

Novel Routes to Polyelectrolytes and Reactive Polymers Via ROMP

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ABSTRACT: Various derivatives of norbornene and 7-oxanorbornenedicarboxylic acid have been synthesized and polymerized via Ring Opening Metathesis Polymerization (ROMP). The introduction of tetrahydropyranyl moieties as protection groups opened a way for the synthesis of polyelectrolytes through well-defined transition metal alkylidene catalysts that are usually deactivated by reactions with acidic protons. The incorporation of methacrylate groups in the polycarboxylic acids was achieved either by copolymerization of methacrylate functionalized norbornene or 7-oxanorbornene derivatives, or by the polymer analogous reaction of the polycarboxylic acids with glycidyl methacrylate (GMA). These materials are soluble in water as well as in ethanol and undergo cross-linking reactions initiated by UV light. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 78: 47–60, 2000

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INTRODUCTION

Polyelectrolytes like polycarboxylic acids have gained increasing interest. Until now mainly poly(acrylic acid) and poly(methacrylic acid) as well as homo- and copolymers of maleic acid have been used.^{1–3} Recently new applications have been found in the production of layered materials. In such cases a connection of the layers by photo-cross-linking is desirable.

Ring Opening Metathesis Polymerization (ROMP) of cyclic and bicyclic alkenylcarboxylic acid derivatives has been shown to be an alternative method to obtain new polyelectrolytes.

So far various examples of monomers containing carboxylic acid and carboxylic anhydride

groups polymerized in aqueous media by transition metal halides such as $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$, $\text{OsCl}_3 \cdot 3\text{H}_2\text{O}$, $\text{IrCl}_3 \cdot 3\text{H}_2\text{O}$, and $\text{Ru}(\text{tos})_2 \cdot 6\text{H}_2\text{O}$ have been reported.^{4–7} However, the polymers obtained by these polymerizations usually show high molecular weight, high polydispersities, sometimes poor solubility, cross-linking from ill defined polymerization mechanisms, and coloration due to high-transition metal content (0.1–0.3%). Control of the molecular weight by addition of chain transfer agents (CTA) can be achieved to a certain extent but the results are barely reproducible. The results of Novak⁸ and Maughon⁹ are in agreement with this observations.

The introduction of new, well-defined catalyst systems for metathesis reactions has opened ways to highly functionalized polymers.¹⁰ Molybdenum-based systems of the type $\text{Mo}(\text{NAr})(\text{CHR}')(\text{OR}_2)$ by Murdzek and Schrock¹¹ and ruthenium alkylidene systems by Grubbs¹² proved

Dedicated to Prof. Dr. Klaus Hummel on occasion of his 70th birthday.

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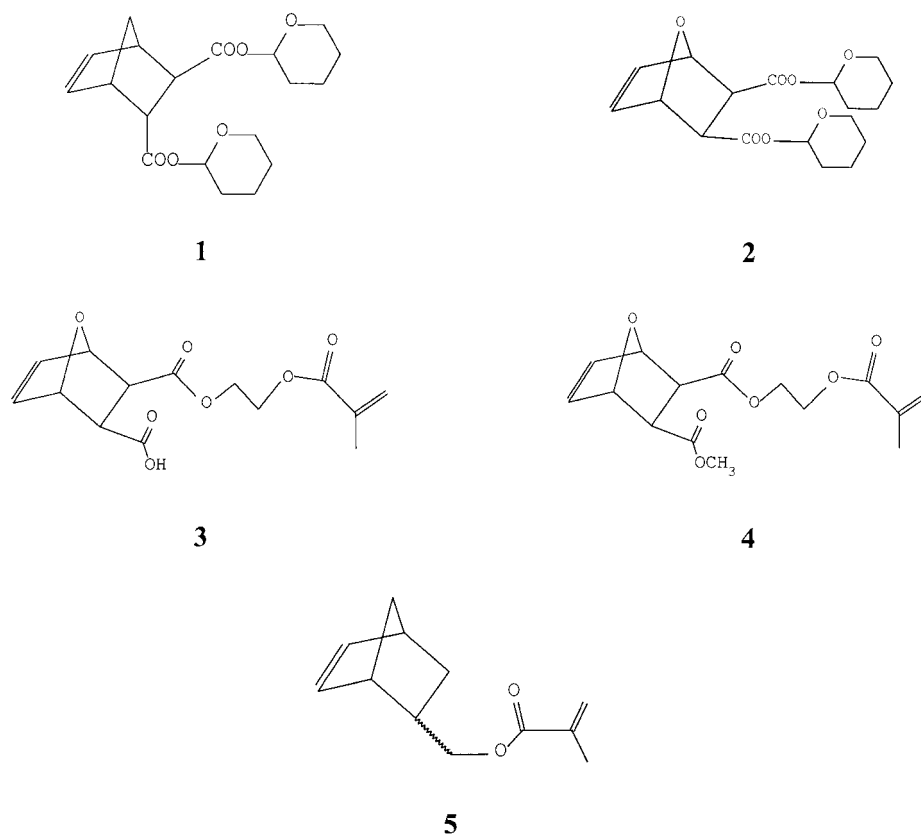


Figure 1 Synthesized monomers.

to be valuable tools in the synthesis of new polymers. The high tolerance of these systems towards various nucleophilic functional groups such as ethers,¹³ esters,¹⁴ amides,^{15,16} amines,^{17,18} and sulfides¹⁹ exist widely in the literature, nevertheless the polymerization of monomers with acidic functionalities still seems to be a challenge. Therefore we decided to protect the carboxylic acid functionality with a suitable protection group. Such a protection group should not interfere with the ROMP and be stable enough to allow proper purification of the monomers and polymers. Also it should offer an easy and clean deprotection from the precursor polymer in a polymer analogous reaction.

The aim of this work was to find a catalyst/monomer system that would allow us to obtain reasonable amounts (on a 10-g scale) of a polyelectrolyte with low metal contamination. Preferred catalysts are the fluorinated type of Schrock's molybdenum alkylidene catalyst ($\text{Mo}(\text{NAr})\text{CH-t-Butyl}(\text{OCCH}_3(\text{CF}_3)_2)^{20,21}$ abbreviated as $\text{Mo}=\text{C}$ and Grubbs' ruthenium alkylidene catalyst ($\text{Cl}_2\text{RuCHC}_6\text{H}_5(\text{PCy}_3)^{22}$ abbrevi-

ated as $\text{Ru}=\text{C}$). The monomers 1-5 are derivatives of norbornene, norbornene dicarboxylic acid, and 7-oxanorbornene dicarboxylic acid that contain a suitable protection group at the carboxylic acid functionality due to the sensitivity of the catalysts towards acidic protons. The monomers are listed in Figure 1.

Furthermore we wanted to obtain polymers containing another polymerizable functionality in order to produce cross-linked materials in a second polymerization step. Due to negative neighboring group effects, methacrylic acids derivatives do not react with the catalyst system in condensation reactions to give a stable catalyst complex or neither act as CTAs.²³ By copolymerizing norbornenes bearing a methacrylic acid functionality and a protected norbornene dicarboxylic acid we synthesized water soluble polyelectrolytes that can be cross-linked in a second step to form hydrogels.

