Macromolecules

Volume 29, Number 13 June 17, 1996

Synthesis of α-Norbornenylpoly(ethylene oxide) Macromonomers and Their Ring-Opening Metathesis Polymerization

Valérie Heroguez, Stefan Breunig, Yves Gnanou,* and Michel Fontanille

Laboratoire de Chimie des Polymères Organiques, Unité mixte CNRS−ENSCPB−Université Bordeaux-1, Avenue Pey-Berland, 33402 Talence Cédex, France

Received December 5, 1995; Revised Manuscript Received April 1, 1996[⊗]

ABSTRACT: This work focuses on the synthesis and the ring-opening metathesis polymerization of α-norbornenylpoly(ethylene oxide) macromonomers. Although obtained in 100% yield and with a narrow distribution of molar masses, the polymacromonomers exhibit degrees of polymerization that are systematically higher than expected. The reasons for this feature are thoroughly discussed.

Introduction

Regardless of their chemical nature, macromonomers have been prepared until recently with a view of subsequently polymerizing them by free-radical processes. Much effort has thus been devoted to end-capping miscellaneous polymeric chains with either styryl or methacryloyl unsaturation.[1] In the case of poly(ethylene oxide) (PEO) macromonomers, several pathways have been described, including the chemical modification of commercial *ω*-hydroxy-PEO[2] and access *via* anionic polymerization of ethylene oxide. In the latter case, the unsaturation was introduced either upon deactivation of living oxanionic sites[3] or *via* the use of an unsaturated oxanionic initiator.[4]

The macromonomer method is being looked into as a privileged way to get access to regular multibranch polymers that are highly compact. Upon polymerization of macromonomers, polymers of extremely high branch density and uniform branch length can, indeed, be obtained, which would not be the case using other synthetic strategies, such as star syntheses. Interest in polymacromonomers arises from their very unique properties in solution as well as in bulk. For instance, polymacromonomers of polystyrene have been shown to exhibit quite peculiar viscosity behavior in toluene, with the intrinsic viscosity being independent of the molar mass for any given branch size.[5] Also remarkable is the tendency of polymacromonomers to form mesomorphic phases and adopt unusual conformations (bottlebrush or sphere) in solution.[5]

One major limitation associated with this technique is the difficulty of obtaining complete conversion and precise size control of the branched structure formed.[1] Curiously enough, the use of ion-mediated processes did not help much and resulted in ill-defined polymacromonomers.

Yet, the above statement about the lack of reactivity of macromonomers should not be indiscriminately generalized, as is shown in the case of PEO macromonomers. Indeed, Ito *et al.*,[5] studying the free-radical homopolymerization of PEO macromonomers, disclosed that these systems undergo fast and complete polymerization, provided that water is chosen as the continuous medium. To achieve this remarkable result, these authors took advantage of the tendency of these hydrophilic macromonomers to organize themselves in micelles, with the hydrophobic polymerizable group entrapped inside the micelle. It has to be mentioned, though, that unusually high molar masses, well above the expected values, have been measured for these polymacromonomers. The authors[6] indeed contended that the $\overline{DP}_n$ of such polymacromonomers is controlled by the micellar behavior of the precursor rather than any other factor, hence their difficulty to prepare polymacromonomer samples of moderate and controlled size by this method.

In a recent addition to the field of macromonomers,[7] we showed that macromonomers could be polymerized under truly living conditions using ring-opening metathesis polymerization (ROMP). Polystyrene samples of controlled size and varying compactness were, indeed, obtained by polymerization of *ω*-norbornenylpolystyrene (PS) with $Mo(NAr)(OC(CH_3)(CF_3)_2)_2(CH\textit{t}\text{-}Bu)$[8] as initiator. Feast *et al.*[9] also exploited the potentialities offered by ROMP and successfully synthesized PS polymacromonomers.

[⊗] Abstract published in *Advance ACS Abstracts,* May 15, 1996.

S0024-9297(95)01797-9 CCC: $12.00

The excellent results obtained with the homopolymerization of PS macromonomers prompted us to extend the same approach to other kinds of ω- or α-norbornenyl polymer chains and particularly to PEOs. It appeared to us of particular interest to investigate the ability of alkylidene complexes to bring about the ROMP of macromonomers containing electron-rich oxygen atoms in their repeating unit. The outcome of such polymerizations is not trivial because of the possible interaction between oxygen and the empty orbitals of the transition metal, which could perturb the overall fate of the metathesis process. Provided the polymerization of such macromonomers occurs as expected, the copolymerization of macromonomers of PS and PEO and the homopolymerization of amphiphilic macromonomers (PS-*b*-PEO) could be envisaged in the near future.

