Macromolecules **1984,** *17,* 1431-1436

and an increase in the lowest unoccupied antibonding level, leading to an increase in energy difference between ground and transition states and the large stability of the compound. Futhermore, it similarly exerts a great influence on the electron-accepting character of these compounds, ascertained with Fieser's reduction potential for the compounds. Consequently, the exocyclic atom of hetero *p*-benzoquinones affects not only the stability of their compounds, that is, the reactivity, but also their electron-accepting character. In the case of the PCA–St system, it is may be presumed that the exocyclic electronegative oxygen atom of PCA affects its stability of PCA more effectively than its electron-accepting character.

Registry No. Acenaphthylene, 208-96-8; butyl vinyl ether, 111-34-2; 2-chloroethyl vinyl ether, 110-75-8; phenyl vinyl ether, 766-94-9; isobutyl vinyl ether, 109-53-5; QBS, 1050-82-4; St, 100-42-5; MAnh, 108-31-6; PCA, 118-75-2; TMCQ, 65649-20-9; TCNQ, 1518-16-7.

References and Notes

(1) Errede, L. A.; Gregorian, R. S.; Hoyt, J. M. *J. Am. Chem. Soc.* **1960,** *82,* 5218.
(2) Acker, D. S.; Hertler, W. R. *J. Am. Chem. Soc.* **1962,** *84,* 3370.
(3) Iwatsuki, S.; Itoh, T.; Shimizu, Y. *Macromolecules* **1983,** *16,* 532.
(4) Iwatsuki, S.; Itoh, T.; Horiuchi, K. *Macromolecules* **1978,** *11,* 497.
(5) Iwatsuki, S.; Itoh, T. *Macromolecules* **1980,** *13,* 983.
(6) Bevington, J. C.; Chanem, N. A.; Melville, H. W. *Trans. Faraday Soc.* **1955,** *51,* 946.
(7) Tüdös, F. *J. Polym. Sci.* **1958,** *30,* 343.
(8) Bevington, J. C.; Chanem, N. A.; Melville, H. W. *J. Chem. Soc.* **1955,** 2822.
(9) Walling, C. "Free Radicals in Solution"; Wiley: New York, 1957; p 161.
(10) Breitenbach, J. W. *Can. J. Res., Sect. B* **1950,** *28,* 507.
(11) Hauser, C. F.; Zutty, N. L. *J. Polym. Sci., Part A-1* **1970,** *8,* 1385.
(12) Hauser, C. F.; Zutty, N. L. *Macromolecules* **1971,** *4,* 478.
(13) Iwatsuki, S.; Itoh, T. *J. Polym. Sci., Polym. Chem. Ed.* **1980,** *18,* 2971.
(14) Willstätter, R.; Mayer, E. *Ber. Dtsch. Chem. Ges.* **1904,** *37,* 1494.
(15) Coppinger, G. M.; Bauer, R. H. *J. Phys. Chem.* **1963,** *67,* 2846.
(16) Gordon, A. J.; Rord, R. A. "The Chemist's Companion"; Wiley: New York, 1972; p 82.
(17) Adams, R.; Nagarkatti, A. S. *J. Am. Chem. Soc.* **1950,** *72,* 4601.
(18) Iwatsuki, S.; Kokubo, T.; Kondo, S. Japanese Patent 7528480; *Chem. Abstr.* **1976,** *85,* 6353*u*.
(19) Iwatsuki, S.; Itoh, T. *Macromolecules* **1982,** *15,* 347.
(20) Iwatsuki, S.; Itoh, T.; Saito, H.; Okada, J. *Macromolecules* **1983,** *16,* 1571.
(21) Iwatsuki, S.; Itoh, T.; Hiraiwa, A. *Makromol. Chem.* **1981,** *182,* 2161.
(22) Iwatsuki, S.; Itoh, T. *Macromolecules* **1979,** *12,* 208.
(23) Pinkus, A. G.; Tsuji, J. *J. Org. Chem.* **1974,** *39,* 497.
(24) Natsuume, N.; Shirota, Y.; Hirata, H.; Kusabayashi, S.; Mikawa, H. *J. Chem. Soc., Chem. Commun.* **1969,** 289.
(25) McElvain, M.; Pinzón, B. F. *J. Am. Chem. Soc.* **1945,** *67,* 650.
(26) Fueno, T.; Matsumura, I.; Okuyama, T.; Furukawa, J. *Bull. Chem. Soc. Jpn.* **1968,** *41,* 818.
(27) Cretcher, L. H.; Koch, J. A.; Pittenger, W. H. *J. Am. Chem. Soc.* **1925,** *47,* 1173.
(28) In the treatment with the equation devised by Ketelaar et al. for the system with a significant absorption of acceptor (Ketelaar, J. A. A.; van de Stolpe, C.; Goudsmit, A.; Dzcubas, W. *Recl. Trav. Chim. Pays-Bas* **1952,** *71,* 1104), K_{CT} and ϵ_{CT} were found to be 0.057 at 20 °C and 0.50 at 30 °C and 837, respectively.
(29) Iwatsuki, S.; Itoh, T.; Yokotani, I. *Macromolecules* **1983,** *16,* 1817.
(30) Foster, R. "Organic Charge-Transfer Complexes"; Academic Press: New York; 1969; p 33.
(31) Chen, E. C. M.; Wentworth, W. E. *J. Chem. Phys.* **1975,** *63,* 3183.
(32) Bovey, F. A.; Tiers, G. V. D.; Filipovich, G. *J. Polym. Sci.* **1959,** *38,* 73.
(33) Iwatsuki, S.; Yamashita, Y. *Makromol. Chem.* **1967,** *104,* 263.

