Studies on Comblike Polymers. 7. ^{13}C NMR Characterization of Poly(oxiranes) Containing Long Hydrocarbon Side Chains

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ABSTRACT: ^{13}C NMR spectra have been measured for some comblike polymers obtained by coordination polymerization of higher epoxides such as octadecyloxirane and decyloxirane. Backbone methine and methylene resonances of the high-melting polymer fractions appear as single unsplit peaks, thus indicating a high degree of stereoregularity (isotactic structure). In contrast, strong tacticity effects have been generally observed for the backbone resonances of the low-melting polymer fractions. These effects have been interpreted in terms of different stereosequences. The complete assignment to the triads mm, mr (rm), and rr and comparison with the spectra of poly(methyloxirane) and anionically prepared poly(octadecyloxirane) allowed us to conclude that the low-melting polymers are atactic and contain substantial amounts of abnormal (head-to-head and tail-to-tail) linkages. Measurement of T_1 of the main-chain carbons and NOE showed their independence of the tacticity. Moreover, the length of the hydrocarbon side chain does not substantially affect the backbone relaxation. As for the side chains, only the T_1 values of the interior atoms showed a marked tacticity effect. Experimental dynamic parameters have been interpreted either on the basis of a single correlation time or with a model based on restricted motion on a diamond lattice.

As part of our studies on the structure–property relations of poly(alkylethylenes) and poly(alkyloxiranes) containing long hydrocarbon side chains,[1-5] we recently carried out NMR measurements of the tacticity of poly(octadecylethylene) samples.[5] This study demonstrated that the immiscible phases revealed by DSC analysis in the unfractionated product of the stereospecific polymerization of octadecylethylene are composed of isotactic and atactic polymer.

To improve our knowledge of the effect of stereoregularity on the properties of comblike polymers, we have extended our NMR investigation to some of the polymers prepared from the epoxides of these olefins. We recently examined[2] the thermal behavior of poly(octadecyloxirane) obtained from the racemic monomer with Kambara's catalyst. This catalytic system is very similar to the alkylaluminum chelate catalysts developed by Vandenberg[6] and has been reported to be very effective in polymerizing oxirane and its derivatives to stereoregular polymers of high molecular weight.[7]

The DSC analysis of poly(octadecyloxirane) showed that the crude product of the polymerization consists of two immiscible, crystalline phases, which can be separated under appropriate fractionation conditions into two polymers melting at different temperatures. On the basis of the differences of molecular weight and solubility, the higher melting material was assumed to be the stereoregular polymer (isotactic), while the lower melting polymer was thought to be predominantly atactic. The present ^{13}C NMR investigation of poly(octadecyloxirane) and poly(decyloxirane) samples allows a direct determination of the microstructure of these polymers and provides information on their dynamic behavior in solution.

No structural study of poly(alkyloxiranes) with alkyl side chains longer than ten carbon atoms has been reported so far.

Experimental Section

Monomers. Octadecyloxirane was prepared as reported.[2] It was purified by repeated crystallization from ethyl ether. The crystalline product (mp 43 °C) was dried under vacuum at 35 °C. Decyloxirane (Schuchardt and Co.) was purified by fractionation under reduced pressure, dried over calcium hydride, and stored under vacuum in calibrated Pyrex ampules equipped with a break seal.

The structural identity of both monomers was checked by IR and 60-MHz ^1H NMR spectra. These spectra agree closely with those reported recently for some epoxides of this homologous series.[8] No extraneous signals were detected in the 200-MHz ^1H NMR spectra of either monomer.

Polymerizations. The stereospecific polymerizations of the oxiranes were carried out with the catalytic system bis(dimethylglyoxime)nickel(II)/$AlEt_3$ ([Al]/[Ni] = 2.5 mol/mol) in heptane at 60 °C. The procedure was essentially that previously reported,[7] except that all operations were performed on a high-vacuum line using Pyrex tubes equipped with break seals.

A nickel compound concentration of 1.5 mol % with respect to the monomer was used. The polymers were recovered as described[2] and purified by repeated precipitation from their $CHCl_3$ solutions into excess methanol.

