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Structural Aspects of the Ring-Opening Polymerization of 2-Methyloxacyclobutane

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ABSTRACT: ^{13}C NMR measurements on polymers of 2-methyloxacyclobutane prepared at −78 to 0 °C have revealed that the number of structural irregularities of the head-to-head type increases with the polymerization temperature. By comparison with results expected on the basis of influence from the neighboring carbons on the chemical shifts for particular carbons in various triad configurations, stereochemical effects are clearly observable. The meso and racemic configurations in head-to-head units are noticeable as are longer range effects. The signal from the methine carbon in head-to-tail units is influenced by the chirality of the corresponding carbon four bond distances removed in the adjoining units. Iso-, syndio-, and heterotactic triads are observed roughly in the ratio 1:1:2, indicating random incorporation of the enantiomeric monomers. The methyl carbons in the same triad are, however, outside the range of influence and appear as a singlet. Stereochemical effects are also noticeable for the irregular sequences.

Oxacyclobutane (oxetane), as well as the 2-methyl, 3-methyl, and 3,3-dimethyl derivatives, will easily undergo cationic polymerization by a ring-opening reaction.[1-4] In the last few years the kinetics of polymerization of these compounds have been studied in detail,[5,6] and recently the oligomer formation accompanying the polymerization of these compounds has received considerable attention.[7-9] The structural aspects have generally not been considered, although, in principle, tacticity is possible in the polymers of the 2-methyl- and 3-methyloxacyclobutanes.[10] It has been pointed out that the amorphous structure of poly(2-methyloxacyclobutane) may be connected with irregularities due to the unsymmetrical monomer.[2] In the case of copolymerization of oxacyclobutane and 3,3-dimethyloxacyclobutane the microstructure with respect to the distribution of the two comonomers has recently been investigated by means of 300-MHz ^{1}H NMR.[11] In the present investigation the structural features related to head-to-head and tail-to-tail irregularities as well as to the presence of asymmetric carbons in poly(2-methyloxacyclobutane) have been studied by ^{13}C NMR and related to polymerization conditions.

Results and Discussion

The polymerization results are summarized in Table I. Two initiators were used, PF_5 and Et_3OPF_6, and experiments were carried out in bulk as well as in CH_2Cl_2 solution. The oxonium salt appears to yield polymers with higher molecular weights than those obtained with PF_5. When the polymerization temperature is lowered, the molecular weights become higher for the polymers prepared with both initiators. After workup of the polymers, no significant amounts of oligomers were present, as indicated by GPC analysis. A detailed polymerization study has not been carried out at this point; the objective of the present investigation has been to detect if any gross changes in the polymer structure occur as a result of changing the polymerization conditions, particularly the temperature.

A typical 22.63-MHz ^{13}C NMR spectrum of a polymer prepared at −50 °C is shown in Figure 1. More signals appear than correspond to the four different carbons in the regular head-to-tail structural units. The additional signals originate first of all from head-to-head and tail-to-tail configurations. It should be expected that the head-to-tail structure would predominate, and this assumption has been verified by evaluating the chemical shifts on the basis of structural parameters and model studies. In the following, the methyl carbon is labeled C-1, the methine carbon is indicated C-2, and the methylene carbons are labeled C-3 and C-4.

The influence of structure on the ^{13}C NMR chemical shifts is known to be predictable by a scheme based on the effects of the carbons in α, β, γ, δ, and ϵ positions relative to the observed carbon.[12,13] Generally a deshielding is observed except for the γ effect, which causes an upfield shift. The effect of the neighboring carbons diminishes with distance and the ϵ effect is very small. This attenuation has also been observed in the case of the configurational splittings in diastereomeric alkanes.[14] In the case of polymers containing heteroatoms in the main chain it was recently pointed out by Ivin[15] that since chemical shifts for carbons in such polymers are sensitive to substitution at a distance only up to four bonds, triad configurational

