

Copolymerizations between cyclic olefins and norbornene lactone

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

Abstract

The ring-opening metathesis polymerization (ROMP) of dicyclopentadiene and cyclooctene with norbornene lactone as a polar comonomer was studied. By incorporation of this rigid molecule the glass transition temperature was significantly increased. Thermal investigations showed a linear correlation between the amount of norbornene lactone in the copolymer and the observed glass transition. Thus, it was possible to vary the T_g within a broad temperature range. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Ring-opening metathesis polymerization (ROMP) has been investigated for some decades now [1]. Nevertheless, there are only a few commercialized polymers made by ROMP. Poly(octenylene), polynorbornene and poly(dicyclopentadiene) are the most important products, because these monomers are quite cheap and readily available.

Especially polymerization of dicyclopentadiene in RIM (reaction injection-molding) process has led to many patents [2–7].

Poly(dicyclopentadiene) shows glass transition temperatures between 140°C and 160°C, depending on the amount of crosslinked units

[8,9]. For certain applications the T_g of poly(dicyclopentadiene) is too low, which limits its industrial use. This was the reason for looking for a comonomer capable of improving the thermal properties. Also poly(octenylene) as a low- T_g polymer could be modified by incorporation of a heteroatom bearing comonomer. High- T_g polymers are usually of great interest for advanced applications like optical lenses or syringes.

It is well known that the incorporation of rigid monomers like norbornene anhydride [10,11] into poly(dicyclopentadiene) leads to increased T_g values up to 210°C. But anhydrides are not stable enough and often crosslink when exposed to moisture. Butyrolactones are usually quite stable and difficult to polymerize by ring-opening polymerization of the lactone ring [12,13]. The norbornene derivative bearing the butyrolactone functionality (4-oxa-tricyclo-

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[5.2.1.0^{2,6}]dec-8-en-3-one, norbornene lactone **3**) was our monomer of choice. It can be polymerized by the well-defined ruthenium carbene complex $\text{RuCl}_2(\text{PCy}_3)_2 = \text{CHPh}$ [14], which tolerates the cyclic ester functionality during polymerization.

In this work, the copolymerization of dicyclopentadiene or cyclooctene with norbornene lactone was investigated.

2. Experimental

2.1. Materials

CH_2Cl_2 was freshly distilled under argon over CaH_2 and degassed prior to use. Dicyclopentadiene **1** and cyclooctene **2** were purchased from Aldrich Chemical.

1 was used after purification by thermal cracking over calcium hydride and redimerization. **2** was distilled under argon over CaH_2 and stored in the dry-box.

Ruthenium carbene catalyst **4** was purchased from Strem Chemicals.

3 was synthesized by controlled reduction of norbornene anhydride in tetrahydrofuran at -55°C with LiAlH_4 according to literature procedure [15]. The raw product was purified by column chromatography (eluent: cyclohexane/ethyl acetate = 3/1).

2.2. Analyses

Glass transition temperatures were measured by differential scanning calorimetry with a Perkin Elmer DSC 4 ($20^\circ\text{C}/\text{min}$) or a Polymer Laboratories Simultaneous Thermal Analysis STA 625 ($15^\circ\text{C}/\text{min}$).

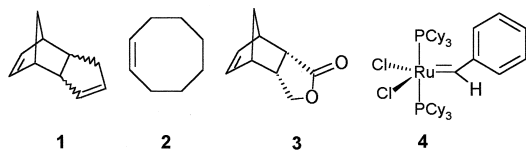


Fig. 1. Monomer and catalyst structures.

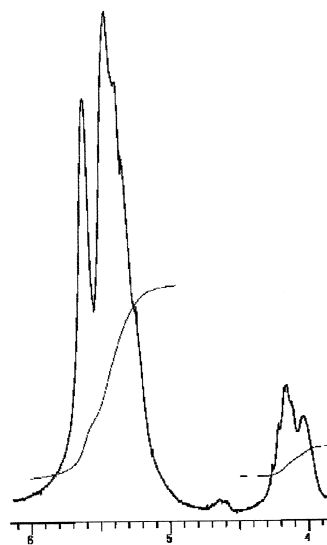


Fig. 2. ^1H NMR spectrum of the copolymer **1/3** — determination of the lactone content.