These crude products of the polymerizations are composed of two crystalline phases with distinct melting temperatures. The DSC traces of unfractionated poly(octadecyloxirane) and poly(decyloxirane) are shown in Figures 1d and 2g, respectively. Appropriate solvent treatments can be used to separate the two crystalline phases. Thus, for poly(octadecyloxirane), an extraction with boiling methylene chloride provides a soluble fraction (sample B) showing only the lower temperature transition (mp 338 K), whereas crystallization from $CHCl_3$, performed by dissolving 2 g of polymer in 100 cm^3 of boiling chloroform and letting the solution cool slowly to room temperature, yields a pure fraction (sample A) displaying the higher temperature transition (mp 375 K). The DSC traces of the two pure crystalline samples are shown in Figure 1a,b.

The highest ratios of the high-melting fraction to the low-melting one (up to about 2) were obtained when the catalyst was produced and used in the form of an insoluble solid phase.

The intrinsic viscosities of the two fractions were of the order of 420 and 35 $cm^3\ g^{-1}$, respectively (Ubbelohde viscometer, in toluene at 35 °C).

The values of the constants k and a of the Mark–Houwink–Sakurada equation for the polymers under consideration are not available. However, the assumption of the k and a values given for poly(methyloxirane)[9] led to viscosity-average molecular weights of ca. 10^6 and 32×10^3 for the high-melting and low-melting polymer fractions, respectively. Furthermore, a number-average molecular weight ($\bar{M}_n$) of 14×10^3 was found for the low-melting fractions by membrane osmometry.

For the case of poly(decyloxirane), only the higher melting phase (mp 369 K) was obtained in a sufficiently pure state by crystallization from heptane, carried out by the same procedure used for poly(octadecyloxirane). The lower melting phase (mp 280 K), as obtained by extraction with cold methylene chloride, still contained a measurable amount of the higher melting ma-

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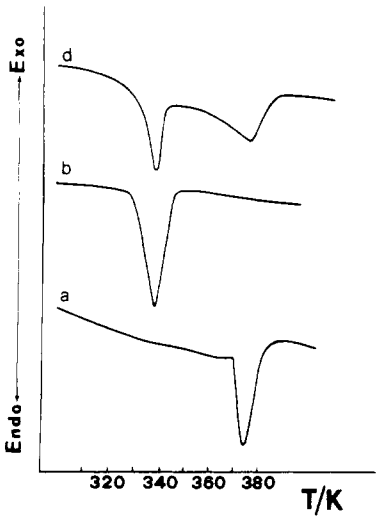


Figure 1. DSC traces of poly(octadecyloxirane) prepared by stereospecific catalyst. Heating and cooling rate 16 K/min. (a) High-melting fraction (sample A); (b) low-melting fraction (sample B); (d) unfractionated polymer (cf. Experimental Section).

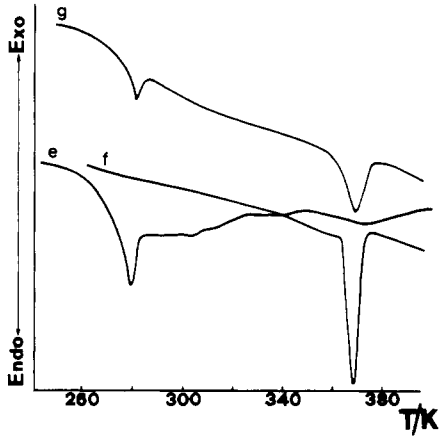


Figure 2. DSC traces of poly(decyloxirane) prepared by stereospecific catalyst. Heating and cooling rate 16 K/min. (e) Low-melting polymer fraction; (f) high-melting polymer fraction; (g) unfractionated polymer (cf. Experimental Section).

terial. The DSC traces of the two fractions are reported in Figure 2, curves f and e, respectively.

The cationic and anionic polymerizations of octadecyloxirane were carried out in Pyrex tubes sealed under vacuum. The conditions were as follows: PF_5 as initiator in 1,2-dichloroethane at 20 °C and KOH as catalyst in toluene at 40 °C, respectively.

The polymers were freed from the residual monomer by repeated precipitations into methanol containing 20% (v/v) methylene chloride.

The DSC traces of all the polymer samples were obtained on a Perkin-Elmer Model DSC-1B calorimeter.