Ring-Opening Polymerization of 3-Methyloxetane: NMR Spectroscopy and Configurational Properties of the Polymer

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ABSTRACT: Poly(3-methyloxetane) was obtained at −78 °C by ring-opening polymerization of 3-methyloxetane, using a cationic initiator with a very stable counterion. The polymerization reaction was rapid and quantitative, suggesting that 3-methyloxetane is much more reactive than initially was suspected. The structure of the polymer was studied by ^1H NMR and ^{13}C NMR spectroscopy. The ^{13}C NMR spectra show that the methine carbons present three peaks, which can be assigned to the isotactic, syndiotactic, and heterotactic triads. The chemical shift differences of these signals (0.017 ppm), much lower than those for poly(2-methyloxetane) (0.14), suggest that the vicinity of the oxygen atom to the methine carbon enhances the splitting of these carbons. Mean square dipole moments $\langle \mu^2 \rangle$ of poly(3-methyloxetane) were determined as a function of temperature by means of dielectric constant measurements in cyclohexane. It was found that the value of the dipole moment ratio $\langle \mu^2 \rangle / nm^2$, where nm^2 is the mean square dipole moment of the chains in the idealization that all the skeletal bonds are freely jointed, is 0.354 at 30 °C and its temperature coefficient is 2.7×10^{-3} K^{-1}. The experimental results were found to be in good agreement with theoretical results based on a 3 × 3 rotational state scheme. The theoretical analysis showed that the dielectric properties are not very sensitive to the stereochemical composition of the chains. The present study also indicates that all of the members of the polyoxetane series have a high degree of conformational randomness.

Introduction

The cationic ring-opening polymerization of oxetane (Ox)[1-3] and its derivatives 3-methyloxetane (MOx)[2,3] and 3,3-dimethyloxetane (DMOx)[2-4] was studied some time ago. The correlation between the reactivity and the monomer ring substitution was discussed from the viewpoint of the propagation rate constants and the corresponding activation parameters. However, a considerable discrepancy was observed in the kinetic results obtained by different authors. As far as we are aware, no additional work to that of ref 3 has been published on the reactivity of MOx.

