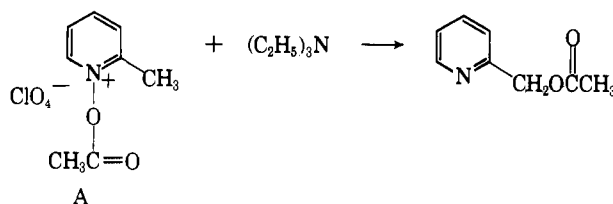


TABLE IV
THE REACTION OF 1-ACETOXY-2-METHYLPYRIDINIUM PERCHLORATE WITH TRIETHYLAMINE



A, mole	CH ₃ CN, ml.	(C ₂ H ₅) ₃ N, mole	CH ₃ CN, ml.	Method	Time, hr.	Temp., °C.	Yield, ^a %
(1) 0.018	40	0.018	10	A	1	0°	23
(2) .0357	80	.0357	10	A	<5 min.	0°	22
(3) .038	70	.038	20	B	1 ^b	0	38
(4) .040	200	.040	100	B	2 ^b	Reflux	60
(5) .040	200	.040	100	B	2 ^b	R.t. ^d	57-62
(6) .040	2850	.040	150	B	2 ^b	R.t. ^d	64

^a Based on distilled material. ^b This represents the time of addition of base. ^c Both solutions were precooled before mixing. ^d Room temperature.

oxide, m.p. 96-98°, was isolated. An analytical sample, m.p. 98.5-100°, was prepared by recrystallization from benzene.

Anal. Calcd. for C₁₂H₉D₂NO²¹: C, 76.97; H, 5.92; D, 18.18 atom % excess. Found: C, 76.75; H, 5.99; D, 17.55 atom % excess.

The n.m.r. spectrum¹² had peaks at: triplet, 1.8 τ (α -proton in pyridine) and multiplet, 2.6-3.2 τ with a sharp peak at 2.7 τ (phenyl and β,γ -pyridine protons). The 5-6 τ region (benzylic protons) showed no absorption.

Reaction of 1-Acetoxy-2-(α,α -Dideuteriobenzyl)pyridinium Perchlorate with Sodium Acetate in the Presence of Acetic Acid.—A solution of 1-acetoxy-2-(α,α -dideuteriobenzyl)pyridinium perchlorate²² (5.9 g., 0.018 mole), sodium acetate (1.47 g., 0.018 mole) in acetonitrile (48 ml.), and acetic acid (27 ml.) was refluxed 30 min., diluted with water, and extracted with chloroform. After the extract was dried over anhydrous sodium sulfate and

(21) The % H was calculated by using the formula weight of the deuterated molecule and the number of hydrogen atoms \times 1.008 of the undeuterated molecule. The conversion factor for regular water was used for the combustion water collected in the absorption tube.

(22) 1-Acetoxy-2-(α,α -dideuteriobenzyl)pyridinium perchlorate, m.p. 129-132°, was prepared in 98% yield by the procedure described above for the nondeuterated 1-acetoxypyridinium salts.

the chloroform, acetonitrile, and acetic acid removed under vacuum, the residue was chromatographed on 35 g. of Fluorosil using benzene and chloroform as eluents. The first compound eluted was phenyl(2-pyridyl)-1-deuteriomethyl acetate and weighed 0.85 g. (21%). The n.m.r. spectrum¹² had peaks at: doublet, center at 1.5 τ (α proton in pyridine); multiplet, center at 2.7 τ (phenyl and β,γ -pyridine protons); singlet, 7.8 τ (methyl protons). The 3.2 τ region (benzylic proton) showed no absorption. An analytical sample, m.p. 46°, was prepared by recrystallization from petroleum ether (b.p. 60-70°).

Anal. Calcd. for C₁₄H₁₂DNO²¹: C, 73.67; H, 5.74; D, 7.69 atom % excess. Found: C, 73.57; H, 5.77; D, 7.34 atom % excess.

A second compound eluted with chloroform was 2-(α,α -dideuteriobenzyl)pyridine N-oxide and weighed 1.2 g. (36%). The n.m.r. spectrum¹² was identical with that of an authentic sample and showed no absorption in the 5.8 τ region (benzyl hydrogens; see n.m.r. of 2-benzylpyridine N-oxide). An analytical sample, m.p. 101-102°, was prepared by recrystallization from anhydrous ether.

Anal. Calcd. for C₁₂H₉D₂NO²¹: C, 76.97; H, 5.92; D, 18.18 atom % excess. Found: C, 76.88; H, 6.12; D, 17.65 atom % excess.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, POLYMER RESEARCH INSTITUTE, POLYTECHNIC INSTITUTE OF BROOKLYN, BROOKLYN, N. Y.]

Stereochemistry of Poly- α -methylvinyl Methyl Ether

BY MURRAY GOODMAN AND YOU-LING FAN¹

RECEIVED MAY 19, 1964

We synthesized stereoregular poly- α -methylvinyl methyl ether (PMVME) employing various cationic catalysts at low temperature. In contrast to the stereochemical configurations of polyvinyl methyl ether (PVME), these polymers were found to be primarily syndiotactic in nature by high-resolution nuclear magnetic resonance and infrared spectroscopy. We interpreted these results in terms of the greater stability of the six-membered oxonium ring formed at the growing chain end which governs the stereochemical configurations of the main chain during the course of propagation. Examination by X-ray diffraction analysis indicates the identity period along the chain axis is 16.4 Å., which requires the main chain to be spiraled in the crystalline state presumably in an eightfold helix with three turns.