^{13}C NMR Measurements. All polymer samples were observed by 50.28-MHz ^{13}C NMR as undegassed 5% (w/v) solutions in chloroform-*d*. Spectra were obtained with a WP 200 Bruker spectrometer employing a 10-mm probe.

T_1 values were measured by the standard inversion–recovery ($\pi - t - \pi/2 - T$) pulse sequence, with T at least 5 times the longest T_1 of interest (accumulating for each t value 1600 transients for α, β, γ, and δ C atoms and 320 transients for all other side-chain C atoms).

Values of the NOEF were obtained from peak areas measured with an accumulation of 12 000 transients in the broad-band or gated ^{1}H decoupling and a 45-s relaxation delay. In every case the temperature was 301 K.

Results and Discussion

Polymer Structure. Octadecyloxirane is a higher homologue of the extensively studied methyloxirane. One

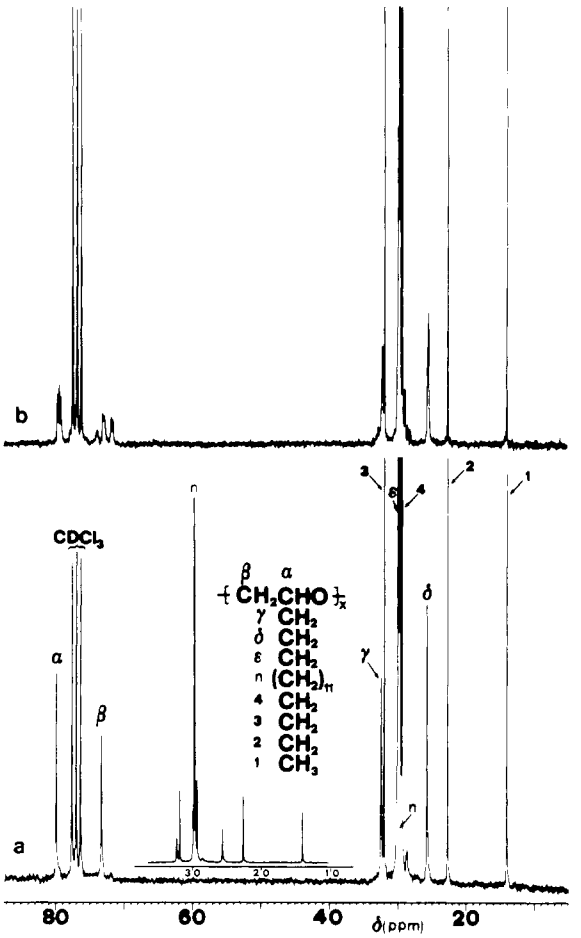


Figure 3. 50.28-MHz ^{13}C{^{1}H} NMR spectra of poly(octadecyloxirane) prepared by stereospecific catalyst: (a) High-melting polymer fraction (sample A); (b) low-melting polymer fraction (sample B); (inset) side-chain carbon resonances of sample A (reduced vertical scale 1:8). Solvent chloroform-*d*, 29 °C, concentration 5% (w/v), 3900 transients.

of the key features of the polymerization of the latter monomer by coordination catalysts is the formation of both isotactic and atactic polymers, the latter containing head-to-head and tail-to-tail units as structural defects.[10] Accordingly, it is expected that under the influence of a coordination catalyst, octadecyloxirane may undergo polymerization to stereoregular and atactic polymer as well.

As described in the Experimental Section, poly(octadecyloxirane) obtained with a coordination catalyst can be separated into two fractions having different melting points.

The 50.28-MHz ^{13}C NMR spectra of samples A (higher melting fraction) and B (lower melting fraction) of poly(octadecyloxirane) are shown in Figure 3, parts a and b, respectively.

The spectrum of sample A consists of sharp and well-defined signals. The resonances in the region 10–35 ppm have been assigned to the side-chain carbons on the basis of the chemical shifts of linear alkanes. Individual assignments are made according to well-known additivity rules[11] except for the resonances between 29 and 30 ppm, which have been assigned on the basis of their relaxation times (T_1).