The first part of this paper is devoted to the synthesis of PEO samples carrying a norbornenyl unsaturation. Of the different pathways that were contemplated, we preferred the one based on the use of an unsaturated initiator, namely a norbornene-containing alcoholate. The second part is concerned with the polymerization of PEO macromonomers by ROMP. The propensity of these macromonomers to polymerize in the presence of a Schrock-type initiator is discussed in the light of the characteristics and the structural features of the polymacromonomers obtained.

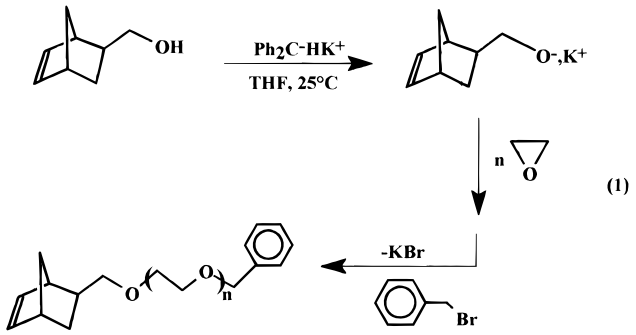
Results and Discussion

Macromonomer Synthesis. We could have derived the targeted PEO macromonomers upon merely coupling α-methoxy-ω-hydroxy-PEOs to 5-norbornene-2-carbonyl chloride. The two products being commercial, the advantage of this procedure can be easily perceived. This pathway would, however, imply a major shortcoming in the sense that an ester linkage would have been introduced between the unsaturation and the rest of the chain. After polymerization of the norbornene ring, the polymacromonomers obtained could not be hydrogenated to fully saturated materials because of the presence of this ester function. Another drawback is the sensitivity of the latter function to hydrolysis, which might inhibit the use of these polymacromonomers in certain applications.

While designing the synthetic scheme that would give access to ester-free PEO macromonomers, we purposely avoided using commercial ω-hydroxy-PEOs, for the latters are known to contain some dihydroxyl species. All these reasons led us to attempt the synthesis of PEO macromonomers by anionic polymerization of ethylene oxide *via* the unsaturated initiator approach.

We actually started from hydroxymethyl-5-bicyclo-[2.2.1]heptene ($NBCH_2OH$), a commercially available product, which we deprotonated by diphenylmethylpotassium (Ph_2CHK) and used to initiate the anionic polymerization of ethylene oxide (EO). Particular attention has been given to the purification of solvent because residual protonic impurities may induce the polymerization of EO after deprotonation and give rise to unfunctionalized chains. Likewise, the amount of diphenylmethylpotassium to be introduced in the reaction medium for the deprotonation of $NBCH_2OH$ has been determined with great care so as to avoid excess or deficiency of the latter deprotonating agent; it would have also yielded unfunctionalized materials. Benzyl bromide was chosen to deactivate the living alcoholates after polymerization of EO.

The PEO macromonomers were thus prepared *via* the following reaction scheme (eq 1):



(1)

The data pertaining to the various macromonomers synthesized are given in Table 1. The samples were characterized by ^{1}H NMR (Figure 1) and SEC, linear PEO standards being used for the calibration of the latter technique. All macromonomers exhibit polydispersity indexes close to unity and $\bar{M}_n$ values in good agreement with the expected values. The α-functionality of these macromonomers was checked by ^{1}H NMR upon comparing the area (I_1) of the signal due to the protons of EO units (δ 3.1−3.5 ppm) with that of the peak (I_2) arising from the ethylenic protons of norbornene (δ 5.5−5.9ppm). The values found for $\bar{g}$, which can be calculated using the relation $\bar{g} = I_1/(2I_2\overline{DP}_n)$, show that functionalities close to unity are systematically obtained. The extent of functionalization was also determined upon dividing the area of the signal (I_3) arising from the methylene protons of the terminal benzylic group by I_2. The fact that $\bar{f}$, the ratio of I_3 to I_2, falls close to the theoretical value of 1 is an additional proof that functionalization had quantitatively occurred.