Introduction

α -Methylvinyl alkyl ethers were polymerized by Shostakovskii and co-workers.²⁻⁴ In their work, the

(1) Submitted by Y. L. Fan in partial fulfillment of the requirements for the degree of Doctor of Philosophy to the Faculty of the Polytechnic Institute of Brooklyn.

(2) M. F. Shostakovskii and E. P. Gracheva, *Zh. Obshch. Khim.*, **23**, 1153 (1953).

(3) M. F. Shostakovskii and E. P. Gracheva, *ibid.*, **27**, 355 (1957).

(4) M. F. Shostakovskii, E. P. Gracheva, and N. K. Kul'bovskaya, *ibid.*, **28**, 2344 (1958).

polymers varied from viscous liquids to transparent solids and were synthesized using a ferric chloride-dioxane catalyst at fairly low temperature. A cationic polymerization mechanism was described by these authors.

Although the chain configurations and crystalline structures of polyvinyl alkyl ethers have been investigated extensively,⁵⁻⁹ no elucidation of the stereochemis-

(5) S. Okamura, T. Kodama, and T. Higashimura, *Makromol. Chem.*, **58**, 180 (1962).

try of poly- α -methylvinyl alkyl ethers (where the α -hydrogen has been replaced by a methyl group) has appeared. We undertook to characterize the structure of the α -methylvinyl methyl ether polymers and compare the results to those obtained for the vinyl ether polymers.

Microtacticity of a polymeric chain is a complex stereochemical problem. We are now able to employ in these studies such sensitive tools as high-resolution nuclear magnetic resonance, X-ray diffraction, and infrared spectroscopy. On the basis of these data we propose a polymerization mechanism based on Cram's scheme for the cationic polymerization of vinyl alkyl ethers.¹⁰

Experimental

A. Monomer Synthesis.— α -Methylvinyl methyl ether was prepared from methylacetylene and methanol by the method given by Shostakovskii and co-workers.² The crude product (b.p. 28–35°, 760 mm.) was refluxed with metallic sodium to remove the unreacted methanol and was twice fractionally distilled with a helical-packed column. The product (b.p. 32.5–33.5°, n_D^{25} 1.3768, d_4^{20} 0.737, yield 36%) gave a single peak in vapor phase chromatography.

Anal. Calcd. for C_4H_8O : C, 66.62; H, 11.25. Found: C, 66.63; H, 11.18.

B. Polymerization by Cationic Catalysis.—Freshly distilled monomer and solvent were introduced into a Pyrex glass ampoule under anhydrous nitrogen atmosphere. The ampoule was then sealed with a rubber cap and adjusted to the desired temperature. After the ampoule reached thermal equilibrium, appropriate amounts of catalyst were introduced slowly into the system by a syringe. The polymerization vessel was continuously shaken. At the end of the polymerization, a small amount of 2% ammonium hydroxide in methanol was added to terminate the catalysis and the ampoule was allowed to come to room temperature. The crude polymer was collected by precipitation in excess cool methanol and was purified by repeated dissolution and precipitation in benzene and methanol, respectively. The purified polymer was then dried at 55° under vacuum.

Anal. Calcd. for C_4H_8O : C, 66.62; H, 11.25. Found: C, 66.75; H, 11.12.

C. Measurement of Physical Properties.—Viscosity measurements were carried out in benzene at 25.2° using an Ubbelohde viscometer. Melting point measurements were carried out using a Thomas-Hoover capillary melting point apparatus. The polymers usually melt within a temperature range of $\pm 2^\circ$; PMVME used for density measurement was cast into rod shapes by heating under nitrogen atmosphere. A pycnometer (2 ml.) was employed and calibrations were made because of the buoyancy of air. The crystallinity of each polymer was examined by comparing the intensity of the concentric rings with that of the diffuse background in the X-ray diffraction pattern.

D. High-Resolution Nuclear Magnetic Resonance Spectrometry.—Spectra were obtained using 10% solutions of the polymers in various solvents. Solutions containing 0.6 ml. were placed in 5-mm. Pyrex tubes. A Varian V-4300-C 60 Mc./sec. spectrograph was employed, together with a Varian heated probe, sample spinner, audio-oscillator, Hewlett-Packard 522-B frequency counter, and Varian recorder. Tetramethylsilane was used as an internal reference standard and was given a τ -value equivalent to 10.

E. X-Ray Fiber Pattern.—Sample 33 obtained with iodine-ether catalyst in toluene at -78° was employed for this purpose. Oriented fibers were obtained by annealing strips of polymer under stress at about 70° under nitrogen atmosphere, followed by unidirectional stretching for 300–400% at about the same temperature. These oriented fibers were further annealed under the same conditions in order to produce maximum sharpness and intensity in the fiber pattern. Exposures ranging from 4 to 12 hr. were made using nickel filtered copper radiation. An

X-ray tube operating at 45,000 v. and 15 ma. and fitted with a copper target was used. Consequently, it is expected that the radiations observed arise from the characteristic $K\alpha$ radiation.

F. Infrared Absorption Spectrometry.—A Perkin-Elmer Model 21 infrared spectrometer with a rock salt prism was used. Spectra of polymers were obtained from films cast from appropriate solvents on salt plates.