For the sake of clarity the side-chain resonances are also shown in the inset spectrum of Figure 3a, where the most intense peak at 29.5 ppm corresponds to the unresolved resonances of the methylene groups denoted by n. The two low-field peaks at 73.2 and 79.8 ppm have been assigned to the backbone carbons. By relaxation experiments

and off-resonance decoupling, they were identified as being due to the methylene and methine carbons, respectively. The prominent feature of the spectrum of sample A is that the resonance of each backbone carbon appears as a single, unsplit peak. This pattern can be considered as indicative of a regular (normal) enchainment of the repeating units, as expected for highly stereoregular monosubstituted oxirane polymers,[12] including isotactic poly(methyloxirane).[13]

Moreover, no extra signals due to structural irregularities can be observed, except for the weak resonance at 72 ppm and the very small shoulder at 79.4 ppm, likely arising from a slight contamination by sample B.

On the basis of these observations and of the well-known fact that the stereospecific catalysts used for the polymerization of oxiranes can give regular polymers with a high ratio of isotactic to syndiotactic sequences,[10] sample A can be assumed to consist of a configurationally homogeneous (isotactic) polymer. In contrast, the spectrum of the lower melting fraction B (Figure 3b) exhibits a more complex pattern showing multiplicity of peaks probably due to sequences of different tacticity, as expected for a stereoirregular polymer. Small sequence effects are also observable on resonance peaks due to γ and δ side-chain methylenes.

It is well-known that the structure analysis of monoalkyl-substituted oxirane polymers is complicated by the possible occurrence of abnormal (head-to-head and tail-to-tail) linkages in the main chain, since this kind of isomerism affects the NMR chemical shifts at least as much as the stereoisomerism.[14] For a correct assignment of the resonances of the spectrum b, we found it helpful to compare this spectrum with that of a reference sample of poly(octadecyloxirane) obtained with KOH catalyst under anhydrous conditions (sample C). It is well established that under such initiation conditions, the ring opening of racemic methyloxirane takes place usually at the CH_2–O bond (normal fission[15]) to give an atactic, almost completely head-to-tail polymer.[16,17]

The expanded backbone carbon regions of the spectra of samples A–C of poly(octadecyloxirane) are shown in Figure 4a–c, respectively.

The methine resonance in both spectra b and c is present as an apparent triplet with a shoulder on the high-field side (more evident in spectrum b). In the methylene carbon region two main peaks are observable, each of them split into an apparent doublet. In addition, a broad poorly resolved band, at approximately 74 ppm, is also observable.

The spectra make it immediately evident that both samples B and C are very irregular. Their pattern reflects clearly an appreciable sensitivity of the observed carbon atoms to different configurational sequences. A comparison of the spectra of Figure 4 with that published for an atactic poly(methyloxirane) containing regular head-to-tail linkages[13] was considered useful for the peak assignments. Peak integration (from low field to high field) for the methine carbon of sample C gives a peak area ratio of 28:46:26, very close to that of atactic poly(methyloxirane) (25:50:25). For the latter polymer the peaks have been assigned, in order of increasing field, to isotactic (mm), heterotactic (mr, rm), and syndiotactic (rr) triads, respectively. Accordingly, it is reasonable to assign the observed peaks at 79.76, 79.60, and 79.44 ppm of spectrum c to isotactic, heteroatactic, and syndiotactic triads, respectively.

The same assignment can be obviously extended to the methine triplet of spectrum b. It follows from the comparison of the three spectra that the presumed isotactic structure of sample A is strongly supported by the coincidence of the single methine resonance of spectrum a with the peak assigned to isotactic triads in spectra b and c.

