



Synthesis of dihydroxy poly(ethylene-co-butadiene) via metathetical depolymerization: Kinetic and mechanistic aspects

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ABSTRACT

We investigate the synthesis of dihydroxytelechelic poly(ethylene-co-1,3-butadiene) via metathetical depolymerization of the corresponding high molar mass copolymers in the presence of first generation Grubbs catalyst and butene diacetate as functionalizing chain transfer agent, followed by hydrolysis of the acetoxy chain ends. Formation of telechelic oligomers is complicated by a fast back-biting reaction leading to cyclohexene and macrocycles production. The thermodynamically favored formation of unsaturated six membered ring results from the presence of 1,7-dienic unsaturations in the starting copolymer. Macrocycles also rapidly and almost quantitatively form in the first reaction stage. Opportunely they can re-open in the presence of functionalizing transfer agent, owing that the later is introduced in molar excess with respect to the macrocycle, finally yielding linear dihydroxytelechelic oligomers.

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1. Introduction

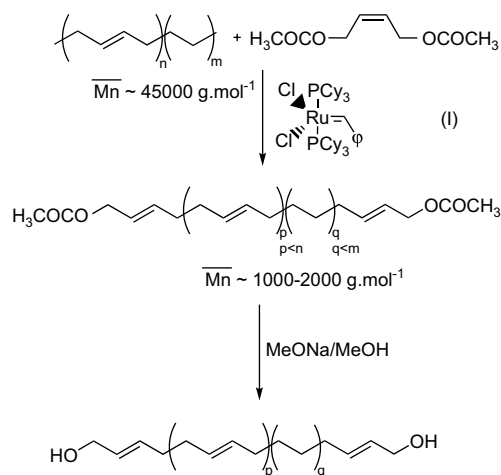
Telechelic oligomers found important applications as precursors for polymeric networks and for the production of block copolymers. Among these materials dihydroxytelechelic polybutadiene (HT-PB) is widely used in polyurethane industry owing to its good elastomeric properties, very low glass transition temperature, resistance to hydrolysis and excellent dielectric properties [1–3]. However, the unsaturated backbone constituted both of 1,2 and 1,4-butadiene units suffers from a relatively important and rapid aging process [4,5] characterized by a loss of the elastomeric properties due to chain crosslinking induced by double bond photo-oxidation [6–8]. To improve chain stability several approaches have been investigated. The first one consists in the synthesis of perfectly 1,4 polybutadiene since 1,2 units are reported to oxidize more rapidly than 1,4 units [9]. This can be achieved by ring opening metathesis (ROMP) of cyclooctadiene in the presence of a functional transfer agent [10,11]. In fact this approach shows a limited impact on aging processes since in chain unsaturations can be also readily oxidized [12]. The ROMP of larger cyclic olefins, which allows reducing the number of backbone unsaturations was also explored [13,14]. The polyalkenamers show an improved stability with decreasing the number of unsaturations [12,15,16]

but at the same time exhibit some undesirable crystallinity as soon as the repetitive units possess more than five methylenic carbons. It was recently shown that crystallinity could be significantly reduced by copolymerizing randomly two large cyclic olefins of different ring sizes [17], the disorder introduced by the presence of two distinct monomer units limiting chain packing. Another way to get more stable telechelic hydrocarbon oligomers consists in the hydrogenation of double bonds to yield the corresponding ethylene–butene hydroxytelechelic copolymers (HT-HPB). To limit the presence of long polyethylene sequences yielding semi-crystalline materials, HT-PB with a high amount of 1,2 units must be used. The major drawback of this strategy is an important increase of the glass transition temperature and of the bulk viscosity of the corresponding HT-HPB.

Recently, some of us [18,19] have achieved the synthesis of high molar masses poly(ethylene-co-1,3-butadiene) with a chain composition quite similar to copolyalkenamers. These random-like copolymers were interesting starting materials for the preparation of new hydroxytelechelic hydrocarbon oligomers of improved stability.

In this paper we investigate the synthesis of dihydroxytelechelic poly(ethylene-co-1,3-butadiene) (HT-PEB) via metathetical depolymerization of high molar mass PEB in the presence of first generation Grubbs catalyst and butene diacetate as functionalizing chain transfer agent (CTA), followed by hydrolysis of the acetoxy chain ends (Scheme 1).

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Scheme 1. Strategy for the synthesis of dihydroxytelechelic copolymer via metathetical depolymerization of poly(ethylene-*co*-1,3-butadiene).

2. Experimental

2.1. Materials

Bis(tricyclohexylphosphine)benzylidene ruthenium(IV) dichloride (first generation Grubbs catalyst) was purchased from Sigma Aldrich France and used as such. Dichloromethane (Atlantic Labo, >99%) was distilled and dried over CaH_2 followed by further distillation over triethylaluminium and stored in glass flasks under dry nitrogen until use. *cis*-1,4-Diacetoxy-2-butene (Sigma Aldrich, 95%) was dried over CaH_2 and then distilled prior use. Other solvents and chemicals were of reagent grade and used without further purification.