Results and Discussion

A. Polymerization.—Results of polymerization of α -methylvinyl methyl ether with various initiating systems are summarized in Table I. Several observations are apparent: (1) Cationic polymerizations with either Lewis-acid type catalysts or modified Friedel-Crafts type catalysts are successful, though the former usually gives higher yields. (2) Temperature is critical in cationic polymerizations. The above catalysts give good yields of polymer at -78° but they fail to initiate at temperatures above 0°. (3) Free-radical polymerization using either conventional initiators or Co^{60} radiation are unsuccessful. (4) Ziegler-Natta and anionic catalysts¹¹ are also ineffective in initiating polymerization. It is not surprising that α -methylvinyl methyl ether, with two electron-donating groups attached to the α -carbon atom, polymerizes only through a cationic mechanism. The fact that the ceiling temperature in the cationic polymerization of α -substituted vinyl alkyl ether is found to be much lower than that of the corresponding vinyl alkyl ether is probably attributed to the difference in stability of the oxonium complexes of these two compounds.³ The oxonium complex of the former is more unstable and its formation and dissociation start at a lower temperature.

B. Physical Properties.—PMVME prepared through cationic polymerization at low temperature is a transparent solid melting between 90 to 100°. Intrinsic viscosities measured in benzene at 25.2° are in the order of 0.2 to 0.3¹⁰⁰ ml./g. which indicates that the molecular weight is similar to that of PVME obtained under the same conditions.¹² Examination by X-ray diffraction analysis shows that these polymers contain moderate crystallinity.

In contrast to PVME,^{12,13} PMVME was found to be insoluble in methanol and water. It is, however, readily soluble in a large number of common solvents such as chloroform, methyl ethyl ketone, ethyl acetate, aromatic compounds, and ethers.

PMVME is stable on aging at room temperature. At elevated temperatures it becomes unstable and decomposes gradually. The degradation is accelerated in the presence of acidic substances which may act as initiator at low temperatures. Figure 1 shows the effect of iodine on the degradation of PMVME at elevated temperature.

Acidic substances, which accelerate the degradation of PMVME in bulk, exert even greater effect in solution, while addition of a basic substance such as phenyl- β -naphthylamine markedly enhances the stability of polymer. Figure 2 indicates the n.m.r. spectrum obtained by adding iodine to PMVME, also the spectrum obtained by adding an equal amount of phenyl- β -naphthylamine to the PMVME. Based on these data, we suggest that the degradation products are not

(6) I. W. Bassi, G. Dall'Asta, U. Campigli, and E. Strepelarola, *Makromol. Chem.*, **60**, 202 (1963).

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(8) R. J. Kern, J. J. Hawkins, and J. D. Calfee, *ibid.*, **66**, 126 (1963).

(9) S. Brownstein and D. M. Wiles, *J. Polymer Sci.*, **2A**, 1901 (1964).

(10) D. J. Cram and K. R. Kopecky, *J. Am. Chem. Soc.*, **81**, 2748 (1959).

(11) M. Goodman and Y. L. Fan, unpublished results.

(12) C. E. Schildknecht, A. O. Zoss, and C. McKinley, *Ind. Eng. Chem.*, **39**, 180 (1947).

(13) C. E. Schildknecht, S. T. Gross, and A. O. Zoss, *ibid.*, **41**, 1998 (1948).

TABLE I
 POLYMERIZATION OF α -METHYL VINYL METHYL ETHER

Sample	Name	Catalyst		Solvent	T, °C.	Amt., g.	Monomer		Convsn., %
		Amount					G./ml. concn.	t, hr.	
20	Al(C ₂ H ₅) ₂ Cl	0.05 ml.		Toluene	-78	1.47	0.1	42	2.4
45	Al(C ₂ H ₅)Cl ₂	0.1 ml.		Toluene	-78	1.47	.15	14	1
25	BF ₃ ·OEt ₂	45%, 0.1 ml.		Toluene	-78	1.47	.15	138	3.1
22	BF ₃ ·OEt ₂	45%, 0.1 ml.		Ether	-78	1.47	.1	42	1.8
21	FeCl ₃	5% in ether, 0.1 ml.		Toluene	-78	1.47	.1	42	33.3
21	FeCl ₃	5% in ether, 0.1 ml.		Toluene	-78	1.47	.15	138	49.9
29	FeCl ₃	5% in ether, 0.1 ml.		Toluene	0	1.47	.15	43	0
30	FeCl ₃	5% in ether, 0.1 ml.		Toluene	50	1.47	.15	43	0
33	I ₂	5% in ether, 0.1 ml.		Toluene	-78	1.47	.15	43	70.2
37	I ₂	5% in ether, 0.1 ml.		Ether	-78	1.47	.15	66	20
40	I ₂	2% in toluene, 0.15 ml.		Toluene	-78	1.47	.15	65	2.5

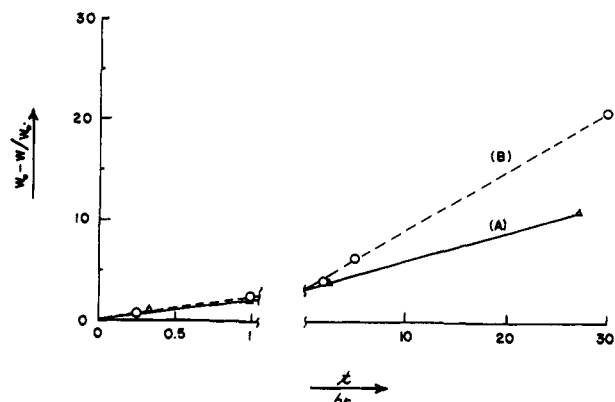


Fig. 1.—Thermal degradation of PMVME (a) 120–125° in air; (b) 120–125° in air and in the presence of a trace amount of iodine, where W_0 and W are the initial weight and weight at time t , respectively.