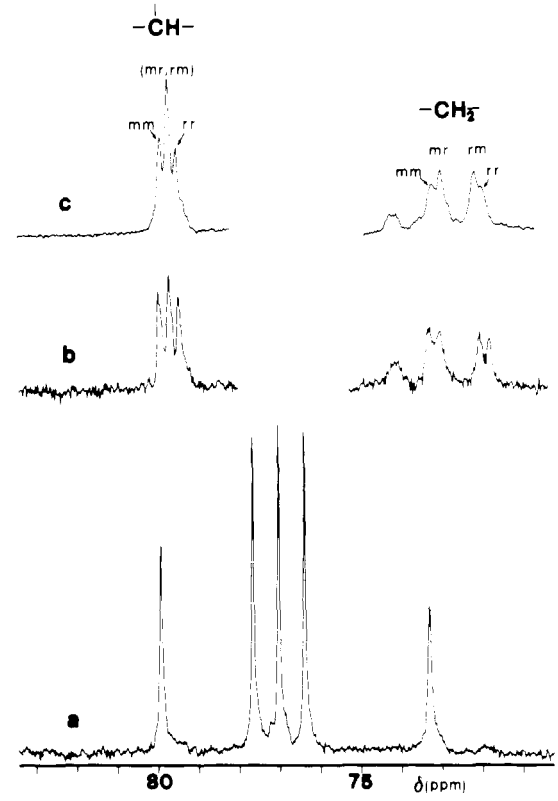


Figure 4. ^{13}C{^{1}H} NMR spectra of poly(octadecyloxiranes): (a) and (b), expanded main-chain carbon region, respectively, of samples A and B (cf. Figure 3); (c) expanded main-chain carbon region of sample C prepared by KOH catalyst. Conditions as in Figure 3.

Similar to the case of poly(methyloxirane), the monomer units of poly(octadecyloxirane) contain a true asymmetric center, and this makes mr and rm triads not equivalent. However, as in the case of poly(methyloxirane), these heterotactic triads are indistinguishable, at least in the methine region, and appear as a single peak.

As regards the resonance of the CH_2 group, the situation is rather different. Indeed, while in poly(methyloxirane) the methylene carbon is only dyad sensitive, in poly(octadecyloxirane) the multiplicity of the methylene resonance points to a remarkable sensitivity of all the possible triads (mm, mr, rm, and rr), with noticeable chemical shift differences.

Owing to the appreciable overlapping of the peaks, the assignments were performed on the basis of a rough, quantitative measurement of the relative intensity of the resonances and of simple statistical considerations. An approximate estimation of the intensities of the four methylene signals between 73.8 and 71.5 ppm for samples B and C gives peak area ratios of 24:28:28:20 and 30:25:24:21, respectively. Since the content of mr and rm triads must be equal, these can be reasonably assigned to the peaks at 72.92 and 71.95 ppm for B and 72.88 and 72.05 ppm for C, which show the same relative intensities. From comparison with sample A, the peaks at 73.20 ppm for B and at 73.15 ppm for C can be attributed to the isotactic (mm) triads, and thus it is straightforward to assign the upfield peak to rr triads.

As mentioned before, some additional resonances, consisting of a shoulder on the high-field side of the methine peak of the syndiotactic triad at ca. 79.3 ppm and of a broad band at ca. 74 ppm, appear in the spectra of samples B and C. These are most probably due to irregular,

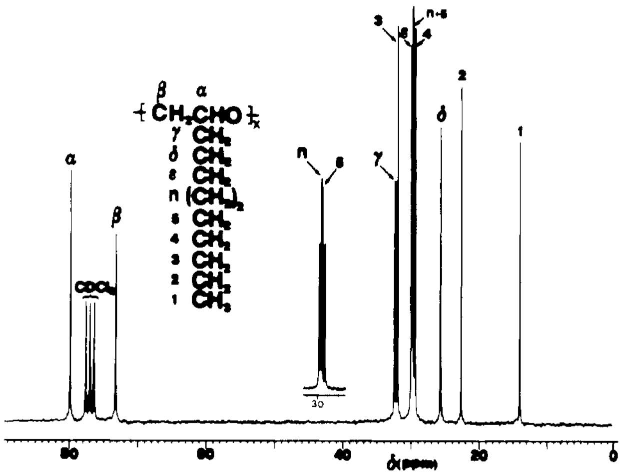


Figure 5. $^{13}C\{^{1}H\}$ NMR spectrum of the high-melting fraction of poly(decyloxirane) prepared by stereospecific catalyst. Conditions as in Figure 3.

head-to-head and tail-to-tail linkages in the polymer chain. Their detailed analysis is very difficult since they are composed of several lines arising from the combination of positional and configurational isomerism. Even for poly(methyloxirane) containing irregular linkages this problem was not resolved. Nevertheless, the correctness of the attribution of these bands to irregular linkages is supported by the finding that these bands appear to have increased intensities in the spectrum of a sample of poly(octadecyloxirane) prepared by ordinary cationic polymerization (PF_5 initiator). It is well-known that under acidic reaction[18,19] or cationic polymerization conditions,[20] the oxirane ring undergoes opening at either the α or β position. Accordingly, poly(octadecyloxirane) obtained under such conditions should contain a large amount of irregular linkages.