Ring-Opening Metathesis Polymerization of PEO Macromonomers. Polymerizing macromonomers to complete conversion and controlled $\overline{DP}_n$ is not an easy task. When nonliving conditions are used to polymerize macromonomers, ill-defined materials that exhibit broad molar mass distributions are generally obtained. Unless particular experimental conditions are worked out—micellization of hydrophilic macromonomers fitted with a hydrophobic head in water[6]—the homopolymerization of macromonomers generally involves incomplete conversion, so a fractionation step is generally required. In the search for a more robust and reliable technique of polymerization of macromonomers than those tried so far, we[7] and others[9] recently demonstrated that the ROMP of ω-norbornenyl-PS chains meets all the criteria of "living" processes.

With PEO as macromonomer, it would be worthwhile to know whether ROMP functions as efficiently as it does with PS macromonomers. Three α-norbornenyl-PEO macromonomers, whose molar masses range from 1500 to 4700 g/mol, were polymerized in toluene using $Mo(NAr)(OC(CH_3)(CF_3)_2)_2(CHt\text{-}Bu)$ as initiator. The first series of experiments was actually carried out with $Mo(NAr)(OC(CH_3)_3)_2(CHt\text{-}Bu)$, a less reactive catalyst than its fluorinated homologue, but it was discontinued because of the lack of reactivity of the growing carbenic species. Polymerization of PEO macromonomers with the bis-*tert*-butoxy initiator gave poor yields, only 20% conversion after 24 h, in the case of the 2800 molar mass macromonomer. The use of $Mo(NAr)(OC(CH_3)(CF_3)_2)_2(CHt\text{-}Bu)$ gave far better results.

In the case of macromonomers exhibiting the lowest molar masses (1500 and 2800 g/mol) and with $Mo(NAr)(OC(CH_3)(CF_3)_2)_2(CHt\text{-}Bu)$ as initiator, complete conversions were systematically obtained, regardless of the

Table 1. Characteristics of α-Norbornenylpoly(ethylene oxide) Macromonomers

$\bar{M}_{n,macro}$ targeted, g/mol	$\overline{DP}_{n,theor}$	$\bar{M}_{n,macro}$[a] (SEC-RI detector), g/mol	$\bar{M}_w/\bar{M}_n$	$\bar{g}$[b]	$\bar{f}$[c]
1100	21	1500	1.05	0.90	1.08
3500	75	2800	1.06	0.95	0.90
5000	109	4700	1.07	1.00	1.18

[a] Calibration by PEO linear standards. [b] $\bar{g} = I_1/(2I_2\overline{DP}_n)$. I_1 and I_2 are the intensities of the signals due to oxyethylene protons ($\delta = 3.1-3.5$ ppm) and to ethylenic protons of the norbornene unit ($\delta = 5.5-5.9$ ppm), respectively. $\overline{DP}_{n,exptl} = (\bar{M}_{n,macro} - \bar{M}_u - \bar{M}_b)/44$, $\bar{M}_u$ and $\bar{M}_b$ being the molar mass of the end-standing norbornene unit and that of the benzylic moiety, respectively. [c] $\bar{f} = I_3/I_2$. I_3 is the intensity of the signal due to the methylene protons of the terminal benzylic group ($\delta = 4.48$ ppm).

$\overline{DP}_n$ targeted (Table 2). The molar masses of the polymacromonomers obtained were characterized by conventional SEC, to which was connected a multiangle laser light scattering (LLS) photometer. The adjunction of a LLS detection to the usual differential refractometer (DR) is particularly helpful when dealing with samples that are dissimilar to the calibration standards. It gives direct access to the absolute molar masses without recourse to any calibration, in contrast to the DR detection.

The molar masses obtained from LLS detection were found to fall consistently well above the targeted values (Table 2), although they conformed to a Poisson-type distribution. The reproducibility of these results was checked upon repeating some homopolymerization reactions, but the same values were systematically obtained for the molar masses. The presence of residual water or other protonic impurities in the PEO sample—after all, PEOs are hydrophilic polymers—was first incriminated to account for the "deactivation" of a large amount of initiator, but this hypothesis was ruled out before the following experimental evidence. In a separate experiment, we sequentially polymerized PS and PEO macromonomers by the very same initiator and did not observe any deactivation of living PS polymacromonomers after introduction of the PEO macromonomer. This will be the subject of a forthcoming article. It has to be also added that further freeze-drying of PEO macromonomers did not improve the results.