The cationic polymerization of the oxetanes gives rise to chains of unusual interest to get a better understanding

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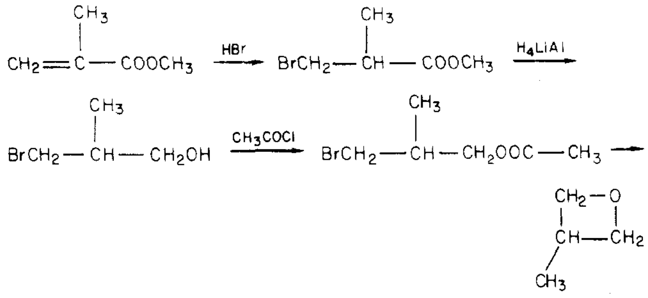
Scheme I



of the correlation between structure and properties in polymers. Poly(trimethylene oxide) (POx), which is obtained by ring-opening polymerization of Ox, has two bonds in the repeating unit that strongly prefer trans states whereas the other two show a strong preference for gauche states.[5] These chains are extremely coiled and, consequently, exhibit the smallest unperturbed dimensions reported for any polymer to date.[6] The substitution of the two hydrogen atoms of the central methylene group of the repeating unit of POx for two methyl groups converts this polymer into poly(3,3-dimethyloxetane) (PDMOx). The dielectric properties of the latter polymer change drastically with regard to those of POx. The dipole moment ratio of PDMOx $\langle\mu^2\rangle/nm^2$, where $\langle\mu^2\rangle$ is the mean square dipole moment of a chain with n skeletal bonds, each of them having an average dipole moment m, is 0.21–0.25,[7,8] significantly lower than the value of this quantity for POx (0.4).[9] The dipole moments and the unperturbed dimensions of PDMOx are more sensitive to temperature than those of POx chains.

It would be interesting to investigate how the substitution of a single hydrogen atom of the central methylene group of the repeating unit of POx for a methyl group would affect the configurational properties of the resulting polymer poly(3-methyloxetane) (PMOx). It is expected that the stereochemical structure will have little effect on the statistical properties of PMOx; however, the dipole moment of these chains will differ significantly from those of PDMOx owing to the fact that the C–O skeletal bonds of PMOx will have accessibility to some rotational states that are excluded in PDMOx. These qualitative predictions are tested in the present study, where the dipole moments of PMOx chains were measured and the results were interpreted in terms of the rotational isomeric state (RIS) model. The effect of the position of the oxygen atom, with respect to the asymmetric carbon, on the splitting of the methine carbons of substituted polyoxetanes was also studied by comparing the ^{13}C NMR spectra of poly(2-methyloxetane) and PMOx.

Experimental Section

Materials. 3-Methyloxetane was prepared by the method described by Searles et al.[10] The synthetic route involves the steps shown in Scheme I. The monomer was purified by fractional distillation, dried over calcium hydride, and distilled several times onto sodium mirrors. Methylene chloride was purified by conventional methods and stored in vacuo over calcium hydride. Acetyl chloride was distilled in an inert atmosphere immediately before use. Silver hexafluoroantimonate was purified as described elsewhere.[11]

Ring-Opening Polymerization. The cationic polymerization of 3-methyloxetane was carried out at −78 °C under vacuum, using methylene chloride as solvent and acetyl hexafluoroantimonate as initiator. The initiator was prepared "in situ" by reaction of equimolecular amounts of silver hexafluoroantimonate and acetyl chloride. The monomer and initiator concentrations were 2 and 1.0×10^{-3} mol L^{-1}, respectively. In spite of the small initiator concentration, total conversion was achieved practically in about 2 min. The polymer was precipitated with methanol, isolated at low temperature, washed several times with water, and, finally, dried in vacuo at room temperature.

