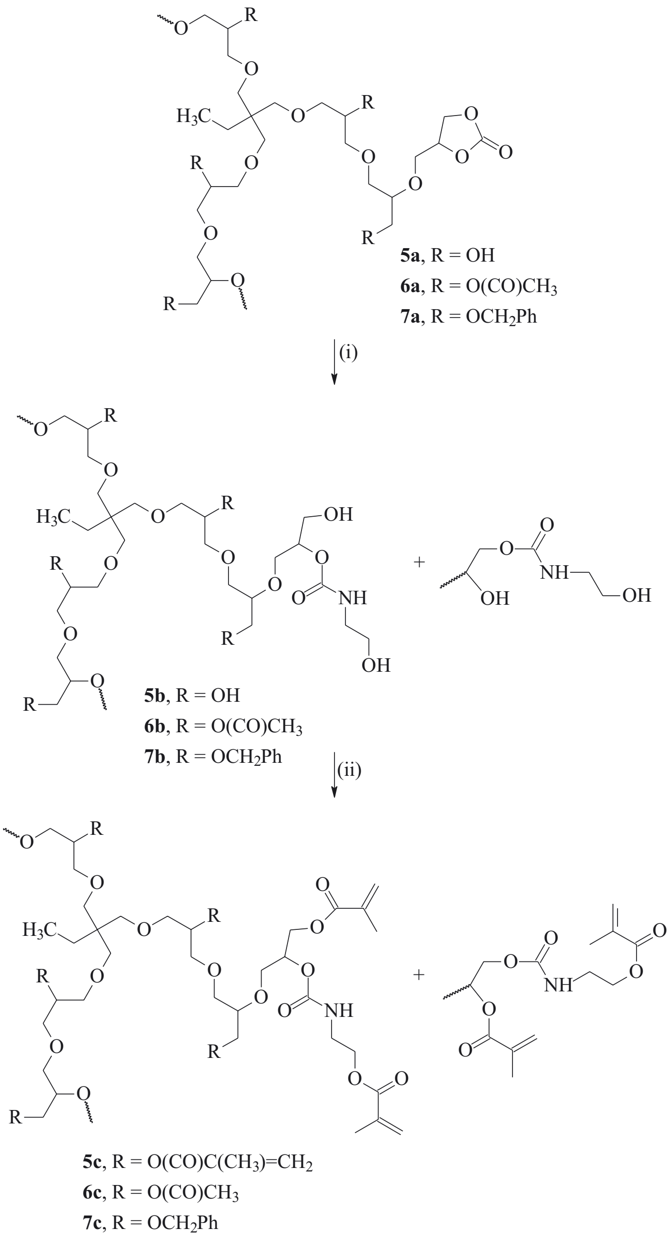
Methacrylate resins containing urethane bonds were synthesized using either isocyanate or non-isocyanate routes. The molecules of polyglycidol were functionalized using known procedures described in the literature. Polymers **5a** and **6a** were synthesized according to [19]. Polymer **7a** was obtained in a series of reactions including: protection of vicinal dihydroxyl groups with benzaldehyde acetal, reaction of remaining hydroxyl groups with benzyl halide, deprotection of vicinal hydroxyl groups described in [20] and reaction with dimethyl carbonate performed similarly to the procedure described in [19]. The reactions of polymers **5a-7a** with 2-aminoethanol yielded derivatives containing urethane bonds and free hydroxyl groups **5b-7b**. In such reaction two types of regioisomers are possible, which are shown in Scheme B.

The methacrylic groups were introduced in the reaction with methacrylic acid chloride in the presence of triethylamine. The synthesized resins were characterized by ^{1}H NMR, FTIR and viscosity measurements.

Figure 5 shows the ^{1}H NMR spectrum of resin **5c**. The presence of methacrylic groups is confirmed by the signals at 1.82 ppm (CH_3), 6.02 and 5.65 ppm (CH_2=). The urethane group is represented by NH signal at 6.98 ppm.

The FTIR spectrum (Figure 6) also confirms the introduction of methacrylate groups into the hyperbranched structure (1638 cm^{-1} C=C band, 1722 cm^{-1} C=O band).

