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Polymerization of 2-Methyltrimethylene Oxide with Organoaluminum Catalysts and a Microstructure Study of Its Polymer by ^{13}C NMR Spectroscopy

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ABSTRACT: The polymerization of 2-methyltrimethylene oxide and its optically active enantiomer was done with an aluminum coordination catalyst and some cationic catalysts. Only the coordination catalyst gave polymer with predominantly head-to-tail linkages. The microstructure of the polymers obtained was determined by ^{13}C NMR spectroscopy from the methine-carbon triads and the *O*-methylene-carbon dyads. The stereospecific ability of the catalysts was also evaluated.

Since the polymerization of trimethylene oxide and its derivatives with BF_3 catalyst was reported by Rose,[1] a large number of papers and patents have appeared on the polymerization of derivatives of trimethylene oxide, particularly 3,3-bis(chloromethyl)oxetane. There has been much research on the polymerization of propylene oxide but little investigation of the polymerization of 2-methyltrimethylene oxide in the past decade. We have reported microstructure results for poly(propylene oxide) by ^1H and ^{13}C NMR spectroscopic methods.[2] In this paper the ^{13}C NMR method was also used for the microstructure analysis of poly(2-methyltrimethylene oxide) obtained with some coordination and cationic catalysts.

Experimental Section

Materials. In general, purification of materials was carried out under a dry argon atmosphere. All solvents were purified by conventional methods, dried over calcium hydride, and distilled just before use. Diethylzinc and triethylaluminum were purified by distillation under reduced pressure.

2-Methyltrimethylene Oxide. This racemic compound was prepared with 1,3-butanediol as a starting material by the method reported by Searles et al.:[3] bp 60 °C; yield 54%. Optically active (+)-2-methyltrimethylene oxide was prepared by asymmetric reduction of methyl acetoacetate with Raney-nickel catalyst treated with D(+)-tartaric acid, followed by reduction with lithium aluminum hydride in dry ether and subsequently by Searles' procedure:[3] yield 46%; $[\alpha]^{22}_D$ −22.4 ° (neat), optical purity 76%.[4]

Polymerization Procedure. 2-Methyltrimethylene oxide was charged by distillation over calcium hydride into the polymerization ampule containing the catalyst solution. The ampule was sealed and allowed to stand at 60 °C for several days. Polymerization was terminated by adding a mixture of benzene and a small amount of methanol. The precipitated catalyst residue was removed by centrifugation and the raw polymer was obtained from the solution by freeze-drying. Intrinsic viscosity, $[\eta]$, was measured at 30 ± 0.1 °C in benzene solution.

Preparation of Catalysts. (a) Diethylzinc–Water (Molar Ratio 1:0.8) Catalyst. An ampule connected to a vacuum line was flushed several times with dry argon, and a solution of diethylzinc (3.0×10^{-4} mol) in benzene (5 mL) was introduced by distillation under reduced pressure; then, while the mixture was stirred at room temperature, water (5.04 μL) was added with a microsyringe. Stirring was continued at room temperature for 2 h and then at 60 °C 3 h. The resulting benzene solution was freeze-dried to remove unreacted diethylzinc. To the residue obtained toluene and monomer were added by distillation seperately in this order under reduced pressure from the graduated reservoirs.

Table I
Polymerization of Racemic 2-Methyltrimethylene Oxide with a Variety of Catalysts[a]

catalyst (molar ratio)	amt of catalyst, mol/mol of monomer	polymerization time, days	polymer yield, %	$[\eta]$,[b] dL/g
t-BuOK	2×10^{-2}	48	0	
$BF_3 \cdot OEt_2$	2×10^{-2}	44	52	0.05
$FeCl_3$	3×10^{-2}	44	62	0.02
$Al(O\text{-}i\text{-}Pr)_3$-$ZnCl_2$ (1:1)	3×10^{-2}	54	14	0.01
$ZnEt_2$-H_2O (1:1)	3×10^{-2}	23	16	0.20
$AlEt_3$-H_2O (1:1)	3×10^{-2}	5	24	0.11
$AlEt_3$-acac-H_2O (1:1:0.5)	3×10^{-2}	9	51	0.90

[a] Polymerization was carried out in toluene solution at 60 °C. The concentration of monomer was 11.8 mol/L. [b] Intrinsic viscosity was measured in benzene at 30 °C.

(b) Triethylaluminum–Water Catalyst. The procedure was the same as that described for the diethylzinc catalyst, except for the reagent used.

