C-13 NMR Spectra and Spin-Lattice Relaxation Times of Poly(alkyl vinyl ether)s

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ABSTRACT: ^{13}C NMR spectra of isotactic-rich poly(alkyl vinyl ether)s were measured in toluene- d_8 at 110°C, with some improvements on peak separation. The ^{13}C spin-lattice relaxation times (T_1 's) for syndiotactic sequences were consistently longer than those for isotactic ones, in contrast to the case of polypropylene and polymethacrylates, in which the T_1 's for isotactic sequences are longer than those for syndiotactic sequences. The nuclear Overhauser enhancement factors for the polymers of methyl and *t*-butyl vinyl ethers were close to the theoretical maximum. These results indicate higher flexibility of the syndiotactic sequences in poly(alkyl vinyl ether)s.

KEY WORDS Carbon-13 NMR Relaxation / Tacticity / NMR Chemical Shift / Methyl Vinyl Ether Polymer / Ethyl Vinyl Ether Polymer / Isopropyl Vinyl Ether Polymer / Isobutyl Vinyl Ether Polymer / *t*-Butyl Vinyl Ether Polymer / Alkyl Vinyl Ether Polymer / Nuclear Overhauser Enhancement (NOE) /

NMR spin-lattice relaxation times (T_1 's) of certain vinyl polymers are known to depend on stereoregularity. Thus, it has been shown for the polymers of propylene,¹ methyl^{2–5} and other alkyl methacrylates,⁴ and vinyl chloride⁶ that T_1 values for *isotactic* polymers or sequences are larger than those for *syndiotactic* polymers or sequences. This difference may be attributed to the fact that isotactic chains are more flexible than syndiotactic chains.

Recently, Angad-Gaur and Sikkema⁷ reported that T_1 for the peak of *racemo* methylene carbon is longer than that for the *meso* peak in poly(allyl vinyl ether). They accounted for this reverse phenomenon by the higher magnetic field (6.34T) employed in the measurements and concluded that the mobility of the *syndiotactic* sequence is lower than that of the isotactic one.

In this study, the ^{13}C T_1 's for poly(alkyl vinyl ether)s (alkyl=methyl, ethyl, isopropyl, isobutyl and *t*-butyl) were measured in toluene- d_8 at 110°C at 25MHz. It was found that for most of the carbons in these polymers, ^{13}C T_1 's are shorter for *isotactic* or *meso* sequences than for *syndiotactic* or

racemo sequences. Nuclear Overhauser enhancement (NOE) factors were measured for the polymers of methyl and *t*-butyl vinyl ethers. From the results obtained, it was concluded that in the poly(alkyl vinyl ether)s studied, the *isotactic* or *meso* sequences are less flexible than the *syndiotactic* or *racemo* sequences, in contrast to the case of polypropylene and polymethacrylates.

EXPERIMENTAL

Materials

Isopropyl and *t*-butyl vinyl ethers were synthesized from the corresponding alcohols and methyl vinyl ether by transesterification reaction.⁸ Other monomers were obtained from commercial sources. All these monomers were purified by fractional distillation, dried over molecular sieves 4A and calcium dihydride, and distilled *in vacuo* before use.

Polymer samples were prepared by polymerizing these monomers with boron trifluoride etherate in toluene at –78°C. Their characteristics are summarized in Table I.

Table I. Characteristics of poly(alkyl vinyl ether)s prepared with $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$ in toluene at -78°C

Alkyl group	Tacticity/%			M_n	T_g °C
	I	H	S		
CH_3	62	30	8	16100	-27
C_2H_5	55	37	8	37300	-31
iso- C_3H_7	62	24	14	26500	-1
iso- C_4H_9	67	24	9	74500	-14
<i>t</i> - C_4H_9	69	25	6	64300	82

Measurements

^{13}C NMR spectra were measured on a JNM-FX100 (25 MHz) or JNM-FX200 (50 MHz) Fourier transform NMR spectrometer (JEOL) at 110°C . Tetramethylsilane (TMS) was used as the internal standard. A given polymer solution (1.0 mol l^{-1}) was sealed in an NMR sample tube (10 mm o.d.) under nitrogen atmosphere. Spin-lattice relaxation times were determined by the inversion recovery method. Nuclear Overhauser enhancement factors were determined by comparing the signal intensities of completely decoupled and gated decoupled NMR spectra.

