Preparation of an ester-terminated telechelic polybutadiene by a two-step olefin metathesis process

P.O. Nubel [*], H.B. Yokelson, C.A. Lutman, W.G. Bouslog, R.T. Behrends, K.D. Runge

Amoco Corporation, Amoco Research Center, Mail Station D-3, P.O. Box 3011, Naperville, IL 60566, USA

Abstract

A two-step olefin metathesis process was devised and utilized to prepare an ester-terminated telechelic 1,4-polybutadiene of high difunctional purity using readily available olefin reactants (methyl undecylenate and 1,5-cyclooctadiene or 1,5,9-cyclododecatriene). In the first step of this process, methyl undecyclenate was self-metathesized in the presence of WCl_6-$SnMe_4$ catalyst to yield an acyclic olefinic diester, dimethyl 10-eicosene-1,20-dioate (DMED), plus ethylene. In the second step, ring-opening metathesis polymerization (ROMP) of 1,5-cyclooctadiene or 1,5,9-cyclododecatriene with DMED as a chain transfer agent was carried out using WCl_6-$SnMe_4$ catalyst to afford the polybutadiene product. The methanol-insoluble fraction of the product, which was isolated in yields of 70–80%, consisted primarily of acyclic ester-terminated 1,4-polybutadiene species. The use of highly pure 1,5-cyclooctadiene and a low catalyst charge in the ROMP reaction yielded product in which the acyclic component was determined to be purely ester-terminated ($F_n = 2.0$) telechelic 1,4-polybutadiene by high-sensitivity ^{13}C-NMR analysis. Further evidence of the high difunctional purity was obtained through chain extension of the telechelic polybutadiene to a high molecular weight polyester material by transesterification with 1,6-hexanediol.

Keywords: Olefin metathesis; Ring-opening metathesis polymerization; Telechelic; Polybutadiene

1. Introduction

Telechelic polymers, which are polymers with reactive chain end groups [1], are useful as macromonomers for synthesis of various types of higher molecular weight polymers including polyurethanes and polyesters. The reactive chain ends are typically hydroxyl or carboxyl groups, but may also be amine, ester, or other moieties. The degree of functionality in a telechelic polymer is typically expressed as a functionality number (F_n), defined as the average number of functional groups per polymer molecule. Telechelic polymers have been synthesized by a variety of techniques, including anionic, cationic, radical, and, more recently, olefin metathesis polymerization. The olefin metathesis synthetic methods include ring-opening metathesis polymerization (ROMP) [2–10], acyclic diene metathesis (ADMET) [11,12], and metathesis depolymerization of unsaturated polymers [13–18]. The work reported herein involves the use of ROMP to prepare an ester-terminated telechelic polybutadiene.

[*] Corresponding author.

The basic ROMP reaction that has been used [2–10] to prepare telechelic polymers is illustrated in Scheme 1, in which a cyclic olefin monomer reacts with a difunctional acyclic olefin to yield a difunctional telechelic polymer. The acyclic olefin acts as a chain transfer agent in the ring-opening metathesis polymerization of the cyclic olefin, regulating the molecular weight of the polymer product. The proposed mechanism of this reaction has been described by others [4–10]. Otton et al. [2], Seyferth et al. [3], and Reyx et al. [4,5] utilized WCl_6-SnR_4 olefin metathesis catalysts to prepare ester-terminated telechelics by reacting C_8 cyclic olefins (cyclooctene or 1,5-cyclooctadiene) with dialkyl 3-hexene-1,6-dicarboxylate ($RO_2CCH_2CH=CHCH_2CO_2R$) as the difunctional acyclic olefin; functionality numbers of the telechelic polymers were not reported. Cramail et al. [6] employed a similar process utilizing norbornene as the cyclic olefin monomer and reported functionality numbers of 1.7–1.9 for the ester-terminated telechelic polymers. Chung et al. [8] utilized 1,5-cyclooctadiene and a difunctional trialkylborane-containing acyclic olefin to produce telechelic polybutadienes with functionality numbers of about 2. Most recently, Grubbs et al. [9,10] have used well-defined molybdenum and tungsten metathesis catalysts to react 1,5-cyclooctadiene with silyl-protected 3-hexene-1,6-diol to yield telechelic polybutadiene diols with functionality numbers of 1.9–1.95; unprotected 3-hexene-1,6-diol has been employed as the chain transfer agent using ruthenium catalysts [10].