^1H NMR spectra were recorded on a 90-MHz Bruker spectrometer (Model WH-52) in deuterated chloroform, ^{13}C NMR spectra on a Bruker MSL 300 with 75 MHz also in deuterated chloroform.

GPC analyses of certain soluble polymer samples were run relative to polystyrene standards in THF or chloroform solutions using a refractive index detector.

2.3. Polymerizations

All work involving air and moisture sensitive compounds was performed under argon or nitrogen using standard Schlenk techniques or a dry-box.

Polymerizations were carried out in dichloromethane inside a dry-box usually for 24 h. The obtained polymers were dried in vacuo to constant weight before further characterization.

2.3.1. Dicyclopentadiene **1** / norbornene lactone **3** copolymerizations

A solution of the initiator **4** (4 mg, 0.005 mmol) in 2 ml dichloromethane and a solution of the various monomer mixtures **1** and **3** (0.7 mmol) in 2 ml solvent were put in the freezer

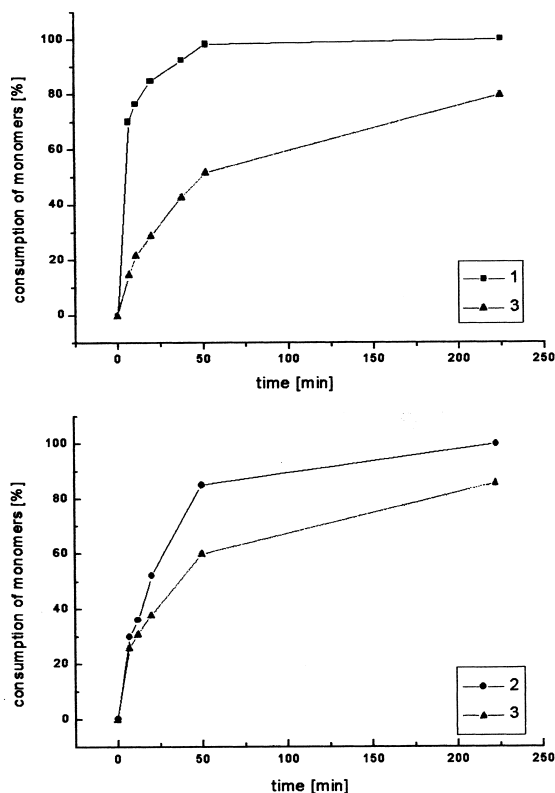


Fig. 3. Consumption of monomers in copolymerization of 1/3 and 2/3 (^1H NMR experiment in CDCl_3).

(-25°C) for 10 min before mixing together. Three different 1/3 ratios were employed containing 30, 60 and 90 mol% 3. The reaction mixtures with 70 and 40 mol% 1 became turbid within the first hour, which indicated cross-linking. The polymerizations were run at room temperature for 24 h and the polymers were precipitated by pouring the solutions in a 10-fold excess of ethanol. The polymer yield was in the range of 65%–70%.

The reaction containing 60 mol% norbornene lactone was carried out a second time using the double amount of dichloromethane in order to obtain a soluble copolymer. The polymer yield was 49%.

For comparing the reaction rate of monomers 1 and 3, 11 mmol of 1 and 11 mmol of 3 were mixed in a 5-mm NMR tube with $1.2\ \mu\text{mol}$ of 4 (room temperature). 1.1 ml CDCl_3 was used as solvent and benzene as an internal standard.

Table 1
Copolymerizations of 1 and 3 initiated by 4^a

Run	1 (mol% in feed)	3 (mol% in feed)	3 (mol% in polymer) ^b	T_g ($^\circ\text{C}$)
1	0	100	100	236
2	10	90	76	206
3	40	60	39	183
4	70	30	21	165
5	100	0	0	140

^aReaction time = 24 h, reaction temperature = 25°C .

^bDetermined by ^1H NMR analysis.