The number-average molecular weight of each sample was measured in benzene at 42.0°C using a Hitachi 117 vapor osmometer.

Glass transition temperature was measured with a Rigaku Denki differential scanning calorimeter Model 8801 SL/C at a heating rate of $10^\circ\text{C min}^{-1}$.

RESULTS AND DISCUSSION

^{13}C NMR Spectra of Poly(alkyl vinyl ether)s

The ^{13}C NMR spectrum of poly(methyl vinyl ether) was first reported by Johnson *et al.*⁹ and showed in the methoxy and methylene carbon resonances stereochemical splittings which could be attributed to pentad and dyad sequences, respectively. The dyad splitting of the methylene resonance was supported by the theoretical investigation of Ando *et al.*¹⁰ using a dimer model. Matsuzaki and his coworkers¹¹ measured the NMR spectra of several poly(alkyl vinyl ether)s in mixed solvents mostly containing halomethanes at 50°C , and made the stereochemical assignments for the polymers of different tacticities. The ^{13}C NMR spectra of the polymers of ethyl and isobutyl vinyl ethers were also measured by Randall.¹² In this work, we reexamined the ^{13}C NMR spectra of various poly(alkyl vinyl ether)s in toluene- d_8 at 110°C and found some improvements on peak separation.

Figure 1 illustrates the 25 and 50 MHz ^{13}C NMR spectra of poly(methyl vinyl ether) in toluene- d_8 at 110°C . The resonances of all carbons are sensitive to

Figure 1. ^{13}C NMR spectra of poly(methyl vinyl ether) (A), (B), and (C) at 25 MHz, (D), (E), and (F) at 50 MHz.

Table II. Peak assignments for methoxy carbon resonance of poly(methyl vinyl ether) at 50 MHz

Peak	Chemical shift (ppm)	Assignment	Relative intensity	
			Obsd	Calcd ^a
1	55.94	<i>mmmm</i>	0.40	0.413
2	56.06	<i>mmmr</i>	0.21	0.192
3	56.14	<i>rmmr</i>	0.10	0.085
4	56.21	<i>mmrm + mmrr</i> ^b	0.17	0.173
5	56.32	<i>mmr + mrrm</i> ^b	0.05	0.068
6	56.39	<i>mrrr</i>	0.04	0.038
7	56.48	<i>rrrr + rrrr</i>	0.03	0.031

^a Calculated assuming first-order Markovian statistics ($P_{m/r}=0.209$, $P_{r/m}=0.604$).

^b This assignment of *mmrr* and *mrrm* pentads is tentative and interchangeable.

Table III. Peak assignment for *meso* methylene carbon resonance of poly(methyl vinyl ether) at 50 MHz

Peak	Chemical shift (ppm)	Assignment	Relative intensity	
			Obsd	Calcd ^a
1	39.37	<i>mmmm</i>	0.307	0.327
2	39.46	<i>mmmmr</i>	0.160	0.157
3	39.54	<i>rmmmr</i>	0.025	0.019
4	39.67	<i>mmmr</i>	0.064	0.067
5	39.73	<i>mmrm + rmmrr</i>	0.150	0.143
6	39.83	<i>rmmrm</i>	0.033	0.030
7	40.02	<i>rmr</i>	0.008	0.029
8	40.09		0.010	
9	40.17		0.014	

^a Calculated assuming first-order Markovian statistics ($P_{m/r}=0.209$, $P_{r/m}=0.604$).

stereochemical configurations, and the separation of peaks is better in the spectrum at 50 MHz than in that at 25 MHz.