The urethane-methacrylate resins **5c-7c** contained only one urethane bond per one starting carbonate group. The number of urethane bonds in the hyperbranched molecule can be doubled when methacrylate fragments containing isocyanate groups reacts with



Scheme B. Synthesis of multimethacrylate resins containing urethane linkages: (i) 2-ethanoloamine, 90 °C; (ii) methacrylic anhydride, 4-dimethylaminopyridine, DMF, room temperature

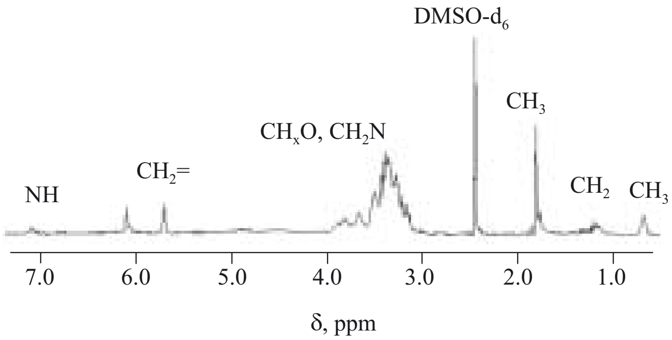


Fig. 5. ^{1}H NMR (400 MHz, DMSO-d$_6$) spectrum of polymethacrylate resin ***5c***

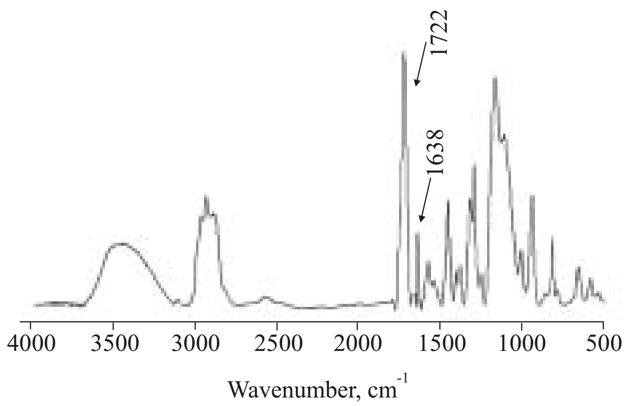
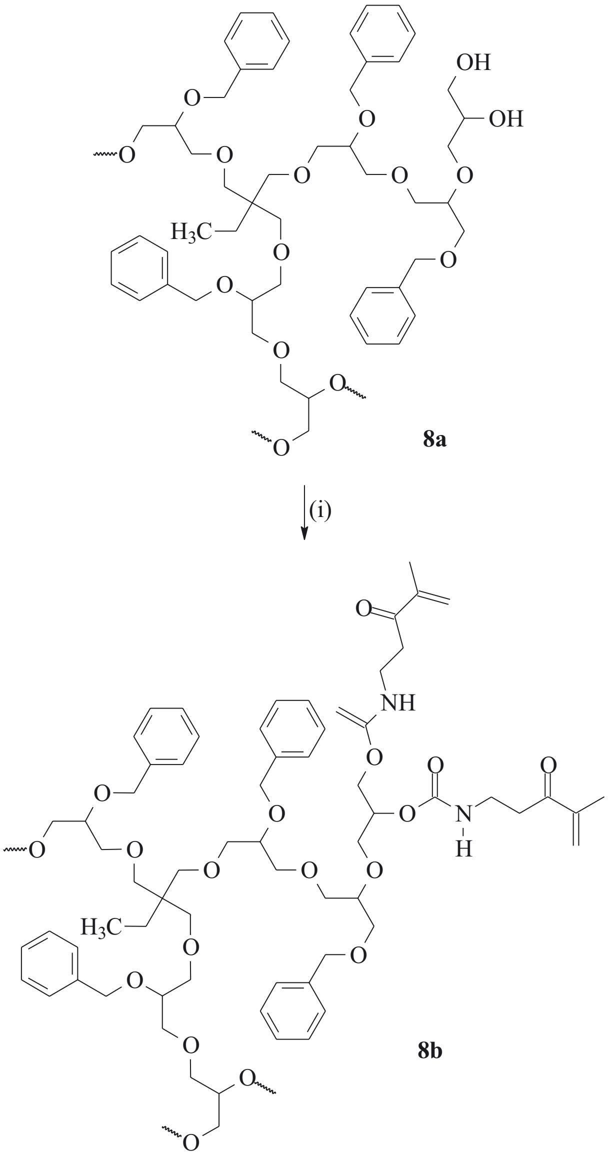


*Fig. 6. FTIR spectrum of polymethacrylate resin **5a***



Scheme C. Preparation of multimethacrylate resin in the reaction with 2-isocyanatoethyl methacrylate

