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Monomers for adhesive polymers

1. Synthesis and radical polymerization of bicyclic monomers

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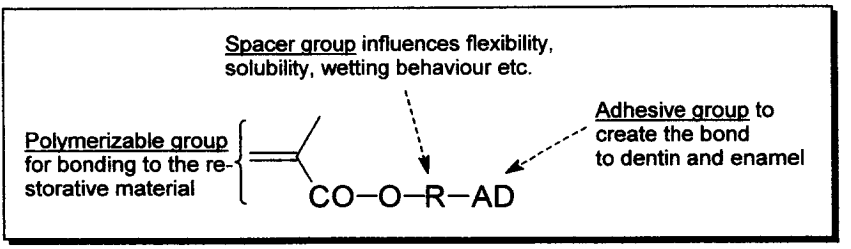
Summary

Bicyclic functionalized methacrylates were synthesized by a Diels-Alder reaction of furfuryl methacrylate with maleic anhydride and subsequent conversion to the corresponding monomers containing carboxylic groups. The structure of the bicyclic functionalized methacrylates was confirmed by elemental analysis, IR, ^{1}H NMR and ^{13}C NMR spectroscopy. The radical photopolymerization of bicyclic monomethacrylates in dimethylformamide with 2,2`-azobisisobutyronitrile (AIBN) resulted in soluble polymers while a bicyclic dimethacrylate resulted in a crosslinked polymer.

Introduction

To achieve a strong bond between the filling material and the tooth substance (dentin and enamel), coupling agents are used in restorative dentistry [1,2]. In general, these coupling agents are bifunctional molecules, containing a) a polymerizable group, which can react with the restorative material by copolymerization, b) an adhesive group AD, such as an ionic or chelating group, capable to react with the tooth substance, and c) a spacer R, designed to influence the hydrophilicity, flexibility and the wetting properties of the adhesive monomer:



Polar bicyclic compounds with 7-oxabicyclo[2.2.1]hept-2-enyl groups attract interest as monomers for aqueous ring-opening metathesis polymerization

catalyzed by ruthenium trichloride [3,4]. Examples of 7-oxabicyclo[2.2.1]hept-2-enyl or 7-oxabicyclo[2.2.1]hepta-2,5-dienyl compounds which also contain radical polymerizable methacrylic groups are only few and concern only 7-oxa-5,6-dicarboxyimide-N-yl-bicyclo-[2.2.1]hept-2-ene acrylate [5] and 1-[2-(propenoyl-oxy)ethyl]-7-oxabicyclo[2.2.1]-hepta-2,5-dien-2,3-dicarboxylic acid dimethyl ester [6].

In previous papers, we reported about the reaction behaviour of polymerizable β-keto esters [7], which are able both to chelate calcium ions and form enamins with amino acids. Therefore they are showing a good adhesion on dentin [8].

In this paper, the synthesis, characterization and polymerization of bicyclic monomers formed by a Diels-Alder reaction of furfuryl methacrylate with maleic anhydride and the subsequent conversion to various carboxylic group containing monomers showing adhesion on dentin are described.

Experimental

Materials

Butyl acetate, ethylene glycol, glycerol, triethylene glycol, dimethylformamide (DMF) and tetrahydrofuran (THF) were dried over molecular sieves. Furfuryl methacrylate (Aldrich) and maleic anhydride were used without further purification. Unless stated otherwise, all other reagents were purchased from Fluka. 2,2`-Azoisobutyronitrile (AIBN) was purified by recrystallization.

Syntheses

1-(Methacryloyloxymethyl)-7-oxabicyclo[2.2.1]hept-5-ene-2,3-*exo,exo*-dicarboxylic acid anhydride **1**:

A mixture of 166.0 g (1.0 mol) furfuryl methacrylate, 107.8 g (1.1 mol) of maleic anhydride and 0.1 g of hydroquinone monomethyl ether (MEHQ, inhibitor) were dissolved in 250 mL butyl acetate and stirred for 2 days at room temperature. The formed precipitate was filtered off, washed with 100 mL butyl acetate and dried under vacuum to constant weight resulting in about 140 g of the product. The mother liquor underwent further stirring. After about 3 weeks, additional 60 g of the product were isolated as described above. Altogether about 200 g (76% yield) of colourless crystals (m.p.: 109-110 °C) were obtained.