2.3.2. Cyclooctene 2 / norbornene lactone 3 copolymerizations

A solution of the initiator 4 (4 mg, 0.005 mmol) in 0.5 ml dichloromethane was added to a solution of the various monomer mixtures 2 and 3 (1 mmol) in 1 ml solvent. Within a few

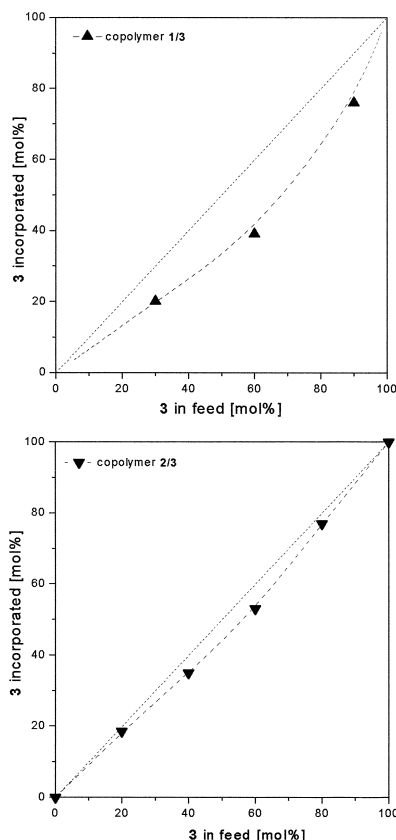


Fig. 4. Comparison of copolymers 1/3 and 2/3 — content in feed versus content in polymer after 24 h reaction time.

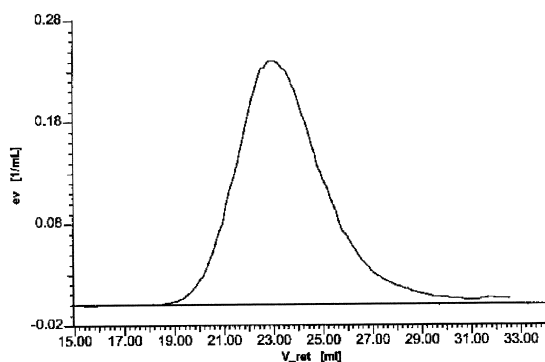


Fig. 5. GPC spectrum of the copolymer **2/3** containing 35 mol% **3**.

seconds, the color of the solution changed, indicating the new propagating carbene species.

Polymerization runs were carried out containing 40, 60 and 80 mol% norbornene lactone. After 24 h reaction time at room temperature, the polymerizations were terminated by precipitation in ethanol. The polymer yield was higher than 90%.

For comparing the reaction rate of monomers **2** and **3**, 10 mmol of **2** and 10 mmol of **3** were mixed in a NMR tube with 1.3 μmol of **4** (room temperature). 1 ml CDCl_3 was used as solvent and benzene as an internal standard (Fig. 1).

2.3.3. Norbornene lactone **3** homopolymerization

A solution of the initiator **4** (4 mg, 0.005 mmol) in 0.5 ml dichloromethane was added to