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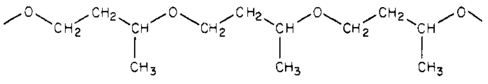
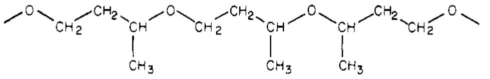
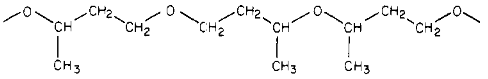
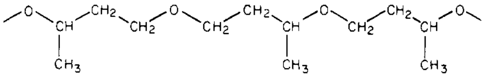
Table I
Polymerization Experiments with 2-Methyloxacyclobutane

no.	polymn temp, °C	mmol of initiator		mmol of monomer	vol of CH_2Cl_2, mL	time, h	yield, %	GPC	
		PF_5	Et_3OPF_6					$\overline{M}_n$	$\overline{M}_w$
1	0	0.188		9.4		22.5	28	710	960
2	0		0.097	9.7	2.8	2	95	2500	6600
3	−25	0.186		9.3		138	60	1600	7200
4	−25		0.094	9.4	1.4	1.5	41	6200	15000
5	−50		0.101	9.2	2.8	47.5	91	9100	20800
6	−78	0.099		9.9	1.4	408	81	4000	9200
7	−78	0.024		9.6		456	78	4200	7800
8	−78	0.097		9.7		184	77	4000	9200
9	20		3.1	5.5	12.0	1	78		

Table II
Number of Neighboring Carbon Interactions Due to the Presence of Methyl Substituent in Poly(2-methyloxacyclobutane)[a]

structural unit	C-1					C-2					C-3					C-4				
	α	β	γ	δ	ε	α	β	γ	δ	ε	α	β	γ	δ	ε	α	β	γ	δ	ε
 A	1	1	2	1	2	1				2		1		1				2		
 B	1	1	2	2	2	1		1		1		1		2				2		1
 C	1	1	2	2	2	1		1				1		1				1		2
 D	1	1	2	1	2	1				1		1						1		1

[a] In-chain interactions excluded.

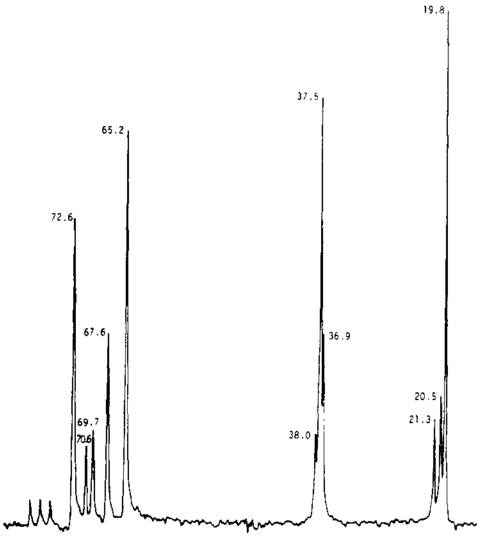


Figure 1. 22.63-MHz ^{13}C NMR spectrum of poly(2-methyloxacyclobutane) prepared at −50 °C (sample 5) (solvent 10% $CDCl_3$; 7000 scans).

or compositional sensitivity can be expected in the case of monomers yielding repeat units with four atoms in the main chain. In the case of five atoms in the repeat units only dyad sensitivity should be expected. Recently, however, long-range steric effects on the ^{13}C chemical shifts were reported for hydrocarbon polymers of monomers with four atoms in the chain repeat unit.[16] In this case the possible distinction between different triads indicated an observable ζ effect.

The configurational variation in the polymer structure, notwithstanding the stereochemical forms, may be analyzed in terms of the four triads A, B, C, and D which are shown in Table II. For each carbon of the center unit of the triads, the number of interactions up to the ε position from the neighboring carbons, which are related to the presence of the methyl substituent, have been counted and tabulated. Since it is only of interest here to assess the differences in the number of neighboring interactions which may influence the chemical shifts, all interactions not related to the presence of the methyl substituent may be disregarded, since these will cancel out in the comparison between the units. Also the heteroatoms will have a fixed influence on each of the four types of carbon since it will not vary for the different structural units. If the contributions from the ε carbons, which are very small, are disregarded, the number of signals (given in parentheses after the carbon type) predicted on this basis is as follows:

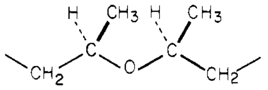
C-1 (2): C-1(A) = C-1(D), C-1(B) = C-1(C)
C-2 (2): C-2(A) = C-2(D), C-2(B) = C-2(C)
C-3 (3): C-3(A) = C-3(C), C-3(B), C-3(D)
C-4 (2): C-4(A) = C-4(B), C-4(C) = C-4(D)

On the other hand, if the ε contribution is counted, the result will be the same for C-1 and C-3, as may be seen in Table II. However, in the case of C-2 and C-4 the signals could possibly be further split due to a difference of one in the number of ε contributions for each pair predicted on the basis of interactions from the other neighboring carbons.