$C_{13}H_{12}O_6$ (264.2) Calc.: C 59.08 H 4.58
Found.: C 58.89 H 4.61

^{1}H NMR (300 MHz, $CDCl_3$, δ (ppm)): 1.91 (s,3H,CH_3); 3.42 and 3.52 (d,2x1H,H-2,3-exo); 4.55 and 4.83 (d,2x1H,CH_2O); 5.33 (s,1H,H-4); 5.67 and 6.04 (s,2x1H, CH_2=); 6.52 (d,1H,H-6) and 6.64 (s,1H,H-5); assignment with COSY.

^{13}C NMR (75 MHz, $CDCl_3$, δ (ppm)): 17.99 (CH_3); 50.07 and 51.82 (C-2,3); 61.00 (CH_2O); 81.69 (C-4); 89.97 (C-1); 126.17 (CH_2=); 135.36 (CH_2=C); 137.06 and 137.72 (C-5,6); 165.89; 169,39 and 170.77 (alle C=O); assignment with 2D-inadequate and DEPT.

IR (film, cm^{-1}): 570 (w), 655 (m), 705 (m), 735 (w), 815 (w), 855 (m), 880 (m), 925 (s,sh), 980 (s,sh), 1025 (w), 1080 (s,sh), 1110 (w), 1145 (w), 1165 (s), 1190 (w), 1230 (s), 1275 (m), 1330 (m,sh), 1370 (w), 1400 (w, sh), 1430 (w), 1450 (w), 1630 (w), 1720 (s), 1780 (s), 1860 (m, sh), 2960 (w), 3025 (w) and 3100 (w).

1-(Methacryloyloxymethyl)-7-oxabicyclo[2.2.1]hept-5-ene-2,3-*exo,exo*-dicarboxylic acid **2**:

To a solution of 0.74 g (41 mmol) of water and 0.01 g of phenothiazine (inhibitor) in 50 mL THF, 10.6 g (40 mmol) of **1** was added. The mixture was cooled to 5-10 °C and a solution of 8.0 g (80 mmol) of triethylamine (TEA) and 0.25 g of 4-dimethylaminopyridine (DMAP) in 15 mL THF was added dropwise under stirring. After stirring at room temperature, the resulting reaction mixture was poured into 115 mL of 2N HCl. The aqueous solution was separated and extracted 3 times with 100 mL diethyl ether. The combined organic extracts were dried over anhydrous sodium sulphate. The solvent was removed under reduced pressure at a maximum temperature of 30 °C. The remaining oil was further dried under high vacuum. The formed solid (about 8.5 g) was washed with butyl acetate and dried under vacuum to constant weight obtaining 6.1 g (54% yield) of colourless crystals (m.p.: 118-120 °C).

$C_{13}H_{14}O_7$ (282.2) Calc.: C 55.32 H 5.00
Found.: C 55.46 H 5.14

^{1}H NMR (300 MHz, DMSO-d_6, δ (ppm)): 1.86 (s,3H,CH_3); 2.82 (s,2H,H-2,3); 4.48 and 4.61 (d,2x1H,CH_2O); 5.13 (s,1H,H-4); 5.67 and 6.00 (s,2x1H,CH_2=); 6.38 (d,1H, H-6); 6.50 (m,1H,H-5) and 12.35 (b,2H,COOH).

^{13}C NMR (75 MHz, DMSO-d_6, δ (ppm)): 17.86 (CH_3); 47.96 and 48.85 (C-2,3); 61.88 (CH_2O); 79.45 (C-4); 88.61 (C-1); 126.31 (CH_2=); 135.48 (CH_2=C); 136.58 and 137.59 (C-5,6); 166.16; 171.81 and 172.20 (all C=O).

IR (film, cm^{-1}): 520 (w), 593 (w), 647 (w), 720 (m), 816 (w), 895 (w), 934 (m), 959 (m), 990 (w), 1019 (w), 1078 (w); 1173 (s), 1248 (m), 1305 (m), 1334 (m), 1394 (m, sh), 1633 (m), 1740 (s, sh), 3200 (b) and 3428 (b).