(c) Triethylaluminum–Acetylacetone (acac)–Water Catalyst. The preparative method was reported by Vandenberg[5] and the typical procedure in this work was as follows: Triethylaluminum (0.0235 mol) was reacted with an equimolar amount of acac in toluene (20 mL) at 60 °C for 2 h; subsequently, water (0.0118 mol) was added with stirring and the mixture was allowed to stand overnight at room temperature.

Measurement of ^{13}C NMR Spectra. ^{13}C NMR (25.1 MHz) spectra of the polymers in deuteriobenzene solution were measured with a Varian XL-100 FT spectrometer. The instrument conditions were as follows: spectrum width, 5 kHz; acquisition time, 2.0 s; transients, 6000; flip angle, 50°; temperature, 30 °C. Tetramethylsilane was used as an internal standard.

Measurement of Molecular Weight Distribution. Chromatographic measurements were performed on a Shimadzu-Du Pont Model 830 liquid chromatograph using a set of three Styragel columns designated 7×10^5–5×10^6, 4×10^3–1.5×10^5, and

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Table II
^{13}C Shifts in Poly(2-methyltrimethylene oxide) in Deuteriobenzene

$$\overset{a}{\text{—O—CH}_2}\text{—}\overset{b}{\text{CH}_2}\text{—}\overset{c}{\text{CH}}\overset{d}{\text{(CH}_3\text{)}}\text{—}$$

sample	δ [a] indicated			
	a (*O*-methylene)	b (methylene)	c (methine)	d (methyl)
polymer obtained with $AlEt_3$-H_2O catalyst	65.37 H-T[b] 67.89 T-T	37.76 H-H (T-T) 38.16 H-T 38.36 H-H (T-T)	69.59 H-H 70.07 H-H 72.88 H-T	20.08 H-T 20.57 H-H 21.47 H-H

[a] Defined to be downfield from the proton line of tetramethylsilane. [b] H-T, head-to-tail; H-H, head-to-head; T-T, tail-to-tail.

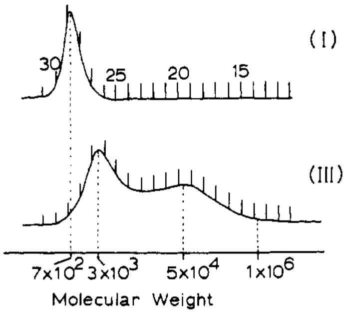

Figure 1. GPC diagram of poly(2-methyltrimethylene oxides) prepared with $AlEt_3$–H_2O (I) and $AlEt_3$–acac–H_2O (III) catalysts.

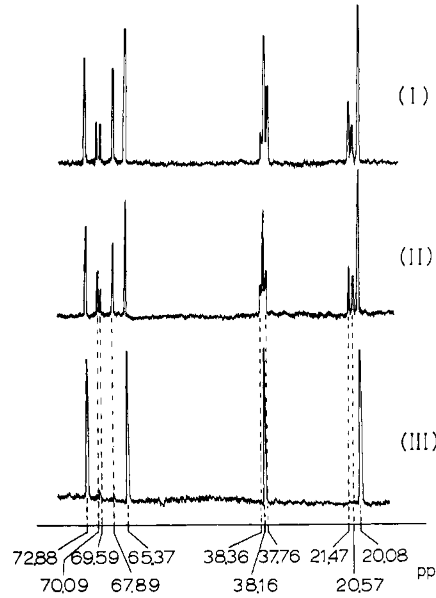

Figure 2. ^{13}C NMR spectra of poly(2-methyltrimethylene oxides) prepared with $AlEt_3$–H_2O (I), $ZnEt_2$–H_2O (II), and $AlEt_3$–acac–H_2O (III) catalysts. Sweep width 5000 Hz.

700–2000. The elution solvent was THF at 30 °C. The flow rate was maintained at 1 cm^3/min. A very sensitive differential refractometer was used to indicate polymer concentration in the eluent. The polymer samples (1 mL) were injected as 1% (w/v) solutions in THF. The polystyrene standard solutions were 0.5% (w/v). They were also injected into the GPC over 1 min. The elution volume was calculated from the initial point of injection to the appearance of the peak-height maximum of the elution curve.