Our two goals in the work we report herein were to prepare an ester-terminated telechelic polybutadiene with a functionality number of 2.0, and to do so using readily available olefin reactants. A pure difunctional ($F_n = 2.0$)
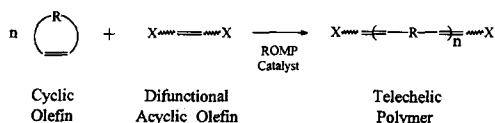
Scheme 1. ROMP reaction to prepare telechelic polymers.

telechelic polymer is a requirement in certain applications where the telechelic is used as a macromonomer to synthesize non-crosslinked condensation polymers of high molecular weight. Economic factors drive the desire to utilize reactants that are readily available commercially rather than materials, such as the 3-hexene-1,6-diesters and diols discussed above, which must be synthesized or are only available in research-scale quantities at high cost. We now report successful results through the use of a two-step olefin metathesis process employing 1,5-cyclooctadiene (COD) or 1,5,9-cyclododecatriene (CDT) as the cyclic olefin and a difunctional acyclic olefin derived from the methyl ester of undecylenic acid.

2. Experimental

Chlorobenzene, 1,2-dichlorobenzene, and methylcyclohexane solvents (Aldrich, HPLC grade) and tetramethyltin (Aldrich, 99 + %) were stored over 4 Å sieves. Tungsten hexachloride (Aldrich, 99.9%) was used as obtained and stored under N_2. Methyl undecylenate, $CH_2=CH(CH_2)_8CO_2CH_3$ (Elf Atochem, 97%) was washed with 1N NaOH and then water to remove acidic impurities, dried with $MgSO_4$, vacuum-distilled, and stored over 4 Å sieves. trans,trans,cis-1,5,9-Cyclododecatriene (CDT) was obtained from DuPont (98–99%) and stored over 4 Å sieves under N_2. cis,cis-1,5-Cyclooctadiene (COD) was obtained from Aldrich ('redistilled' grade, 99 + %) and stored over 4 Å sieves under N_2. This 'as-received' COD was employed in Experiment No. 1 of Tables 1 and 2 (see Section 3); it was determined to have a purity of 99.3% by GC and contained 0.2% 4-vinyl-1-cyclohexene (4-VCH). Fractionally-distilled COD was employed in Experiments 2 and 3 (Tables 1 and 2). Batch fractional distillation of COD (b.p. 150°C) was performed at 1 atm under N_2 using a 1-inch diameter, 20-tray Oldershaw column at a 15:1 reflux ratio. A 'heart cut' was collected; low-boiling fractions

Table 1
Experimental data and yield results for ROMP reactions of COD and DMED

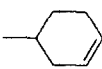| Exp. No.	COD Purity (4-VCH [a] content)	COD/WCl$_6$ molar ratio	PhCl/COD volume ratio	Reaction time(h)	% COD conv.	% DMED conv.	Yield MeOH-soluble product	Yield MeOH-insoluble product
1	99.3%(0.2%)	500	2:1	4	99.6	85	12%	83%(9.5 g)
2	99.9%(< 0.01%)	500	2:1	2.5	99.9	94	8%	67%(7.5 g)
3	99.9%(< 0.01%)	2500	1.5:1	22	99.9	87	10%	77%(44.0 g)

[a] 4-VCH = 4-vinyl-1-cyclohexene.

containing 4-VCH (b.p. 129°C) and high-boiling fractions were discarded. The fractionally-distilled COD was analyzed to be 99.9% pure by GC with < 0.01% 4-VCH present; it was stored under nitrogen over 4 Å sieves. 1,6-Hexanediol (Aldrich, 99 + %) and titanium(IV) butoxide (Aldrich, 99%) were employed for the chain-extension experiment.