1-(Methacryloyloxymethyl)-7-oxabicyclo[2.2.1]hept-5-ene-2,3-*exo,exo*-dicarboxylic acid mono(2-hydroxyethyl) ester **3**:

To a solution of 2.6 g (41 mmol) of ethylene glycol and 0.01 g of phenothiazine in 50 mL THF, 10.6 g (40 mmol) of **1** was added. The suspension was cooled to -15 °C and a solution of 4.0 g (40 mmol) of TEA and 0.25 g DMAP in 10 mL THF were added dropwise under stirring over a period of 45 minutes. The mixture was left to warm to room temperature, while stirring continued for another 5 h to complete the reaction. The reaction product was taken up in a mixture of 100 mL of a 10% aqueous $NaHCO_3$ solution and 50 mL of diethyl ether. The aqueous phase was separated, washed again with 50 mL of diethyl ether and then adjusted to a pH of about 1-2 with approx. 10 mL of concentrated hydrochloric acid. The obtained oil was taken up in 300 mL diethyl ether and insoluble material were removed from the solution by filtration. The filtrate was dried over anhydrous sodium sulphate, evaporated under vacuum at a maximum temperature of 30 °C. The remaining solid was dried under vacuum to constant weight resulting in 6.1 g (51% yield) of a colourless sticky product.

$C_{15}H_{18}O_8$ (326.3) Calc.: C 55.21 H 5.56
Found.: C 55.45 H 5.63

^{1}H NMR (300 MHz, DMSO-d_6, δ (ppm)): 1.87 (s,3H,CH_3); 2.96-3.12 (m,2x1H,H-2,3); 3.70-3.90 (m,2H,CH_2OH); 4.05-4.35 (m,2H,$COOCH_2$); 4.55-4.75 (d,2H, methacryloyl-OCH_2); 5.47 (d,1H,H-4); 5.78 and 6.10 (s,2x1H,CH_2=); 6.42-6.68 (m,2H,H-5,6) and 7.80 (s,b, 2H,OH H/D-exchange).

IR (film, cm^{-1}): 408 (w), 512 (w), 594 (w), 715 (m), 814 (m), 876 (b, w), 934 (m, sh), 1022 (m, sh), 1166 (s,sh), 1301 (s, sh), 1382 (s, sh), 1451 (m), 1635 (m), 1726 (s) and 2960 (s, b).

1,2-Bis-[1-(methacryloyloxymethyl)-7-oxabicyclo[2.2.1]hept-5-ene-2(3)-*exo*-dicarboxylic acid-3(2)-*exo*-carbonyloxy]ethane **4**:

Analogous to the synthesis of **3**, 1.25 g (20 mmol) of ethylene glycol was brought to react with 10.6 g (40 mmol) of **1**. 8.0 g (68% yield) of a highly viscous liquid was obtained.

$C_{28}H_{30}O_{14}$ (590.5) Calc.: C 56.95 H 5.12
Found.: C 56.86 H 5.31

^{1}H NMR (300 MHz, DMSO-d_6, δ (ppm)): 1.87 (s,6H,CH_3); 3.00-3.20 (m,4H,H-2,3); 3.95-4.30 (m,4H,CH_2CH_2); 4.41-4.60 (m,4H,methacryloyl-OCH_2); 5.27-5.50 (m,2H,H-4); 5.68 and 6.02 (s,2x1H,CH_2=); 6.3-6.6 (m,4H,H-5,6) and 12.5 (s,b,2H,COOH).
IR (film, cm^{-1}): 532 (w), 596 (w), 668 (w), 716 (m), 814 (m), 856 (b, w), 934 (m, sh), 1014 (m, sh), 1166 (s,sh), 1299 (s, sh), 1378 (s, sh), 1453 (m), 1636 (m), 1724 (s) and 2960 (s, b).

1-(Methacryloyloxymethyl)-7-oxabicyclo[2.2.1]hept-5-ene-2,3-*exo,exo*-dicarboxylic acid mono(2,3-dihydroxypropyl) ester **5**:

The reaction of 11.3 g (0.12 mol) of anhydrous glycerol with 10.6 g (40 mmol) of **1** was carried out analogous to the synthesis of **3**. 1.3 g (9% yield) of a highly viscous liquid was obtained.