The deviation of heterotacticity of sample B from ideal randomness may be attributed to its high content of abnormal linkages. Such a tendency is less evident for sample C, and this trend is consistent with a structure containing less irregularities, as expected from the adopted preparation procedure.

In the course of our work we have examined other poly(oxiranes) closely related to poly(octadecyloxirane) but having an alkyl substituent slightly shorter than the octadecyl group. As mentioned in the Experimental Section, we succeeded in obtaining samples of poly(decyloxirane) with different thermal behavior.

The ^{13}C NMR spectrum of a carefully purified sample of the higher melting fraction of poly(decyloxirane) is shown in Figure 5. The close similarity with the poly(octadecyloxirane) spectrum of Figure 3a has been taken as a clear indication of the high degree of stereoregularity (isotacticity) of the examined poly(decyloxirane) sample. The only (predictable) difference lies in the number of the distinguishable side-chain carbon resonances, as evident from the ^{13}C chemical shift values listed in Table I.

Close spectral patterns and analogous observations stem also from the comparison between the lower melting fractions of poly(octadecyloxirane) and poly(decyloxirane), to which also a stereoirregular (atactic) structure can be assigned.

As far as the polymerization mechanism is concerned, the results obtained in the present investigation do not allow the formulation of a precise mechanistic scheme for the coordination process. In general, the mechanism of polymerization of oxirane monomers with coordination catalysts is rather complex, since it often involves the formation of aggregates of as-yet ill-defined structure. In

Table I
Observed ^{13}C Resonance Chemical Shifts of Isotactic Poly(decyloxirane) and Poly(octadecyloxirane),

$$-(\overset{\beta}{C}H_2-\underset{R}{\overset{\alpha}{C}}HO)_n-$$

R = decyl		R = octadecyl	
signal[a]	shift[c]	signal[b]	shift[c]
α	79.85	α	79.89
β	73.20	β	73.24
γ	32.30	γ	32.37
δ	25.70	δ	25.66
ϵ	29.96	ϵ	29.95
n	29.78	n	29.64
5	29.73		
4	29.42	4	29.31
3	31.94	3	31.90
2	22.67	2	22.62
1	14.04	1	13.92

[a,b] See Figures 1 and 3, respectively. [c] Ppm from $SiMe_4$.

spite of the extensive progress made during the past years in this area, much more work is necessary for elucidating the true nature of the propagating centers of these polymerizations.

However, in the case of decyloxirane and octadecyloxirane polymerization initiated by $AlEt_3$–$Ni(dmg)_2$ our observation that polymer fractionated into two parts of different microstructures strongly suggests the existence of at least two kinds of active centers: some stereospecific, giving the isotactic polymer, and others neither specific nor selective, giving the atactic polymer.

It is probable that the steric control experienced in this polymerization process may proceed according to an enantiomorphic catalyst site control mechanism, which is known to operate in many highly stereospecific polymerizations to isotactic polymers, including poly(methyloxirane).[21]

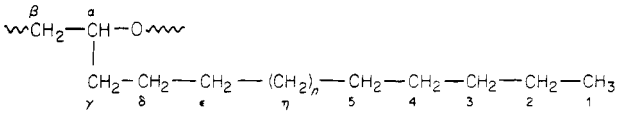
Solution Dynamics. Over the past few years, considerable interest has arisen on the dynamic parameters of polymers with long side chains[22-24] or, more generally, of molecules with anchored and flexible portions.[25]

As a further step in the present investigation, we considered it interesting to provide insight into the motional behavior of the main and side chains of the polymers under study, by determining dynamic parameters such as the spin–lattice relaxation time (T_1) and the nuclear Overhauser enhancement factor (NOEF).

Dynamic measurements were carried out on samples of isotactic and atactic poly(octadecyloxirane) and poly(decyloxirane). T_1 of poly(octadecyloxirane) was considered to be independent of the molecular weight, the latter being higher than 10^4. The same assumption was also extended to T_1 of poly(decyloxirane) on the basis of the similarity of the preparation conditions used for both the polymers. The T_1 and NOEF data of the above-mentioned poly(alkyloxirane) samples are presented in Table II.