A different approach to obtain hydrogels via ROMP is the polymerization of norbornene dicarboxylic acid anhydride in presence of diols,²⁴ fol-

lowed by hydrolysis of the anhydride groups in a polymer analogous reaction.

EXPERIMENTAL

Materials

Furane, fumaric acid, maleic acid, 3,4-dihydro-2H-pyrane, pyridinium tosylate, *p*-toluenesulfonic acid, methyl iodide, 2-hydroxyethyl methacrylate HEMA, glycidyl methacrylate, K₂CO₃, Na₂SO₄ basic aluminum oxide type 5016 A and all other chemicals and solvents were used as obtained from Fluka. Cyclopentadiene was cracked freshly from dicyclopentadiene. Flash chromatography was performed using silica gel K60 from Merck.

Deuterated solvents such as CDCl₃, toluene-d₈, benzene-d₆, and dimethyl sulfoxide (DMSO)-d₆ for NMR measurements were obtained from Chemotrade Inc. and dried by passing through basic aluminum oxide type 5016 A.

Solvents used for polymerization reactions were obtained from Fluka and dried over sodium/potassium alloy (tetrahydrofuran [THF]) and phosphorous pentoxide (chlorobenzene, dichloromethane), respectively.

Molybdenum and ruthenium catalysts were prepared according to published procedures.^{19–21}

Methods

NMR spectra were recorded on a Varian, Gemini 200 MHz instrument. Gel permeation chromatography (GPC) were done at flow rates of 1 mL/min of THF using columns from polymer standard services packed with SDV gels and simultaneous viscosity and refractive index (RI) detection. Molecular weights were determined versus polystyrene standards.

Monomer Synthesis

exo,endo-bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic acid (**a**), exo-7-oxabicyclo [2.2.1]hept-5-ene-2,3-dicarboxylic acid anhydride (**b**), and exo/exo-7-oxabicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic acid (**c**) were synthesized according to the literature.^{25–27}

(**a**): ¹H-NMR (DMSO-d₆): (δ = 12.5–12.0 (2H, COOH), 6.3 (1H, dd, H-6), 6.0 (1H, dd, H-5), 3.2 (2H, bs, H-4, H-3), 3.1 (1H, bs, H-1), 2.6 (1H, bs, H-2), 1.6 (1H, d,

H-7_{anti}), 1.3 (1H, dd, H-7_{syn}), melting point (mp) = 186–189°C.

(**b**): ¹H-NMR (DMSO-d₆): (δ = 6.60 (2H, s, H-1, H-2), 5.28 (2H, s, H-1, H-4), 3.31 (2H, s, H-2, H-3), mp = 118–121°C.

(**c**): ¹H-NMR (DMSO-d₆): (δ = 9–6.5 (2H, COOH), 6.50 (2H, s, H-5, H-6), 4.95 (2H, s, H-1, H-4), 2.60 (2H, s, H-2, H-3), mp = 146–148°C

Di(tetrahydropyranyl) exo,endo-bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylate 1

Thirty-six grams (200 mmol) of exo,endo-bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic acid and 2.0 g (8 mmol) of pyridinium tosylate were suspended in 700 mL of dichloromethane and 25 g (300 mmol) of 3,4-dihydro-2H-pyrane were added slowly. The dicarboxylic acid dissolved during of the reaction. After 16 h the solution was washed twice with 200 mL of a 5% solution of sodium hydrogen carbonate and then with 100 mL water. The organic phase was dried with anhydrous sodium sulfate. The solvent and excess of 3,4-dihydro-2H-pyrane were removed under reduced pressure. The oily residue was dissolved in 600 mL hot *n*-hexane, filtered through basic aluminum oxide, and the volume was reduced to 400 mL and the product crystallized at –30°C.

Yield: 59.5 g (85%) ¹H-NMR (CDCl₃): δ 6.27 (1H, dd, H-6), 6.08 (1H, dd, H-5), 5.99, 5.91 (1H, bs, OCHO), 3.85, 3.65 (2H, m, OCH₂C), 3.42 (1H, ddd, H-3), 3.30 (1H, bs, H-4), 3.14 (1H, m, H-1), 2.74 (1H, m, H-2), 1.9–1.5 (13H, m, OCH₂(CH₂)₃, H-7_{anti}), 1.46 (1H, dd, H-7_{syn}).

¹³C-NMR (CDCl₃): δ 173.1 (C=O), 171.9 (C=O), 137.7 (C-6), 135.0 (C-5), 93.0 (O-CH-O), 63.0 (CH₂CH₂O), 48.1–47.3 (C-3, C-1, C-7, C-2), 47.2 (C-4), 29.2 (OCHCH₂CH₂), 25.0 (OCHCH₂-CH₂), 18.5 (OCH₂CH₂CH₂).

Di(tetrahydropyranyl)-exo/exo-7-oxabicyclo[2.2.1]hept-5-ene-2,3-dicarboxylate 2

We dispersed 18.4 g (100 mmol) *exo/exo*-7-oxabicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic acid in 100 mL dry dichloromethane and 1.0 g (4 mmol) pyridinium tosylate was added. We slowly added 25.2 g (300 mL) of 3,4-Dihydro-2H-pyrane. The solution became transparent. After 16 h, 50 mL dichloromethane were added and the solution was washed three times with 200 mL 5%

NaHCO₃ solution and then once with water. The organic phase was dried over Na₂SO₄ and the solvent was evaporated leaving a white, solid residue that was recrystallized twice from a mixture of 20 mL dichloromethane and 200 mL diethyl ether.

Yield: 25.2 g (71%). ¹H-NMR (CDCl₃): δ = 6.44 (2H, s, H-6, H-5), 5.94, (2H, m, OCHO), 5.25 (2H, m, H-4, H-1), 3.84 (2H, m, OCH₂C), 3.65 (2H, m, OCH₂C), 2.81 (2H, dpt, H-2, H-3), 1.9–1.4 (12H, m, OCH₂(CH₂)₃CH).

¹³C-NMR (CDCl₃): δ = 170.0 (C=O), 136.0 (C-6, C-5), 93.5 (O-CH-O), 81–80 (C-1, C4), 62.0 (CH₂-CH₂-O), 47.4–46.9 (C-3, C-2), 29.2 (OCH-CH₂CH₂), 25.0 (OCH₂CH₂CH₂), 18.5 (OCH₂CH₂-CH₂).

3-[2-(2-Methylpropenoxy)ethoxy]carbonyl-*exo*-*exo*-7-oxabicyclo[2.2.1]hept-5-ene-2-carboxylic acid 3

We dispersed 16.6 g (100 mmol) *exo*-7-oxabicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic acid anhydride in 130 mL ethyl acetate with 15 g (190 mmol) pyridine. Next, 23.6 g (200 mmol) 2-hydroxyethyl methacrylate (HEMA) were added dropwise. After 16 h the solution was washed three times with 100 mL 1N HCl, and the aqueous phases were extracted with 100 mL ethyl acetate. The combined organic phases were dried over Na₂SO₄ and evaporated to small volume. The oily residue was recrystallized from 200 mL diethyl ether to give **3**.