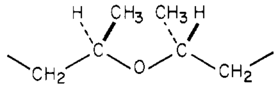
Table III
^{13}C NMR Signal Intensity Distribution (%) for Each Type of Carbon in the Chain Repeat Units in Polymers Prepared under Various Conditions

	polymn	^{13}C reson	C-1 signals, ppm			C-2 signals, ppm			C-3 signals, ppm			C-4 signals, ppm	
no.	temp, °C	freq, MHz	19.8	20.5	21.3	69.7	70.6	72.6	36.9	37.5	38.0	65.2	67.6
1	0	22.63	60	23	17	25	14	61	23	62	15	54	46
2	0	67.89	60	23	17	24	19	58	23	63	14	57	43
3	−25	22.63	57	27	17	22	17	61	23	60	17	57	43
4	−25	67.89	60	23	16	23	16	61	24	64	11	60	40
5	−50	22.63	69	19	12	19	13	68	20	70	10	68	32
6	−78	22.63	70	20	10	17	12	71	20	68	12	77	23
7	−78	22.63	81	12	7	8	7	85	10	82	8	82	18
8	−78	22.63	80	11	9	9	10	81	15	77	8	78	22

By comparison with the spectrum in Figure 1 the following actual assignments of the signals are made (Table III summarizes the results). The signal at lowest field, 72.6 ppm, is assigned to the deshielded methine carbons, C-2, next to oxygen in the head-to-tail units, and the neighboring peaks of lower intensities at 69.7 and 70.6 ppm are assigned to the methine carbons in the head-to-head configuration. The upfield shifts in case of the latter carbons are due to the γ effect on these methine carbons from the methyl carbons in the neighboring units. The size of the shift is of the right order for such a γ effect. Furthermore, the signal is split into two signals of roughly equal intensity. This is attributed to meso and racemic configurations present in the head-to-head adjoined units:



meso



racemic

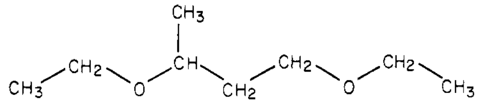
Therefore three signals in all are observed for C-2 and not two as predicted merely on the basis of the effect of the methyl substituent on the chemical shifts in the four different triads. Such splittings have been observed for various branched paraffins[13] and also in the case of 2,4-dichloropentane.[17] The magnetic nonequivalence of this type will typically cause splittings of the order of 1 ppm.

The methyl carbons, C-1, appear partly as a singlet at the highest field at 19.8 ppm and partly as two signals of lower intensity at 20.5 and 21.3 ppm. The singlet originates from the carbons in the head-to-tail units and the doublet from the corresponding carbons in the head-to-head units. In this case the carbons in the head-to-head units appear at lower field. However, this is to be expected since each methyl carbon in this configuration will experience an additional δ interaction from the methyl carbon in the neighboring unit, causing a deshielding and downfield shift (see Table II). The signal is also split in this case and this reflects the nonequivalence of the methyl groups in the meso and racemic configurations of the head-to-head units. Just as discussed for the methine carbon, C-2, three signals are observed for the methyl carbon, C-1, instead of the two predicted on the basis of the substituent effect.

The methylene carbons, C-4, next to oxygen, are deshielded, although less than C-2, and the methylene carbons in the head-to-tail units appear at 65.2 ppm while those in the tail-to-tail units appear downfield at 67.6 ppm. In this case the γ effect on C-4 from the methyl carbon in a neighboring unit comes into play only in the case of the head-to-tail structure, causing an upfield shift of about 2 ppm for the methylene C-4 carbons.

Finally, the remaining signals around 37.5 ppm must be due to the C-3 carbon. A complicated multiplet appears and this reflects the position of these carbons in the center of a unit with equal distance to the carbons of the adjoining two units which will tend to maximize the neighboring effects.

A model compound was prepared, the diethyl ether of 1,3-butanediol, the parent diol of 2-methyloxacyclobutane:



The methine ^{13}C signal appears at 72.3 ppm in accordance with the assignment given above for the methine carbons in the head-to-tail repeat units. The methyl group attached to the methine carbon appears at 20.0 ppm while the less deshielded methyl carbons at the ends give signals at 15.2 and 15.6 ppm. Thus the peak assignment for the methyl carbons in the head-to-tail units is in accordance with the model prediction. For the methylene carbons adjacent to oxygen three signals were recorded at 63.8, 66.2 and 67.3 ppm, respectively. The latter signal is assigned to the methylene carbon in the middle part corresponding to the structure of the repeat unit, while the methylene carbons in the ethyl groups are less deshielded and appear at the higher fields. The methylene carbon at 67.3 ppm in this model corresponds closely to the tail-to-tail configuration and the signal position to that of the methylene carbon in the tail-to-tail units of the polymer which, as already indicated, is found at 67.6 ppm. Finally, the remaining methylene carbon signals are found around 37.1 ppm, which also is in the range of that found for C-3 in the polymer.

