

The synthesis and properties of triethyleneoxy-methylether and crown-ether functionalized metathesis polymers

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

Abstract

The synthesis and characterization of metathesis polymers functionalized with triethyleneoxy-methylether and crown-ether side groups is reported. The triethyleneoxy-methylether substituted norbornene and acetylene derivatives and the 14-crown-4 functionalized norbornene were synthesized and metathesis polymerization with carbene complexes of molybdenum or ruthenium provided the substituted polynorbornene or polyacetylene backbone. The polymers were characterized with NMR, GPC, FT-IR and DSC. Addition of lithium ions to these amorphous polymers results in increasing of the glass transition temperature, T_g , because the oxygen–metal coordination leads to an enhanced order. The triethyleneoxy-methylether-bearing polymers show a low T_g even at high O:Li ratios. This is in contrast to the crown-ether-modified polynorbornene where the crown-ether ring stiffens the main chain and leads to higher T_g . © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Metathesis polymerization; Crown-ether; Poly(ethyleneoxide), PEO; Polymer electrolytes

1. Introduction

The use of polymeric materials bearing oligoethyleneoxy or crown-ether side chains as solid electrolytes is well described [1–3]. Such ionically conducting materials continue to be studied because of various technological applications such as low weight, all solid-state lithium batteries, polymer light-emitting electrochemical cells (LECs) or sensors [4,5].

Since 1973, when Fenton et al. [6] first reported the ionic conductivity of poly(ethylene oxide) (PEO) and the following suggestion of Armand [7] for the use of PEO as a solid electrolyte system, much work has been reported on this field. In pure PEO the dissolution of lithium ions causes a considerable increase in glass transition temperature T_g because the lithium ions cross-link the PEO chains and the increased order diminishes the ionic mobility. Various attempts have been made to modify PEO by plasticizers, cross-linking, or grafting to improve the properties [8]. The aim was to get a noncrystalline polymeric material wherein lithium addition is not accompanied by an in-

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crease in T_g above room temperature. This is important because ion conduction takes place in the amorphous regions of the polymer where the ion transport is assisted by the liquid-like chain relaxation processes occurring in the polymer above its glass transition temperature [3].

It is desired to produce polymeric materials with high stereoregularity because such highly ordered structures give the possibility for the oligo(ethyleneoxide) units to arrange in regular tunnels. Such “ion channel formation” is assumed to be responsible for the high ion conductivity in polymer gel electrolytes [8]. In these systems ion transport does not depend directly on chain flexibility [3].

Also, crown ethers have been found to be excellent cation binding agents and it is desired to form regular stacks of the crown structures for building up an oxygen coated tunnel which works as an ion conductor. 14-Crown-4 is known to form relatively strong 1:1 complexes in which the lithium ion sits in the plane of the ring [9].

The monomers and their method of synthesis are shown in Fig. 1. By the ring-opening metathesis polymerization [10] of the norbornene derivatives using well-defined molybdenum or ruthenium carbene complexes [11,12] we hoped to obtain polymers with high stereoregularity. In addition due to the nonpolar main chain a self-assembling of the polar moieties could be possible.

By metathesis polymerization of acetylene derivatives [13–15] with molybdenum carbene complexes it is possible to get a polyacetylene main chain with a high density of the triethyleneoxy-methylether side chains. In this case the advantage should be to combine a rigid, stiff and nonpolar backbone with a cover of regular, polar side chains.

We studied the microstructure of the polymers obtained with different catalysts and finally we investigated the thermal behavior after lithium salt addition.

We could show that it is possible to produce polymers with a regular, nonpolar backbone via metathesis polymerization and that the polar