Yield: 11.5 g (40%). ¹H-NMR (CDCl₃): δ = 9.9 (1H, COOH), 6.45 (2H, m, H-6, H-5), 6.10 (1H, bs, CH₂= (Z)), 5.61 (1H, m, CH₂= (E)), 5.25 (2H, m, H-1, H-4), 4.32 (4H, bs, OCH₂CH₂O), 2.85 (2H, s, H-2, H-3), 1.95 (3H, m, CH₃).

¹³C-NMR (CDCl₃): δ = 176.12 (COOH), 171.38 (C-COO-CH₂), 167.37 (=C-COO-CH₂), 136.66; 136.62 (C-5; C-6) 135.90 (CH₃-C=), 126.31 (H₂C=), 88.68; 88.42 (C-1, C-4), 62.90; 62.39 (O-CH₂CH₂-O), 46.99; 46.95 (C-2, C-3).

2-[2-(2-Methylpropenoxy)ethyl]-3-methoxy-carbonyl-*exo*-*exo*-7-oxabicyclo [2.2.1]hept-5-ene-2-carboxylate 4

We added 5.7 g (20 mmol) **3** to a suspension of 4.2 g K₂CO₃ (30 mmol) in 50 mL acetone. After 20

min, 3.2 g (23 mmol) methyl iodide were added. After 16 h the solution was filtered and the acetone removed under reduced pressure. The residue was dissolved in dichloromethane, the solution was filtered again, and the solvent was removed under reduced pressure to give 5.14 g dark yellow oil, which was purified by column chromatography using silica gel and cyclohexane/ethyl acetate 30/1 als the eluant.

Yield: 4.5 g (73%), colorless oil. ¹H-NMR (CDCl₃): δ = 6.38 (2H, m, H-6, H-5), 6.05 (1H, bs, CH₂= (Z)), 5.61 (1H, m, CH₂= (E)), 5.15 (2H, m, H-1, H-4), 4.32 (4H, bs, OCH₂CH₂O), 3.65 (3H, s, OCH₃), 2.86 (2H, s, H-3, H-2), 1.95 (3H, m, CH₃). ¹³C-NMR (CDCl₃): δ = 171.80 (COO-CH₃), 171.36 (C-COO-CH₂), 167.35 (=C-COO-CH₂), 136.73; 136.65 (C-5; C-6) 135.97 (CH₃-C=), 126.15 (H₂C=), 80.60; 80.56 (C-1; C-4), 62.88; 62.33 (O-CH₂CH₂-O), 47.03; 46.79 (C-2, C-3).

[*exo*,*endo*-(Bicyclo[2.2.1]hept-2-ene-5-yl)methyl]-2-methyl propenoate 5

We dissolved 31.7 g (150 mmol) 2-(Hydroxymethyl)-5-norbornene, 26.8 g (270 mmol) triethylamine, and 0.01 g 2,6-di-tert.-butyl-4-methyl-phenol (0.045 mmol) in 400 mL dry THF under argon. After cooling to 0°C a solution of 29.5 g (280 mmol) methacrylic acid chloride in 100 mL dichloromethane was added dropwise. A white solid precipitated and the solution was warmed up to 5°C. After further warming to room temperature and stirring for another hour the solid was removed by filtration, the filtrate was washed with 150 mL acidic (pH 1–2, acidified with 1 mL HCl concentration), neutral, and then basic (pH 8–9, containing 2% w/v Na₂CO₃) NaCl-solution. The organic phase was dried over Na₂SO₄ and the solvent was evaporated. A distillation at 0.05 mbar and 110°C gave a colorless oil, which was not pure enough for ROMP. The pure product was obtained by column chromatography using cyclohexane as eluent.

Yield: 23.5 g (81%). ¹H-NMR (toluene-d₈): δ = 6.04 (1H, s, CH₂= (Z)), 5.87 (1H, dd, H-3), 5.73 (1H, dd, H-2), 5.07 (1H, pt, CH₂= (E)), 4.1–3.5 (2H, m, CH₂O, *exo* and *endo*), 2.64 (1H, bs, H-4), 2.50–2.48 (2H, bs, H-1, H-7_{syn}), 2.05 (1H, m, H-7_{anti}), 1.79 (3H, s, CH₃), 1.53 (1H, dt, H-5_{exo}), 1.30 (1H, d, H-6_{exo}), 0.92 (1H, d, H-6). ¹³C-NMR (CDCl₃): δ = 166.5 (C=O), 137.4 (C-2, C-3), 136.3 (CH₂=C-C), 132.3 (CH₂=), 67.8 (CH₂O), 49.5 (C-

Table I NMR Scale Polymerizations of Various Monomers with Ru=C and Mo=C in Benzene-d₆

Monomer	Ratio Mon./ Ru=C	Conversion by Ru=C (%)	Ratio Mon./ Mo=C	Conversion by Mo=C (%)
(1)	35	0	107	> 98%
(2)	28	> 98%	14	> 98%
(4)	25	> 98%	20	> 98%
(5)	42	30%	63	> 98%

7), 44.2 (C-1), 42.5 (C-4), 38.2 (C-6), 29.0 (C-5), 18.2 (CH₃).

Polymerizations: General Procedures

All polymerizations were carried out in dry solvents in a drybox under argon. Large-scale polymerizations were carried out in solutions containing ca. 10–25 wt % of monomer and the calculated amount of CTA, 1-hexene, to which a solution of the initiator was added at once. The polymers were obtained by precipitation from ethanol.

Cleavage of the tetrahydropyranyl groups was achieved by dropping the THF-solution into a stirred solution of 20 mg *p*-toluenesulfonic acid in ethanol. After stirring for 30 min at 60–70°C the poly(carboxylic acid)s were precipitated by adding the polymer-tetrahydrofuran solutions dropwise to 400 mL diethyl ether/pentane mixtures and dried in vacuo. These protected polymers were named with single letters, deprotected polymers with letter*, respectively.

Other chemicals were used as purchased; solvents used in the drybox were dried and degassed by standard methods.²⁸

Polymerizations on NMR-Scale

For preliminary investigations by ¹H-NMR spectroscopy a solution of the calculated amount of initiator dissolved in 0.2 mL of benzene-d₆ was prepared in an NMR tube to which a solution of ca. 50 mg of the monomer in 0.6 mL benzene-d₆ was added. Spectra were taken on a Varian Gem-

ini 200 MHz or a Bruker MSL 300 MHz after 90 min.

Conversions were determined by comparison of the integrals of the olefinic signals of the polymer formed to the signals of the remaining monomer (Table I). NMR scale polymerizations were carried out with the compounds **1**, **2**, **4**, and **5**.

Calculated amounts of the monomers together with 1-hexene were dissolved in benzene-d₆ and added to a solution of Mo=C in an NMR tube. Spectra were taken after 15 min and the ratios of the different repeating units in the polymer chain were determined by ¹H-NMR spectroscopy. Results are given in Table II.

Laboratory Scale Polymerizations

Polymerization of **1** in presence of 1-hexene as CTA

We dissolved 10.0 g (29 mmol) of **1** in 25 mL of THF together with 78 mg (0.93 mmol) of 1-hexene. Then a solution of 55 mg (0.079 mmol) of Mo=C in 1 mL of THF was added (monomer/CTA/initiator=800/31/1).