The variation in the relative intensities of the ^{13}C NMR signals for the polymers corresponding to those of Table I is presented in Table III. The problems associated with applying the ^{13}C NMR technique in a quantitative fashion are well-known; however, in the present analysis the intercomparison of the integrated peak areas is restricted to the same types of carbons only. Thus the results may be utilized to analyze the gross changes in the structure of the polymers. The chemical shifts for the same carbons showed some minor changes due to different NMR instruments and to the varying molecular weights of the polymer prepared under different conditions. In case of the polymer with the lowest molecular weights (1 and 3 in Table I) some additional minor peaks were observed due to the end groups.

When the polymerization temperature is lowered it is seen that the signals from the carbons assigned to the regular head-to-tail units (A) become relatively stronger. The C-1 signal at 19.8 ppm follows the same pattern as that of the C-2 signal at 72.6 ppm. Also, the fraction of C-1 and respective C-2 carbon atoms appearing in the head-to-head units should be the same. With reference to Table II this corresponds to the signals originating from the structural units B and C. As seen in Table III this is reflected in the ^{13}C NMR data since the sum of the C-1 signals at 20.5 and 21.3 ppm generally corresponds to the

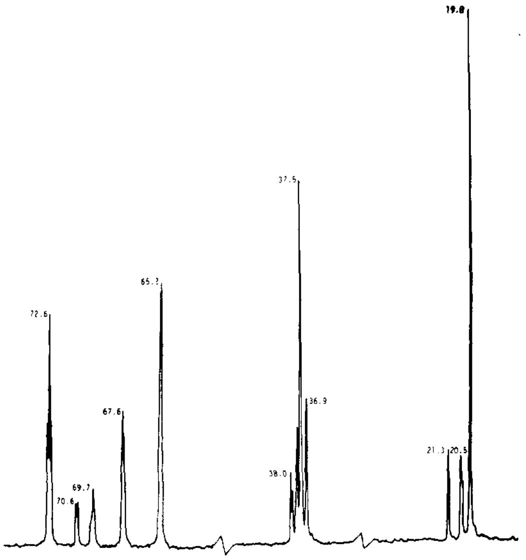
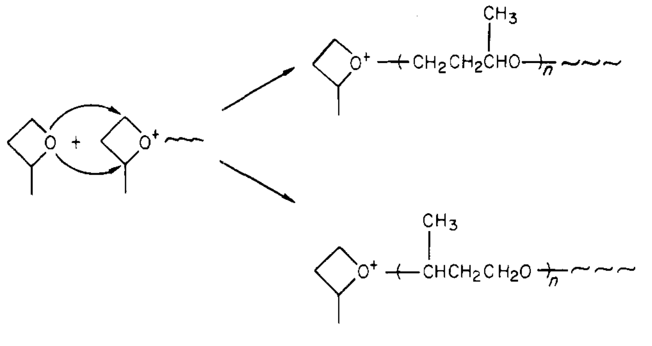


Figure 2. 67.89-MHz ^{13}C NMR spectrum of poly(2-methyloxacyclobutane) prepared at −50 °C (sample 5) (solvent 10% $CDCl_3$; 600 scans).

sum of the C-2 signals at 69.7 and 70.6 ppm. In case of C-4, the signal at 65.2 ppm increases in intensity with lower polymerization temperature and this signal represents the carbons of structures A and B, including the carbons of the head-to-tail units.

Obviously, at the lower polymerization temperature the ring opening occurs in a preferred way while at the higher temperature it tends to occur in a more random fashion. The data do not allow any conclusion with regard to which carbon is preferentially attacked at the lower temperature. Obviously, the predominant head-to-tail structure may be formed by repeated nucleophilic attack of monomer oxygen at either methylene or methine carbon adjacent to the oxonium ion in the propagating species.