monomers but probably include acetone, methanol, and sirupy low polymers.¹²

C. Stereochemical Configurations of PMVME Prepared through Cationic Polymerization.—In Fig. 3 are shown typical n.m.r. spectra for 10% solutions of three PMVME prepared with different polymerization systems. In Fig. 4 are shown n.m.r. spectra of PMVME prepared with FeCl₃-ether catalyst measured in three different solvents. Because of the absence of adjacent protons, no spin-spin coupling should occur. The singlet at 6.86 to 6.87 τ is attributed to the methoxyl protons which, according to Bovey,¹⁴ *et al.*, and Kern, *et al.*,⁸ in an analogous case, PVME, are not sensitive to stereochemical configuration. However, Brownstein and Wiles¹⁵ and Ramey, Field, and Hasegawa¹⁶ observed a complex methoxyl proton spectrum and assigned each peak to a particular configuration of chain. In the case of PMVME, we observed only a singlet for methoxyl protons for samples prepared with various cationic catalysts. This observation indicates either the methyl protons are not sensitive to the stereochemical configurations or that these polymers acquire primarily one stereochemical configuration.

There is a singlet attributable to the α -methyl protons at 8.55 to 8.64 τ for all polymers examined regardless of polymerization system employed. The α -methyl protons of typical α,α -disubstituted vinyl polymers such

(14) F. A. Bovey, E. W. Anderson, D. C. Douglas, and J. A. Manson, *J. Chem. Phys.*, **39**, 1199 (1963).

(15) S. Brownstein and D. M. Wiles, *J. Polymer Sci.*, **2A**, 1901 (1964).

(16) K. C. Ramey, N. D. Field, and I. Hasegawa, *ibid.*, in press. We wish to thank these authors for showing us a copy of their paper prior to its publication.

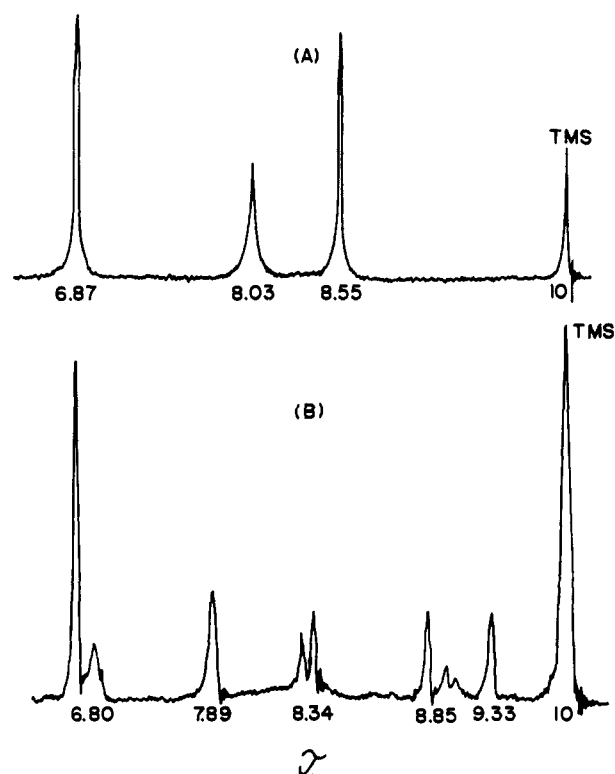


Fig. 2.—N.m.r. spectra of PMVME in benzene measured at (a) 175°, 0.3% of phenyl- β -naphthylamine added; (b) 145°, 0.3% of iodine added.

as polymethylmethacrylate¹⁷ and poly- α -methylstyrene^{18,19} which have similar structure to PMVME were found to show different magnetic environments for the backbone methyls in different configurations. Although the spectrum of α -methyl protons of polypropylene-2-*d* was not resolved by Stehling,²⁰ the dependence of the position of the methyl proton bands on the stereochemical configurations was successfully demonstrated by Woodbrey²¹ using both 60 Mc. and 100 Mc. n.m.r. instruments.

We assume that the singlet from the α -methyl protons arises from one stereochemical configuration of the main chain. To assign this configuration, we examined the nature of the methylene proton signal.¹⁷ In the isotactic form, the methylene protons become nonequiv-

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(18) S. Brownstein, S. Bywater, and D. J. Worsfold, *Makromol. Chem.*, **48**, 127 (1961).

(19) Y. Sakurada, M. Matsumoto, K. Imai, A. Nishioka, and Y. Kato, *Polymer Letters*, **1**, 633 (1963).

(20) F. C. Stehling, *J. Polymer Sci.*, **2A**, 1815 (1964).

(21) J. C. Woodbrey, *Polymer Letters*, **2**, 315 (1964).