Olefin metathesis reactions were performed under N$_2$ atmosphere due to the moisture sensitivity of WCl$_6$. Liquid reagents and mixtures were charged into glass reaction vessels (3-neck round-bottom flasks, magnetically stirred) by syringe or cannula methods under N$_2$. Reaction flask temperature was controlled using a thermostated silicone oil bath. Reaction temperatures reported refer to the oil bath temperature; internal reaction vessel temperatures were not measured. GC analyses were performed using an HP-5790 FID GC with a 30-meter DB-1 capillary column. Conversions of reactants were determined by GC analyses, generally using the solvent as an internal standard for quantifica-

tion. Metathesis reactions were quenched by bubbling dry gaseous ammonia through the reaction solution at room temperature, followed by filtration of the solution to remove precipitated tungsten catalyst residue.

In a typical ROMP reaction (Experiments 1 and 2 in Tables 1 and 2), a solution of COD (10.0 g, 92 mmol) and dimethyl 10-eicosene-1,20-dioate (DMED, 1.40 g, 3.80 mmol) in PhCl (22.5 ml) was charged into a reaction vessel. WCl$_6$ (73 mg, 0.18 mmol) was added to the solution and dissolved at room temperature, followed by addition of SnMe$_4$ (0.051 ml, 0.37 mmol). The reaction vessel was then immersed in a preheated oil bath at 100°C and the solution was stirred at 100°C for the desired reaction time. Afterward, the solution was cooled to room temperature and then quenched and filtered as described above. Evaporation of solvent afforded the crude product, typically a clear amber viscous liquid. Crude products were precipitated into methanol by dissolution in a minimum volume of CH$_2$Cl$_2$ and addition of the

Table 2
Characterization of methanol-insoluble products from ROMP reactions of COD and DMED based on ^{13}C-NMR spectral data

Exp. No.	Reaction conditions		Product characterization			
	COD purity (4-VCH [a] content)	COD/WCl$_6$ molar ratio	Backbone trans/cis	Endgroup proportion [b] (%)		
				–CO$_2$Me	–CH = CH$_2$	cyclohexenyl
1	99.3% (0.2%)	500	54:46	88	7	~ 5%
2	99.9% (< 0.01%)	500	67:33	98.5	1.5	< 1% (n.d.)
3	99.9% (< 0.01%)	2500	59:41	100	< 1 (n.d.)	< 1% (n.d.)

[a] 4-VCH = 4-vinyl-1-cyclohexene.
[b] Ester endgroup (–CO$_2$Me) quantification was performed using an average of the integrated intensities of the carbonyl and methoxy carbon resonances. Vinyl endgroup quantification was performed using an average of the integrated intensities of the two vinylic carbon resonances. Cyclohexenyl endgroup quantification was performed using the olefinic carbon resonances of the C$_6$ ring.

solution to a large excess of methanol (at room temperature). The precipitation procedure was performed two additional times. Methanol-soluble fractions were isolated by vacuum removal of solvent. Methanol-insoluble fractions were typically clear yellow viscous liquids; residual solvents were removed by vacuum.

Chain extension of the telechelic polybutadiene diester (ROMP reaction product) was carried out by the following procedure. To a 50-ml round-bottom flask with N_2 atmosphere containing 5.00 g (1.4 mmol) telechelic polybutadiene diester ($M_n = 3660$ by ^{13}C-NMR; IV = 0.11 dl/g in PTCE) and 0.821 g (7.0 mmol) 1,6-hexanediol was added 0.02 g titanium(IV) butoxide. In a Kugelrohr 'thin film' reactor, the mixture was heated to 150°C and maintained at this temperature for 3 h under 1 atm N_2. The pressure was then reduced to 0.005 mm Hg (dynamic vacuum) and the mixture was maintained at 150°C at the reduced pressure for an additional 3 h. The resultant polyester polymer (5.09 g, 99%) was a clear rubbery solid.