Results and Discussion

Polymerization of 2-Methyltrimethylene Oxide. The results obtained for the polymerization of 2-methyltrimethylene oxide with a variety of catalysts are shown in Table I. The catalysts used in this work are well-known to be effective for the polymerization of propylene oxide. The typical free anionic catalyst *t*-BuOK was inactive, but the coordination anionic catalyst systems $ZnEt_2$–H_2O and Al(O-*i*-Pr)$_3$–$ZnCl_2$ showed catalytic activity for the polymerization of 2-methyltrimethylene oxide. The cationic catalyst systems $BF_3{\cdot}OEt_2$, $FeCl_3$, and $AlEt_3$–H_2O gave only low molecular weight oily polymer, but the coordination catalyst system $AlEt_3$–acac–H_2O afforded high molecular weight polymer. Polymer obtained with the last catalyst was a tacky or glassy solid. It was previously reported by Vandenberg that high molecular weight polymer was obtained with the catalyst in the polymerization of trimethylene oxide.[6]

The GPC diagram of poly(2-methyltrimethylene oxide) obtained with the aluminum catalysts is shown in Figure 1. The molecular weight distribution of the polymer obtained with the $AlEt_3$–H_2O catalyst ranged between several hundreds and several thousands and that of the polymer obtained with the $AlEt_3$–acac–H_2O catalyst from several thousands to one million.

^{13}C NMR Spectra of Poly(2-methyltrimethylene oxide). ^{13}C NMR spectra of poly(2-methyltrimethylene oxide) obtained with $AlEt_3$–H_2O (I), $ZnEt_2$–H_2O (II), and $AlEt_3$–acac–H_2O (III) are shown in Figure 2. There are only four peaks for the ^{13}C NMR spectrum of the polymer obtained with catalyst III. By comparison with its undecoupled spectrum, all peaks were assigned; the peak at 20.08 ppm originated from the methyl carbon, the one at 38.16 ppm from the methylene carbon, the one at ca. 65 ppm from the *O*-methylene carbon, and the peak at ca. 73 ppm from the methine carbon. In the spectra of the polymers obtained with catalysts I and II, additional peaks were observed. Since these polymers do not contain any cyclic and linear oligomers,[7] the splitting of these absorptions should be based on the configuration and sequence of the asymmetric carbon atoms in the polymer main chain. The chemical method applied to poly(propylene oxide) by Price[8] and Vandenberg[5] showed that the polymer obtained with $AlEt_3$–H_2O catalyst contained a certain amount of head-to-head and tail-to-tail linkages in the polymer main chain. These abnormal linkages were also determined from the ^{1}H and ^{13}C NMR studies of poly(propylene oxide) done by us.[2] As reported by Searles et al.[3] the anionic ring-opening reaction of 2-methyltrimethylene oxide occurs predominantly between oxygen and *O*-methylene carbon, and the cationic ring opening occurs between oxygen and methine carbon to the extent of 30% in addition to the normal opening reaction.[3] In the polymerization of this compound similar phenomena should occur. The occurrence of these abnormal linkages in poly(2-methyltrimethylene oxide) should produce a complicated spectrum in which the presence of at least three lines for each carbon atom is expected, in principle, corresponding to the structural isomeric units (Figure 3), if the configurational isomers (triad and/or dyad) were neglected. Actually three peaks for each methyl-, methylene-, and methine-carbon atom and two peaks for the *O*-methylene-carbon atom were observed. Magnetic resonance of the two *O*-methylene carbons in the tail-to-tail

Table III
^{13}C Shifts in Poly(2-methyltrimethylene oxide) and Assignments in Deuteriobenzene

$-O-\overset{a}{CH_2}-\overset{b}{CH_2}-\overset{c}{CH}(\overset{d}{CH_3})-$

sample	δ [a] indicated: a	b	c	d
polymer obtained with $AlEt_3$-acac-H_2O catalyst	65.37, isotactic 65.43, syndiotactic	38.16	72.25, isotactic 72.88, heterotactic 73.00, syndiotactic	20.08

[a] Defined to be downfield from the proton line of tetramethylsilane.

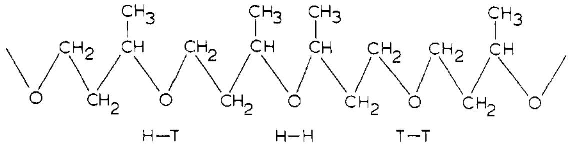

Figure 3. Polymer sequences containing head-to-tail, head-to-head, and tail-to-tail linkages.