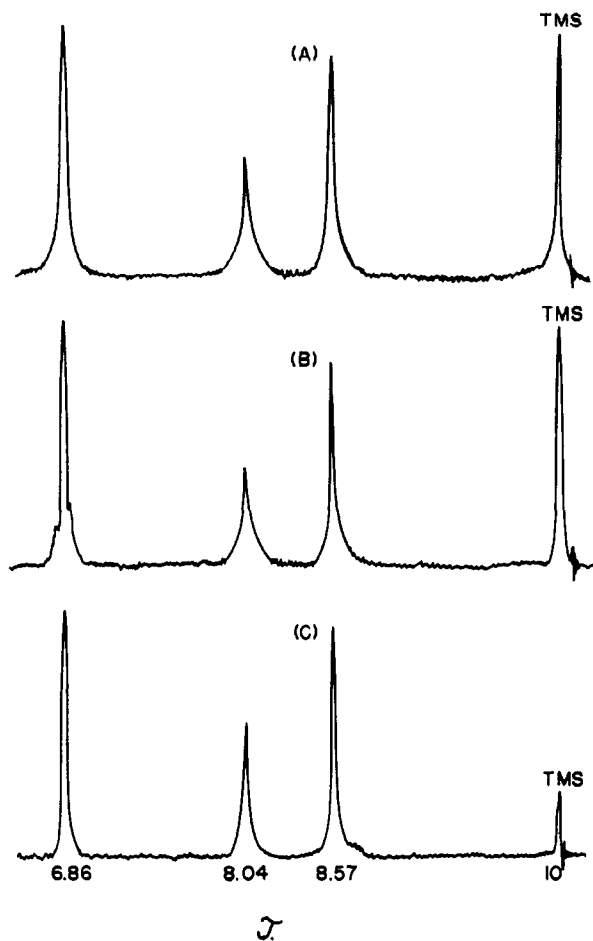


Fig. 3.—N.m.r. spectra of PMVME measured at 140° in chlorobenzene prepared with (a) FeCl_3 -ether in toluene at -78° , (b) I_2 -ether in toluene at -78° , (c) I_2 -ether in ether at -78° .

alent and should yield an AB quartet. In the syndiotactic structure, the two methylene protons become equivalent and yield a singlet. We observe only a singlet for the methylene protons of PMVME at 8.03 to 8.15 τ , which supports the hypothesis that the polymer is primarily syndiotactic.

An identical approach to the methylene proton signals has been successfully applied to such polymers as polymethylmethacrylate,¹⁷ poly- α -methylstyrene,^{18,19} polyvinyl methyl ether,^{8,14-16} and polypropylene.²⁰ Although there are known cases where the two methylene protons of isotactic structure have accidentally equivalent chemical shifts and therefore give a singlet in the absence of spin-spin coupling^{14,22-25} no example has been found where a syndiotactic structure yields a complex spectrum.

Were the singlet for the methylene in PMVME to arise from an isotactic structure, we would, in general, expect the polymer to be highly crystalline. Actually, the PMVME was found to be only partially crystalline as is typically found for many syndiotactic vinyl poly-

(22) U. Johnsen, *J. Polymer Sci.*, **54**, 57 (1961).

(23) W. C. Tincher, *ibid.*, **62**, 3148 (1962).

(24) D. Doskocilova, *Polymer Letters*, **2**, 421 (1964).

(25) We wish to thank Dr. F. A. Bovey for transmitting unpublished results to us on n.m.r. results on isotactic polystyrene. Dr. Bovey and his co-workers measured the spectrum for the aliphatic region in dichlorobenzene at 200° . The methylene signal consisted of a distorted triplet with a true chemical shift of 8.36 τ . The coupling constant is 6.8 c./sec. This result is an example of accidental equivalence of the methylene protons.

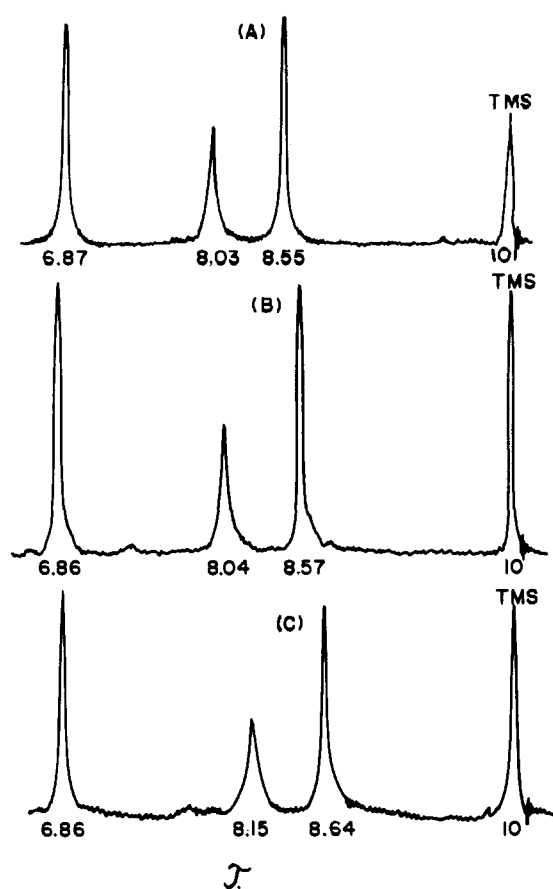


Fig. 4.—N.m.r. spectra of PMVME (sample 21) measured in (a) benzene containing 0.3% of phenyl- β -naphthylamine at 175° , (b) chlorobenzene at 144° , and (c) chloroform at 91° .