After 2 h the polymerization was quenched by addition of 0.3 mL of benzaldehyde, polymer **A** was precipitated in ethanol, dried in vacuo and characterized by GPC (see Table V) and ¹H-NMR spectroscopy.

Yield: 96%.

Polymer **A** was then dissolved in 5 mL of THF and dropped into 30 mL of hot ethanol containing

Table II Copolymerization of **1** and **5**

Used Monomers and Catalyst	Polymer C	Polymer D	Polymer E
(1)	0.07 mmol	0.047 mmol	0.094 mmol
(5)	0.07 mmol	0.095 mmol	0.047 mmol
Mo=C	0.0014 mmol	0.0014 mmol	0.0014 mmol
Ratio (1)/(5)/Mo=C	50/50/1	33/66/1	66/33/1

20 mg (0.11 mmol) of *p*-toluenesulfonic acid in order to cleave the tetrahydropyranyl groups. After 30 min the poly(carboxylic acid), polymer **A*** was precipitated from diethyl ether/pentane=1/5, dried in vacuo, and characterized (Fig. 2; see Table V).

Polymerization of 2

We dissolved 1.1 g (3.1 mmol) of **2** in 5 mL of THF and a solution of 10 mg (0.012 mmol) of Ru=C in 1 mL of THF was added (monomer/initiator = 259/1). The color changed from purple to pale brown. After 16 h the mixture was highly viscous, hence polymer **B** was precipitated from ethanol and characterized by GPC (see Table V) and ¹H-NMR spectroscopy.

Yield: 1.0 g (93%).

Polymer **B** was then dissolved in 5 mL THF and dropped into 30 mL hot ethanol containing 25 mg (0.14 mmol) of *p*-toluenesulfonic acid. After 30 min the polycarboxylic acid, polymer **B*** was precipitated from diethyl ether/pentane=1/3, then dried in vacuo and characterized (Fig. 3; see Table V).

Polymerization of 5

To a solution of 250 mg (1.30 mmol) **5** in 2.50 mL chlorobenzene, 6 mg (0.008 mmol) of Mo=C in chlorobenzene (1 mL) were added. An insoluble gel, polymer **C**, was formed almost immediately probably due to cross-linking via the methacrylate groups. Whether this occurred via a metathesis mechanism or by radical addition was not investigated. Repeated attempts to produce homopolymers of **5** always led to cross-linked polymers.

Copolymerization of 1 and 5 in presence of CTA (1-hexene)

We dissolved 10.0 g (28.5 mmol) of **1**, 1.4 g (7.3 mmol) of **5** and 31 mg (0.38 mol) of 1-hexene in 40 mL of chlorobenzene. A solution of 31 mg (0.044 mmol) of Mo=C was added and the mixture stirred for 4 h with the exclusion of light to avoid radical formation and additional polymerization of the methacrylate groups. Polymer **D** was precipitated from ethanol and the tetrahydropyranyl groups were removed as described above to give polymer **D***, which was characterized by GPC and ¹H-NMR spectroscopy (Fig. 4; see Table 5).

Yield: 4.5 g (68%).

Copolymerization of 2 and 4

We dissolved 600 mg (1.70 mmol) **2** and 160 mg (0.54 mmol) **4** in 3 mL chlorobenzene and a solution of 10 mg (0.012 mmol) Ru=C in 0.5 mL chlorobenzene was added. After 10 min the initially purple solution changed into pale brown and the mixture was polymerized for 18 h under exclusion of light. The polymer **E** was precipitated from ethanol, dried and characterized by GPC and NMR spectroscopy (see Table V and Fig. 7).

Cleavage of the tetrahydropyranyl groups as described above gave polymer **E***, which was precipitated from diethylether/pentane = 2/1, dried in vacuo, and characterized with GPC (see Table V) and NMR spectroscopy.

Yield: 330 mg (70%).

Investigation of the chain transfer by 1-hexene in the polymerization of 2 by Ru=C

Each polymerization was carried by treating 200 mg (0.567 mmol) of **2** with 0.093 mg (1.1×10^{-4} mmol) of Ru=C in presence of various amounts of 1-hexene as CTA in 1 mL dichloromethane. The ratio of **2**/(Ru=C) was 500, the ratios of 1-hexene/(Ru=C) were 0, 1, 2, 4, 9, and 19. To transfer the minimal amounts of 1-hexene a stock solution was prepared. 1-Hexene (45 mg) was diluted with 4.5 mL dichloromethane (10 mg/mL), 100 μ L of this solution were diluted with 900 μ L dichloromethane to obtain a solution with 1 mg 1-hexene/mL.

Molecular weights were determined by GPC. Results are listed in Table III (see also Fig. 6).

Investigation of the solubilities of the polymers

The different solubilities of the synthetic polymers in H₂O, 10% NaHCO₃ in H₂O, ethanol, THF, HEMA, ethyl acetate, and dichloromethane was examined. Typically 20 mg polymer were added to 2 mL of solvent in a vial and the mixture was stirred at room temperature for 24 h. The polymer was considered to be soluble if a clear, homogeneous solution was obtained.

Polymer-Analogous Reaction of ROMP Polymers

Modification of poly(*exo,endo*-norbornene-2,3-dicarboxylic acid) with glycidyl methacrylate

To a solution of 5.0 g (27.2 mmol) of poly(*exo,endo*-norbornene-2,3-dicarboxylic acid) **1** ($M_n = 14\ 000$