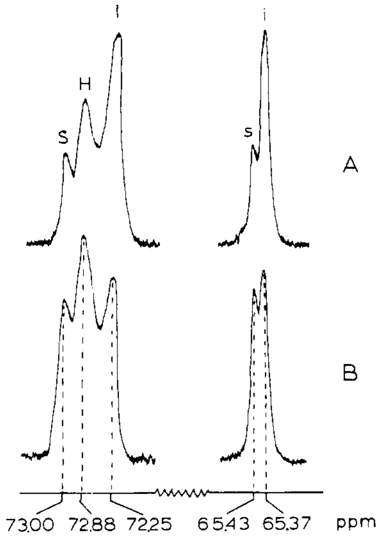

Figure 4. ^{13}C NMR spectra of poly(2-methyltrimethylene oxides) obtained from optically active monomer (A) and racemic monomer (B) with $AlEt_3$-acac-H_2O catalyst.

Table IV
Tactivity of a Variety of Optically Active Poly(2-methyltrimethylene oxides)[a]

starting monomer			microstructure, triad %[b]		
$[\alpha]^{25}{}_D$ (neat), deg	optical purity, %	$[\alpha]^{25}{}_D$ of polymer in benzene, deg	*I*	*H*	*S*
−18.7	76	−38.0	68	20	12
−11.3	46	−23.2	55	28	17
−3.9	16	−9.2	51	33	16
±0	0	0	32	48	20

[a] Polymers were obtained with $AlEt_3$-acac-H_2O catalyst. [b] ±3%.

Table V
Specific Rotation, $[\alpha]^{25}{}_D$, of Poly(2-methyltrimethylene oxide) in Various Solvents

solvent	$[\alpha]^{25}{}_D$ (*c* 1.00), deg	solvent	$[\alpha]^{25}{}_D$ (*c* 1.00), deg
chloroform	−20.4	methanol	−33.5
acetonitrile	−26.4	diisopropyl ether	−37.0
acetone	−27.0	benzene	−38.0

linkage is presumably nearly equivalent. The results obtained in terms of the above sequences are shown in Table II. The polymer obtained with catalyst III contained only a very small amount of abnormal linkages.

On the other hand, in the wide-sweep spectrum of the polymer obtained with catalyst III, splitting of the absorption originating from the *O*-methylene carbon into 65.37 and 65.43 ppm and splitting of the absorption originating from the methine carbon into 72.75, 72.88, and 73.00 ppm were observed (Figure 4). It is resonable to assign the three peaks of the methine carbon and the two peaks of the *O*-methylene carbon with small values of chemcial shift to the absorption based on the different stereochemical isomers, that is, triad and dyad, respectively. The ^{13}C NMR spectrum of the polymer obtained from optically active monomer (optical purity 76%) shows an absorption at 65.37 ppm which is of higher intensity than the two peaks originating from the *O*-methylene carbon. It is assignable to an isotactic dyad. The peak at 65.43 ppm is naturally assignable to the syndiotactic one. Concerning the splitting of absorptions based on methine carbon, the highest peak at 72.75 ppm is determined as the isotactic triad and the residual two peaks at 72.88 and 73.00 ppm are assigned to heterotactic and syndiotactic triads, respectively, so that the relationships of $i = (I + H)/2$ and $s = (S + H)/2$ between triads and dyads were satisified. The order of these chemical shifts was the same as that in the ^{13}C NMR spectrum of poly(propylene oxide). The polymer obtained from racemic monomer does not have a stereoregular structure ($I = 32$, $H = 48$, $S = 20$), whereas the polymer obtained from the 76% optical purity monomer had $I = 68$, $H = 20$, and $S = 12$ ($i = 78$ and $s = 22$). These results show that the $AlEt_3$-acac-H_2O system has little stereospecific catalytic ability for the polymerization of 2-methyltrimethylene oxide. The assignments of the resonances and the microstructure of the polymers obtained with aluminum catalysts are summarized in Tables III and IV.

Optical Activity of Poly[(+)-2-methyltrimethylene oxide] in Solution. The optical activity of poly(propylene oxide) prepared from (+)-propylene oxide is positive (+25°) in chloroform and negative (−33°) in benzene solution. This solvent dependence of optical activity has interested many researchers and was explained by taking into account the interaction between main-chain protons and solvents.[9] According to this interpretation a similar phenomenon should be observed also for the optical activity of poly[(+)-2-methyltrimethylene oxide] in a variety of solvents. While the sign of the optical activity of poly[(+)-2-methyltrimethylene oxide] in all solvents used was negative, a large deviation of −17.6° was observed between the values in chloroform and benzene (Table V).