mers.^{17,26,27} A syndiotactic nature of PMVME seems to be supported by the presence of 1460 cm^{-1} band in the infrared which was found to be characteristic of syndiotactic polymethylmethacrylate.²⁸ Lastly, results obtained from the optical rotatory studies of optically active poly- α -methylvinyl alkyl ethers²⁹ are consistent with these considerations. Furthermore, the polymer solutions exhibit low viscosity. Since we carried out our measurements at high temperature, we cannot attribute to poor resolution the lack of splitting of the backbone methylene or the α -methyl protons. Rather we suggest that the singlet at 8.03 to 8.15 τ arises from a racemic methylene, *i.e.*, these polymers are primarily in the syndiotactic form.^{17,30} In terms of Bovey's¹⁷ probability parameters, the value of δ , which is the probability that a growing chain will add a monomer unit to give the same configuration as that of the last monomeric unit at its growing end, must be nearly zero. Therefore, P_i and P_h both approach zero and P_s approaches unity. However, we reserve the possibility that variations of configuration may occur occasionally along the main chain which then create a small amount of heterotactic structure which is not resolved from the intense syndiotactic peaks. It is interesting that, through cationic polymerizations, vinyl methyl ether

(26) I. Sakurada, A. Nakajima, O. Yashizaki, and K. Nakamae, paper presented at the Fifteenth Meeting of the Japanese Chemical Society, Kyoto, Japan, April, 1962.

(27) G. Natta and F. Danussa, *J. Polymer Sci.*, **34**, 3 (1959).

(28) V. U. Baumann, H. Schreiber, and K. Tessmar, *Makromol. Chem.*, **36**, 81 (1960).

(29) M. Goodman and Y. L. Fan, unpublished results.

(30) A. Nishioka, H. Watanabe, I. Yamaguchi and H. Shimizu, *J. Polymer Sci.*, **45**, 232 (1960).

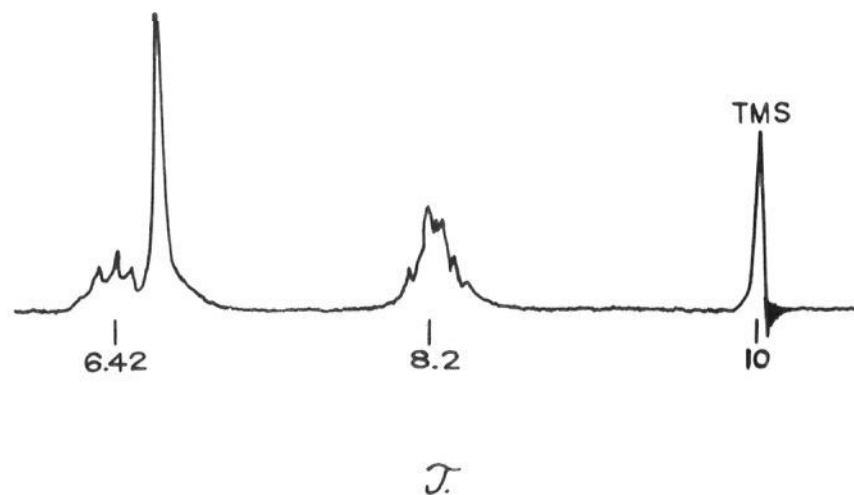


Fig. 5.—N.m.r. spectrum of polyvinyl methyl ether measured in chlorobenzene from data reported by Bovey, *et al.*⁹

forms predominantly isotactic polymers (n.m.r. spectrum of PVME is shown in Fig. 5^{8,14,31}) while α -methylvinyl methyl ether gives primarily syndiotactic polymers. We think that this difference in main-chain configurations arises probably as a result of greater stability of the six-membered oxonium ring formed at the end of the growing chain which governs the stereochemical configurations of the main chain (see later section of this paper).

D. Crystalline Structure of PMVME.—Figure 6 shows the X-ray fiber pattern of PMVME. The identity period along the chain axis was found to be roughly 16.4 Å. (accurate examination was not possible because of the diffuse nature of the reflections). The interpretation of the fiber pattern of this polymer by the methods of the reciprocal lattice allows us to attribute all reflections on the basis of a tetragonal unit cell having the dimensions: $a = 15.2$ Å. and $c = 16.4$ Å. (chain axis). The density of this polymer calculated by assuming that 32 monomeric units are contained in each unit cell is 1.011 g./ml., which agrees with the experimental value of 0.950 g./ml. On the basis of eight monomeric units per each identity period, the distance of projection of each monomeric unit on the chain axis is 2.05 Å. which is considerably smaller than the value of 2.52 Å. expected for that of a planar zigzag main chain. We suggest, therefore, the syndiotactic PMVME is probably coiled in an eightfold helix in the crystalline state. Some reflections also indicate that this eightfold helix may contain three turns. This result is not surprising in view of the fact that polymers of α,α -disubstituted vinyl compounds such as polyisobutylene³² and syndiotactic polymethylmethacrylate³³ both acquire helical conformations in the crystalline state.

E. Infrared Analysis of PMVME.—Infrared spectroscopy has been employed extensively for the study of the stereoregularity of various polyvinyl alkyl ethers. Kern, *et al.*,⁸ determined the degree of stereoregularity of PVME prepared under different conditions by comparing the ratio of optical densities of bands at 12.40 and 12.65 μ . Similarly, Vandenberg³¹ reported the absolute percentage crystallinity of PVME from bands present which are characteristic only of either the crystalline polymer (at 12.13 μ) or the amorphous polymer (at 12.65 μ).