Characterization of the Polymer. The polymer was fractionated by precipitation at 25 °C, using chloroform–methanol as the solvent–nonsolvent system. The second fraction, which amounted to 10% of the total polymer, was used for the dielectric measurements. The molecular weight of the fraction, measured with a Knauer 01.00 membrane osmometer, was 125 000.

The ^{1}H and ^{13}C NMR spectra of the unfractionated and fractionated polymer were registered on a Bruker WP80SY and a Bruker WM-360 at 80 and 90.55 MHz, respectively, using deuterated chloroform as solvent and Me$_4$Si as internal standard. Similar spectra were obtained in both cases.

The glass transition temperature of the polymer (T_g) was determined with a DuPont 900 calorimeter at a heating rate of 10 °C/min and turned out to be −62 °C.

Dielectric Measurements. Dielectric measurements were carried out on solutions of the polymer in cyclohexane at several temperatures, using a capacitance bridge (General Radio 1620 A) and a three-terminal cell (Foxboro Model 3HV35). Values of the increments in index of refraction of the solutions were determined at 632.8 nm with a Chromatix KHX laser differential refractometer.

Results and Discussion

The ring-opening polymerization of 3-methyloxetane, carried out at −78 °C in methylene chloride solution and initiated by acetyl hexafluoroantimonate, proceeds in less than 2 min and is almost quantitative. Apparently, these results are in disagreement with those obtained by Saegusa et al.[3] These authors found that the value of the propagation rate constant of MOx, determined at −40 °C with the BF$_3$·THF complex as initiator and methylene chloride as solvent, amounted to 6.8×10^{-3} L mol^{-1} s^{-1}, which means that the lower bound for the value of the time necessary to convert at −40 °C 50% of the monomer into polymer, using an initiator concentration similar to that utilized in our experiments (10^{-3} mol L^{-1}), would be 10^5 s. Since the nature of the anion seems to have little influence on the propagation rate constants of heterocycles through free and pair ions,[12,13] the great differences observed in the reactivity of MOx with BF$_3$·THF and acetyl hexafluoroantimonate should not be attributed to counterion effects. It is more likely due to the fact that the former initiator is not a good system to study the reactivity of the oxetanes. Actually, BF$_3$-catalyzed oxetane polymerization does not occur when water or hydroxyl compounds are removed from the reaction system and, as a consequence, incomplete drying was used, which could affect the kinetic mechanism. It should be pointed out in this regard that, according to Saegusa et al.,[3] the reactivity of the oxetanes increases in the order DMOx > MOx > Ox. However, this was not supported by Bucquoye and Goethals,[4] who studied the copolymerization reactions between Ox and DMOx and found that the former heterocycle is more reactive than the latter. In view of these controversial results, it is desirable to carry out further experimental work on the cationic polymerization of oxetanes using initiators with very stable counterions, in order to determine the true reactivity of these heterocycles and to obtain reliable values of the propagation rate constants through free and pair ions.

NMR Spectroscopy of Poly(3-methyloxetane). The structure of PMOx was studied by ^{1}H NMR and ^{13}C NMR spectroscopy. The ^{1}H NMR spectrum, shown in Figure 1, presents a doublet at 0.92 ppm, a multiplet at 2.0 ppm, and two quadruplets between 3.12 and 3.48 ppm, corresponding to the methyl, methine, and methylene protons, respectively. The presence of the methine group produces magnetic nonequivalence of the two protons of each

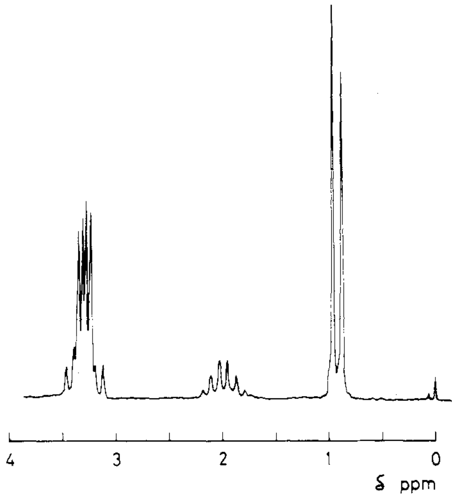


Figure 1. ^{1}H NMR spectrum of poly(3-methyloxetane).