$C_{16}H_{20}O_9$ (356.3) Calc.: C 53.93 H 5.66
Found.: C 54.22 H 5.67

^{1}H NMR (90 MHz, $CDCl_3$, δ (ppm)): 1.98 (s,3H,CH_3); 3.08 (s,2H,H-2,3); 3.50-4.45 (m,5H,CH_2CHCH_2);4.70 (s,2H,methacryloyl-OCH_2), 5.47 (s,1H,H-4); 5.67 and 6.18 (s,2x1H,CH_2=) and 6,35-6,95 (m,b,5H,H-5,6+OH,H/D-exchange).
IR (film, cm^{-1}): 716 (w), 814 (w), 860 (w, sh), 934 (m, sh), 985 (w), 1023 (w, sh), 1115 (w), 1169 (s, b), 1300 (m sh), 1405 (w, sh)1455 (w, sh), 1636 (w), 1732 (s, b), 2958 (s, sh) and 3474 (w, b)

1-(Methacryloyloxymethyl)-7-oxabicyclo[2.2.1]hept-5-ene-2,3-*exo,exo*-dicarboxylic acid mono(3-hydroxy-2,2-dimethylpropyl) ester **6**:

The reaction of 12.8 g (0.12 mol) of anhydrous 2,2-dimethyl-1,3-propanediol with 10.6 g (40 mmol) of **1** was carried out analogous to the synthesis of **3**. 3.0 g (20% yield) of colourless crystals (m.p.: 108°C) was obtained.

$C_{18}H_{24}O_8$ (368.4) Calc.: C 58.69 H 6.57
Found.: C 58.71 H 6.53

^{1}H NMR (300 MHz, $CDCl_3$, δ (ppm)): 0.85 and 0.89 (s,2x3H,CH_3-propyl); 1.94 (s,3H,$\underline{CH_3}$-C=CH_2); 2.90 and 3.05 (d,2x1H,H-2,3); 3.30 and 3.40 (d,2x1H, CH_2OH); 3.78 and 3.89 (d,2x1H,$C\underline{H_2}C(CH_3)_2$); 4.57 and 4.77 (d,2x1H, methacryloyl-OCH_2); 5.46 (s,1H,H-4); 5.60 and 6.14 (s,2x1H,CH_2=); 6.41 and 6.51 (d,2x1 H,H-5,6) and 8.0 (s,b,2H,OH+COOH).
^{13}C NMR (75 MHz, $CDCl_3$, δ (ppm)): 18.2 ($\underline{CH_3}$-C=CH_2); 21.6 (C($\underline{CH_3}$)$_2$); 35.4 ($\underline{C}(CH_3)_2$); 48.9 and 49.6 (C-2,3); 61.9 (methacryloyl-O$\underline{C}H_2$); 66.9 and 69.6 ($CH_2\underline{O}$-propyl); 79.9 (C-4); 89.3 (C-1); 126.6 (C=$\underline{CH_2}$); 135.5 ($\underline{C}$=CH_2); 137.2 and 137.3 (C-5,6); 166.8; 171.2 and 174.6 (all C=O).
IR (film, cm^{-1}): 726 (w), 814 (w), 932 (w, sh), 1027 (w, sh), 1178 (m, sh), 1267 (w), 1302 (w), 1383 (w), 1636 (w), 1720 (s, sh), 2961 (w, sh) and 3488(m, b).

1-(Methacryloyloxymethyl)-7-oxabicyclo[2.2.1]hept-5-ene-2,3-*exo*,*exo*-dicarboxylic acid mono(8-hydroxy-3,6-dioxaoctyl) ester **7**:

The reaction of 6.2 g (41 mmol) of anhydrous triethylene glycol with 10.6 g (40 mmol) of **1** was carried out analogous to the synthesis of **3**. 3.2 g (20% yield) of a viscous oil was obtained.