Quantitative ^{13}C-NMR spectra were obtained using $CDCl_3$ solvent with chromium acetylacetonate added as a relaxation agent. A Varian VXR-300 spectrometer was employed to obtain 75-MHz proton-decoupled spectra, with chemical shifts reported in ppm downfield from TMS. Long-duration NMR acquisitions (28 000–32 000 pulses) were employed to obtain high S/N ratios (typically 100–400/1 for the ester endgroup carbonyl carbon signals of ROMP products). GPC analyses of ROMP reaction products were performed using polybutadiene standards (peak molecular weights from 760 to 10 000 g/mole; Polymer Laboratories, Inc.) and THF solvent with sulfur added as a retention time marker.

3. Results and discussion

A two-step olefin metathesis process, illustrated in Scheme 2, was devised to synthesize an ester-terminated telechelic polybutadiene

starting with a readily available olefinic ester, methyl undecylenate. (Undecylenic acid is derived from castor oil; it and the methyl ester are available commercially in bulk quantities.) In the first step of this process, methyl undecylenate undergoes self-metathesis in the presence of a WCl_6-$SnMe_4$ catalyst system to yield the acyclic olefinic diester, dimethyl 10-eicosene-1,20-dioate (DMED), plus ethylene. The second process step is the ROMP reaction of 1,5-cyclooctadiene (COD) or 1,5,9-cyclododecatriene (CDT) with the difunctional acyclic olefin (DMED) using WCl_6-$SnMe_4$ catalyst to yield a linear, telechelic polybutadiene diester. This second step is the same basic reaction depicted in Scheme 1.

The first process step, self-metathesis of methyl undecylenate to DMED, has been reported previously [19]. In our process we isolated and purified the DMED product for use in the ROMP reaction step. The self-metathesis reaction was performed by addition of $SnMe_4$ (4 mmol, 0.72 g) to a 50°C solution of methyl undecylenate (100 mmol, 19.8 g) and WCl_6 (2 mmol, 0.79 g) in 1,2-dichlorobenzene (10 ml). The solution was then heated to 75°C and a continuous slow N_2 purge of the reactor headspace was initiated to effect removal of evolved ethylene. After 20 h GC analysis indicated 59% conversion of methyl undecylenate and > 95% selectivity to DMED (cis + trans). After reaction quench and filtration to remove tungsten catalyst residue, solvent and unreacted
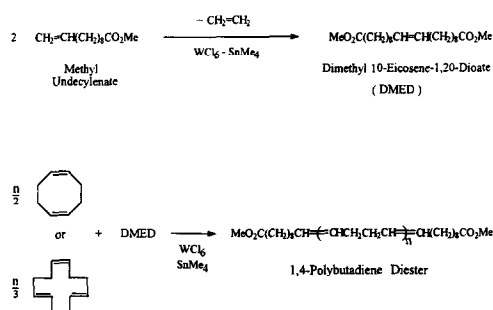
Scheme 2. Two-step olefin metathesis process to prepare an ester-terminated telechelic polybutadiene.

methyl undecylenate were removed by evaporation (150°C, ~ 1 mm Hg). The crude product (an orange solid) was dissolved in methanol, decolorized with charcoal, recrystallized from methanol/water at 0°C, and dried under vacuum, yielding white crystalline DMED (8.3 g, 75% yield based on converted methyl undecylenate, m.p. 43–44°C). GC analyses indicated the DMED product was typically 65–70% *trans* and contained < 0.5 wt.% residual methyl undecylenate.

