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.

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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.

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^{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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Table I
Polymerization of (−)-Menthyl Vinyl Ether in the Presence of Different Cationic Initiators

	polymerization conditions[a]						
			solvent				
run	catalyst	mon/cat molar ratio	type	mL	temp, °C	duration, h	conv,[b] %
M1	$C_7H_7SbCl_6$	1000	CH_2Cl_2	20	0	0.5	65.6
M2	$C_2H_5AlCl_2$	50	$C_6H_5CH_3$	30	−78	24	91.2
M3	$BF_3\cdot O(C_2H_5)_2$	100	CH_2Cl_2	30	−78	24	89.4
M4	$[(i\text{-}C_3H_7O)_2AlO]_2SO_2$	50	$i\text{-}C_8H_{18}$	16	25	48	82.2

[a] Monomer, 27.5 mmol. [b] Determined as (weight of polymer)/(weight of monomer) × 100.

Table II
Characteristics of Poly(menthyl vinyl ether) Samples Prepared under Different Experimental Conditions

	fractionation solvent					
			n-hexane			
	acetone					
run	wt %	$[\Phi]^{25}_{D}$ [a]	wt %	$[\Phi]^{25}_{D}$ [a]	$[\eta]$ [b]	isotactic dyads, %
M1	3.8	−60.4	96.2	−357	0.34	75
M2	0.0		100	−379	0.56	75
M3	0.4	−218	99.6	−379	0.45	78
M4	4.3	−282	95.7	−359	0.29	75

[a] In toluene. [b] In toluene at 30 °C.

Experimental Section

(−)-Menthyl vinyl ether (1), having bp 94 °C (20 mm), $[\alpha]^{25}_{D}$ −73.6 (neat), and optical purity 100%, was prepared as already reported.[1] (−)-Menthyl ethyl ether (3), having bp 98 °C (20 mm) and $[\alpha]^{25}_{D}$ −89.0 ($CHCl_3$), was obtained in 96% yield by catalytic hydrogenation (Pd/C) of 1 in ethanol solution.

Polymerization experiments were carried out in the presence of different cationic initiators as previously reported[2] (Table I), and the polymers obtained were fractionated by extraction with acetone and *n*-hexane. In Table II some properties of the investigated samples are collected.

Optical rotatory measurements were performed at 25 °C with a Perkin-Elmer Model 141 spectropolarimeter with a sensitivity of ±0.003°. Viscosity measurements at 30 °C in toluene were performed with a Desreux-Bischoff dilution viscometer.

^{13}C NMR spectra of 5% (w/v) solutions of the polymers in $CDCl_3$ were recorded at room temperature with a Bruker WH-90 spectrometer operating at 22.63 MHz and a Bruker WP-200 spectrometer operating at 50.28 MHz under conditions of full proton decoupling. Spectral conditions at 22.63 MHz were as follows: spectral width, 6000 Hz; pulse length, 4 μs (~30° pulse); acquisition time, 1.4s; number of scans, 40 000. Spectral conditions at 50.28 MHz were as follows: spectral width, 8000 Hz; pulse length, 11 μs (50° pulse); relaxation delay, 3 s; acquisition time, 1 s; number of scans, 15 000. ^{13}C NMR dynamic parameters: spin–lattice relaxation times (T_1) and nuclear Overhauser enhancement factors (NOEF) were measured at two different field strengths (21.14 and 46.15 kG). At 21.14 kG the T_1 spin–lattice relaxation times were measured by the inversion–recovery pulse sequence (π–τ–$\pi/2$) with a delay between the sequences of 10 s. NOEFs were measured by the inverse gated irradiation technique.

At 46.15 kG the spin–lattice relaxation times and the NOEFs were measured with the unique sequence ($\pi/2$–τ–$\pi/2$) as a function of the preirradiation period with a 5-s delay between sequences. Data were analyzed as a single-exponential decay with an exponential regression routine.