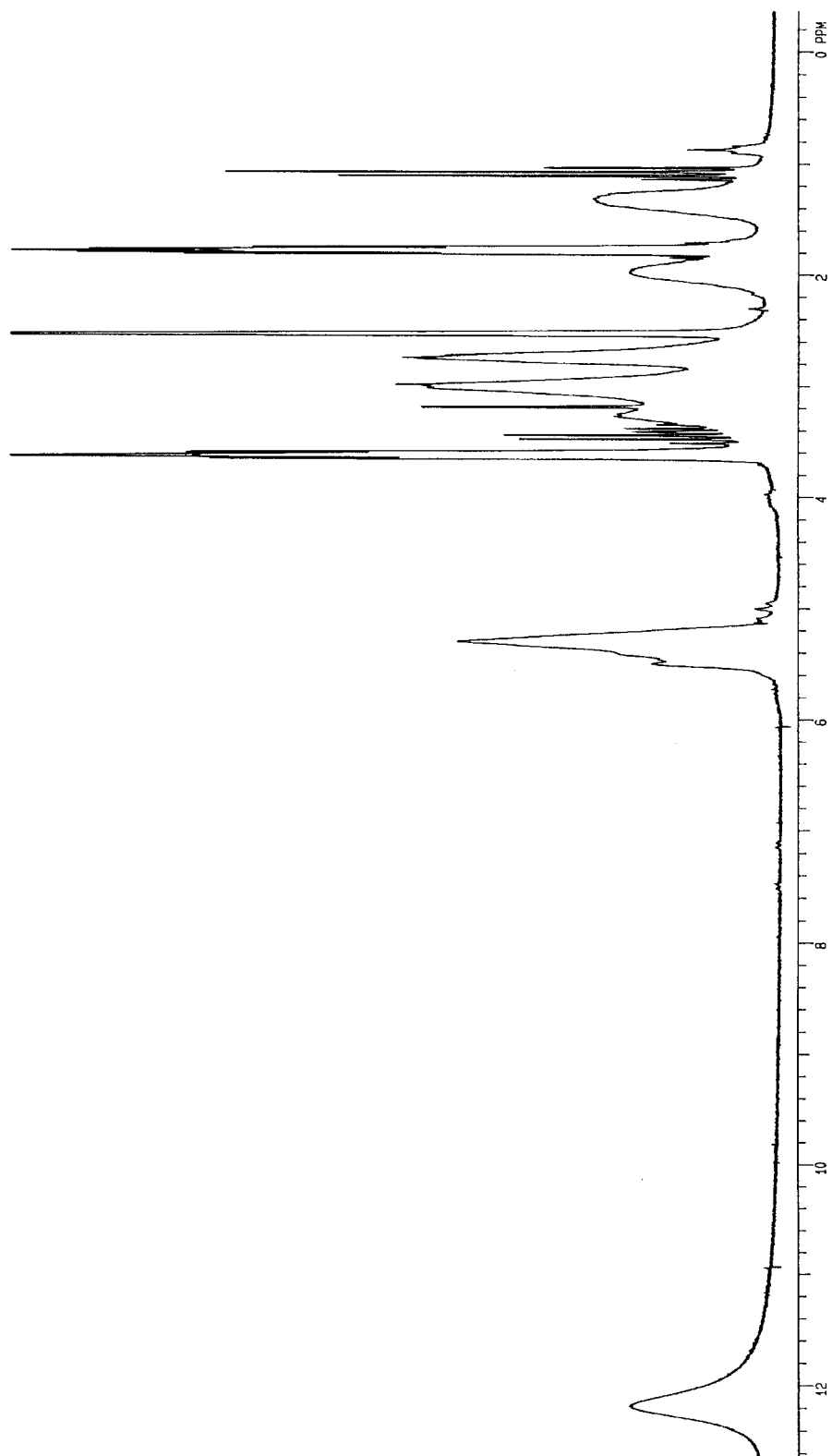


Figure 2 $^1\text{H-NMR}$ of Polymer A*.

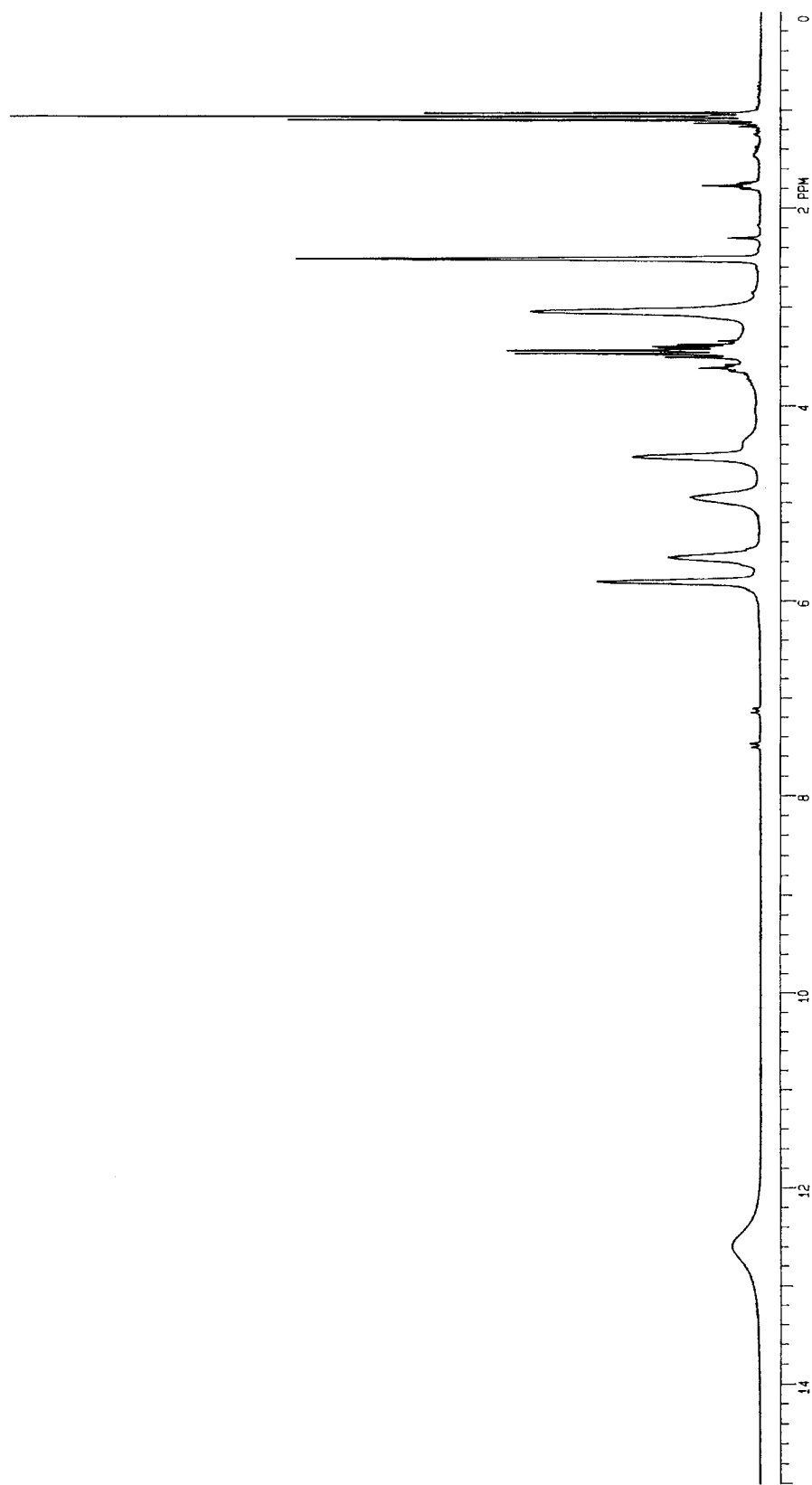


Figure 3 ¹H-NMR of Polymer B*.