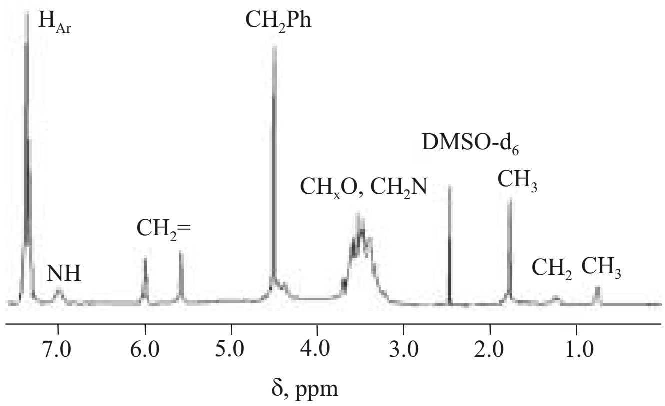


*Fig. 7. ^{1}H NMR (400 MHz, DMSO-d_6) spectrum of polymethacrylate resin **8b***

existing hydroxyl groups. The multimethacrylate resin containing urethane bonds **8b** was synthesized in a simple one-step procedure in the reaction of polyglycidol containing benzyl groups in the inner sphere **8a** with 2-isocyanateethylmethacrylate (Scheme C).

The application of isocyanate allowed to obtain a material containing equal numbers of urethane and methacrylic bonds. The reaction was performed in dry THF in the atmosphere of nitrogen with tin 2-ethylhexanoate as a catalyst. The product appeared to be a viscous oil of viscosity similar to those obtained for resins **5c-7c** (see Table 1). Figure 7 shows the ^{1}H NMR spectrum of the product. Again, the spectrum contained signals characteristic for methacrylate groups (6.02, 5.59 and 1.78 ppm) and urethane NH protons at 7.0—6.8 ppm as well as the aromatic at 7.2 ppm and benzylic CH_2 at 4.55 ppm.

Characterization of the multimethacrylate resins

In spite of the large number of urethane bonds capable of forming of hydrogen bonds, the viscosity of urethane-methacrylate resins **5c-7c** and **8b** remained low (2.1—2.7 Pa · s see Table 1). The structures of hyperbranched molecules cause that methacrylate and urethane bonds are positioned one next to the other. This leads to the formation of intramolecular hydrogen bonds which do not cause an increase in viscosity.

In case of methacrylic resins **4a-c** an increase in viscosity from 2.1 to 8.5 Pa · s with increasing size of the molecule is observed. The reason of such behavior can be the rigid bisphenol core of the molecules. It does not allow the functional groups to organize and form intramolecular hydrogen bonds. Instead, intermolecular bonds are formed leading to increased viscosity.

Density of the synthesized resins was in the range of 1.25 to 1.30 g/cm^3. The polymerization shrinkage was calculated as described in the experimental part. The results are shown in Table 1.

All the samples showed low values of polymerization shrinkage. The highest shrinkage was observed for molecules of the smallest size (**4a**) and having no substituents other than methacrylic esters (**5c**). The introduction of bulky substituents to the inner sphere of the hyperbranched structure as well as increasing of the size of the hyperbranched structure leads to lowering of the polymerization shrinkage.

Table 1. Characteristics of the multimethacrylate resins

Resin	Viscosity, Pa · s	Shrinkage, %
4a	2.1	6.6 ± 0.21
4b	6.2	4.8 ± 0.19
4c	8.5	4.9 ± 0.15
5c	2.4	6.8 ± 0.24
6c	2.5	5.9 ± 0.32
7c	2.1	5.4 ± 0.12
8b	2.7	5.0 ± 0.25

The urethane-methacrylate resins were hardened with a Megalux lamp in the presence of a photoinitiator (5 wt. % of camphorquinone, 5 wt. % 2-diethylaminoethyl methacrylate). The obtained samples showed flexural strength in the range of 58 MPa to 64 MPa. The coatings of **5c-7c** and **8b** were obtained in a similar manner. The glass plates were covered with a 60 μm thick layer of the monomer/initiator mixture and then hardened under UV-light at ambient conditions for 5 minutes. The hardness of the coatings was determined by König pendulum and ranged from 55 to 78 (Table 2). The surfaces of all the obtained materials were hard, without signs of sticky material. This proves that the materials **5c-7c** and **8b** containing urethane bonds are resistant to oxygen inhibition.