In the study of polymerization of bicyclic ethers the direction of ring opening has been found to vary with the structure of the monomer. In the case of 2-oxabicyclo[2.2.2]octane[18] the ring opening occurs predominantly by attack on the tertiary rather than on the secondary carbon adjacent to the oxonium ion. On the other hand, in the case of severe steric hindrance at the tertiary position, the attack of the monomer may occur solely at the methylene carbon. This was found to be the case in the polymerization of the bicyclic ethers *trans*-7-oxabicyclo[4.3.0]nonane[19] and *trans*-2-oxabicyclo[3.3.0]octane.[20] The structures of these polymers were investigated by ^{13}C NMR.[21] In the polymerization of 2-methyloxacyclobutane the secondary and tertiary neighboring carbons adjacent to the oxonium ion appear to be equally accessible. Thus attack at the tertiary position may be expected with reference to the result quoted above for *trans*-2-oxabicyclo[2.2.2]octane. However, further experimental work is needed to establish the actual mechanism in the present case.

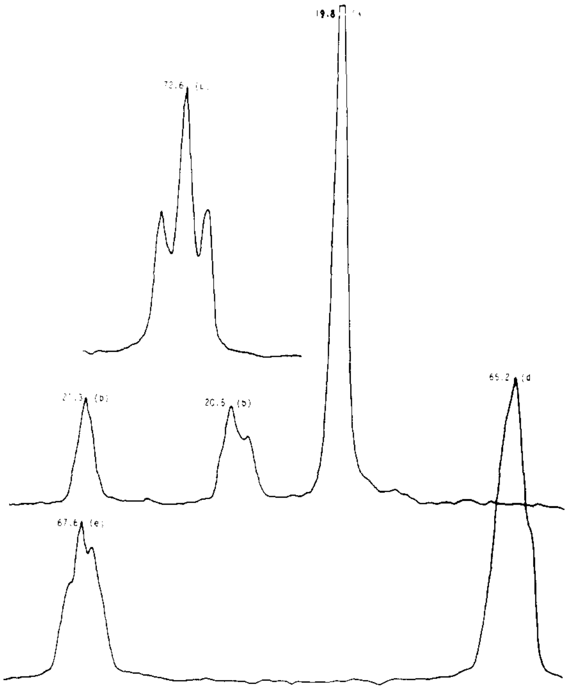
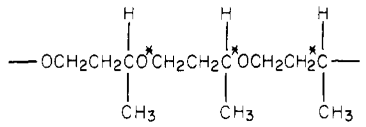


Figure 3. 67.89-MHz ^{13}C NMR spectrum (expanded) of poly(2-methyloxacyclobutane) prepared at −50 °C (sample 5) (solvent 10% $CDCl_3$; 600 scans): (a) C-1 (head-to-tail); (b) C-1 (head-to-head); (c) C-2 (head-to-tail); (d) C-4 (head-to-tail); (e) C-4 (tail-to-tail).

The poly(2-methyloxacyclobutane) possesses true asymmetric centers which give rise to different stereochemical forms. In the head-to-head adjoined units it has already been discussed that different signals are observed in ^{13}C NMR, depending on whether the head-to-head configuration is meso or racemic, i.e., whether the methine carbons are of opposite or of the same chirality. In the regular head-to-tail structure



$$-OCH_2CH_2\overset{H}{\underset{CH_3}{\overset{*}{C}}}OCH_2CH_2\overset{H}{\underset{CH_3}{\overset{*}{C}}}OCH_2CH_2\overset{H}{\underset{CH_3}{\overset{*}{C}}}-$$

tacticity is possible, and iso-, syndio-, and heterotactic forms may be found, depending on the variation in the configurations along the chain. In the 67.89-MHz spectrum in Figure 2 the signal from the methine carbon, C-2, in the head-to-tail units appears as a triplet (72.75, 72.64, and 72.52 ppm). This triplet is magnified in Figure 3 and the intensities are roughly in the ratio 1:2:1. The signals are attributed to isotactic, syndiotactic, and heterotactic triads. By assuming random propagation with respect to the enantiomeric monomers, the observed ratio of signals is expected, with the strongest signal representing the methine carbons in the heterotactic triads. This result is in accordance with Ivin's[15] prediction that triad sensitivity should be observable for polymers containing four main-chain atoms, including a heteroatom in the repeat units. The methyl carbons, C-1, in the head-to-tail units appearing at 19.8 ppm do not show any sign of splitting. These methyl carbons are located five bond lengths from the asymmetric carbons in the adjoining unit. Thus the carbons are outside the range of interaction. The C-3 and C-4 methylene carbons in the head-to-tail units are found, by the same kind of analysis, to be influenced only by the carbon in two adjoining units. Whether the C-3 is actually dyad sensitive cannot be stated since the complicated multiplet representing all the C-3 carbons has not been resolved. The C-4 signal at 65.2 ppm is not a clean singlet. As stated above it represents carbons of structural units A and B, and the influence of the dyad structure appears to be small.