Under the experimental conditions used, it seems that a good amount of the initiator remains entrapped within the PEO chains, being not available for the coordination with the macromonomer olefinic unsaturation and hence for the metathesis process. Obviously, both electron-rich oxygen atoms and carbon−carbon double bonds of the cycloalkenyl macromonoer compete for coordination to the vacant site of transition metal carbenes, leaving little chance for all initiator molecules to participate in the metathesis process. One could argue that such competition should not affect the overall efficiency of the initiator but rather the rate of polymerization, for the complexation−decomplexation process is generally considered faster than the propagation itself. This argument holds whenever molecules of small size such as those of a solvent like THF, participate in the interaction with the metal carbene; in the latter case, the entropy factor is large enough to compensate the enthalpy term so that the different entities that could potentially interact with the metal are liable to rapidly interchange. Replacing molecules of small size by polymeric chains as possible sites of interaction is bound to decrease the entropy factor and dramatically affect the rate at which the exchange between the two kinds of sites occurs. The complexation−decomplexation process of the molybdenum catalyst to PEO ether functions seems to be slower than the propagation. This is our explanation for the rather low efficiency of the initiator when it is used to polymerize macromonomers of PEO.

A feature which further substantiates the above analysis is the quasiconstant efficiency of the initiator for a given family of macromonomers, regardless of the $\overline{DP}_n$ targeted. For a series of experiments carried out with the same macromonomer ($\bar{M}_n = 2800$ g/mol) and at the concentration of 0.014 mol/L, the efficiency factor systematically revolves around 30%. Comparison of the efficiency of the initiator for other families of macromonomers would be meaningless because the corresponding homopolymerizations were carried out under different conditions of dilution. The parameter which turns out to be essential for the control of the initiator efficiency is thus the concentration ratio of the two kinds of sites—oxygen and olefinic unsaturation—normally constant for a given macromonomer.

The case of macromonomers of larger size ($\bar{M}_n = 4700$ g/mol) is even more eloquent, and it calls for specific comments (Table 3). With this latter family of macromonomers, the polymerization yield always reached the plateau value of 30%, despite the precautions taken to thoroughly dry the macromonomer. This rather low yield was not due to uncontrolled deactivation of growing carbenes but is believed to mirror the difficulty of the macromonomer double bonds to get coordinated to the vacant site of the transition metal. With PEO macromonomers of higher molar masses ($\bar{M}_n = 11\,000$ g/mol) no polymerization occurred at all.

Exchange of toluene for 1,2-diethoxyethane as solvent of the reaction medium brought about dramatic changes. The polymerization yield rose to almost complete conversion (90%) in the presence of the latter solvent, which was chosen for its similarity to PEO chains. As a matter of fact, the use of a solvent that is a stronger base than the repeating units of PEOs helps to prevent the coordination of the metal vacant sites by the oxygen atoms of PEO and allows the polymerization to proceed almost to completion.

Two other experiments were carried out to add further credit to this interpretation. In the first experiment, 400 mg of the 2800 molar mass macromonomer were polymerized in toluene under the same conditions as those described above. After removal of an aliquot from the reaction medium, 2 mL of 1,2-diethoxyethane were introduced on the living medium, along with a further amount of the same macromonomer. Characterization of these two samples by SEC and comparison of their SEC traces show a shift toward the high molar mass domain and a broadening of the molar mass distribution in the second case, likely due to the "release" of the trapped initiator after addition of 1,2-diethoxyethane (Figure 2). A similar experiment was carried out with the 4700 molar mass macromonomer. Subsequently to the addition of 1,2-diethoxyethane, it can be seen that the macromonomer is almost entirely converted into polymacromonomer (Figure 3). These results add further credit to our reasoning as to the determining influence of the size of the species carrying the oxygen atoms on the outcome of the metathesis polymerization.

As additional proof of the complexing ability of PEO chains toward the carbenic initiator, a series of homopo-