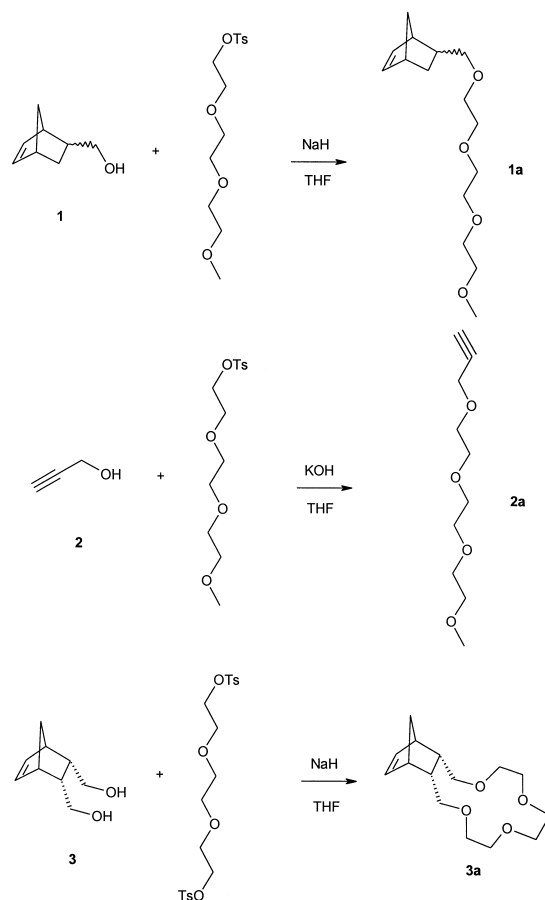


Fig. 1. Synthesis of monomers.

side chains are able to dissolve high amounts of Li salts.

2. Experimental

2.1. Chemicals and analysis

THF was purified by distillation from Na/K alloy. Dichloromethane was distilled from CaH_2 prior to use.

Propargyl alcohol and the methoxy-triethylene-glycol were ordered from Fluka and used as received.

The molybdenum carbene complexes were prepared as described in the literature [11]. The

ruthenium benzylidene catalyst was obtained from Strem Chemicals.

All polymerizations were carried out in a dry box filled with nitrogen. All monomers were degassed before the transfer into the dry box.

^1H and ^{13}C NMR spectra were recorded on a 300-MHz Bruker MSL, Varian Gemini 200 or a 90-MHz Bruker WH-52 spectrometer.

Glass transition temperatures were measured by differential scanning calorimetry with a Perkin-Elmer DSC 4 (20°C/min) or a Polymer Laboratories simultaneous thermal analysis STA 625 (15°C/min).

Molecular weights were determined, relative to polystyrene standards, by gel permeation chromatography (GPC) of THF or chloroform solutions of the polymer using a UV or refractive index detector.

FT-IR spectra were recorded on a Perkin-Elmer Spectrum One FTIR as thin films on NaCl plates.

2.2. Synthesis of monomers

The starting materials for the monomer synthesis were the alcohols **1**, **2** and **3**. Compounds **1** and **3** were synthesized according to literature [16]. The introduction of the oligoethyleneoxy functionalities was achieved by etherification of the various alcohols with triethylene-glycol-ditosylate or the tosylate of the triethylene-glycol-monomethylether [17] using sodium hydride or potassium hydroxide as a base and THF as a solvent in order to obtain monomers **1a**, **2a** and gel permeation chromatography.

The reaction of the disodium salt of the bis-5,6-(hydroxymethyl)-norbornene **3** with the triethylene-glycol ditosylate was made under high dilution conditions (THF solution) to obtain the norbornene-14-crown-4 in 22% yield.

Description of the syntheses in detail:

2.2.1. 5-{2-[2-(2-Methoxy-ethoxy)-ethoxy]-ethoxymethyl}-bicyclo[2.2.1]hept-2-ene **1a** (endo, exo mixture)

A 60% sodium hydride suspension in mineral oil (0.45 g, 0.011 mol) was washed several

times with dry THF. THF (50 ml) were added to the sodium hydride and warmed slightly. A solution of 5-(hydroxymethyl)-norbornene **1** (0.57 g, 0.004 mol) in 3 ml dry THF was added (bubbling). The mixture was heated until reflux and a solution of methoxy-triethylene-glycol tosylate (1.9 g, 0.006 mol) in 5 ml dry THF was added with a syringe. The mixture was stirred under reflux overnight. After cooling the solid salts were removed by filtration and the solvent was removed under reduced pressure to get a slightly yellow colored oil which was purified by column chromatography on silica (eluent: cyclohexane/ethylacetate = 3/1) to yield a colorless oil (0.79 g, 64 %, endo, exo mixture 2:1).

δ_{H} (CDCl_3): 6.10 (m), 5.92 (m), 3.55–3.65 (14 H, m), 3.4 (3 H, s), 3.12 (2 H, m), 2.9 (1 H, b s), 2.78.

(1 H, b s), 2.35 (1 H, b s), 1.80 (1 H, m), 1.4 (1 H, m), 1.26 (1 H, d) 0.5 (1 H, m) ppm.