2.2. Instrumentation

^1H and ^{13}C NMR polymer analysis were performed in CDCl_3 on a Bruker 400 ultra shield spectrometer at room temperature.

Copolymer and oligomer molar masses were measured by SEC (Varian apparatus) at 20°C , in THF using a dual refractive index /UV Varian detector fitted with four TSK columns ($300 \times 7.7 \text{ mm}^2$, 250, 1500, 10^4 , and 10^5 \AA , respectively) calibrated with polystyrene standards and using a correction factor of 0.6 for the calculation of PEB molar masses.

The MALDI-TOF mass spectrometry measurements were performed on a Bruker REFLEX II mass spectrometer (Bruker Daltonics, Bremen, Germany). The instrument is equipped with a pulsed N_2 laser (337 nm) and a time-delayed extracted ion source. Polymers were dissolved in THF at 10 g L^{-1} . The dithranol matrix solution was prepared by dissolving 10 mg in 1 mL of THF. A THF solution of cationisation agent (Agtrifluoroacetate at 10 g L^{-1}) was also prepared. The solutions were combined in a 10:1:1 volume ratio of matrix to sample to cationisation agent and spotted on the sample holder.

Cyclohexene formation was titrated via gas chromatography (GC). The apparatus was equipped with a FID detector (Varian 3,650) coupled and filled with a hydrophobic capillary column BP1-30 m and N_2 as vector gas. Nonane was used as an internal reference.

2.3. Synthesis of poly(ethylene-*co*-butadiene)

The original synthesis of poly(ethylene-*co*-1,3-butadiene) random copolymers using a neodymocene catalyst as well as the

copolymer characterization has been reported by Boisson et al. in previous papers [18,19]. Briefly, copolymer **A**₁ was prepared as follows: 28 mL of butadiene (0.31 mol) were added to a solution of toluene (500 mL) containing the bridged complex $[\text{Me}_2\text{Si}(\text{3-Me}_3\text{SiC}_5\text{H}_3)_2]\text{NdCl}$ (52 mg, 102 μmol) and *n*-butyl-*n*-octylmagnesium (ratio Mg/Nd = 2). The solution was transferred into a 1 L stainless steel reactor. The reactor was charged with ethylene (17.5 bar) and heated up to 80°C . The polymerization was stopped after 1 h. The copolymer was then precipitated into methanol, washed and dried under vacuum (15.75 g). Ethylene-butadiene copolymers with high butadiene content, mainly present as isolated 1,4-butadiene units between ethylene sequences were obtained in these conditions. Copolymers with $\overline{M}_n = 45,000 \text{ g mol}^{-1}$ ($\overline{M}_w/\overline{M}_n = 2.5$) and $\overline{M}_n = 51,000 \text{ g mol}^{-1}$ ($\overline{M}_w/\overline{M}_n = 1.4$) respectively noted **A**₁ and **A**₂ were used in this study.

2.4. Depolymerization reaction protocols

- In the absence of CTA*: in a typical experiment, PEB sample (1 g) was solubilized in a small amount of dichloromethane (1 mL), in a 200 mL glass reactor under argon, and 2 mg (2.4 μmol) of Grubbs catalyst in 1 mL of dry dichloromethane was added by syringe under nitrogen atmosphere at room temperature under continuous stirring. Rapidly after the catalyst addition, the viscosity of the solution was observed to drop. The reaction was quenched after 20 h by the addition of an excess of acidic methanol (2 mL). The polymer was purified three times by redissolution in THF and precipitation in methanol solution.
- In the presence of CTA*: similar procedure was applied except that a known amount of *cis*-1,4-diacetoxy-2-butene (DAB) was added to the dichloromethane polymer solution before adding the catalyst.

2.5. Hydrolysis of the acetate polymer ends

A solution of sodium methanolate in methanol (10 mL, 10 g L^{-1}) was added to a THF solution of the acetoxy ended copolymer (20 mL, 40 g L^{-1}) and the mixture was stirred over night at 25°C . Finally the polymer was precipitated into a large excess of methanol, and dried under vacuum until constant weight before NMR and SEC analyses.

3. Results and discussion

Prior works concerning the metathetical depolymerization of unsaturated polymers have shown that an important polymer molar mass reduction already takes place in the presence of metathesis catalysts, in the absence of any additional chain transfer agent (CTA) [20,21]. This was explained by the formation of cyclic oligomers and the *in-situ* generation of chain limiters [20]. This led us to investigate first the action of the ruthenium carbene catalyst (I) onto the poly(ethylene-*co*-1,3-butadiene) chains in the absence of DAB.

Table 1
Characteristics of initial high molar mass poly(ethylene-*co*-butadiene) samples **A**₁ and **A**₂ used in this work

Ref.	Butadiene content ^a (mol%)	1,4 units ^a (mol%)	1,2 units ^a (mol%)	\overline{M}_n^b (g/mol)	$\overline{M}_w/\overline{M}_n^b$	BEB triads ^c (mol%)
A ₁	38	97	3	46,000	2.5	24
A ₂	42	96	4	51,000	1.4	30

^a Determined by ^1H NMR in CDCl_3 .