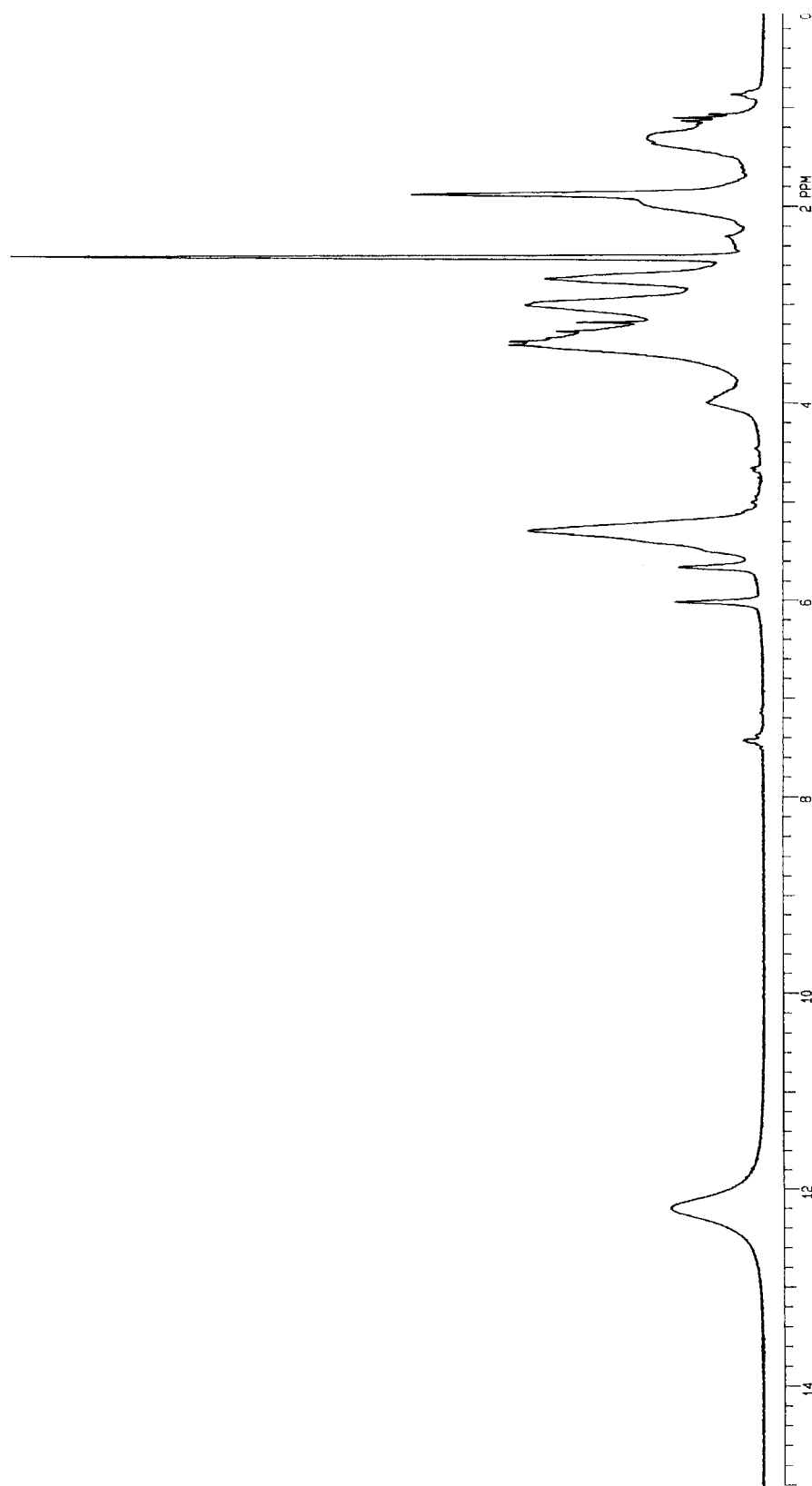


Figure 4 $^1\text{H-NMR}$ of Polymer D*.

Table III Chain Transfer by 1-hexene: Estimated and Determined Molecular Weights of Poly(2)

Exp.	Cat + CTA	P_n Estim.	M_n Estim. $\times 10^{-3}$ g/mol	M_n Det. $\times 10^{-3}$ g/mol	PDI
1	1	500	176.0	115.6	1.09
2	2	250	88.0	86.4	1.27
3	3	167	58.6	60.1	1.44
4	5	100	35.2	35.5	1.60
5	10	50	17.6	18.9	1.68
6	20	25	8.8	9.6	1.71

g/mol) in 20 mL of *sec*-butanol and with 1.55 g (10.9 mmol) of 2,3 epoxypropyl methacrylate, 11.6 mg of lithium perchlorate and a spatula tip of hydroquinone monomethyl ether (HQME) were added. The reaction mixture was stirred for 48 h at 60°C. The reaction product was then precipitated by pouring the mixture into 150 mL of ethyl acetate. Then the polymer was dissolved in methanol and precipitated again by dropwise addition to ethyl acetate. The precipitated white polymer was dried under vacuum to constant weight forming 3.8 g of a light brown solid.

$^1\text{H-NMR}$ (methanol- d_4): δ = 5.63–6.14 (2s, =CH₂), 5.20–5.65 (br, -CH=), 3.30–4.25 (m, OCH₂CHO), 2.80–3.60 (br, -CHCOO and CH), 2.00 (s, CH₃) and 1.10–1.70 (br, CH₂).

The intensity ratios of the signals show that the degree of 2,3 epoxypropyl methacrylate modification is about 8 mol %.

Modification of poly(*exo*-7-oxanorbornene-2,3-dicarboxylic acid) with glycidyl methacrylate

To a solution of 1.3 g (7.0 mmol) of poly(*exo*-7-oxanorbornene-2,3-dicarboxylic acid) (formed by ROMP of monomer **2**) in 10 mL of *sec* butanol were added 1.0 g (7.0 mmol) of 2,3 epoxypropyl methacrylate and 10 mg of lithium perchlorate. The reaction mixture was stirred for 48 h at 60°C. The reaction product was then precipitated by pouring into 150 mL of diethyl ether. The precipitated white polymer was dried under vacuum to constant weight forming 0.2 g of a white solid.

$^1\text{H-NMR}$ (methanol- d_4): δ 5.63–6.12 (2s, =CH₂), 4.95–5.57 (br, -OCH< and =CH-), 3.30–4.22 (m, OCH₂CHO), 2.91–3.30 (br, >CHCOO), and 1.94 (s, CH₃).

The intensity ratios of the signals show that the degree of GMA-modification is about 20 mol %.

RESULTS AND DISCUSSION

Monomer Synthesis

The monomers were prepared following well known organic reactions. The norbornene units were formed via Diels Alder reactions of cyclopentadiene and furan with fumaric acid and maleic anhydride, respectively. The introduction of the protection group was achieved by reacting the carboxylic groups with 3,4-dihydro-2*H*-pyrane in the presence of catalytic amounts of pyridinium tosylate. Compound **4** was obtained from 7-oxabicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic acid anhydride by first estrification with HEMA than with methyl iodide. Structure **5** was formed through the esterification of methacrylic acid chloride with 2-(hydroxymethyl)-5-norbornene in the presence of triethylamine.

Polymerization Reactions

All monomers were exposed to both catalysts in NMR spectroscopy experiments. The results are given in Table I. If these small-scale experiments showed promising results, larger scale polymerizations at higher concentrations were attempted.

The polymers obtained were characterized by GPC, eluent: THF, calibration versus polystyrene), and NMR spectroscopy in CDCl₃ and DMSO- d_6 , respectively.

Tetrahydropyranyl moieties were the protecting groups of choice because the monomerization reaction occur readily, the monomers are crystalline and can be obtained in sufficient purity and acceptable yields (85% for **1** and 71% for **3**, respectively).

Monomers **1** and **2** were easily converted by Mo=C on NMR scale, although in the latter case a change in color from yellow to brown was observed within 3 min, leading to the conclusion that some deactivation of the catalyst occurred.