It can be seen from Figure 1 that the resonance of methine carbon splits into three peaks which can be assigned to *isotactic*, *heterotactic* and *syndiotactic* triads in order of decreasing magnetic field. The resonance of methoxy carbon splits into pentad peaks (Figures 1B and 1E), as has already been reported.^{9,11} By assuming first-order Markovian statistics,¹¹ pentad fractions were calculated from the triad values, and the calculated values were

Figure 2. ^{13}C NMR spectra of poly(ethyl vinyl ether). **Figure 3.** ^{13}C NMR spectra of poly(isopropyl vinyl ether).

compared with the measured peak intensities at 50 MHz. The resulting assignment of seven peaks is presented in Table II. The agreement between the calculated and measured intensities is fairly good. The present assignment is somewhat different from that made on the spectrum measured in a methanol-dichloromethane mixture at 50°C.¹¹

The methylene carbon resonance consists of two multiplets situated at 39.5 and 41.4 ppm due to dyad tacticity. The resonance of *meso* methylene carbon splits into nine peaks. These peaks were assigned to hexad sequences as indicated in Table III by comparing the peak intensities with the calculated fractions of hexad sequences. The *racemo* resonance also shows splitting probably due to hexad sequences, although peak separation was not satisfactory enough to make complete stereochemical assignment of the peaks.

^{13}C NMR spectra of the polymers of ethyl, isopropyl, isobutyl and *t*-butyl vinyl ethers were also measured in toluene- d_8 at 25 MHz and 110°C. The results are shown in Figures 2–5. The resonances of main-chain methylene carbons except for that of poly(*t*-butyl vinyl ether) clearly show dyad splitting. The *meso* methylene resonances are more

Figure 4. ^{13}C NMR spectra of poly(isobutyl vinyl ether).

Figure 5. ^{13}C NMR spectra of poly(*t*-butyl vinyl ether).

sensitive to tetrad configurations than the *racemo* methylene resonances and split into multiplets as in the case of poly(methyl vinyl ether) (Figures 2C, 3C, and 4C). The methylene carbon of poly(*t*-butyl vinyl ether) gives only a broad signal as has already been reported¹¹ (Figure 5C).

The resonances of the main-chain methine carbons of these polymers split into three peaks reflecting tactic triads. The peak resolution is good in the spectra of the polymers of isopropyl and *t*-butyl vinyl ethers (Figures 3A and 5A), but not so in those of the polymers of ethyl and isobutyl vinyl ethers (Figures 2A and 4B). The resonances of the α -carbon to the oxygen in the side-chains are sensitive to stereochemical configurations, and most of them reflect the triad tacticity of the polymers.

For poly(isopropyl vinyl ether), pentad splitting was also observed in the signal for *isotactic* triad (Figure 3B). For poly(isobutyl vinyl ether), the resonances of the methyl carbon as well as the methylene carbon in the side-chain showed triad splitting (Figures 4A and 4D).

Matsuzaki *et al.*¹¹ found the methine carbon

resonance of poly(*t*-butyl vinyl ether) in a mixture of chloroform and dichloromethane to split into five peaks reflecting pentad tacticity. In our spectrum, however, this resonance splits into three peaks which can be assigned to *mm*, *mr*, and *rr* triads in the order of decreasing magnetic field. The triad tacticities determined from the methine carbon resonance (I 68.7, H 25.3, S 6.0%) agreed well with those obtained from the quaternary carbon signal (I 68.8, H 25.3, S 5.9%).

In summary, our newly observed peaks and their stereochemical assignments are as follows:

Poly(methyl vinyl ether):

CH (triad), CH₂ (hexad)

Poly(isopropyl vinyl ether):

CH (triad), CH₂ (tetrad)

Poly(isobutyl vinyl ether):

CH (triad), CH(CH₃)₂ (triad), CH₂ (tetrad)

Poly(*t*-butyl vinyl ether):

CH (triad)

The chemical shift values are listed in Table IV.