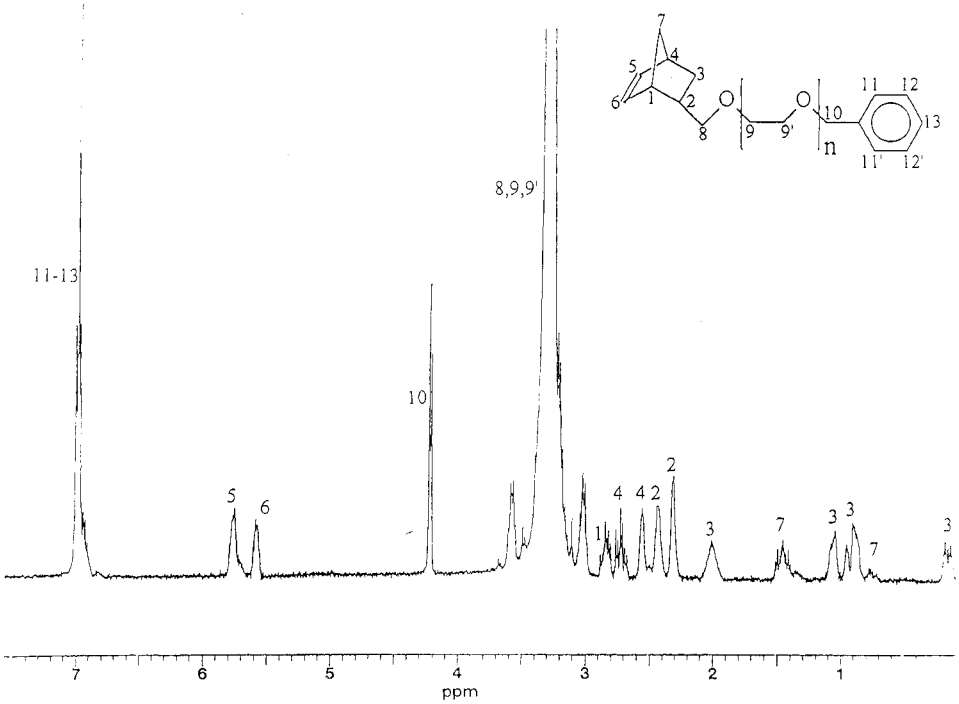


Figure 1. ^{1}H NMR spectrum ($CDCl_3$) of a norbornene-terminated poly(ethylene oxide) macromonomer.

Table 2. Characteristics of PEO Polymacromonomers

$\bar{M}_{n,macro}$,[a] g/mol	$\bar{M}_{n,polym}$ targeted, g/mol	conversion, %	$\bar{M}_{n,polym}$[a] (SEC-RI detector), g/mol	$\bar{M}_{n,polym}$ (SEC-LLS detector), g/mol	$\bar{M}_w/\bar{M}_n$ (SEC-LLS detector)
1500	7 500	100	10 400	47 500	1.35
	15 000	100	12 600	46 500	1.30
	30 000	100	31 600	112 000	1.11
2800	14 000	100	19 000	46 400	1.25
	28 000	100	28 000	84 000	1.05
	56 000	100	31 000	100 000	1.12
	70 000	100		215 000	1.19

[a] Calibration by PEO linear standards.

Table 3. Characteristics of the Polymacromonomers Obtained by ROMP of 4700 g/mol Macromonomer

$\bar{M}_{n,polym}$ targeted, g/mol	conversion, %	solvent	$\bar{M}_{n,polym}$ (SEC-LLS detector), g/mol	$\bar{M}_w/\bar{M}_n$ (SEC-LLS detector)
47 000	30	toluene	90 000	1.1
47 000	30	toluene	118 000	1.7
23 500	90	1,2-diethoxyethane	50 000	1.3
117 500	85		326 000	1.3

lymerizations of PS macromonomers was run in the absence and presence of PEO chains. In absence of PEO chains, the polymerization of PS macromonomers in toluene proceeds quickly to completion and affords samples with expected molar masses. In the presence of α,ω-bis(benzyloxy)-PEOs, the rate of polymerization of the same macromonomers dramatically decreases, and the polymacromonomers obtained exhibit quite higher molar masses than those targeted (Table 4).

^{1}H NMR Analysis of Metallaalkylidenic Species. ^{1}H NMR studies on the carbenic initiator were carried out with a view of identifying the nature of metallaalkylidenic species that are formed in the presence of PEO chains (Figure 4). This series of experiments was not meant to precisely determine the amount of molybdenum complex sequestred by the PEO chains but rather to qualitatively show the propensity of initiator molecules to get complexed by PEO. Conducting the same NMR analysis on the polymerization medium would not have given any interpretable result because of the very low concentrations of initiator and macromonomer. They are, indeed, much lower in a homopolymerization reaction than they are in this study.