δ_{C} (CDCl_3): 137.3, 136.8, 132.7, 120.7, 76.2, 75.3, 72.2, 70.4–70.8 (4 C), 59.27, 49.6, 45.2, 44.15, 43.83, 42.40, 41.73, 38.9, 29.9, 29.34 ppm.

2.2.2. 3-{2-[2-(2-Methoxy-ethoxy)-ethoxy]-ethoxy}-propyne **2a**

A solution of propargyl alcohol (1.5 g, 0.027 mol) in 4 ml THF was treated with potassium hydroxide (1.2 g, 0.021 mol). Methoxy-triethylene-glycol tosylate (4.3 g, 0.013 mol) was added and the mixture was stirred 5 h at room temperature. During this time a white solid precipitates.

Hydrochloric acid was added and the mixture was extracted three times with diethylether. The organic layers were dried with sodium sulfate and the solvent was removed under reduced pressure to get a slightly colored liquid which was purified by vacuum distillation (b.p. 175°C/0.2 mm Hg). Yield: 1.55 g (59%).

δ_{H} (CDCl_3): 4.18 (2 H, d), 3.67 (10 H, m), 3.58 (2 H, m), 3.35 (3 H, s), 2.42 (1 H, t) ppm.

δ_{C} (CDCl_3): 79.69, 74.55, 71.96, 70.63 (2 C), 70.59, 70.44, 69.14, 59.07, 58.43 ppm.

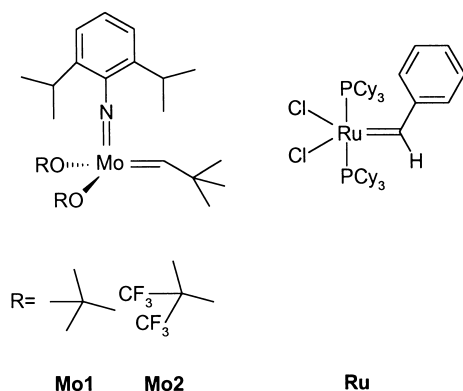


Fig. 2. Initiators.

2.2.3. *Endo, exo-4,7,10,13-tetraoxa-tricyclo[14.2.1.0^{2,15}]nonadec-17-ene 3a*

A 60% sodium hydride suspension in mineral oil (0.5 g, 0.0125 mol) was washed several times with dry THF. THF (100 ml) was added to the sodium hydride and heated until reflux. A solution of bis-5,6-(hydroxymethyl)-norbornene (0.5 g, 0.00325 mol) in 3 ml dry THF was added with a syringe. After 10 min a solution of triethylene-glycol ditosylate (1.5 g, 0.00325 mol) in 150 ml of dry THF was added slowly during the next 3 h. The reaction mixture was kept under reflux for 3 days. After cooling the solvent was removed under reduced pressure and the white solid was extracted with 100 ml chloroform. After filtration the solvent was again removed and the residual oil was purified by

column chromatography on silica (eluent: cyclohexane/ethylacetate = 4:1) to get a colorless oil. Yield: 0.192 g (22%).

δ_{H} (CDCl_3): 6.08 (2 H, t), 3.55–3.7 (12 H, m), 3.45 (2 H, m), 3.18 (2 H, m), 2.84 (2 H, b s), 2.44 (2 H, m), 1.39 (2 H, dd) ppm.

δ_{C} (CDCl_3): 135.38 (2 C), 71.6–71.9 (8 C), 49.78, 45.90 (2 C), 42.27 (2 C) ppm.

2.3. Polymerization

The monomers **1a–3a** were polymerized using well-defined molybdenum (**Mo1**, **Mo2**) or ruthenium carbene (**Ru**) complexes (Fig. 2).

In a typical polymerization procedure the monomer (1 mmol) was dissolved in 1 ml dichloromethane and a solution of the catalyst (0.003 mmol) was added. In the case of the molybdenum catalyst after 2 h benzaldehyde was added to quench the reaction. After 10 min the reaction mixture was filtered through a silica column in order to remove the molybdenum. By pouring the polymer solution in pentane the highly viscous (**1b**, **2b**, **4b**) or solid (**3b**) polymer could be separated (Fig. 3).

In the case of **Ru** after 2 h ethyl vinyl ether was added as a quenching reactant. After 1 h the polymer solution was poured into pentane. A highly viscous (**1b**) or solid (**3b**) polymer precipitated.