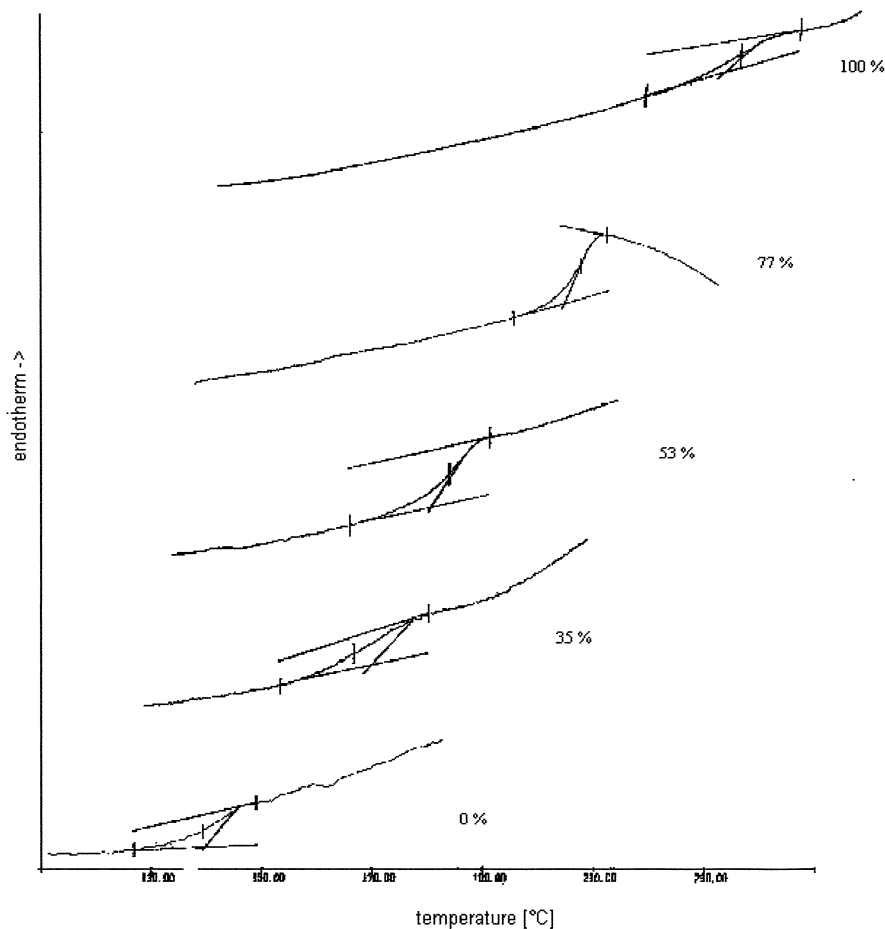


Fig. 6. Glass transitions of the copolymers **1/3** containing different amounts of **3** (second run, heating rate 20°/min).

a solution of the norbornene lactone (106 mg, 0.7 mmol) in 1 ml solvent. After a reaction time of 24 h at room temperature, the polymerization was quenched by precipitation in ethanol. The polymer yield was 95%.

3. Results and discussion

3.1. Copolymerization

The copolymerizations of **1** or **2** with the rigid **3** were studied. The amount of the lactone moiety **3** incorporated in the resulting copolymer was determined by ^1H NMR analysis comparing the integrals of the olefinic protons in the main chain and the lactone ring protons as shown in Fig. 2.

When copolymerizing **1** and **3**, even after 24 h the yields were only in the range of 70%. NMR experiments showed a faster incorporation of **1** than **3** (Fig. 3). This result was in accordance with a lower amount of **3** incorporated in the polymers (Table 1, Fig. 4). During polymerization, the ratio of **1/3** was decreasing because of the higher reaction velocity of **1**. So the composition of the copolymers might change in the course of the polymerization process, but

as can be seen from Figs. 2 and 5, the difference in the reaction rate is not big enough to yield fully separated blockcopolymer. A detailed study of the copolymerization parameters is underway. Nevertheless, only one broad glass transition temperature of each polymer was found (Fig. 6), so we assume that no phase separated block copolymers were formed. ^{13}C NMR analyses of the copolymers showed a complex splitting in the olefinic area due to the unsymmetrical substitution of the norbornene lactone (Fig. 7). So a detailed interpretation of the microstructure of the copolymers has not been possible yet.

Some copolymers of **1** with **3** contained an insoluble part that was only swelling, indicating that these parts were crosslinked. Even though reactions were carried out under high dilution conditions (0.17 M) and at low initial temperature, the experiments containing 70 and 40 mol% **1** provided crosslinked polymer, but only in a small amount. If the insoluble part was separated (e.g. by flash chromatography), the soluble part of these polymers showed a multimodal molecular weight distribution. The crosslinking could be caused either by a ROMP reaction of the dicyclopentadiene or by a ring opening of the lactone. In previous investigations, the for-

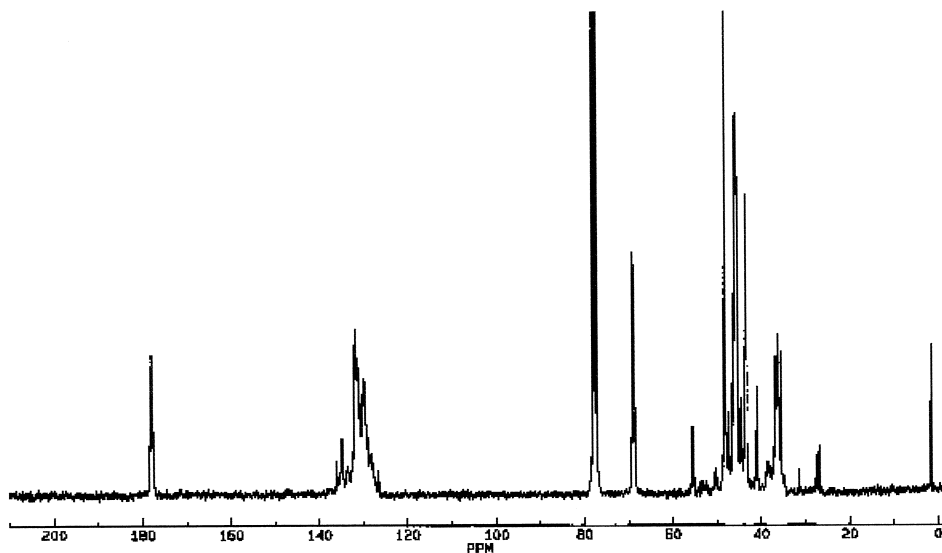


Fig. 7. 75 MHz ^{13}C NMR spectrum of the copolymer **1/3**.