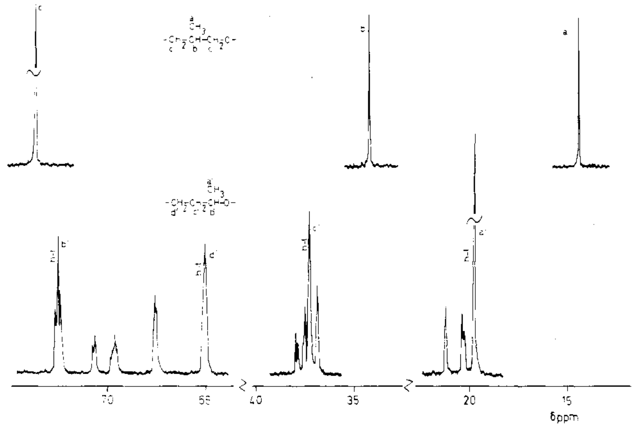


Figure 2. ^{13}C NMR spectra of poly(3-methyloxetane) (top) and poly(2-methyloxetane) (bottom).

methylene group, giving rise to the apparently abnormal signals of these protons. This behavior also occurs in substituted ethanes,[14] poly(propylene oxide),[15] and poly(propylene sulfide).[16] The stereoregularity of the polymer cannot be detected by ^{1}H NMR spectroscopy, because four skeletal atoms separate two consecutive asymmetric centers; the analysis of the spectrum shows, however, the high purity of the polymer obtained.

The ^{13}C NMR spectrum of PMOx, determined at 90.55 MHz in a solution of deuterated chloroform in which the concentration of polymer was 100 mg/mL, is shown in Figure 2. For comparison, the ^{13}C NMR spectrum of poly(2-methyloxetane) is also shown. It can be observed that the spectrum corresponding to the former polymer does not present any splitting in its resonance signals, in sharp contrast with what occurs in the latter, where different stereochemical triads (isotactic, syndiotactic, and heterotactic), are easily detected in the methine carbon of the head-to-tail units.[17-19] Since the methine carbons are separated by four skeletal bonds in both polymers, the relatively simple spectrum obtained for PMOx would suggest that the cationic ring-opening polymerization of MOx produces a practically 100% stereoregular (isotactic or syndiotactic) polymer. This possibility, however, seems unlikely because it would require very strong stereospecific effects by the initiator, which have never been observed in other cases. Moreover, the symmetry of the monomer suggests that an atactic polymer should be formed. The most plausible explanation for the appearance of the splitting in poly(2-methyloxetane) and not in PMOx may be that the vicinity of an oxygen atom to the asymmetric carbon in the former polymer enhances strongly the splitting of the methine carbons. In order to check this assumption, new spectra of PMOx were obtained at the same high field by using a concentration of polymer of 10 mg/mL at 44 °C; 32K of memory were used for the acquisition of the free induction decay (FID). The resolution was slightly enhanced by means of a Lorentz–Gauss multiplication of the FID. The spectrum recorded under these conditions is shown in Figure 3. It can be seen that the methine carbon resonance presents three peaks, which can be assigned to the isotactic, syndiotactic, and heterotactic triads. The chemical shift differences of these signals are only 0.017 ppm, much lower than those for poly(2-methyloxetane), which are about 0.14 ppm. The fact that these peaks appear at the same chemical shift in all the spectra recorded on PMOx assures that the splitting observed is not due to noise. It should be stressed in this regard that the wide band of the methine carbon in comparison with that of the others also indicates a true splitting. Although the very small separation between signals precludes an accurate measurement of the areas, the values observed for the ratio of the intensities (about 1:2:1) suggest an atactic structure for the polymer.