In the second process step, ROMP reactions of 1,5-cyclooctadiene (COD) with DMED were performed using WCl_6-$SnMe_4$ (1:2 mole ratio) catalyst. A 24:1 COD/DMED mole ratio was employed in order to obtain polymer product with a number-average molecular weight of approximately 3000. Experimental data and isolated yields for three illustrative experiments are given in Table 1. These three reactions were run at 100°C at 1 atm in chlorobenzene solvent. High conversions of both COD and DMED were obtained even with a COD/WCl_6 mole ratio as high as 2500:1 (Experiment No. 3). The crude products contained a small amount (~ 10 wt.%) of very low molecular weight material that was easily extracted upon precipitation into methanol. Both GPC data (Fig. 1) and GC analyses indicate that this extractable material probably consisted mainly of cyclic butadiene oligomers (in addition to unreacted DMED), which are typically produced to some extent in ROMP reactions of COD with WCl_6 catalysts [20]. GC analyses of reaction solutions showed the presence of cyclic butadiene oligomer products: clusters of GC peaks corresponding to ~ C_{12}, C_{16}, C_{20}, and C_{24}, probably cyclic (–$CH_2CH=CHCH_2-)_n$ species with $n = 3–6$. These species were detected at both low (~ 50%) and high (> 99%) COD conversions. The methanol-insoluble product fractions, which were isolated in ~ 70–80% yield, were of substantially higher molecular weight than the extractable material (see Fig. 1). GPC-determined molecular weights for the insoluble product of Experiment No. 3 were $M_n = 2980$, $M_W =$
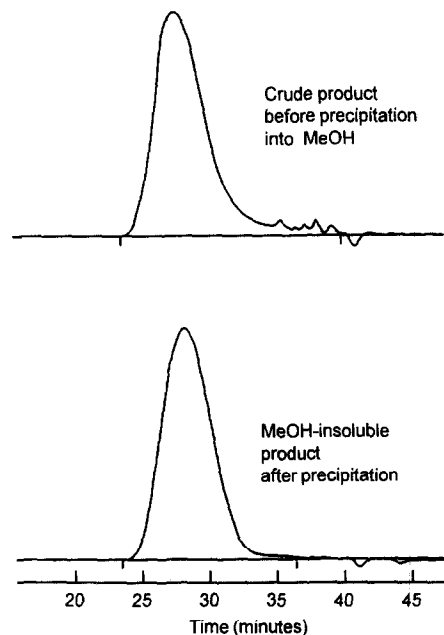

Fig. 1. GPC chromatograms of products from ROMP reaction of COD and DMED, Experiment No. 3 (see Table 1).

7150, and $M_W/M_n = 2.4$. The methanol-insoluble product fractions probably contained only very low amounts of cyclic oligomers, since it is known that concentrations of cyclic oligomer products decrease with increasing ring size [21].

The methanol-insoluble products of the ROMP reactions were analyzed by ^{13}C-NMR spectroscopy (Figs. 2 and 3) in order to deduce their structure and difunctional purity. The spectra are all consistent with the ester-terminated 1,4-polybutadiene structure shown in Scheme 2. Backbone resonances are assigned as follows: =CH (multiplet at 129–131 ppm), CH_2 adjacent to *trans* double bond (singlet at 32.6 ppm), and CH_2 adjacent to *cis* double bond (singlet at 27.3 ppm) [22]. Resonances associated with the ester endgroup, –$(CH_2)_8CO_2CH_3$, which are much weaker signals than the backbone resonances, are assigned as follows: OCH_3 (singlet at 51.1 ppm), C=O (singlet at 173.5 ppm), CH_2 α to C=O (singlet at 33.8 ppm), CH_2 β to C=O (singlet at 24.8 ppm), CH_2 adjacent to double bond (unseen, presumably hidden by backbone CH_2 resonances), and the five other

CH$_2$'s (multiplet at 29.0–29.5 ppm). The end-group assignments were made by comparison to spectra of DMED and methyl undecylenate.