Table IV Solubilities of Polymers A, A*, B, B*, D, D*, E, E* in Various Solvents

Solvent	A	A*	B	B*	D	D*	E	E*
H ₂ O	—	—	—	+	—	—	—	+
10% NaHCO ₃ in H ₂ O	—	+	—	+	—	+	—	+
10% ethanol in H ₂ O	—	±	—	+	—	—	—	+
20% ethanol in H ₂ O	—	+	—	+	—	±	—	+
Ethanol	—	+	—	+	—	+	—	+
THF	+	+	+	+	+	+	+	+
HEMA	+	+	+	+	+	+	+	+
Ethyl acetate	+	—	+	—	+	—	+	—
CH ₂ Cl ₂	+	—	+	—	+	—	+	—

+, soluble; —, insoluble.

Attempts to obtain polymers from **1** with Ru=C failed, the solution showed an immediate color change from purple to yellow. This might be due to a change in the oxidation state of the ruthenium from Ru (II) to Ru (IV), more detailed investigations on the reasons for this behavior are necessary.

On larger scale only the polymerization of **1** was successful yielding polymer **A**. The signals of the tetrahydropyranyl groups are found at δ : 6.0–5.7 ppm (OCHO) and in the region of δ : 3.8–3.4 ppm and 2.2–1.0 ppm (-CH₂-) respectively. The molecular weight was determined to be $M_n=10.10^3$ g/mol, poly dispersity index (PDI) = 2.23 by GPC (see Table V). To obtain the polyelectrolyte the protection groups were cleaved, yielding polymer **A***. The ¹H-NMR spectrum of **A*** (Fig. 2) still showed small contents of THF and ethanol even after drying in vacuo for 1 week, but clearly proved the quantitative loss of the protection groups. The molecular weight of **A*** was determined to be $M_n=3.43 \cdot 10^3$ g/mol, PDI=1.62. (see Table V)

Comparative studies of the solubilities of **A** and **A*** in various solvents are shown in Table IV.

The synthesis of poly(*exo*-7-oxanorbornene-2,3-dicarboxylic acid) **B*** via polymerization of 7-oxanorbornenedicarboxylic anhydride with Ru=C in THF always led to a gel that was insoluble in THF, DMSO, ethanol, and hot aqueous NaHCO₃, although the mixtures were stirred overnight to obtain esterified and hydrolyzed polymers respectively.

Polymerization of **2** by Ru=C in presence of 1-hexene gave polymer **B**. The molecular mass was found to be $M_n=1.89 \times 10^5$ g/mol, PDI=1.30 (Table V). The NMR spectrum showed signals from residual THF and ethanol in addition to the

expected signals. After cleavage of the protection group a ¹H-NMR spectrum (Fig. 3) was obtained showing that polymer **B*** is a very pure, very well-defined polymer. The -CH=CH- and -CHO resonances were both split into major and minor peaks, which has been attributed to *cis/trans* isomerism of the double bond. Unfortunately we were unable to obtain GPC results for that polymer because it never passed the filters before the GPC columns, either because of agglomeration and cross-linking or just because of the very high-molecular weight.

Investigation of the chain transfer by 1-hexene in the polymerization of **2** by Ru=C

To find a system where short chain polymers of **2** could be obtained at low consumption of catalyst, we investigated the polymerization in presence of 1-hexene as CTA.

Approximately, every molecule of 1-hexene could terminate a growing chain, thus creating a

Table V GPC Results of Polymers A, A*, B, B*, D, D*, E and E*

Polymer	[M]/[Kat]	Yield	PDI	M_n^+ [g/mol]
A	25	—	2.23	10.000
A*	—	60	1.62	3.400
B	259	—	1.3	189.000
B*	—	93	◆	◆
D	85	—	—	—
D*	—	68	3.0	13.600
E	185	—	1.4	57.000
E*	—	73	1.2	3.000

+, M_n were calculated vs. monodisperse PS standards.
◆, Not passable through syringe filters used for GPC.

new active species of the initiator to start a new chain, which leads to a number average polymerization degree of

$$P_n = \frac{[\text{monomer}]}{[\text{catalyst}] + [\text{CTA}]}$$

This assumption does not consider different reactivities of 1-hexene and the monomers towards the metathesis reaction, but is good enough to estimate the molecular weights of the resulting polymers. Correlation of these estimated data with the values of M_n determined by GPC was found to be more than acceptable. Table III gives estimated and determined molecular weights of the different polymers. Figure 6 shows the decrease in molecular weight as a function of increasing amounts of CTA.

We assume that the comparably low-molecular weight polymer found in experiment 1 was due to the formation of macro cycles through backbiting reactions of the active species according to the ring-chain equilibrium of metathesis polymerizations.

Structure **4** was readily polymerized by both catalysts in NMR spectroscopy experiments.

Homopolymerization of **5** with Mo=C was successful in the NMR spectroscopy experiment but led to cross-linked gels (polymer **C**) in larger scale experiments. Cross-linking involving metathesis reactions seems to be unlikely because acrylates have been shown not to undergo metathesis reactions. Therefore we rather assume that addition reactions are the cause of this observation.

Copolymerization of **1** and **5** was carried out on NMR spectroscopy scale (Table II) employing Mo=C with mixtures containing different ratios of **1** / **5** = 0.5; 1; 2. The ¹H-NMR spectra of the polymer implied that in all cases both monomers were incorporated in the polymer chain at approximately the expected ratio given by the starting concentrations.

For larger scale polymerizations a ratio of **1** / **5** = 4 was chosen. **1** and **5** were copolymerized by Mo=C in presence of 1-hexene to obtain a short-chain polymer **D**. The polymer was stable enough to be isolated and dried without forming cross-links.

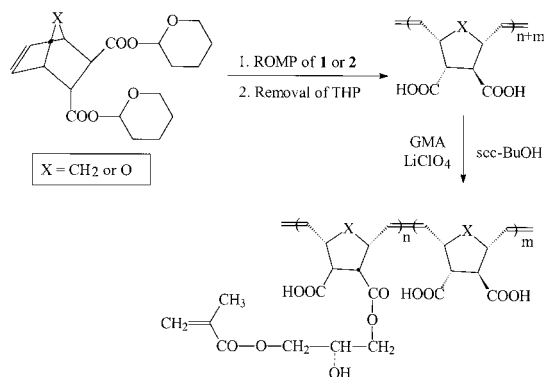
The ¹H-NMR spectrum of polymers **D** and **D*** (Fig. 4) showed the expected signals with intensities that correlated very well with the comonomer ratio. Molecular weights were low as desired due to chain transfer reactions involving the 1-hexene. After cleavage of the tetrahydropyranyl group the molecular weight was reduced from $M_n = 2.7 \times 10^4$ g/mol

with polymer **D** to 1.4×10^4 g/mol with polymer **D***, determined by GPC (Table V).

The solubilities of the resulting polymers in different solvents are shown in Table IV.

Copolymerization of **2** and **4** at a ratio of **2** / **4** = 3.15 yielded polymer **E**, which was also stable enough to be isolated. After cleavage of the protection group the molecular mass was reduced from 5.7×10^4 g/mol to 3.0×10^3 g/mol (Table V) for Polymer **E***. This dramatic loss in molecular weight cannot be explained by breaking up the main chain reducing the average polymerization degree because the conditions for cleaving of the tetrahydropyranyl groups are relatively mild. More likely this very polar polymer seems to be coiled much more densely in solution so that its hydrodynamic volume can no longer be compared to polystyrene. Formation of such very dense coils that are eventually coordinated to others might be an explanation why Polymer **B*** never passed membrane filtration through 0.45 μm filters. ¹H-NMR Spectra (Fig. 5) showed the incorporation of both monomers in **E*** in good correlation with the initial monomer ratio.