The typical infrared spectra of PMVME are shown

(31) E. J. Vandenberg, *J. Polymer Sci.*, **1C**, 207 (1963).

(32) C. S. Fuller, C. J. Frosch, and N. R. Pape, *J. Am. Chem. Soc.*, **62**, 1905 (1940).

(33) J. D. Stroupe and R. E. Hughes, *ibid.*, **80**, 2341 (1958).

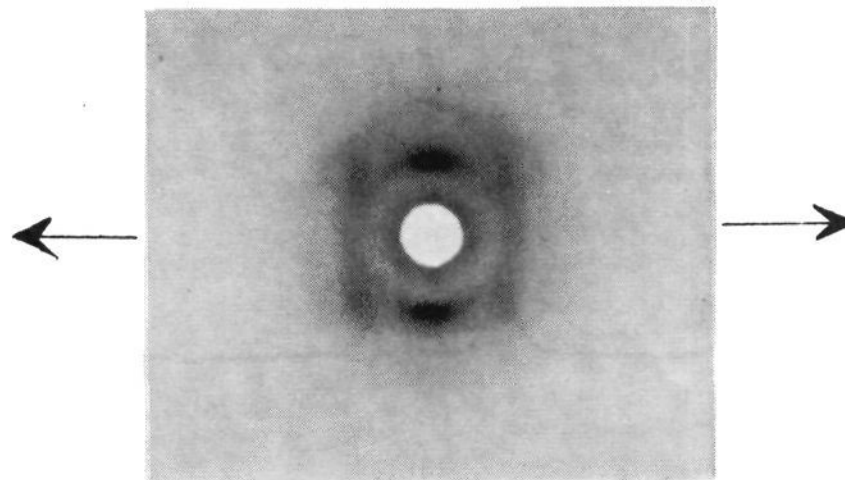


Fig. 6.—X-Ray fiber pattern of PMVME (arrows indicate the direction of stretching).

in Fig. 7 and the wave numbers of the observed adsorption maxima are listed in Table II.³⁴⁻³⁶

TABLE II

THE WAVE NUMBERS OF ABSORPTION BANDS OF PMVME

Wave number, cm. ⁻¹	Rel. intensity	Type of vibration
2970	S	CH ₃ CH ₂ stretching
2920	S	
2820	M	
1460	M	CH ₃ bending, asym.
1372	M	CH ₃ bending, sym.
1360	M	O-C stretching
1233	M	
1184	S	
1124	M	C-C stretching, asym.
1075	VS	
940	W	C-C stretching, sym.
893	VW	CH ₂ rocking mixed with CH ₃ rocking
810	VW	
766	M	

As shown in Fig. 7, PMVME obtained with different cationic catalysts gave essentially identical infrared spectra. Besides, both soluble and insoluble fractions of PMVME fractionated with a benzene-methanol system showed no differences in their infrared spectra. The difference in solubility of these two fractions is probably attributed to differences in molecular weight rather than stereoregularity. If the stereoregularities were different, some variations in their spectra would have been observed. A strong absorption at 1460 cm.⁻¹ which corresponds to CH₃ asymmetric bending³⁶ and which is characteristic of syndiotactic polymethylmethacrylate was also found in our PMVME. These observations are consistent with the n.m.r. results presented earlier, *i.e.*, PMVME prepared through cationic polymerization is syndiotactic in nature.

F. Mechanism.—The formation of isotactic polyvinyl alkyl ethers through cationic polymerizations has been interpreted by various mechanisms,^{8,10,37-40} depending on the particular catalytic system employed. In the cationic polymerization of α -methylvinyl methyl ether, polymerizations were carried out under homo-

(34) A. Kawasaki, I. Furukawa, T. Tsuruta, S. Inoue, and K. Ito, *Makromol. Chem.*, **36**, 260 (1960).

(35) Y. Mikawa, *Bull. Chem. Soc. Japan*, **29**, 110 (1956).

(36) V. U. Baumann, H. Schreiber, and K. Tessmar, *Makromol. Chem.*, **36**, 81 (1960).

(37) C. E. Schildknecht, *Ind. Eng. Chem.*, **50**, 107 (1958).

(38) C. E. H. Bawn and A. Ledwith, *Proc. Chem. Soc.*, 165 (1962):

(39) T. Higashimura, S. Okamura, T. Yonezawa, and K. Fukue, *J. Polymer Sci.*, **39**, 487 (1959).

(40) S. Nakano, K. Iwasaki, and H. Fukutani, *ibid.*, **1A**, 3277 (1963).