More careful ^{13}C-NMR analyses (Fig. 3 and Table 2), however, revealed that the ROMP products of Experiments 1 and 2 were not purely ester-terminated. The spectrum of the methanol-insoluble product of Experiment No. 1 (Fig. 3) shows small but significant resonances associated with a vinyl endgroup (–CH=CH$_2$, singlets at 138.0 and 114.3 ppm) and a cyclohexenyl endgroup (probably 4-substituted as shown in Table 2, singlets at 126.1 and 126.6 ppm assigned as the ring olefinic carbons by comparison to the spectrum of 4-vinyl-1-cyclohexene). Evidently, the major source of the vinyl and cyclohexenyl endgroups was 4-vinyl-1-cyclohexene impurity in the COD reagent, as the use of purified COD in Experiment No. 2 gave a product with much less vinyl and no detectable cyclohexenyl endgroup. 4-Vinyl-1-cyclohexene can act as a chain transfer reagent in ROMP reactions in a manner similar to Scheme 1 [23], with metathesis occurring at the vinyl double bond to yield polymers with vinyl and cyclohexenyl endgroups. However, to
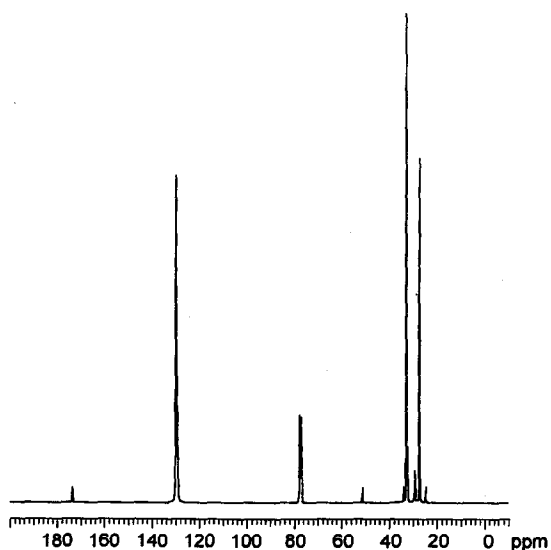

Fig. 3. Expanded ^{13}C NMR spectra of the methanol-insoluble products from ROMP reactions of COD and DMED, Experiments 1–3 (see Table 1).

obtain a product with no detectable vinyl endgroup it was necessary to employ a smaller catalyst charge (higher COD/WCl$_6$ ratio) in addition to the pure COD (Experiment No. 3). We postulate that the low level of vinyl endgroup detected in Experiment No. 2 was the result of initiation (and perhaps termination) reactions involving the WCl$_6$-SnMe$_4$ catalyst, in accordance with the results of Grubbs et al. [24]. Thus, the use of fewer initiating species (less catalyst) resulted in fewer vinyl endgroups produced from initiation, although this also had the effect of lowering the overall reaction rate.

No non-ester endgroups of any type were detected in ^{13}C-NMR spectrum of the methanol-insoluble polymer product of Experiment No. 3 within the detectability limit (< 1% of the ester endgroup signals). This indicates that the acyclic component of the product was purely ester-terminated ($F_n = 2.0$) telechelic 1,4-polybutadiene. As mentioned above, the product probably also contained very low amounts of cyclic 1,4-butadiene oligomers. Indirect evidence for this was seen in the comparison of NMR- and GPC-determined molecular