Results and Discussion

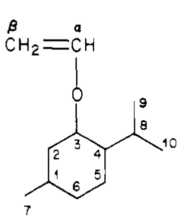
(a) Synthesis and Characterization of Polymer Samples. Poly(menthyl vinyl ether) [poly(1)] samples were obtained by polymerization under homogeneous conditions using a free-ion cationic initiator (run M1), conventional cationic catalysts (runs M2 and M3), and diisopropoxyaluminum sulfate (run M4), a catalyst that displays a controllable activity even at room temperature[3] (Table I). It is worth mentioning that menthyl vinyl ether gives no polymer under heterogeneous conditions in the presence of a Vandenberg-type catalyst based on triisopropoxyaluminum and sulfuric acid.[4] In all these experiments, polymeric products having fairly high molecular weights were obtained in good yields although the catalyst of run M4 seems to be less active than the others.

Fractionation with boiling solvents (Table II) of the crude polymeric products allows one to isolate a fraction of more than 96% which is insoluble in acetone and extractable in *n*-hexane. The latter fractions, within the limits of experimental error, are characterized by the same molar optical rotation, which is very close to the maximum value reported for poly(menthyl vinyl ether).[5] It is worth noting that, whatever the route of preparation, poly(menthyl vinyl ether) shows upon X-ray inspection a crystalline structure analogous to that observed for a sample obtained with a heterogeneous catalyst.[6]

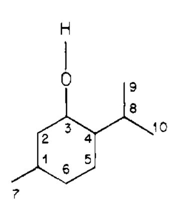
(b) ^{13}C NMR: Tacticity Evaluation. The ^{13}C NMR proton-decoupled spectra of poly(menthyl vinyl ether) (sample M1, Table I) at 22.63 and 50.28 MHz are shown in Figure 1, parts a and b, respectively.

Apart from slight variations in the intensity and width of the lines, all the polymer samples have identical spectra.

Resonance assignments were made by comparison with model compounds [(−)-menthol (2)[7,8] and menthyl ethyl ether (3)], by off-resonance decoupling experiments, and by using ^{13}C T_1 relaxation times. Resonance assignments of menthyl ethyl ether were made by off-resonance decoupling and ^{1}H selective decoupling experiments. Chemical shifts of carbon atoms in the polymers and model compounds and their corresponding assignments are reported in Table III.



1



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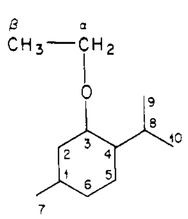

3

Methylenic carbon atom C_β and C_2 resonances cannot be unequivocally assigned due to the broadening and overlapping of the corresponding peaks centered at 41.36 ppm. The peaks at 68.18 and 73.48 ppm due to methine carbon atoms C_3 and C_α can be tentatively assigned only on the basis of slightly different relaxation times. This assignment is in keeping with what is observed for poly(isopropyl vinyl ether) in which the resonance signal of the main-chain methine carbon atom is placed at lower field value with respect to the methine carbon in the side chain.[9] It should be noted, however, that in the case of (−)-menthol (2) and the model compound (−)-menthyl ethyl ether (3) the methine carbon atom of the six-membered ring in the α-position to the oxygen atom is rather markedly shifted to lower field values (Table IV).

Table III
^{13}C NMR Experimental Chemical Shifts[a] and Relative Assignment of Poly(menthyl vinyl ether) [Poly(1)], (−)-Menthol (2), and (−)-Menthyl Ethyl Ether (3)

carbon atom	2	3	poly(1)[b]
C_1	31.70	31.87	31.51
C_2	45.11	41.11	41.36[c]
C_3	71.35	79.01	68.18
C_4	50.12	48.70	48.74
C_5	23.23	24.05	23.55
C_6	34.60	34.95	34.60
C_7	22.23	22.39	22.67
C_8	25.68	26.19	24.88
C_9	16.16	15.87	16.49
C_{10}	21.14	20.97	21.12
C_α		63.75	73.48
C_β		16.70	41.36[d]

[a] In ppm from Me_4Si. [b] Average values observed for polymers obtained by different catalytic systems. [c] Coincides with the C_β resonance. [d] Coincides with the C_2 resonance.

In the case of poly(menthyl vinyl ether) no information on main-chain configurational placements can be obtained from the resonance of the β-CH_2 carbon because of overlapping with the signal of the 2-CH_2 of the aliphatic ring.