For the carbons in the irregular structures some stereochemical influence may be noted besides that which has already been indicated. In the head-to-head units the C-2 methine carbon may interact not only with the methine group in β position (the meso–racemic effect) but also with the methine carbon located in the δ position in the other direction (see structure B in Table II). The C-2 signal at 70.6 ppm appears as a doublet and the signal at 69.7 ppm shows a tendency to split further in a more complicated manner. The C-4 methylene carbon signal at 67.6 ppm, which represents the carbons in tail-to-tail units, shows a tendency to split. In structures C and D in Table II it may be seen that C-4 is located in such a way that the asymmetric carbons in the adjoining units are within four bond distances and may therefore influence the ^{13}C NMR signal. In case of structure C C-4 is seen to be influenced by all three asymmetric carbons of the triad, and the signal also has a triplet form.

The present investigation has shown that ^{13}C NMR is a useful tool to investigate the structural variations in polymers prepared by ring-opening polymerization of 2-methyloxacyclobutane. In the case of this monomer the chain irregularities as well as the stereochemical configuration in terms of triads have been determined. In the case of β-substituted β-propiolactones which also yield four-atom repeat units it has been reported, on the basis of ^{13}C NMR analysis at 25.16 MHz,[22] that only dyad tacticity could be observed. We have previously found that for polyethers with five-atom repeat units only dyad tacticity could be observed by ^{13}C NMR at 22.63 MHz.[21] Thus it has been demonstrated that in the case of the polyethers it is possible with the proper ^{13}C NMR technique to observe stereochemical effects related to substituted carbons removed up to four bond distances, in accordance with previous predictions for polymers with heterochains.[15]

Experimental Section

Materials. 2-Methyloxacyclobutane was prepared according to the literature either by ring closure of 1,3-butanediol directly[23] or from the chloro ester 3-chloro-1-butyl acetate.[24] The crude oxetane was dried with NaOH and distilled on a spinning-band column to a purity of better than 99.9%, as determined by gas chromatography (bp 58.8–60 °C; lit.[24] bp 60 °C). ^{13}C NMR showed only four sharp signals (relative to Me_4Si) at 24.1 (methyl (C-1)), 29.4 (C-3), 67.4 (C-4), and 79.4 ppm (C-2).

Polymerization Experiments. The polymerizations were carried out on a high-vacuum line by techniques described previously.[20,25] After termination, all the polymer was dissolved in CH_2Cl_2, the solvent was evaporated, and the polymers were dried at 50 °C (1 mmHg) to constant weight.

Characterization of the Products. The polymers were analyzed by gel permeation chromatography in THF solution. A Waters Model 200 instrument equipped with polystyrene gel columns (porosities 10^3, 10^4, 2×10^4, and 10^6 Å) was used. On the basis of a calibration curve obtained with narrow-molecular-weight polystyrenes, approximate molecular weight average values were calculated by the well-known extended chain-length method and a Q value (weight per Å) of 15.4. This type of average value is adequate in this study for assessing the influence of the polymerization parameters.

The ^{13}C spectra of the polymers were recorded on a Bruker WH90 Fourier transform NMR spectrometer, operating at 22.63 MHz with proton decoupling, in deuteriochloroform (10%) at room temperature with tetramethylsilane as an internal reference. Generally, 3000 scans were sufficient, although in some cases more scans were accumulated. In addition, spectra were recorded at 67.89 MHz on a Bruker HX-270, generally on the basis of only 600 scans since improved signal-to-noise resolution is possible for this instrument.

Preparation of the Model Ether. The diethyl ether of 1,3-butanediol was prepared by adding pure, dry 1,3-butanediol (10 mmol) to an agitated suspension of sodium hydride (60 mmol) in dry tetrahydrofuran (35 mL) followed by addition of ethyl iodide (74 mmol). After agitation at room temperature for 1 week, the workup consisted of removing the sodium iodide by filtration, evaporation of the THF, and extraction with diethyl ether of the residue after addition of water. After drying of the ether phase with $MgSO_4$, rotary evaporation was performed at 10 mmHg and 50 °C and the model ether was used as obtained without further purification.

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