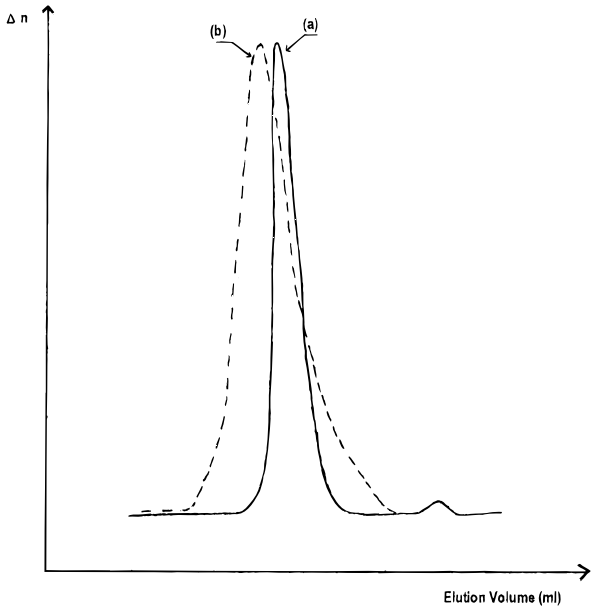


Figure 2. (a) SEC traces of the PEO polymacromonomer obtained by ROMP of the 2800 molar mass macromonomer in toluene. (b) SEC traces of the sample obtained after addition of 1,2-diethoxyethane and of a further amount of 2800 molar mass macromonomer to the above reaction medium.

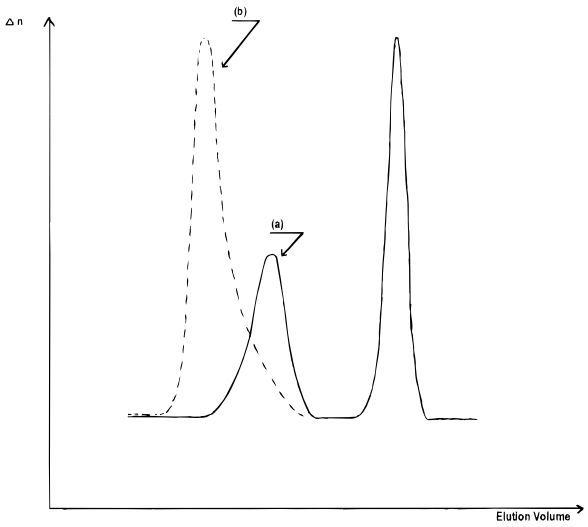


Figure 3. (a) SEC traces of the PEO polymacromonomer obtained by ROMP of the 4700 molar mass macromonomer in toluene. (b) SEC traces of the same sample obtained after addition of 1,2-diethoxyethane to the above reaction medium.

Table 4. Characteristics of PS Polymacromonomers Obtained in the Absence and Presence of α,ω-Bis(benzyloxy)-PEO ($\bar{M}_n$ = 7800 g/mol) in Toluene

α-NBPS,[a] g	PEO, g	time, h	conversion, %	$\bar{M}_{n,polym}$ targeted, g/mol	$\bar{M}_{n,polym}$ (SEC-LLS detector), g/mol
1	0	1	100	50 200	53 000
0.97	0.43	1	45	22 000	68 000
0.97	0.43	8	95	46 300	140 000

[a] See ref 10 for the synthesis and the ROMP of this macromonomer.

The NMR spectrum of the initiator in deuterated toluene (^{8}D) shows that the methine proton of the metallaalkylidenic species absorbs at 12.07 ppm as a sharp singlet. On addition of a small amount of 1,2-diethoxyethane, the same methine proton shifts downfield to 12.34 ppm. Addition of a few drops of THF in the toluene solution of the initiator causes a marked change in the electron distribution on this proton, which results in a further downfield shift of the signal to 12.7 ppm. The existence of a single peak in the two latter cases indicates that the ether functions of 1,2-diethoxyethane and of THF rapidly associate and dissociate from the molybdenum catalyst.

In sharp contrast, with α,ω-bis(benzyloxy)-PEOs, such coalescence into a single peak was not observed. The signal due to the methine proton actually splits into two peaks (12.07 and 12.23 ppm), bearing out the existence of an equilibrium between two species in slow exchange on NMR time scale. In the experimental conditions used for this NMR study, about one-fourth of the carbenic species get complexed to PEO chains and behave as if it were buried within the ether-containing macromolecular chain. The aforementioned lack of efficiency of the initiator can be better accounted for in the light of this NMR study, which reveals the importance of the entropy factor and the slow interconversion process it implies.

Conclusions

PEO macromonomers that are meant to be subsequently polymerized by ring-opening metathesis were derived by the unsaturated initiator approach. Based on the use of norbornene-containing alcoholates to initiate the anionic polymerization of ethylene oxide, this method was shown to provide access to macromonomer samples with functionalities close to unity.