The 22.63-MHz ^{13}C NMR spectra of all the polymer samples fail to provide any well-defined stereochemical information. The 50.25-MHz ^{13}C NMR spectra, however, contain serveral resonance areas having profiles that may be sensitive to stereosequence effects. The most pronounced effect is that detectable in the resonance due to the asymmetric methine carbon 4-CH, clearly split into two peaks (Figure 2). By assuming that no racemization of the chiral centers present in the starting optically pure monomer takes place under the polymerization conditions,[4] one can attribute the observed splitting to tacticity effects. In particular, taking into account that menthyl vinyl ether preferentially gives isotactic polymers under different polymerization conditions,[1,6] one can attribute the highest intensity peak (A) located at higher field to *m* dyads, whereas the lower field peak (B) can be assigned to *r* dyads. The relative intensity ratio of the two peaks gives therefore a quantitative measure of the tacticity. Comparable values of the tacticity (75–78% isotactic dyads) were obtained for all the samples studied.

(c) ^{13}C NMR: Dynamic Parameters. To gain information about the conformational influence of the bulky side chain on the backbone and vice versa, we performed a ^{13}C relaxation study (see Table IV). The dipolar relaxation mechanism ^{13}C–^{1}H has been found to predominate in polymers in solution.[10,11] An isotropic overall tumbling model with a single correlation time does not agree with the different values found for the individual carbon atoms

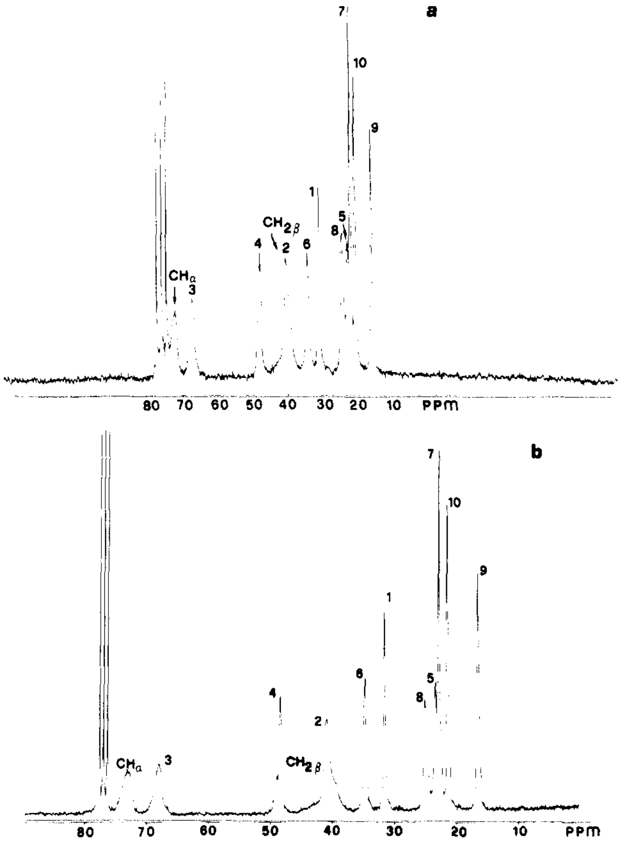

Figure 1. ^{13}C NMR proton-decoupled spectra of poly(menthyl vinyl ether) (sample M1, Table I) at (a) 22.63 MHz and (b) 50.28 MHz.

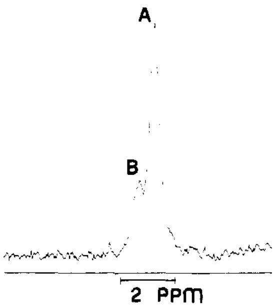

Figure 2. Expanded ^{13}C NMR (50.28 MHz) signal relevant to the 4-CH carbon atom (sample M1, Table I): (A) signal associated with meso dyads; (B) signal associated with racemic dyads.