$C_{19}H_{26}O_{10}$ (414.4) Calc.: C 55.07 H 6.32
Found.: C 55.22 H 6.52

^{1}H NMR (90 MHz, $CDCl_3$, δ (ppm)): 1.98 (s,3H,CH_3); 2.9-3.1 (m,2H,H-2,3); 3.55-3.9 (m,10H,OCH_2CH_2O); 4.1-4.5 (m,2H,COOCH_2CH_2); 4.55-4.95 (m, methacryloyl-OCH_2.); 5.45 (d,1H,H-4); 5.66 and 6.18 (s,2x1H,CH_2=); 6.40-6.68 (m,2H,H-5,6) and 6.90 (s,2H,COOH+OH).
IR (film, cm^{-1}): 490 (s,b), 715 (m), 814 (m), 877 (m), 935 (s), 990 (s), 1049 (s,sh), 1166 (s,sh) 1300 (s,sh), 1400 (s), 1452 (s), 1636 (m), 1727 (s), 2963 (s,sh) and 3500 (s,b).

Polymerization

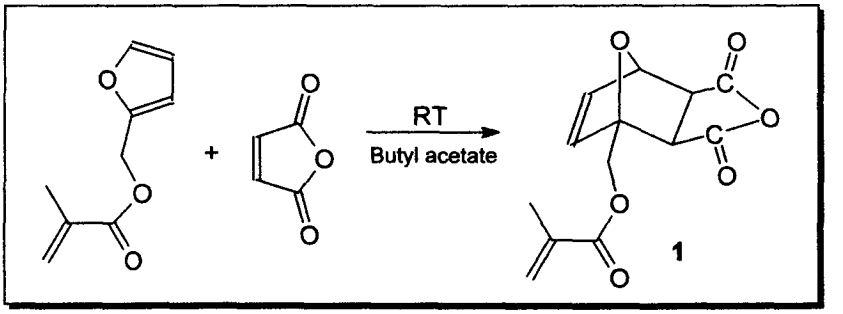
Radical polymerization was carried out in a solution of DMF in sealed glass tubes containing a given amount of AIBN dissolved in DMF. Subsequently, the monomer and a Teflon-coated magnetic stirrer were added. The tubes were sealed and degassed through three freeze-thaw cycles (liquid nitrogen), before they were irradiated with UV light using a SUNTEST CPS (Heraeus) rapid radiation table top unit at 25 °C in a thermostat-controlled stirring bath. The polymerization was terminated after 1 h by the addition of large excess diethyl ether to the polymerization mixture to precipitate the polymer. The monomer conversion was calculated from the gravimetrically determined yields of the dried polymers.

Measurements

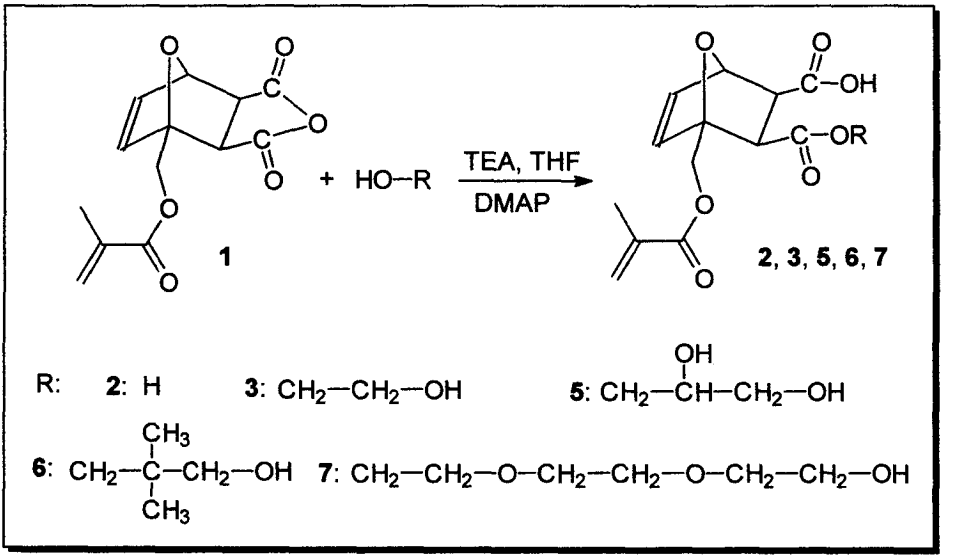
^{1}H NMR measurements were recorded on an EM 390 (Perkin-Elmer, 90 MHz), or AC 300F (Bruker, 300 MHz), using tetramethylsilane (TMS) as the standard. ^{13}C NMR spectroscopic measurements were performed with a AC 300F spectrometer (Bruker, 75 MHz), using $CDCl_3$ or dimethylsulfoxide-d_6 as a solvent. An FT-IR spectrometer 1600 (Perkin-Elmer) was used to record IR spectra. The number-average molecular weights of polymers were determined by GPC, using an isocratic pump IsoChrom (Spectra-Physics) and THF as an eluent, a detector RI-4 (Varian) and columns calibrated with poly(methyl methacrylate) standards. The elemental analysis were performed with an elemental analyzer EA 1108 (Fisons Instr.). The shear bond strengths were measured using a universal testing machine (Zwick) at a cross head speed of 0.8 mm/min. as previously described [8].