The T_1 and NOEF values of the backbone carbons in each pair of sterically different polymers are equal within experimental error. This fact clearly shows that for these monoalkyl-substituted poly(oxiranes), no discernible tacticity effect is present on the skeletal dynamic parameters of comparable carbons. Moreover, the equality of the corresponding NT_1 values indicates that the simple inverse proportionality between spin–lattice relaxation times of the main-chain carbons and the number of directly bonded protons is preserved. Given the dominance of the dipolar mechanism, the equality of NT_1 values shows that the CH and CH_2 groups have the same correlation functions.

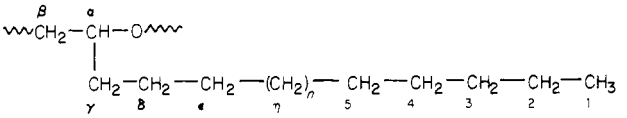
Table II
^{13}C Dynamic Parameters of Comblike Polyoxiranes



carbon	poly(octadecyloxirane) (n = 10) T_1[a]/s isotactic	T_1[a]/s atactic	NOEF[b]	poly(decyloxirane) (n = 2) T_1[a]/s isotactic	T_1[a]/s atactic	NOEF[b]
α	0.160	0.165	1.0	0.234	0.250	1.0
β	0.090	0.095	1.0	0.123	0.120	1.0
γ	0.170	0.165	1.5	0.138	0.158	1.5
δ	0.223	0.202	1.6	0.282	0.348	1.6
ϵ				0.384	0.500	1.8
η			1.8	0.651	0.770	1.8
5				1.13	0.850	1.8
4	2.78	1.98	1.8	1.45	1.48	1.8
3	3.65	2.15	1.8	2.43	2.43	1.8
2	3.94	3.93	1.7	3.17	3.39	1.7
1	4.60	4.45	1.5	3.95	4.15	1.5

[a] T_1 values are ±5%. [b] NOEF values are ±10%.

Table III
Motional Correlation Times (s) Derived from T_1 and NOEF Values for Comblike Poly(alkyloxiranes)[a]



carbon	poly(octadecyloxirane) (n = 10) isotactic and atactic τ_{ov}[b]	isotactic and atactic τ_j[b]	isotactic τ	atactic τ	poly(decyloxirane) (n = 2) isotactic and atactic τ_{ov}[b]	isotactic and atactic τ_j[b]	isotactic τ	atactic τ
α	(3-4) × 10^{-9}	(1.5-1.7) × 10^{-10}			(3-4) × 10^{-9}	(1.7-1.9) × 10^{-10}		
β	(3-4) × 10^{-9}	(1.5-1.7) × 10^{-10}			(3-4) × 10^{-9}	(1.7-1.9) × 10^{-10}		
γ	2 × 10^{-10}	9 × 10^{-11}			2 × 10^{-10}	8 × 10^{-11}		
δ	4 × 10^{-10}	8 × 10^{-11}			4 × 10^{-10}	7 × 10^{-11}		
ϵ							6 × 10^{-11}	4.8 × 10^{-11}
η							3.6 × 10^{-11}	3.1 × 10^{-11}
5							2.3 × 10^{-11}	2.9 × 10^{-11}
4			8 × 10^{-12}	1.2 × 10^{-11}			1.7 × 10^{-11}	1.7 × 10^{-11}
3			6.5 × 10^{-12}	1.1 × 10^{-11}			10^{-11}	10^{-11}
2			6 × 10^{-12}	6 × 10^{-12}			7.5 × 10^{-12}	7.0 × 10^{-12}
1			3 × 10^{-12}	3 × 10^{-12}			6 × 10^{-12}	6 × 10^{-12}

[a] τ = single correlation time; $\tau_{ov} = \tau_{overall}$; slow component of the correlation time; $\tau_j = \tau_{jump}$; fast component of the correlation time. [b] Owing to the experimental errors and to the uncertainty in the function adopted,[26] the values of τ_{ov} and τ_j were obtained by the mean T_1 values of atactic and isotactic polymers.

The length of the hydrocarbon side chain does not seem to affect substantially the backbone relaxations; an increase in the length from 10 to 18 carbon atoms slightly decreases the T_1 values.