^{13}C NMR Relaxation

Table V gives the ^{13}C - T_1 values for poly(alkyl vinyl ether)s in toluene-*d*₈ at 110°C. The T_1 values for the main-chain methine carbons are about twice as large as those for the main-chain methylene carbons. This suggests that these two carbons have similar mobilities; that is, the motion of the poly(alkyl vinyl ether) backbone is essentially isotropic. The T_1 's for the main-chain carbons decrease with increasing side-chain bulkiness (CH₃ < C₂H₅ < iso-C₃H₇ ≤ iso-C₄H₉ < *t*-C₄H₉), indicating that the segmental mobility of poly(alkyl vinyl ether) decreases with an increase in the bulkiness of the side-chain alkyl groups. A similar relation was found for polymethacrylates.⁴ The side-chain carbons have longer T_1 than the main-chain carbons since the former have rotational freedom.

The ^{13}C - T_1 values for the peaks of *racemo* or *syndiotactic* sequences are larger than those for the peaks of *meso* or *isotactic* sequences except in a few cases. The ratios of these two T_1 values range from 1.1 to 1.4. Angad-Gaur and Sikkema⁷ reported the same dependence of T_1 on stereosequence for poly(allyl vinyl ether) at 22°C. On the basis of the lower NOE value (2.0) at 6.34 T (270 MHz for ^1H and 68 MHz for ^{13}C), they concluded that the T_1 values appear to the right of the minimum point in the log T_1 -log τ diagram and that the syndiotactic

Table IV. ¹³C NMR chemical shifts (ppm) for poly(alkyl vinyl ether)s in toluene-*d*₈ at 110°C and 25 MHz^a

Alkyl group	Main-chain				Side-chain		
		CH ₂		CH	CH ₃ ^b		Others
CH ₃	<i>mmm</i>	39.37	<i>mm</i>	76.33			
	<i>mmr</i>	39.73	<i>mr</i>	76.49			
	<i>rmr</i>	40.17	<i>rr</i>	76.64			
	<i>mrmm</i>	41.20					
	<i>mrr</i>	41.34					
	<i>rrr</i>	(41.5)					
C ₂ H ₅	<i>mmm</i>	40.54				CH ₂	<i>mm</i> 64.01
	<i>mmr</i>	40.97		74.65	16.02		<i>mr</i> 64.16
	<i>rmr</i>	(41.4)					<i>rr</i> (64.3)
	<i>r</i>	42.21					
iso-C ₃ H ₇	<i>mmm</i>	42.37	<i>mm</i>	71.88		CH	<i>mm</i> 69.07
	<i>mmr</i>	42.61	<i>mr</i>	72.27	23.46		<i>mr</i> 68.67
	<i>r</i>	43.3	<i>rr</i>	72.66			<i>rr</i> (68.5)
iso-C ₄ H ₉	<i>mmm</i>	40.58				CH	<i>mm</i> 29.66
	<i>mmr</i>	40.91		74.85	19.92		<i>mr</i> 29.75
	<i>rmr</i>	41.16					<i>rr</i> 29.85
	<i>r</i>	42.41				CH ₂	76.16
<i>t</i> -C ₄ H ₉			<i>mm</i>	67.83		-C-	<i>mm</i> 73.75
		46.54	<i>mr</i>	68.30	30.13		<i>mr</i> 73.56
			<i>rr</i>	(68.6)			<i>rr</i> 73.28

^a The chemical shift values in parentheses refer to shouldered peaks.^b The chemical shift and the peak assignment for poly(methyl vinyl ether) at 50 MHz are shown in Table II.

sequence has a longer correlation time, that is, a lower flexibility than the *isotactic* one.