mation of insoluble material during dicyclopentadiene polymerization was attributed to an addition polymerization process initiated by the exothermic ROMP of the norbornene moiety [16,17]. When the polymerization is conducted at half the concentration, heat was dissipated more easily and a soluble polymer with a dicyclopentadiene content of about 70% was obtained. Also, the fact that a copolymer of **1** and **3** containing 76% of **3** is completely soluble in chloroform confirms the assumption that crosslinking is caused by the olefin addition of **1** and not by the ring-opening of the lactone moiety.

The copolymerization of **3** with the less strained monomer **2** was also studied. In this case, the total yields after 24 h were higher than 90%. Copolymerizations were again run with different ratios of **2** and **3** (Table 2). The content of **3** in the polymer is nearly the same as in the feed (Fig. 4). This is caused by a more similar reaction velocity (NMR experiment, Fig. 3) and by a high conversion of both monomers (conversions > 90%). Again no separated blocks of the monomers were built, which is confirmed by only single glass transition points. Copolymers **2/3** showed no crosslinkage. Fig. 5 shows an example of a GPC plot of a sample containing 35% of **3** ($M_w = 80.000$, $M_n = 35.000$, calibration vs. polystyrene).

3.2. Thermal characterization of copolymers

DSC measurements of the obtained copolymers exhibit an almost linear dependence of the T_g on the content of **3**. It was possible to

Table 2

Copolymerizations of **2** and **3** initiated by **4**^a

Run	2 (mol% in feed)	3 (mol% in feed)	3 (mol% in polymer) ^b	T_g (°C)
1	0	100	100	236
6	20	80	77	131
7	40	60	53	61
8	60	40	35	3
9	100	0	0	-60

^aReaction time = 24 h, reaction temperature = 25°C.

^bDetermined by ¹H NMR analysis.

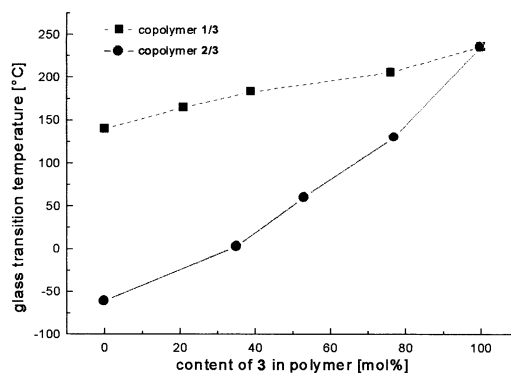


Fig. 8. Glass transition temperature of different copolymers **1/3** and **2/3**.

increase the T_g of **1/3** copolymers from 140°C up to 206°C (76 mol % **3**) by incorporating various amounts of **3** in poly(dicyclopentadiene) (Fig. 8). The homopolymer of the **3** had a very high T_g of 236°C. This value is close to the T_g of poly(norbornene anhydride) ($T_g = 231^\circ\text{C}$) [10].

Copolymers of cyclooctene and norbornene lactone also showed a similar dependence of T_g on the incorporated amount of **3**. Copolymers with T_g values between -60°C and 131°C (77 mol% **3**) were obtained as can be seen from Fig. 8.

4. Conclusions

The copolymerization of dicyclopentadiene and cyclooctene with norbornene lactone was investigated. Dicyclopentadiene tended to form crosslinked copolymers. Only under highly diluted conditions was crosslinking avoided. Thermal investigations exhibited an almost linear correlation between the amount of norbornene lactone **3** in the copolymer and the glass transition temperature. All copolymers showed only one single glass transition, which confirmed that no phase separated blocks of the monomers were built. By copolymerization with norbornene lactone polymers with glass transition temperatures higher than 200°C were obtained.

Acknowledgements

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