Results and Discussion

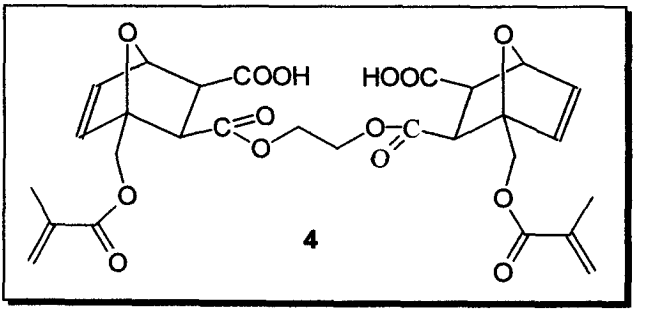
The bicyclic monomeric anhydride **1** was prepared by a Diels-Alder reaction of furfuryl methacrylate and maleic anhydride as a crystalline compound in a yield of 76%:



The bicyclic monomers **2**, **3**, **5**, **6** and **7** were obtained by the reaction of water or the corresponding alcohols with the anhydride **1**:



Using ethylene glycol and **1** in molar ratio of 1:1 the dimethacrylate **4** was formed:



The characterization of the new bicyclic monomers was carried out by ^{1}H NMR, ^{13}C NMR, IR spectroscopy and elemental analysis. The spectral data are in agreement with the expected structure. For example, in case of monomer **2**,

the formation of the bicyclic unit is supported by the presence of the peaks assign-able to =CH of the 7-oxabicyclo[2.2.1]hept-5-ene unit at 6.38 and 6.50 ppm in the ^{1}H NMR spectrum. The chemical shift of the singuletts of the methylene protons of the methacrylic group are at 5.61 and 6.00 ppm in the ^{1}H NMR spectrum whereas the signal arising from carbon atoms 5 and 6 are at about 136.53 and 137.59 ppm in the ^{13}C NMR spectrum. Unfortunately, the NMR spectra do not offer the regioselectivity of the esterification. However, it can be assumed that mixtures of isomers with the ester group in the 2 or 3 position are formed. The synthesized bicyclic monomers are colourless compounds which are well-soluble in polar solvents, like for example methanol, ethanol, aceton or DMF, and also in mixtures of these solvents with water, which is very important for dental application.

The radical photopolymerization of some selected bicyclic monomers was carried out in the presence of AIBN at 25 °C under irradiation with UV-light. Soluble polymerizates of the monomers **1-3** with a number-average molecular weight of 4300 to 11100 g/mol were obtained. In contrast, the radical polymerization of the dimethacrylate **4** yielded a crosslinked polymer (Tab. 1).

Table 1 Polymerization of bicyclic monomers (1.0 mol/L) in the presence AIBN (0.02 mol/L) under irradiation with UV-light at 25 °C, polymerization time 1 h

Monomer	Monomer conversion (%)	M_n (g/mol)
1	53.0	11100
2	14.4	4300
3	74.2	8100
4	98,2	-[a)]

[a)] Insoluble polymer

Solutions of the new bicyclic monomers in ethanol or acetone could be used as dentin primer and result in shear bond strengths of corresponding adhesives of about 19-21 MPa [8].

Finally, it should be mentioned that the synthesized bicyclic monomers are hybride monomers capable of both a radical vinyl polymerization and a ring-opening metathesis polymerization. This could be of interest for dual-curing systems or the step-by-step synthesis of polymer networks

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