^b Determined by SEC (THF).

^c Determined by ^{13}C NMR in CDCl_3 . Calculations are performed according to Ref. [37].

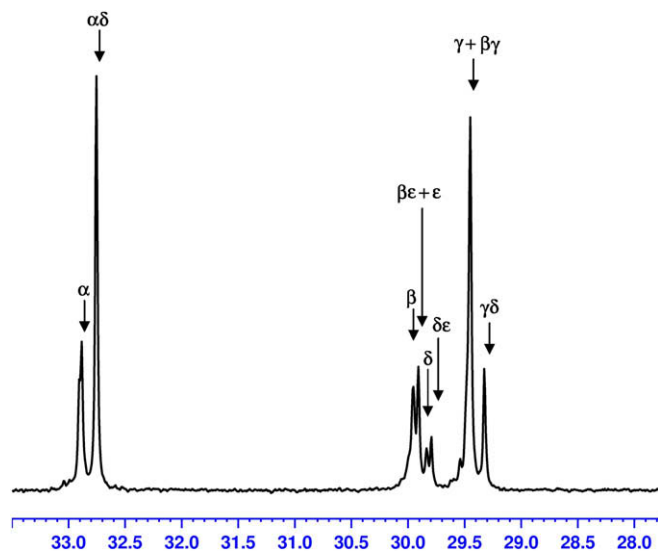


Fig. 1. ^{13}C NMR spectra of PEB copolymer **A**₂ and peak attribution of methylenic carbon according to their relative positions with respect to neighbouring 1,4-butadiene units (notation according to Ref. [37]).

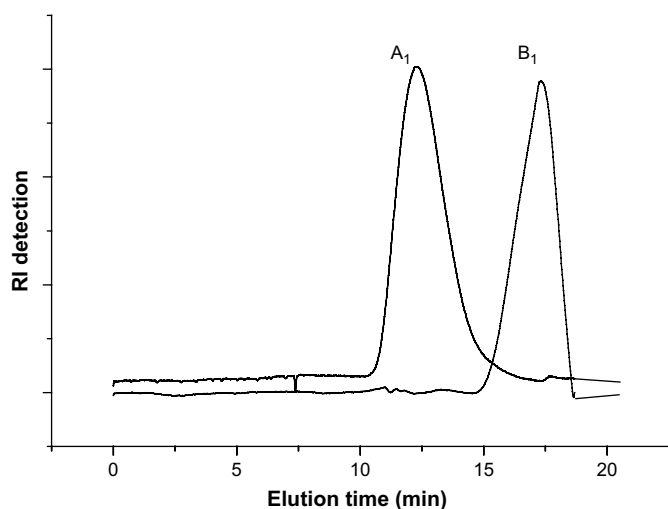


Fig. 2. SEC chromatograms of PEB copolymer (**A**₁) and of the final oligomers (**B**₁).

3.1. Depolymerization in absence of a CTA

The characteristics of the random PEB samples used in this work, **A**₁ and **A**₂ are given in Table 1. A typical ^{13}C NMR spectrum (sample **A**₂) as well as methylenic carbon peaks attribution is given in Fig. 1. The copolymers contain about 40% in moles of butadiene, with more than 96% of *trans*-1,4 units. They are characterized by the

absence of butadiene sequences (less than 3% BB diads) and a tendency to alternation as shown by the quite high percentage of BEB triads.

Reacting PEB copolymers **A**₁ and **A**₂ in dichloromethane with catalyst (I) resulted in an important decrease of their molar mass as shown on SEC chromatograms Fig. 2. After 20 h of reaction, the resulting oligomers **B**₁ and **B**₂ exhibit molar masses in the range of 1000–2000 g mol⁻¹ (see Table 2). As first approximation the ratio between initial and final polymer molar mass suggests about 25–50 scissions for each chain.

Several mechanisms can be considered to explain the products formed and the observed molar mass decrease, Scheme 2:

- (1) Formation of macrocycles by back-biting reaction, a side process which often occurs in ROMP [22–25]. PEB “depolymerization” by intramolecular reaction of metallocarbene chain terminus with 1,4-butadiene units could also yield such macrocycles (Scheme 2). Thanks to the absence of chain ends, cyclic oligomers can be distinguished from linear homologues by MALDI-TOF analysis. Nevertheless this characterization method cannot be directly applied to co-oligomers due to their complex peak pattern. Therefore a high molar mass polycyclooctadiene (pCOD) was prepared as model system and submitted to metathetical depolymerization in conditions reported in Table 2 for PEB and the resulting oligomers were analyzed by MALDI-TOF (Fig. 3). Results confirm the almost quantitative formation of macrocycles ($\bar{M}_n = 800\text{--}1000\text{ g mol}^{-1}$, $M_{\text{peak}} = n54\text{ g mol}^{-1}$ (n butadiene units) + 107 g mol^{-1} (Ag^+ cation)), supporting thus the predominant depolymerization of PEB in presence of catalyst (I) by cyclization, via back-biting reactions.
- (2) Formation of cyclohexene in large amount. This can be related to the particular structure of PEBs, which contains a significant amount of BEB triads (see Table 1). As illustrated in Scheme 3, BEB sequences can readily yield the six membered cyclohexene ring by back-biting. In contrast to other rings, the latter accumulates in the reacting medium since it is resistant to ROMP [26]. The number of cyclohexene molecules formed by PEB chain and by initial BEB sequence are indicated in Table 2. Data shows that formation of cyclohexene increases with both the butadiene content and the proportion of BEB sequences in the initial copolymer. Cyclohexene formation proceeds until almost quantitative consumption of BEB triads, thus yielding new PEB copolymers with very limited number of BEB sequences and a larger fraction of ethylene units, as shown by ^{13}C NMR for oligomer **B**₂, Fig. 4. With respect to the initial copolymers, the average weight percentage of cyclohexene formed reaches about 35%, which corresponds to the generation of approximately 200 cyclohexene molecules per PEB chain.
- (3) Other chain scission processes, involving either reaction of the carbene catalyst with 1,4-butadiene units (Scheme 2,

Table 2

Characteristics of oligomers **B**₁ and **B**₂ recovered after reaction with catalyst (I) at room temperature for 20 h

Ref.	Butadiene content ^a (mol%)	1,4 units ^a (mol%)	1,2 units ^{a,b} (mol%)	BEB triads ^c (mol%)	\bar{M}_n^d (g/mol)	\bar{M}_w/\bar{M}_n^d	Nb cyclohexene molecules ^e generated	
							By copolymer chain	By initial BEB triads
B ₁	33	97	3 [4]	2	1800	1.7	180	0.98
B ₂	35	97	3 [4]	6	1000	1.8	250	0.88

[Butadiene unit] = 1.6 mol L⁻¹ in CH₂Cl₂; [catalyst] = 0.4 mmol L⁻¹.

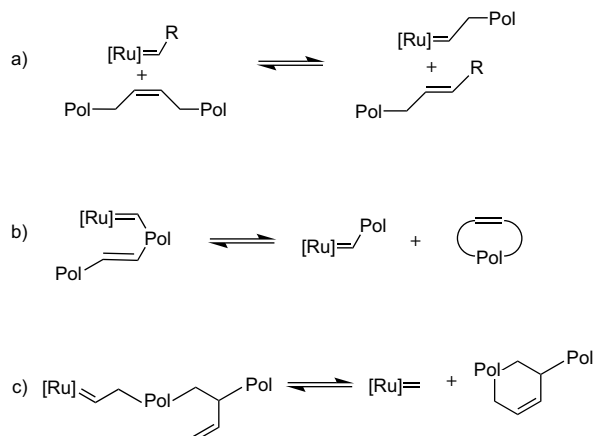
^a Determined by ^1H NMR in CDCl₃.

^b Value into brackets are recalculated to take into account the total amount of initial polymer considering that the formation of cyclohexene only consumes 1,4-butadiene units.

^c Determined by ^{13}C NMR, in CDCl₃ at 20 °C.

^d Determined by SEC (THF).

^e Measured by GC.



Scheme 2. Main reaction processes yielding PEB chain fragmentation in absence of any chain transfer agent.

R = phenyl) or *in-situ* formation of chain limiters [20] by carbene reaction with vinylic bonds of 1,2 butadiene units (Scheme 2) are negligible in comparison to processes (1) and (2). The lack of reactivity of 1,2 butadiene units towards metathesis is supported by results given in Table 2. It may be due to steric congestion.

The evolution of PEB molar mass (sample **A**₁) with increasing reaction time is presented in Fig. 5. It shows that “depolymerization” proceeds in two relatively distinct steps. A very rapid decrease of the polymer molar mass, corresponding to a M_n drop from 46,000 to about 18,000 g mol^{-1} , is first observed. Kinetics of cyclohexene release indicates that the cyclic olefin is mainly formed during this first stage (more than 80%). Then in a second period, from about 10–20 to 300 min, copolymer molar masses continuously but slowly decreases to finally reach a plateau corresponding to the formation of PEB oligomers with a molar mass of about