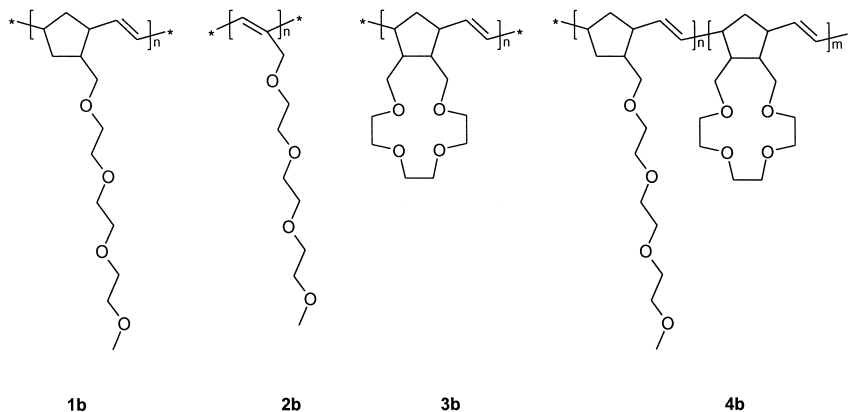


Fig. 3. Polymer structures.

2.4. Lithium salt complexation

Lithium addition was carried out in the dry box filled with nitrogen as follows. Fifty milligrams polymer (5% solution in THF) was weighed into a 10-ml flask equipped with a stirrer bar. The amount of anhydrous lithium perchlorate required to give the desired O:Li ratio (varies from 40:1 to 4:1) was added as a stock solution containing 100 mg/g THF. After 1 h stirring the solvent was removed under reduced pressure and the sample was dried under vacuum at 40°C for several hours. This was repeated for each different O:Li ratio and differential scanning calorimetric analyses were carried out.

3. Results and discussion

3.1. Polymerization

Ring-opening metathesis polymerization of the norbornene derivatives **1a** and **3a** was achieved with catalyst **Mo1**, **Mo2** and **Ru**. With all catalysts we obtained the polymers **1b** and **3b** in quantitative yield under mild conditions (room temperature, 2 h).

The copolymer **4b** was produced with catalyst **Mo2** and a 1:1 mixture of the monomers **1a** and **3a** with 75% yield.

Metathesis polymerization of the acetylene derivative **2a** was achieved using catalyst **Mo1** [14]. The polymerization reaction was carried out in a 10% monomer solution for 16 h (monomer:catalyst = 100:1). We obtained a maximum yield of 85% of the polymer **2b** which showed

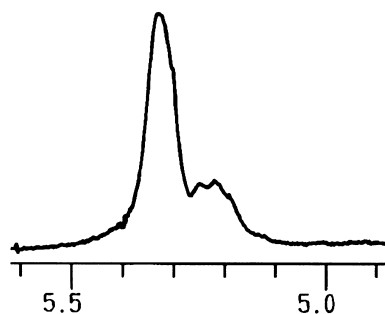


Fig. 4. ^1H NMR of polymer **1b** initiated by **Ru** (olefinic region).

low molecular weight. The polymer structures are shown in Fig. 3. The data from GPC and DSC analyses are reported in Table 1.

^{13}C and ^1H NMR studies of the obtained polymers provide elucidation of the microstructure [18,19]. Polymer **1b** synthesized by **Ru** showed an amount of about 70% *trans* double bonds in the backbone. The *trans* vinylene units were found in the ^1H NMR at 5.33 ppm and *cis* at 5.23 ppm (Fig. 4). With catalyst **Mo1** we obtained nearly the same microstructure (about 80% *trans*). Employing **Mo2** as catalyst resulted in a polymer with a *cis* content > 95%.

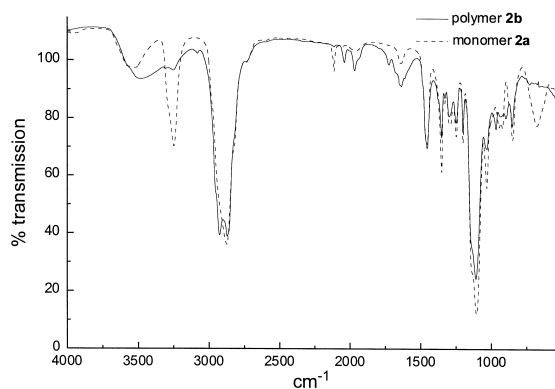
3a polymerized with **Ru** gave a polymer with 82% *trans* vinylene units, whereas **Mo2**-initiated polymerization resulted in a 75% *cis* polymer. Here *trans* and *cis* vinylene units were, in ^1H NMR, nearly at the same chemical shifts (*trans* 5.44 ppm, *cis* 5.40 ppm). For determination of the *cis/trans* ratio the peaks at 3.0 ppm (*cis*) and 2.65 ppm (*trans*) were integrated.