Table 2. Mechanical properties of urethane-methacrylate resins

Resin	Flexural strength, MPa	König hardness of the surface a)
5c	62 ± 4	55
6c	63.5 ± 2	78
7c	61.5 ± 3	67
8b	58 ± 3	68

a) The number of pendulum swings.

Photopolymerization of the multimethacrylate resins

The progress of the photopolymerization has been investigated by means of FTIR spectroscopy. During the polymerization the number of unsaturated methacrylate bonds decreases, which results in lowering of the absorption band at 1640 cm^{-1}. At the same time the intensity of the ester band at 1722 cm^{-1} remains unchanged. It can be used as a reference.

The investigated multimethacrylate resins show relatively high conversions of double bonds — up to 27 % for **4a** resin (Fig. 8, $p = 0{,}27$). In the **4a-c** series one can observe the decrease in conversion with an increase in molecule size. Among the macromonomers of largest size, the elasticity of polyether bonds should be taken into consideration as a main reason of high double bonds conversion because this elasticity leads to low rotation barrier and ease of conformation changes. Moreover, the hyperbranched structure increases the possibility of intramolecular polymerization occurring. This can be observed by an increase in the conversion of double bonds, while the viscosity increases slower that in case of typical crosslinking process. The expansion of polymeric network is in this case slower.

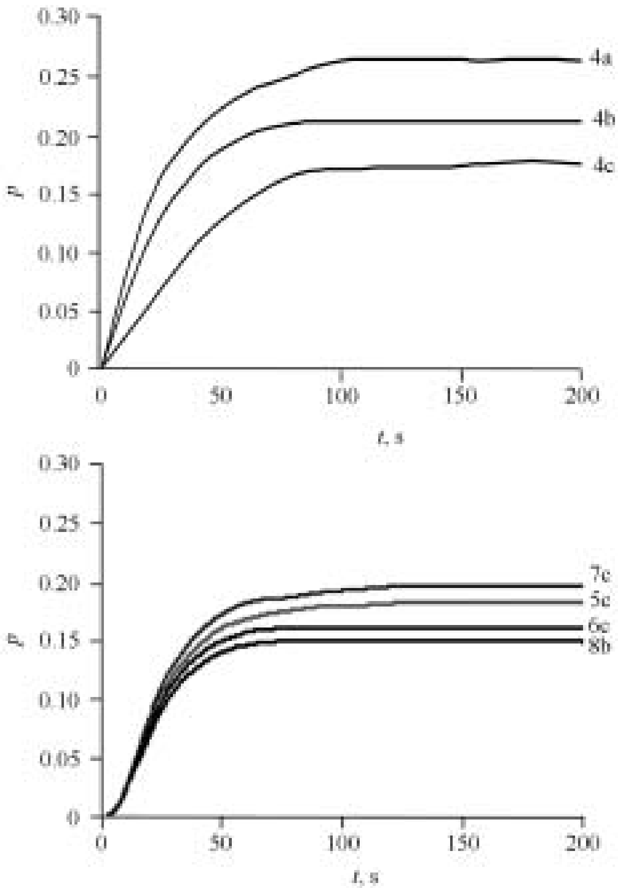


Fig. 8. Conversion (p) of methacrylic groups versus time (t) (2 % of Irgacuce 651, 25 °C, an air atmosphere, different samples of polymethacrylate resins)

It can be seen from Fig. 8 that the double number of urethane bonds in the monomer (**8b**) does not increase the conversion of the double bonds in presence of an air. The conversions obtained for monomers **5c-7c** were of the same level. This is important since the urethane linkages in monomers **5c-7c** were obtained by the environmentally friendly non-isocyanate method. The monomers **4a-4b** showed the highest double bonds conversions due to small molecule sizes.

CONCLUSIONS

Two types of multimethacrylate resins were synthesized. One based on bisphenol A core and polyether branches and the other one based on trimethylolpropane (TMP) and polyether structure containing urethane bonds obtained with isocyanate or non-isocyanate urethane syntheses methods. The functionalization of hyperbranched polymers resulted in new materials showing both: low viscosity and low oxygen inhibition. The monomers were characterized by spectroscopic methods. The conversion of double bonds was investigated by FTIR. The physical properties of multimethacrylate resins such as viscosity, density and polymerization shrinkage were determined. Based on the obtained results it was shown that such resins are attractive materials to use in composites, especially dental composites.

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