Acknowledgment. We express thanks to Professor Y. Izumi of this university for assistance in preparing optically active 2-methylbutyrate.

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Polymer–Solvent Interaction Effects in Oscillatory Flow Birefringence Studies of Polybutadienes and Polyisoprenes in Aroclor Solvents

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ABSTRACT: Oscillatory flow birefringence measurements for solutions of 500 and 150 000 MW polybutadienes (PB) and 1000 and 57 000 MW polyisoprenes (PI) in high-viscosity Aroclors (1248 and 1254) are reported. These data show substantial reductions in the solvent birefringence contributions to the total solution value when small amounts of polymer are present, suggesting that polymer–solvent interactions occurring in these systems somehow modify the solvent–solvent interactions responsible for the unusually large and strongly temperature-dependent viscosity of Aroclors. Similar large reductions in the effective solvent viscosity are detected. These Aroclor solvent modifications due to the presence of PB or PI are strong functions of temperature and concentration but appear to be independent of polymer molecular weight and are insensitive to moderate variations in microstructure. When the normal correction procedure for determination of the polymer contribution to the observed total birefringence is applied to these data, time–temperature superposition appears to be invalid and both PB and PI seem to be dynamically "stiffer" than polystyrenes in Aroclors, for example. However, if modified solvent birefringences deduced from the oligomer-containing solutions are employed, time–temperature superpositions are obtained and the dynamic "stiffness" of PB and PI appears to be substantially less than for polystyrenes. These polymer–solvent interactions for these systems clearly influence both oscillatory flow birefringence and viscoelastic properties, and hence configurational dynamics interpretations obtained from such measurements for these solutions; polystyrenes, poly(α-methylstyrenes), and several poly(2-substituted methyl methacrylates) in Aroclors have not shown any evidence of similar interaction effects.

Extensive studies of the frequency dependence of oscillatory flow birefringence (OFB) and dynamic viscoelastic (VE) properties of polymer solutions have provided considerable insight into the dynamics of conformational change in these systems.[1-14] By employing Aroclors (chlorinated biphenyls) as solvents, both experiments have provided data apparently extending over sufficiently wide effective frequency ranges (as much as 7 decades) to detect the influence of motions ranging from the slowest overall chain rearrangements (low frequency) to very short-range configurational changes and side-group motions (high frequency).[4,12-14] The instrumentation employed for the studies noted above typically has a maximum working frequency of the order of 10^4 Hz or less.[4,15,16] The high-frequency/local-motion information has been obtained with these apparatuses by employing time–temperature superposition; the large temperature dependence of the viscosity of the Aroclor solvents, together with their relatively high viscosities, has been essential to shift the time scales of the various configurational rearrangements down to instrumentally accessible frequencies.[15,17] Thus the solvent requirements for such studies are almost unique to such materials as the Aroclors or tricresyl phosphate;[18] the large temperature dependence of viscosity for these materials suggests significant solvent–solvent interaction, perhaps leading to the formation of small solvent clusters which exhibit temperature-dependent dimensions. For OFB measurements, the Aroclors exhibit one undesirable feature in that they are weakly birefringent when undergoing a shearing deformation, so that the total birefringence observed for a given polymer solution has contributions from both the polymer and solvent constituents. The temperature dependence of the birefringence and viscosity for a given Aroclor is almost identical.[19]

The polymer contribution to the OFB data is obtained by correcting the measured values for the solvent contribution. The procedure generally utilized is based on the assumption of simple additivity of the polarizability tensors for the various constituents.[19-21] Thus the tensor sum of the polarizability contributions of the volume fractions of pure solvent and polymer is assumed to correspond to the solution properties; i.e., the net solution polarizability is essentially unaffected by long-range interactions between polymer and solvent. For the low velocity gradient conditions employed in the thin fluid layer OFB instrument, the principal directions of the polarizability tensors for both solution and solvent remain at 45° with respect to the streamline direction throughout the cycle of deformation,[1,19] which leads to the particularly simple vector subtraction correction procedure described below. This approach gives results for dilute solutions of polystyrene, poly(α-methylstyrene), and poly(2-substituted methyl acrylates) that are consistent with theoretical predictions[22-24] as well as measured viscoelastic properties except at high effective frequencies or extremely low degrees of polymerization.[3,4,7,14]

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