The subsequent ROMP of these PEO macromonomers gave rise to an entire array of polymacromonomers, all characterized by a moderate to narrow distribution of molar masses. Compared to other polymerization processes,[11] ROMP turns out to be the best suited method of polymerization of PEO macromonomers, as it generally affords 100% conversion. Previous attempts using free-radical polymerization and water as reaction medium yielded similar conversions, but uncontrolled and very high molar masses were obtained.

Because the oxygen atoms of the macromonomer are prone to interact with the metal carbene, the proportion of initiator really available for coordination with the olefinic unsaturation of the macromonomer obviously decreases, entailing larger $\overline{DP}_n$ values for the polymacromonomers than expected.

Experimental Part

Materials. $NBCH_2OH$ (Aldrich, purity 98%) was used without further purification. Benzyl bromide (Aldrich, purity 98%) was stirred overnight over CaH_2 and purified upon cryodistillation.

Tetrahydrofuran (THF), ether, and toluene were distilled from sodium benzophenone. Ph_2CHK in THF was synthesized according to well-established procedures. Ethylene oxide (Fluka, purity 99.8%) was stirred over sodium at −30 °C for 3 h and subsequently cryodistilled.

Methods. All reagents were stored and used under inert atmosphere. Polymerizations of ethylene oxide were performed under anhydrous inert atmosphere. Ring-opening metathesis polymerizations were performed in a glovebox. NMR spectra were obtained using a Brucker AC 200 spectrometer. Size exclusion chromatography (SEC) consisted of a JASCO HPLC pump type 880-PU, TOSOHASS TSK gel columns, a Varian series RI-3 refractive index detector, and a JASCO 875 UV/vis absorption detector with THF as mobile phase. The calibration curve was established by means of poly(ethylene oxide) standards. Characterizations of the samples by SEC fitted with a light scattering detector[7] were performed by A. Rameau at Institut Charles Sadron, Strasbourg, France.

Catalyst Synthesis. The Schrock complex MoNAr(CH*t*-Bu)$(OC(CF_3)_2(CH_3))_2$ was synthesized according to literature methods.[9]

Macromonomer Synthesis. In a typical reaction, hydroxymethyl-5-bicyclo[2.2.1]heptene (1.06 mL, 8.77 mmol) ($NBCH_2OH$) was first dissolved in 600 mL of THF. Diphenylmethylpotassium in THF solution (19.24 mL, 8.77 mmol) was slowly added to the above reaction medium over a period of 1 h. The deprotonation of $NBCH_2OH$ was considered to be complete as soon as the Ph_2CHK falling in a reaction mixture retained its characteristic red-orange color. The solution was then cooled to −30 °C, and 35 mL of ethylene oxide (700 mmol) was added. The solution was allowed to rise to room temperature overnight. Deactivation of the reaction medium was performed by addition of 2 mL of benzyl bromide. The KBr salt formed was removed by filtration over Celite.

Precipitation was performed using ether as solvent, after partial evaporation of the solvent. The process of filtration and precipitation was then repeated twice.

Three successive freeze-drying processes were carried out from dioxane solution prior to the ROMP of macromonomers.

Polymacromonomer Synthesis. The synthesis of polymacromonomers was carried out in a glovebox under moisture-free conditions. In a typical synthesis, 10 mg (14.2 μmol) of Schrock-type catalyst was weighed into a flask, and 2 mL of toluene was added. Next, 398 mg (142 μmol) of macromono-