In ^{13}C NMR we were not able to resolve the vinylene units clearly by using the Bruker 300 MSL. Further investigations are going on.

The NMR analysis of copolymer **4b** showed AB blocks in the backbone. In the ^{13}C NMR only the signals of the homopolymers were visible. GPC nevertheless showed a monodispersed polymer with an M_w of 55 000 and a PDI of 2.3. We assume that a block copolymer is formed due to a higher rate of incorporation of the monosubstituted norbornene derivative

Table 1
Molecular weight and glass transition temperature (T_g) of the metathesis polymers

Polymer	1b	2b	3b	4b
M_w	62 000	10 000	66 000	55 000
M_n	34 000	4 200	33 500	24 000
T_g [°C]	-53	-68	78	-18

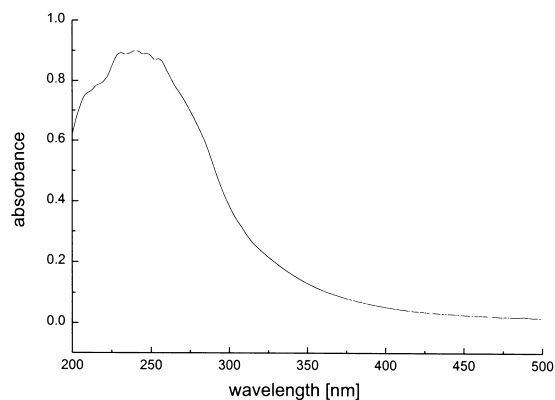
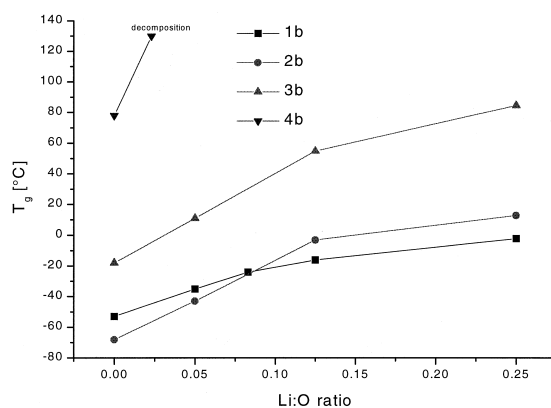
Fig. 5. FT-IR spectra of monomer **2a** and polyacetylene **2b**.

1a. Thus, after the formation of a block of mainly **1a** units, units of **2a** began to be incorporated in the polymer main chain.

In the ^1H NMR analysis of polyacetylene **2b** a broad signal of the olefinic hydrogen at 6.3 was found. No separated peaks for *cis* or *trans* double bonds were observable. In Fig. 5 the FT-IR spectra of monomer **2a** and polymer **2b** are shown. The UV spectrum of **2b** showed an absorption maximum at 245 nm and is illustrated in Fig. 6.

3.2. Lithium complexation studies

Addition of anhydrous lithium perchlorate to the polymers **1b–4b** resulted in an increase in the glass transition temperatures because the oxygen–metal coordination leads to an enhanced order (Fig. 7). The triethyleneoxy-meth-

Fig. 6. UV spectrum of polyacetylene film **2b**.Fig. 7. Dependence of T_g on lithium salt amount.

ylether functionalized polymers remained in the amorphous phase even at high O:Li ratios and DSC measurements showed that T_g was still below room temperature.

We were not able to determine a T_g of the crown-ether functionalized polymer even at very low Li:O ratio (1:40 = one Li per 10 rings) because decomposition took place below the T_g . We assume that the building of strong 1:1 complexes of crown ether and lithium cation is responsible for the drastic increase of T_g . During lithium addition to the rigid crown-ether polymers ($T_g = 78^\circ\text{C}$) we could observe that at an oxygen to lithium ratio of 12:1 the polymers become insoluble in THF.