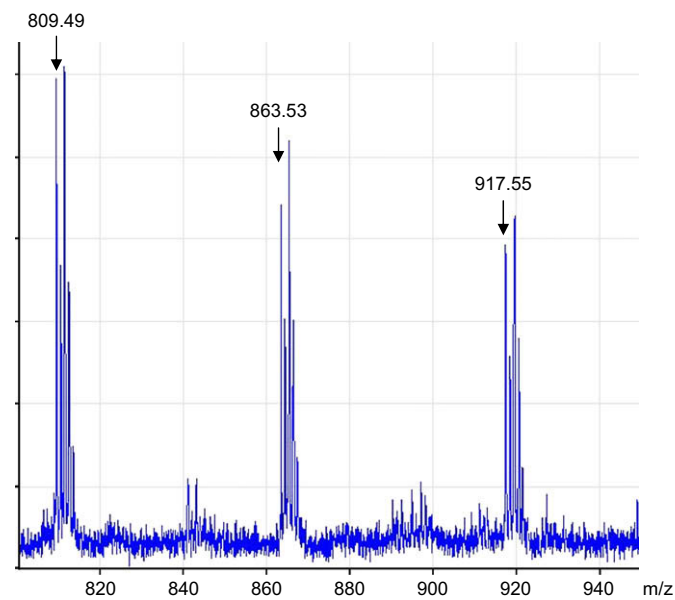
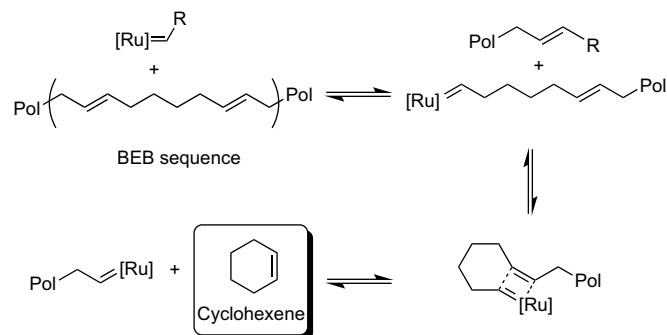


Fig. 3. MALDI-TOF mass spectra of cyclic pCOD oligomers obtained by reaction of high molar mass pCOD with catalyst (I). Reaction conditions: $[\text{COD}] = 0.9 \text{ mol L}^{-1}$ in CH_2Cl_2 ; $[\text{catalyst}] = 0.2 \text{ mmol L}^{-1}$. Reaction at room temperature for 20 h. $M_{\text{peak}} = n \times 54 + 107$ where 107 is the Ag^+ cation. The satellite peaks corresponds to isotropic profiles of Ag^+ cation.



Scheme 3. Cyclohexene formation by back-biting reaction involving BEB sequences.

1800 g mol^{-1} . This is expected to correspond to the thermodynamic equilibrium of the system.

These results point out that in the very initial stage of the reaction, a large majority of 1,4-butadiene units are involved into the metathesis process. The catalyst scrambling is likely accompanied by (i) inter-chain exchanges of polymer blocks (Scheme 2, R = polymer chain), difficult to quantify since they only affect the polydispersity and (ii) back-biting reactions responsible for the observed decrease of the PEB molar masses. When a BEB sequence is concerned, the back-biting results into a fast and irreversible cyclohexene formation, while the slower formation of macrocycles involves in chain butadiene units of longer ethylene/butadiene sequences. These different processes yield a final system, at the

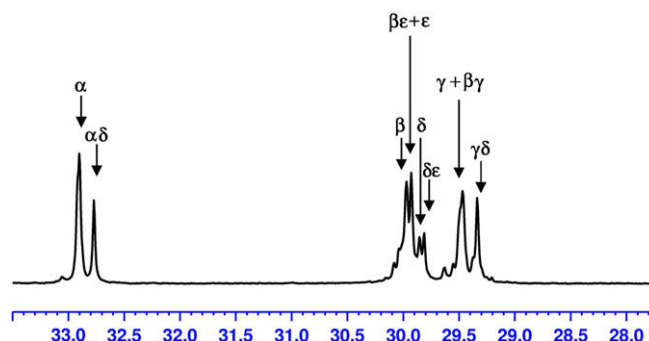


Fig. 4. ^{13}C NMR spectra of PEB oligomers **B**₂ recovered after metathetical reaction with the corresponding peak attribution (notation according to Ref. [37]).

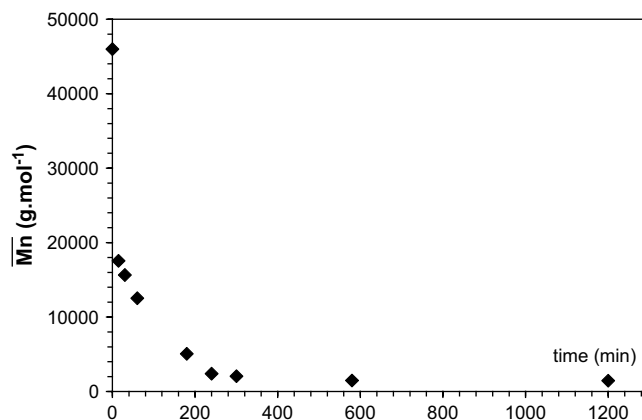


Fig. 5. Evolution of the PEB (sample **A**₁) average molar mass as a function of reaction time with catalyst (I) in dichloromethane at room temperature [$\text{butadiene unit}] = 1.0 \text{ mol L}^{-1}$ in CH_2Cl_2 ; $[\text{catalyst}] = 1.2 \text{ mmol L}^{-1}$.