Table VI shows the NOE and *T*₁ values for the polymers of methyl and *t*-butyl vinyl ethers. Even at 27°C, the NOE values for poly(methyl vinyl ether) come close to the theoretical maximum (2.99) calculated using a model for dipolar relaxation mechanism.¹³ Those for poly(*t*-butyl vinyl ether) do not reach this maximum but are close to it. That the NOE values obtained are larger than those for poly(allyl vinyl ether) should reflect a higher flexibility of poly(alkyl vinyl ether)s. These results indicate that the correlation time (τ) of poly(alkyl vinyl ether) is smaller than that for the minimum *T*₁ value in the log *T*₁–log τ diagram.^{14,15} The *T*₁ values for the main-chain carbons change with the glass transition temperatures of the polymers (Tables I and V). This is additional evidence that the *T*₁ values appear to the left of the minimum *T*₁ value.

Therefore, it may be concluded that in the poly(alkyl vinyl ether) chains, the *syndiotactic* sequence has a higher mobility than the *isotactic* one.

In all the cases so far reported^{1–6} where *T*₁ depends on the stereosequence of the polymers, the *isotactic* sequence gave a longer ¹³C-*T*₁, and hence was more flexible than the *syndiotactic* one. The finding that the *syndiotactic* sequence is more flexible than the *isotactic* one is probably the first instance showing the reverse of these previous observations. The implication is that the stereoregularity dependence of chain conformation in poly(vinyl ether)s should be different from that in polymethacrylates and polypropylene. However, according to a conformational analysis of poly(alkyl vinyl ether),¹⁶ the *TG* conformation should be preferable for *meso* sequences and the *TT* conformation for *racemo* dyads, as in the case of polymethacrylates and polypropylene. Further in-

Table V. ^{13}C - T_1 's (s) for poly(alkyl vinyl ether)s in toluene- d_8 at 110°C and 25 MHz

Alkyl group	Main-chain				Side-chain			
		CH_2		CH		CH_3^a		Others
CH_3	<i>mmm</i>	0.64	<i>mm</i>	1.23	(1)	3.69		
	<i>mmr</i>	0.64	<i>mr</i>	1.20	(2)	3.97		
	<i>mrr</i>	0.75	<i>rr</i>	1.53	(4)	4.06		
C_2H_5	<i>mmm</i>	0.40		0.73		2.75	CH_2	<i>mm</i> 1.19
	<i>r</i>	0.44						<i>mr</i> 1.15
iso- C_3H_7	<i>mmm</i>	0.22	<i>mm</i>	0.44		2.22	CH	1.02
	<i>r</i>	0.25	<i>mr</i>	0.53				
iso- C_4H_9	<i>mmm</i>	0.20		0.40		3.31	CH_2	0.56
	<i>r</i>	0.25					CH	1.80
<i>t</i> - C_4H_9		0.10	<i>mm</i>	0.17		1.47	$-\text{C}-$	<i>mm</i> 7.14
			<i>mr</i>	0.20				<i>mr</i> 7.49

^a The parenthesized numbers for poly(methyl vinyl ether) refer to those in Figure 1B.

Table VI. NOE and ^{13}C - T_1 (s) values for the polymers of methyl and *t*-butyl vinyl ethers

Alkyl group	Temp °C	Main-chain			Side-chain	
			CH_2	CH	OCH_3	$\text{OC}(\text{CH}_3)_3$
CH_3	110	{ NOE	2.9	3.0	2.8	—
		{ T_1	0.64 (<i>m</i>)	1.23 (<i>mm</i>)	3.69 ^a	—
			0.75 (<i>r</i>)	1.53 (<i>rr</i>)		—
	27	{ NOE	2.8	2.8	2.6	—
		{ T_1	0.14 (<i>m</i>)	0.25 ^b	1.42 ^a	—
			0.17 (<i>r</i>)			—
<i>t</i> - C_4H_9	110	{ NOE	2.6	2.6	—	2.9
		{ T_1	0.10	0.17 (<i>mm</i>)	—	1.47

^a T_1 values for the peak (1) seen in Figure 1B.

^b Splitting due to tacticity was not observed at 27°C.

vestigation will be necessary for giving an understanding of the NMR relaxation mechanism in poly(alkyl vinyl ether)s.

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