The modification of polymer **A*** and polymer **B***, respectively, with 2,3 epoxypropyl methacrylate was carried out using *sec*-butanol (*sec*-BuOH) as solvent and lithium perchlorate (LiClO₄) as catalyst according to the following reaction (Scheme 1):



Scheme 1 Polymer-analogous modification of poly(*exo,endo*-norbornene-2,3-dicarboxylic acid) and poly(*exo*-7-oxanorbornene-2,3-dicarboxylic acid).

¹H-NMR spectroscopy characterization of the reaction products confirmed the introduction of the methacrylic side-groups. Peaks at 5.63 and 6.12 ppm were assigned to =CH₂ and the signal of CH₃ appeared at 2.00 ppm in the ¹H-NMR spectrum of

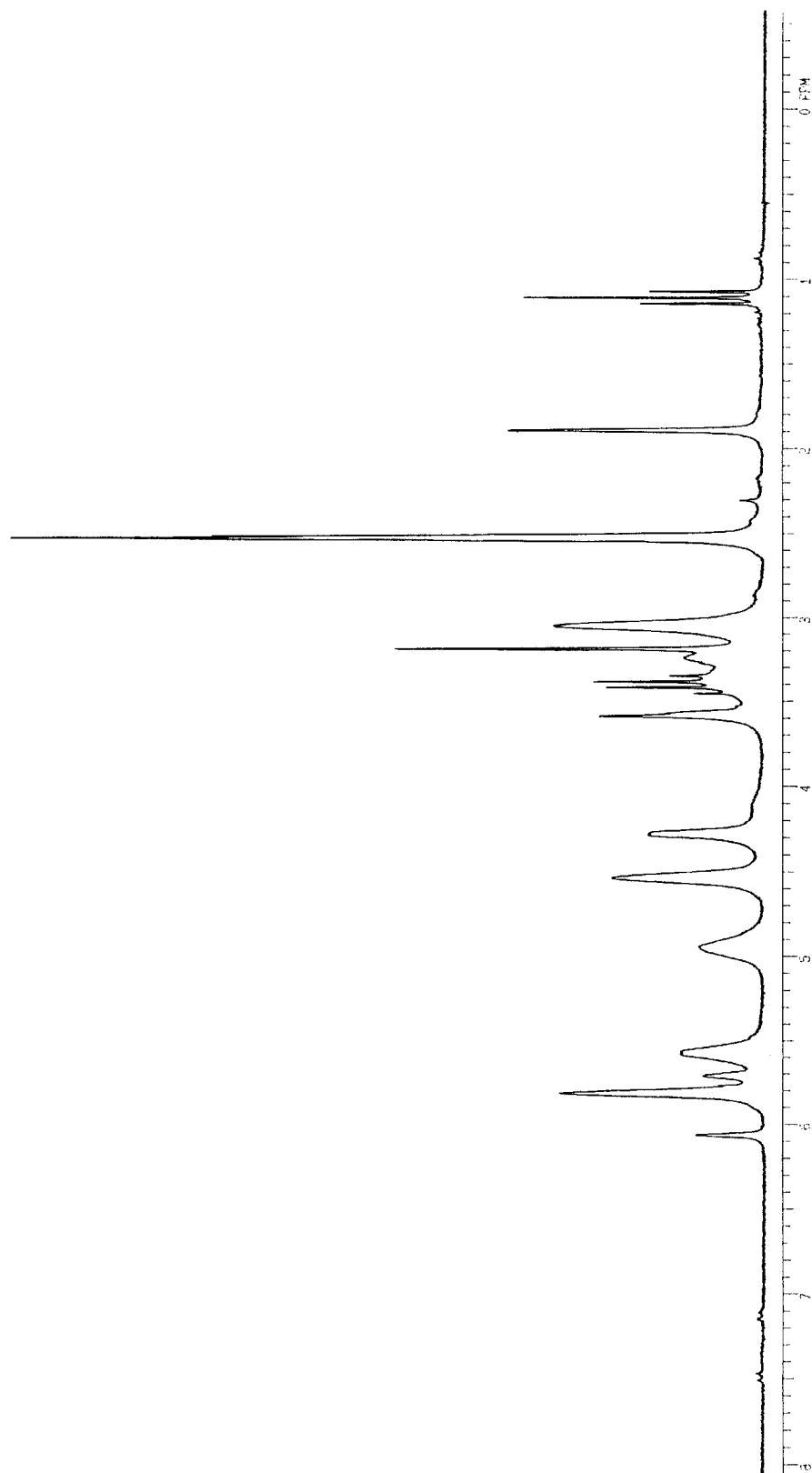


Figure 5 $^1\text{H-NMR}$ of Polymer E*.

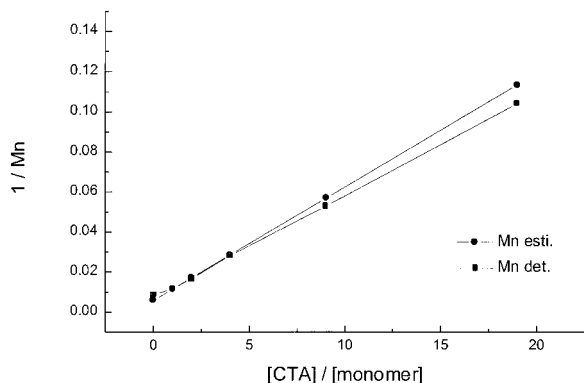


Figure 6 Estimated and determined values M_n of poly(2) as a function of various amounts of CTA present in the polymerization mixture.

GMA-modified poly(*exo*-7-oxanorbornene-2,3-dicarboxylic acid). Furthermore, the formation of polymerizable side groups was also confirmed by the fact that the GMA-modified poly(acid)s tended to polymerize spontaneously. The methacrylic group content was about 8 mol % in case of poly(*exo,endo*-norbornene-2,3-dicarboxylic acid) and about 20% in the case of poly(*exo*-7-oxanorbornene-2,3-dicarboxylic acid). The modified poly(acid)s were soluble in water and ethanol. They can be cross-linked in the presence of radical photo initiators.

CONCLUSIONS

ROMP employing well-defined transition metal alkylidene catalysts has again been shown to be a useful method to obtain highly functionalized polymers with defined microstructures.

Through the synthesis and polymerization of monomers bearing suitable protection groups even highly polar structures such as polyelectrolytes are accessible. These polymers are soluble in water as well as in ethanol. Copolymerization of monomers carrying methacrylate groups gave polymers, which contained another functional group. This allows the formation of cross-linked materials via addition polymerization initiated by UV light. Similar properties were obtained by the polymer analogous reaction of the polycarboxylic acids with GMA.

Such properties make the modified poly(acid)s attractive as a component of dental adhesives. Therefore, solutions of GMA-modified poly(acid)s in ethanol were used as dentin primer and resulted in shear bond strengths of corresponding adhesives of about 15 Mpa.²⁹

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