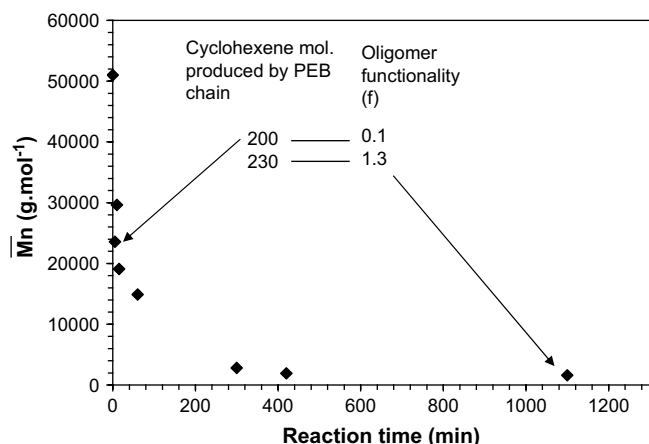


Fig. 6. Evolution of the PEB (sample **A**₂) average molar mass and functionality as a function of reaction time with catalyst (**I**) and DAB as functional transfer agent in dichloromethane at room temperature [butadiene unit] = 1.0 mol L⁻¹ in CH₂Cl₂; [catalyst] = 1.2 mmol L⁻¹.

thermodynamic equilibrium, mainly constituted of cyclohexene and cyclic oligomers, with a small amount of linear PEB oligomers bearing either a metal carbene terminus or one of the initial copolymer end-groups (predominantly -CH₂-CH₃).

3.2. Functional depolymerization in the presence of a CTA

In order to prepare hydroxytelechelic (ethylene-*co*-1,3-butadiene) oligomers, a functional CTA was introduced during the “depolymerization” reaction of PEB. The use and efficiency of butene diacetate (DAB) as CTA in the ROMP of several cyclic olefins have been reported [10,27,28]. During metathetical polymerization

Table 3
Effect of initial copolymer concentration on PEB oligomer functionality

[Butadiene unit] ₀ ^a (mol L ⁻¹)	\bar{M}_n ^b (g mol ⁻¹)	Functionality in acetoxo end-groups ^c
0.7	800	0.8
2.5	1400	1.1
5.0	2300	1.4
20.0	3700	1.6

Initial $n_{\text{DAB}}/n_{\text{copolymer}} = 14$; reaction at room temperature for 20 h.

^a Initial concentration of **A**₁ butadiene units in CH₂Cl₂.

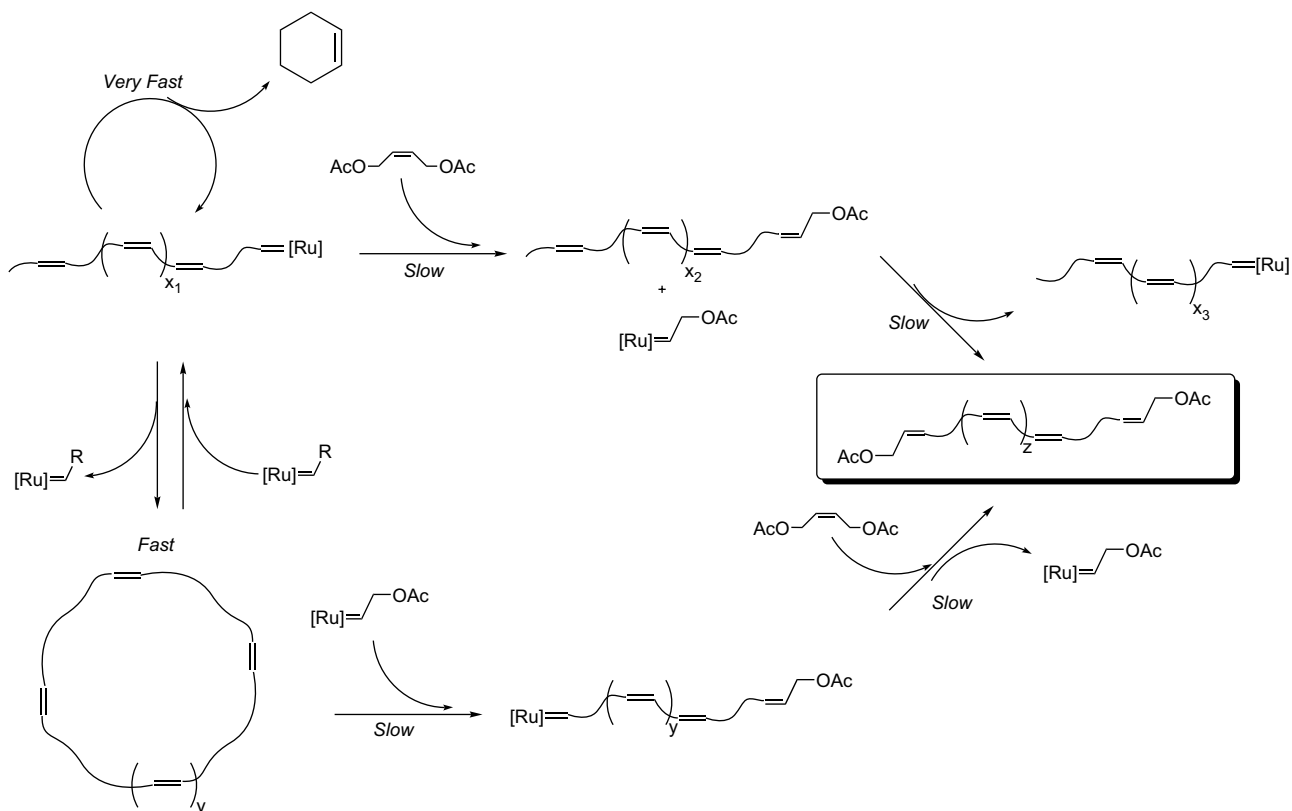
^b Determined by SEC (THF).