Fig. 2. ^{13}C NMR spectrum of the methanol-insoluble product from ROMP reaction of COD and DMED, Experiment No. 3 (see Table 1). (Triplet resonance at 77 ppm from CDCl$_3$ solvent.)
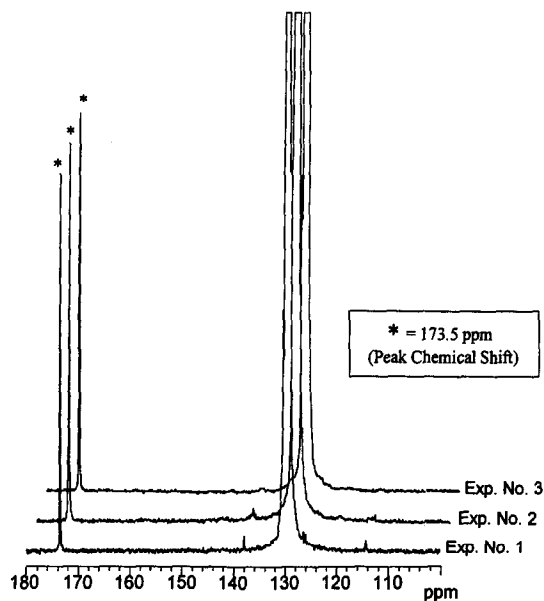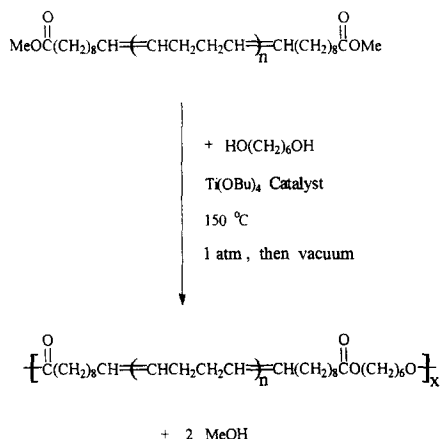
weights. Using ^{13}C-NMR data, the number-average molecular weight (M_n) was computed to be 4030 assuming a purely linear structure (shown in Scheme 2) without cyclic species; the backbone olefinic carbon resonance (129–131 ppm, relative intensity 465.7) and an average of two ester endgroup signals (carbonyl at 173.5 ppm, relative intensity 6.87; methoxy at 51.1 ppm, relative intensity 6.70) were employed in the computation. The fact that the NMR-determined M_n is higher than the GPC value (2980) implies the presence of cyclic species, which cannot be distinguished from acyclic species by NMR. If the cyclic species were predominantly lower molecular weight components of the material, as is likely based on previous studies [21], then the observed difference between the NMR and GPC molecular weights could have been caused by a very small weight fraction of cyclics.

Further evidence of the high difunctional purity of the telechelic polybutadiene was obtained through the chain extension experiment illustrated in Scheme 3. An ester-terminated telechelic polybutadiene (> 99% ester endgroup proportion and $M_n = 3660$ by ^{13}C-NMR) prepared by the same methodology as described above for Experiment No. 3 was employed for this experiment. The telechelic polybutadiene was chain-extended by transesterification with 1,6-hexanediol, yielding a high molecular weight

Scheme 3. Chain extension of ester-terminated telechelic polybutadiene by transesterification with 1,6-hexanediol.

polyester (IV = 0.76 dl/g in 1,2,4-trichlorobenzene; $M_n = 64\,000$ by GPC using a polypropylene standard calibration) plus methanol. The high molecular weight of the polyester product implies that the macromonomer from which it was formed, the telechelic polybutadiene diester, was of very high difunctional purity [25,26].

A ROMP reaction of trans,trans,cis-1,5,9-cyclododecatriene (CDT) with DMED was also performed to demonstrate that CDT can be used in place of COD in the second process step (Scheme 2). This reaction was carried out at 75°C using methylcyclohexane solvent (2:1 solvent/CDT by volume) and a 340:21:1:2 mole ratio of CDT/DMED/WCl$_6$/SnMe$_4$, with the CDT/DMED ratio chosen to target a product M_n of ~ 3000. After 20 h reaction time, 70% CDT conversion and 87% DMED conversion were observed. The isolated methanol-insoluble product (56% yield) was a viscous, slightly cloudy, pale yellow liquid. The ^{13}C-NMR spectrum of the product was very similar to those of the COD reaction products and indicated that the material consisted of essentially the same ester-terminated 1,4-polybutadiene structure (as shown in Scheme 2). The trans/cis double bond proportion in the backbone was 72:28, the endgroup proportion was 99% ester and 1% vinyl, and the NMR-determined M_n was ~ 2500.