As in most high molecular weight polymers, NOEF and T_1 values of the backbone carbons are incompatible with a single correlation time. A restricted motion of a diamond lattice allowing three-bond transitions combined with an overall motion[26-28] satisfactorily fits the experimental data.

For this treatment two correlation times were obtained: $\tau_j \sim 1.7 \times 10^{-10}$ s and $\tau_{ov} \sim 4 \times 10^{-9}$ s. τ_j is the time required for a jump on the diamond lattice, while τ_{ov} is the time constant for a slower motion probably due to segmental motion,[26] as shown in Table III.

Examination of the side-chain relaxation times clearly reveals a variation of mobility along the interior of the hydrocarbon chain itself. Comparison of the T_1 values for the different carbon positions in each given side chain shows their dependence on the relative chain length. In particular, longer T_1 values are observed in carbon positions 1–4 with increasing length of the side chain in both isotactic and atactic samples.

T_1 values appear to be independent of tacticity only near both ends of the side chain (see Table II). For both polymers the central carbon atoms show quite different values of T_1, and this dependence on different configurational structures is particularly evident in carbon positions 3 and 4 of poly(octadecyloxirane) and in positions 5, η, and ϵ of poly(decyloxirane).

As also reported in Table II, the NOEF values are independent, within experimental error, of both chain length and tacticity and reach their maximum value for the interior carbons of the side chain.

All these data and observations point to the probable existence of different conformations for the internal part of the side chain in the isotactic and atactic polymer, giving rise to the observed differences of the interior mobilities. On the other hand, owing to the polymer concentrations (of the order of 5% (w/v)) used in this work, entanglement effects (already observed for polystyrene[29]) may be considered very low. This is also consistent with the high NOEF values of the side-chain carbons.

Actually, it is difficult to establish if the irregular linkages present (up to 25%) in the atactic polymer samples,

affect conformational changes as well as side-chain mobility. Nevertheless, in light of the present results, this hypothesis cannot be completely excluded. The high values of NOEF allow a description of the motion of the central and terminal parts of the side chain of each polymer sample in terms of a single correlation time (see Table III).

Because of the incompatibility of the T_1 and NOEF values of the C_γ and C_δ carbons with a single correlation time, a model based on a restricted motion on a diamond lattice (τ_j) combined with a slower motion was adopted to fit the experimental values.

It has been previously pointed out that this model is by no means unique.[26] In poly(decyloxirane) this model seems to be appropriate, since by considering the fast motion component (τ_j) of the backbone and of the C_γ and C_δ carbons, together with the value obtained for the single correlation time of all other side-chain carbons, a monotonous trend is found.[30]

Registry No. Poly(decyloxirane), 28325-87-3; poly(octadecyloxirane), 71332-27-9; isotactic poly(decyloxirane), 85803-24-3; isotactic poly(octadecyloxirane), 73935-11-2.

References and Notes

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(30) The appearance of a consistent trend in correlation times does not necessarily prove the proposed model. However, if no monotonous trend were observed in the correlation times calculated in the extreme narrowing limit and in those calculated with the Valeur's theory, the suggested model would be inappropriate.

^{13}C NMR Study of Poly(menthyl vinyl ether) Obtained by Different Catalytic Systems

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ABSTRACT: Optically active poly(menthyl vinyl ethers) prepared under different polymerization conditions have been studied by ^{13}C NMR. Resonance assignments, relaxation times T_1, and nuclear Overhauser enhancement factors (NOEF) were obtained at 21.14 and 46.15 kG. Analysis of these parameters gives information about main-chain configuration, in terms of dyad tacticity, and about side-chain mobility. The results are attributed to strong steric interactions between the bulky menthyl group and the growing chain during the polymerization process.

Introduction

In a previous paper considerations on the stereoregulation observed in the polymerization of optically active alkyl vinyl ethers carried out under free-ion propagation conditions were put forward exclusively on the basis of optical rotation measurements.[1]

In light of our recent mechanistic studies of the "cationic coordinate" polymerization of alkyl vinyl ethers performed under either heterogeneous or homogeneous conditions in the presence of organoaluminum sulfates,[2] a more detailed picture of the microstructure of poly(alkyl vinyl ethers) was essential to the interpretation of the experimental findings.

In the present paper we report the results of a ^{13}C NMR investigation performed on poly(menthyl vinyl ether) samples prepared in the presence of different catalysts.

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