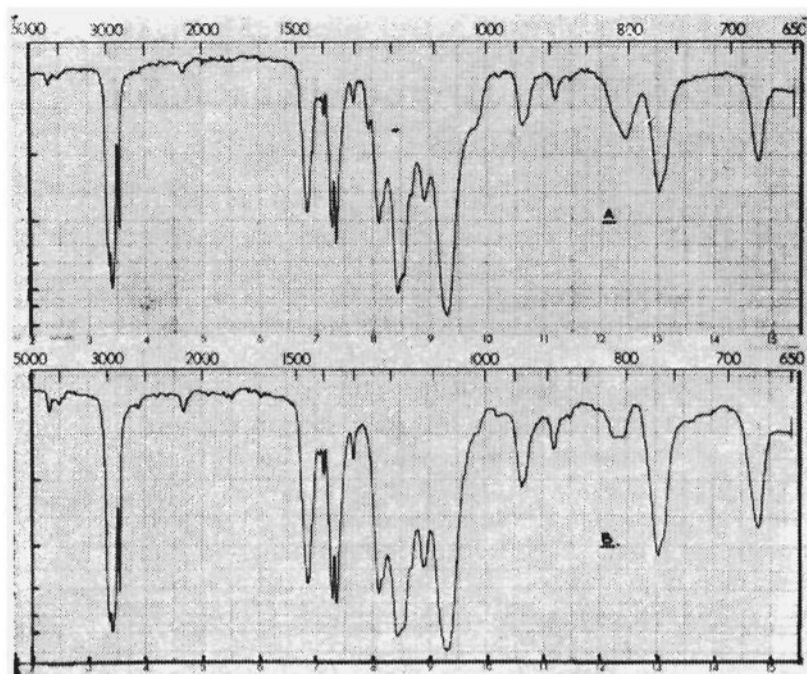


Fig. 7.—Infrared spectra of PMVME prepared with (a) FeCl_3 -ether in toluene at -78° , (b) iodine-ether in toluene at -78° .

geneous conditions at low temperature. We believe that the polymerization involves a growing oxonium ion formed as a pseudo-six-membered ring by the interaction of the carbonium ion of the ultimate residue with the ether oxygen of the prepenultimate unit in the growing chain. This is similar to Cram's mechanism for the polymerization of vinyl alkyl ether. Such a postulate is reasonable, since oxonium ions appear to be intermediates in the polymerization of cyclic ethers⁴¹ and certain epoxides⁴² with cationic catalysts. A schematic representation of the propagation step of such a mechanism is shown in Fig. 8. The growing chain cyclizes to form a pseudo-six-membered oxonium ring (I) at its growing end. In I, since P (polymer chain) is much larger than the methyl group in size, we have assigned it to the equatorial position at C-5. The methyl at C-1 takes an equatorial position to avoid the otherwise unfavorable interaction between axial methyl at C-1 with the axial methyl at C-5. This consideration seems reasonable because a methoxyl is more flexible and farther removed from the ring than a methyl while it differs little in size from the latter. For the same reason methyl at C-3 also takes an equatorial position. Addition of monomer inverts the configuration of C-1 in the

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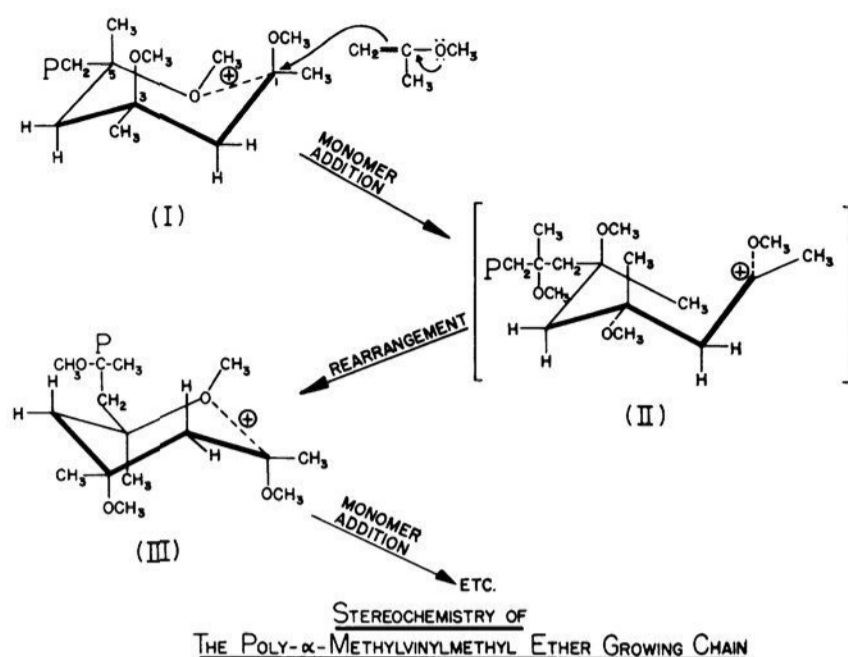


Fig. 8.—Mechanism of stereospecific cationic propagation of poly- α -methylvinyl methyl ether.

ring-opening step and II results. The open-chain intermediate II rearranges, *via* a cyclohexane type flipping mechanism, into the more stable, original pseudo-six-membered oxonium ring (III). This process is repetitive. The over-all configuration of the chain is determined by the relative configurations of the two asymmetric carbons in the penultimate and prepenultimate positions. If their configurations are similar, the polymer chain becomes isotactic. If they are different, as we found, the stereochemistry is syndiotactic. Thus, in contrast to the polymerization of vinyl alkyl ethers, syndiotactic polymer is favored in the polymerization of α -methylvinyl methyl ether. As we discussed earlier, the oxonium complex of α -methylvinyl methyl ether is unstable, which limits the polymerization to a rather low ceiling temperature. If the energy of activation for the syndiotactic placement is smaller than that for the isotactic placement,^{19,43} formation of the latter would be more favored at elevated temperatures. However, at elevated temperatures, the polymerization is probably stopped by the dissociation of the oxonium complex. Consequently, we obtained primarily syndiotactic PMVME.

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