4. Conclusions

A two-step olefin metathesis process was devised and utilized to prepare an ester-terminated telechelic 1,4-polybutadiene of high difunctional purity using readily available olefin reactants (methyl undecylenate and 1,5-cyclooctadiene or 1,5,9-cyclododecatriene). In the first step of this process, methyl undecylenate was self-metathesized in the presence of WCl$_6$-SnMe$_4$ catalyst to yield an acyclic olefinic diester, dimethyl 10-eicosene-1,20-dioate (DMED), plus ethylene. In the second step, a

ROMP reaction of 1,5-cyclooctadiene or 1,5,9-cyclododecatriene with DMED was carried out using WCl_6-$SnMe_4$ catalyst to afford the polybutadiene product. The methanol-insoluble fraction of the product, which was isolated in yields of 70–80%, consisted primarily of acyclic ester-terminated 1,4-polybutadiene species but also appeared to contain very low amounts of cyclic 1,4-polybutadiene oligomers. The use of highly pure 1,5-cyclooctadiene and a low catalyst charge in the ROMP reaction yielded product in which the acyclic component was determined to be purely ester-terminated ($F_n = 2.0$) telechelic 1,4-polybutadiene by high-sensitivity ^{13}C-NMR analysis: no non-ester endgroups were detected within the detectability limit of the analysis ($< 1\%$ of the ester endgroup signals). Further evidence of the high difunctional purity was obtained through chain extension of the telechelic polybutadiene to a high molecular weight polyester material by transesterification with 1,6-hexanediol.

Acknowledgements

References

[1] E.J. Goethals (Ed.), Telechelic Polymers: Synthesis and Applications, CRC Press, Boca Raton, 1989.

[2] J. Otton, Y. Colleuille and J. Varagnat, J. Mol. Catal., 8 (1980) 313.

[3] K. Seyferth, R. Taube and M. Dahlke, (East) German Patent 146052 (1981).

[4] D. Reyx, I. Campistron and P. Heiling, Makromol. Chem., 183 (1982) 173.

[5] D. Reyx, I. Campistron and M. Hamza, J. Mol. Catal., 36 (1986) 101.

[6] (a) H. Cramail, M. Fontanille and A. Soum, J. Mol. Catal., 65 (1991) 193; (b) H. Cramail, M. Fontanille and A. Soum, Makromol. Chem., Macromol. Symp., 42/43 (1991) 281.

[7] H. Balcar and J. Dybal, React. Kinet. Catal. Lett., 30 (1986) 17.

[8] T.C. Chung and M. Chasmawala, Macromolecules, 25 (1992) 5137.

[9] M.A. Hillmyer and R.H. Grubbs, Macromolecules, 26 (1993) 872.

[10] M.A. Hillmyer and R.H. Grubbs, Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.), 34 (1993) 388.

[11] D. Tao and K.B. Wagener, Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.), 34 (1993) 469.

[12] P.O. Nubel, C.A. Lutman and H.B. Yokelson, Macromolecules, 27 (1994) 7000.

[13] K. Seyferth, R. Taube and M. Dahlke, (East) German Patent 146053 (1981).

[14] D. Reyx and I. Campistron, Makromol. Chem., 191 (1990) 251.

[15] T.C. Chung, J. Mol. Catal., 76 (1992) 15.

[16] M. Chasmawala and T.C. Chung, Macromolecules, 28 (1995) 1333.

[17] J.C. Marmo and K.B. Wagener, Macromolecules, 26 (1993) 2137.

[18] J.C. Marmo and K.B. Wagener, Macromolecules, 28 (1995) 2602.

[19] J. Levisalles, H. Rudler, D. Cuzin and T. Rull, J. Mol. Catal., 26 (1984) 231.

[20] K.J. Ivin, Olefin Metathesis, Academic Press, London, 1983, p. 194.

[21] K.J. Ivin, Olefin Metathesis, Academic Press, London, 1983, p. 51.

[22] K.J. Ivin, Olefin Metathesis, Academic Press, London, 1983, p. 202 and references cited therein.

[23] K.J. Ivin, Olefin Metathesis, Academic Press, London, 1983, p. 282.

[24] R.H. Grubbs and C.R. Hoppin, J. Chem. Soc., Chem. Commun., (1977) 634.

[25] B. Ivan and J.P. Kennedy, Polymer Bulletin, 2 (1980) 351.

[26] G. Odian, Principles of Polymerization, McGraw-Hill, New York, 1970, Chapter 2.