^c Determined by ¹H NMR, CDCl₃.

of cyclic olefins, inter and intramolecular cross-metathesis reactions and chain end functionalization proceed concurrently to finally yield diacetoxo terminated oligomers, which can be easily deprotected into dihydroxytelechelic oligomers [10]. Only a limited number of studies have concerned the synthesis of dihydroxytelechelic oligomers by direct “depolymerization” reaction of unsaturated polymers, as depicted for PEB in Scheme 1 [29–36].

In a first set of depolymerization experiments targeting the preparation of functional oligomers with $\bar{M}_n = 30,000$ g mol⁻¹ ([CTA]/[polymer chain] = 14), low molar mass PEB of $\bar{M}_n = 1000$ g mol⁻¹ with an average acetate end-group functionality close to one were obtained. These results can be interpreted by a significant contribution of back-biting reactions which leads to the formation of nonfunctional cyclic oligomers, which accompany the important formation of the six membered ring, despite the presence of DAB.

The evolution of the number-average molar mass of PEB **A**₂ in the presence of DAB with increasing reaction time is plotted in Fig. 6. The functionality and the number of cyclohexene molecules produced per chain after 15 min reaction and at the final molar mass plateau are also indicated. As may be seen, the same two-



Scheme 4. General mechanistic pathway for the metathetical reaction of PEB with catalyst (**I**) in the presence of DAB.

Table 4
Effect of initial DAB concentration on molar mass and functionality and PEB oligomers

Ref.	[DAB] ₀ (mol L ⁻¹)	n _{DAB} /n _{copolymer} ^a	\bar{M}_n (g mol ⁻¹)		Functionality in acetoxy end-groups ^d	Efficiency of DAB ^e (%)
			Theoretical ^b	Observed ^c		
A ₁	0.004	5.6	11,000	2800	0.9	87
A ₁	0.010	14.0	3000	1400	1.1	85
A ₁	0.031	42.0	1000	2100	2.0	34
A ₂	0.010	15.2	3000	1400	0.9	71
A ₂	0.020	30.4	1600	1600	1.3	45
A ₂	0.031	45.6	1400	1100	1.9	64

[Catalyst] = 0.5 mmol L⁻¹; [butadiene unit] = 1.6 mol L⁻¹ in CH₂Cl₂; reaction at room temperature for 20 h.

^a Initial ratio between DAB and copolymer chains [23].

^b Calculated according to \bar{M}_n final oligomer = $n/(n+x+b) \times \bar{M}_n$ initial copolymer where n is the initial number of polymer chain, x the number of catalyst molecules and b the number of DAB.

^c Determined by GPC (THF).

^d Determined by ¹H NMR, CDCl₃.

^e Corresponds to acetate functions inserted ($m_{\text{oligomer}} \times f/\bar{M}_n$ oligomer) to acetate functions introduced ($2 \times n_{\text{CTA}}$) ratio.

steps profile without CTA (Fig. 5) is observed. The first stage is again characterized by the rapid generation of cyclohexene and the fast disappearance of BEB sequences. Then formation of macrocycles and finally acetoxy end-terminated oligomers occur, as shown respectively by the molar mass decrease and oligomer functionality increase with time (Fig. 6). This behavior is consistent with the lower reactivity of carbene species towards unstrained molecules such as DAB, as compared to unimolecular back-biting reactions yielding cyclohexene as well as larger macrocycles. Competition between bimolecular chain end functionalization and back-biting reactions is illustrated in Scheme 4. Although cyclohexene formation is irreversible, macrocycles can opportunely undergo metathesis reaction with butene diacetate to finally yield functionalized linear oligomers.

On these grounds we investigated the influence of various reaction parameters, i.e. the polymer concentration and the relative amount of CTA in respect to PEB to improve the formation of telechelic PEBs.