Table IV
^{13}C NMR Spin-Lattice Relaxation Times (T_1) and Nuclear Overhauser Enhancement Factors (NOEF) for Poly(menthyl vinyl ether) in $CDCl_3$ Solution at 22.63 and 50.28 MHz

	T_1, s		NOEF		τ_d,[d] ns	
assignment	22.63 MHz[a]	50.28 MHz[b]	22.63 MHz[c]	50.28 MHz[b]	22.63 MHz[e]	50.28 MHz[f]
C_α	0.059	0.133	0.68	0.64	3.0	1.2
C_3	0.070	0.137	0.78	0.64	1.2	0.92
C_4	0.071	0.136	0.86	0.60	1.0	0.94
C_2 and C_β	0.063	0.093	0.69	0.56	0.24	0.24
C_6	0.052	0.085	0.67	0.61	0.27	0.35
C_1	0.082	0.106	0.76	0.61	0.076	0.16
C_8	0.079	0.145	0.86	0.60	0.69	0.67
C_5	0.065	0.081	0.86	0.48	0.16	0.41
C_7	0.205	0.249	1.20	0.80	0.0027	0.0063
C_{10}	0.245	0.289	0.97	0.75	0.0027	0.0045
C_9	0.283	0.325	1.10	0.75	0.0012	0.0035

[a] ±0.002. [b] ±0.01. [c] ±0.05. [d] For methyl group, τ_d means τ_R; see text. [e] τ_0 = 30 ns. [f] τ_0 = 10 ns.

in the side chain. A diamond lattice conformational jump model[10,12,13] gave us a reasonably good agreement of the T_1 relaxation times and of the NOEFs in both magnetic fields used.

The conformational jump over three bonds (correlation time τ_d) combined with an overall segmental motion (correlation time τ_0) gives calculated T_1 and NOEF values that agree within the limits of experimental error with the experimental data. The calculated T_1 and NOEF values and the τ_0 and τ_d values are reported in Table IV.

The T_1 values for the methyl groups were fitted according to the model proposed by Woessner.[10,14] In this case τ_d (see footnote *d* in Table IV) represents the correlaton time for the internal rotational motion of the methyl groups.

The τ_d values for individual carbon atoms determined at the two frequencies are in quite good agreement. The motional behavior of the ether side chain is mainly characterized by long correlation times along the C_α–O–C_3–C_4 moiety, thus indicating that the dominant motion of the side chain is a slow rotation around these bonds. The τ_d correlation time of the C_8 carbon is substantially longer than the τ_d correlation times of the C_4, C_5, C_6, C_1, and C_2 carbons. This decrease of the τ_d correlation time points to an increased mobility of this part of the side chain compared to C_8 and C_4. This result can be attributed to a high flexibility of the C_2–C_1–C_6–C_5 portion of the ring and to a reduced mobility of the C_3–C_4–C_8 fragment, perhaps due to steric hindrance of the main chain. It may be noted that the methyl groups, in particular C_9 and C_{10}, have very short internal correlation times indicative of fast rotations. The steric interaction associated with the decreased mobility of the C_3–C_4–C_8 fragment should thus be attributed to the proximity of this part of the ring with the backbone.

In conclusion, (–)-menthyl vinyl ether (1) was polymerized in the presence of different catalytic systems, and in contrast to other optically active alkyl vinyl ethers, it does yield polymers in which the stereochemical configuration is not sensitive to the catalytic system.[1]

Fractionation of the polymers (M1–M4) with solvents gives rise to a very large fraction (>95%) with a molar optical rotation very close to the maximum value reported for poly(1).[5] Furthermore, the investigated samples show under X-ray inspection a crystalline structure analogous to that observed for a partially isotactic sample obtained with a heterogeneous catalysts.[6]

Tacticity studies by ^{13}C NMR spectroscopy performed on samples prepared with different catalytic systems show a 75–78% content of isotactic dyads in all cases. This unusual behavior agrees with the findings by optical rotation[1] and circular dichroism[15] measurements. In particular, no substantial differences in either the profile or relative intensity of the dichroic bands related to the n → σ^* electronic transition of the ether chromophore have been reported.[15]

A ^{13}C NMR study of the dynamics of polymer chains in solution, performed at two different magnetic field strengths, clearly indicates reduced mobility of that part of the side group closest to the polymer backbone. This steric interaction can be considered a characteristic feature of this polymer, in contrast to other poly(alkyl vinyl ethers).[9,10]

It appears that both the presentation and the subsequent insertion of the monomer into the growing chain are controlled to some degree by the stringent stereochemical requirements connected with the interaction of the polymer backbone with the asymmetric bulky side group. At present, however, no detailed scheme can be put forward, even on the basis of molecular models, which explains the rather high stereospecificity of the polymerization process.

Registry No. Poly(menthyl vinyl ether), 26099-46-7.

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