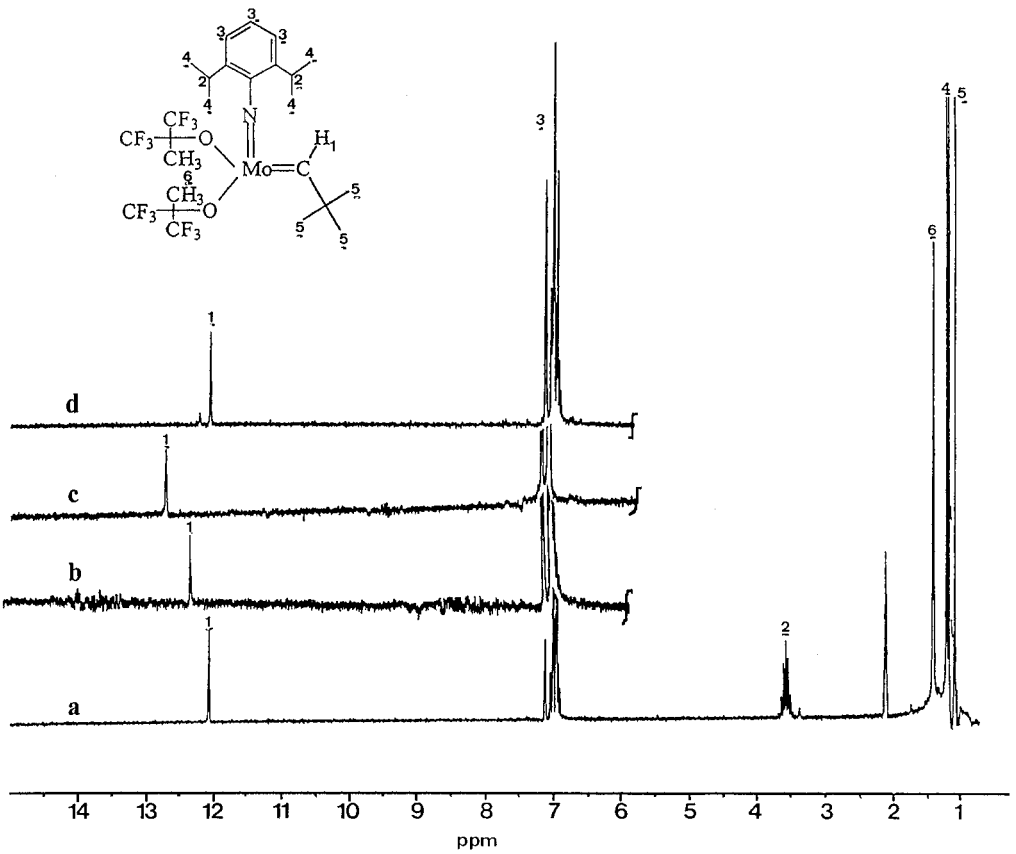


Figure 4. ^{1}H NMR spectra of MoNAr(CH*t*-Bu)(OC(CF$_3$)$_2$(CH$_3$))$_2$ (1.4×10^{-5} mol) and chemical shifts of methine proton signal in (a) deuterated toluene, (b) deuterated toluene + 1,2-diethoxyethane, (c) deuterated toluene + THF, (d) deuterated toluene + PEO chains ([ethylene oxide units] = 3.6×10^{-5} mol).

mer ($\bar{M}_n$ = 2800 g/mol) was dissolved in 8 mL of toluene, and the solution was added to the catalyst solution under stirring. Deactivation of the reaction medium was performed after 30 min of polymerization by addition of 0.1 mL of benzaldehyde. Precipitation in ether yielded the pure polymacromonomer.

References and Notes

(1) Gnanou, Y. *Ind. J. Technol.* **1993**, *31*, 317.
(2) Gnanou, Y.; Rempp, P. *Makromol. Chem.* **1987**, *188*, 2111.
(3) Masson, P.; Beinert, G.; Franta, E.; Rempp, P. *Polym. Bull.* **1982**, *7*, 17. Hamaide, T.; Revillon, A.; Guyot, A. *Eur. Polym. J.* **1984**, *20*, 855.
(4) Takaki, M.; Asami, R.; Tanaka, S.; Hayashi, H.; Hogen-Esch, T. *Macromolecules* **1986**, *19*, 2900.
(5) Ito, K.; Tanaka, K.; Tanaka, H.; Imai, G.; Kawaguchi, S.; Itsuno, S. *Macromolecules* **1991**, *24*, 2348. Tsukahara, Y. *Macromol. Rep.* **1995**, *A32 (Suppl. 5, 6)*, 821.
(6) Ito, K.; Kobayashi, H. *Polym. J.* **1992**, *24*, 199.
(7) Breunig, S.; Heroguez, V.; Gnanou, Y.; Fontanille, M. *Polym. Prepr., Am. Chem. Soc. Div. Polym. Chem.* **1994**, *35* (2), 526; *Macromol. Symp.* **1995**, *95*, 151.
(8) Schrock, R. R.; Murdzek, J. S.; Bazan, G. C.; Robins, J.; Dimare, M.; O'Regan, M. *J. Am. Chem. Soc.* **1990**, *112*, 3875.
(9) Feast, W. J.; Gibson, V. C.; Johnson, A. F.; Khosravi, E.; *Polymer* **1994**, *35*, 3542.
(10) Heroguez, V.; Gnanou, Y.; Fontanille, M. *Macromol. Rapid Commun.*, in press.
(11) Rempp, P.; Lutz, P.; Masson, P.; Chaumont, P.; Franta, E. *Makromol. Chem. Suppl.* **1985**, *13*, 47.

MA951797V