This was the reason for preparing the copolymer **4b** which consisted of about 35% of crown-ether moieties. We can see that the in-

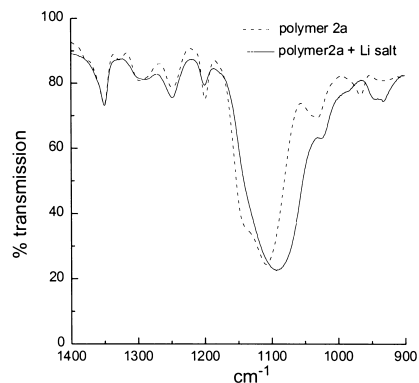


Fig. 8. Lithium complexation detected by FT-IR.

crease in T_g in polymer **4b** is more sensitive to the amount of added lithium than in polymer **1b**. We assume that this is due to the crown-ether compound.

We could also detect the oligo-ethyleneoxy–lithium salt complexes interacting by IR measurements of polymer **2b** and the corresponding lithium doped sample (Fig. 8).

The coordination between the cation and the ether oxygens was proved by a broadening of the C–O–C stretching and the shifting to lower wave numbers [8].

4. Conclusions

We have shown that it is possible to prepare metathesis polymers with a polynorbornene or polyacetylene main chain and triethyleneoxy-methylether or crown-ether side chains with defined microstructure. These polymers are able to dissolve high amounts of lithium salt. The increase in T_g is low using polymer **1b** and **2b** bearing triethyleneoxy-methylether side groups. Crown-ether-containing polymers **3b** and **4b** show higher T_g values after incorporating lithium ions.

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References

- [1] J.E. Denness, D. Parker, H.St. Hubbard, *J. Chem. Soc., Perkin Trans.* (1994) 1445.
- [2] L. Collie, J.E. Denness, D. Parker, F. O'Carroll, C. Tachon, *J. Chem. Soc., Perkin Trans.* (1993) 1747.
- [3] J.M.G. Cowie, *Macromol. Symp.* 98 (1995) 843.
- [4] Q. Pei, Y. Yang, G. Yu, C. Zhang, A.J. Heeger, *J. Am. Chem. Soc.* 118 (1996) 3922.
- [5] F. Sanniccolo, E. Brenna, T. Benincori, G. Zotti, S. Zecchin, G. Schiavon, T. Pilati, *Chem. Mater.* 10 (1998) 2167.
- [6] D.E. Fenton, J.M. Parker, P.V. Wright, *Polymer* 14 (1973) 589.
- [7] M.B. Armand, J.M. Chabagno, M. Duclot, *Extended Abstracts, Second International Conference on Solid Electrolytes*, 1978 St. Andrews, Scotland.
- [8] V. Chandrasekhar, *Adv. Polym. Sci.: Polymer Solid Electrolytes* 135 (1998) 140–200.
- [9] L. Collie, D. Parker, C. Tachon, H.V.St.A. Hubbard, G.R. Davis, I.M. Ward, S.C. Wellings, *Polymer* 34 (1993) 1541.
- [10] K.J. Ivin, J.C. Mol, *Olefin Metathesis and Metathesis Polymerization*, Academic Press, London, 1997.
- [11] R.R. Schrock, J.S. Murdzek, G.C. Bazan, J. Robbins, M. DiMare, M. O'Regan, *J. Am. Chem. Soc.* 112 (1990) 3875.
- [12] P. Schwab, R.H. Grubbs, J.W. Ziller, *J. Am. Chem. Soc.* 118 (1996) 100.
- [13] S. Koltzenburg, E. Eder, F. Stelzer, O. Nuyken, *Macromolecules* 32 (1999) 21–26.
- [14] L.Y. Park, R.R. Schrock, S.G. Stieglitz, W.E. Crowe, *Macromolecules* 24 (1991) 3489.
- [15] F.J. Schattenmann, R.R. Schrock, W.M. Davis, *J. Am. Chem. Soc.* 118 (1996) 3295.
- [16] H.N. Miller, K.W. Greenlee, *J. Org. Chem.* 26 (1961) 3734.
- [17] M. Ouchi, Y. Inoue, T. Kanzaki, T. Hakushi, *J. Org. Chem.* 49 (1984) 1408.
- [18] D.M. Lynn, S. Kanaoka, R.H. Grubbs, *J. Am. Chem. Soc.* 118 (1996) 784.
- [19] K.J. Ivin, L.-M. Lam, J.J. Rooney, *Macromol. Chem. Phys.* 195 (1994) 1189.