3.2.1. Influence of polymer concentration

The equilibrium between linear and cyclic macromolecular species can be shifted towards the formation of linear chains by increasing the polymer concentration [14]. In addition, depolymerization at high polymer concentration should also favor the bimolecular reaction between DAB and the polymer, thus reducing the fraction of cyclic oligomers formed by back-biting. Results are collected in Table 3. As expected depolymerizations performed in concentrated solutions of PEB yield an increase in the average number of acetoxy end-groups per chain, which reaches 1.6 at polymer concentrations close to the bulk. However the functionality remained lower than two and rapid cyclohexene formation was still observed.

3.2.2. Influence of initial ratio [DAB]/[polymer chain]

The effect of initial concentration of DAB on PEB depolymerization was also studied using concentrated polymer solutions (20 wt% of PEB in dichloromethane). Results are summarized in Table 4. As expected in the presence of higher amounts of DAB the average functionality of PEB oligomers reaches 2, indicating that linear telechelic oligomers have been almost selectively formed to the detriment of macrocycles, although the production of cyclohexene is still observed. The low efficiency of DAB observed to reach a chain functionality of 2 could be explained by its low reactivity. Functional oligomers exhibit molar masses in the range 1100–2800 g mol⁻¹ with no significant dependence on the DAB concentration. ¹H NMR spectra of a diacetoxytelechelic PEB and the dihydroxytelechelic oligomer recovered after hydrolysis are shown in Fig. 7.

A general reaction pathway taking into account the different reactions involved is proposed in Scheme 4. Depolymerization studies of PEB with catalyst (1), both in the absence and the presence of DAB, have shown that cyclohexene and macrocycles rapidly form in the first stage, while the bimolecular reaction of DAB with PEB is much slower. Consequently macrocycles formed should be quantitatively re-opened by DAB to yield telechelic PEB oligomers. As a result the oligomer molar mass mainly depends on the molar mass of macrocycles and not on the size of initial PEB. This also implies the presence in the reacting medium of a ratio [DAB]/[macrocycles] higher than 1 to reach an average functionality close to two. The addition of DBA after PEB metathetical

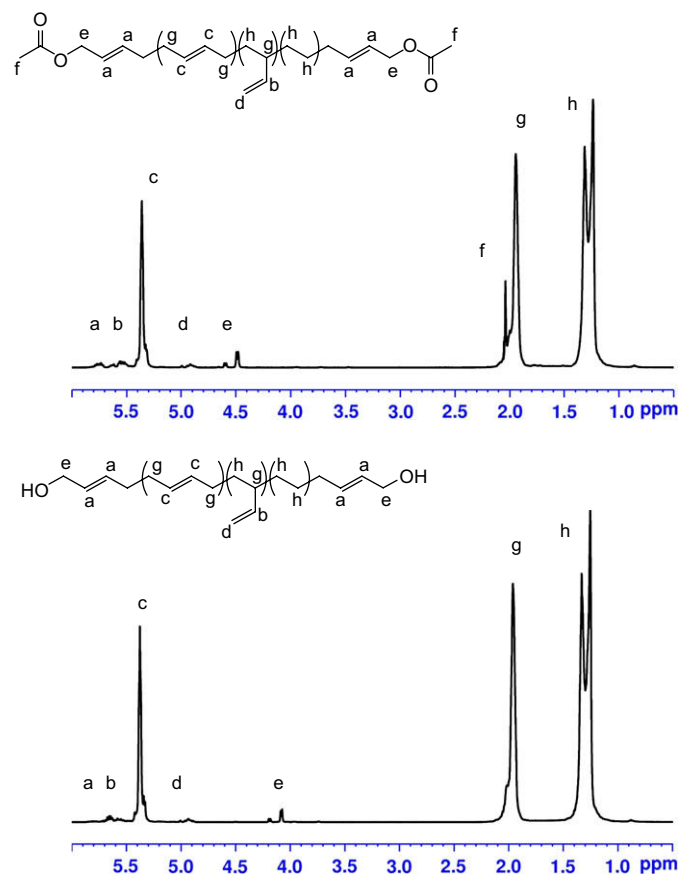


Fig. 7. ¹H NMR spectra of diacetoxytelechelic PEB oligomers **B**₂ recovered after metathetical depolymerization and dihydroxytelechelic PEB oligomers obtained after hydrolysis.

depolymerization reaction, at the thermodynamic state, should thus yield oligomers with similar molar mass and functionality characteristics.

4. Conclusions

A new synthetic route to dihydroxytelechelic poly(ethylene-co-1,3-butadiene) via metathetical depolymerization has been investigated. Formation of telechelic oligomers is complicated by the presence of back-biting reactions leading to cyclohexene and macrocycles production. Indeed, in polymers containing 1,7-dienic unsaturations, such as PEB, the formation of unsaturated six membered ring is thermodynamically favored. Macrocycles are also rapidly and almost quantitatively formed in the first reaction stage. Opportunely, when ratios $[DAB]/[macrocycles] \geq 1$ are used, cyclics are quantitatively re-opened to yield linear telechelics. We are currently extending this work to metathetical depolymerization of other copolymers containing butadiene and isoprene units.

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