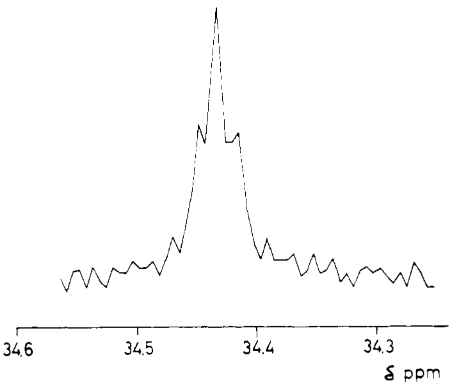


Figure 3. Expanded resonance signals of the methine carbon in the ^{13}C NMR spectrum of poly(3-methyloxetane).

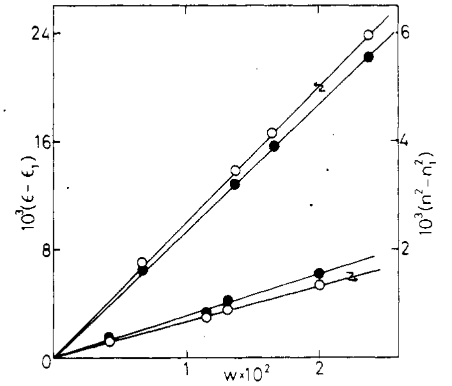


Figure 4. Concentration dependence of the increments in dielectric constant and squared index of refraction at 30 (○) and 60 °C (●) for poly(3-methyloxetane).

Experimental Dipole Moments of Poly(3-methyloxetane). The dielectric constant ϵ and the index of refraction $\tilde{n}$ of four solutions of PMOx in cyclohexane were measured at 30, 40, 50, and 60 °C. Both parameters were expressed relative to the corresponding values ϵ_1 and $\tilde{n}_1$ for the pure solvent in the incremental quantities $\Delta\epsilon = \epsilon - \epsilon_1$ and $\Delta\tilde{n}^2 = \tilde{n}^2 - \tilde{n}_1^2$. From the plots $\Delta\epsilon$ and $\Delta\tilde{n}^2$ against the weight fraction w of the polymer, the values of $d(\epsilon - \epsilon_1)/dw$ and $d(\tilde{n}^2 - \tilde{n}_1^2)/dw$ at each temperature of interest were obtained. Illustrative plots of this kind are shown for two extreme temperatures in Figure 4. Values of $d(\tilde{n}^2 - \tilde{n}_1^2)/dw$ and $d(\epsilon - \epsilon_1)/dw$ determined in this way are given

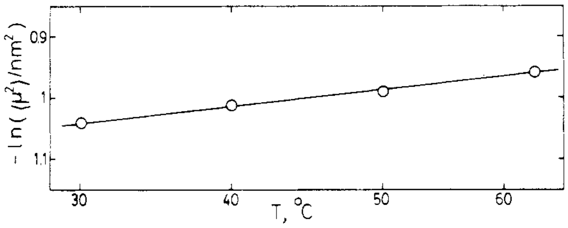


Figure 5. Natural logarithm of the dipole moment ratio against temperature.

Table I
Summary of Dielectric Results

T, °C	$d(\tilde{n}^2 - \tilde{n}_1^2)/dw$	$d(\epsilon - \epsilon_1)/dw$	$\langle\mu^2\rangle/nm^2$
30	0.067	1.001	0.354
40	0.073	0.979	0.363
50	0.076	0.956	0.372
60	0.077	0.940	0.384

in the second and third columns of Table I. The dipole moment ratio corresponding to PMOx chains was calculated at each temperature by means of the equation of Guggenhein and Smith[20,21]

$$\langle\mu^2\rangle/nm^2 = \frac{27kTM}{4\pi\rho N_A(\epsilon_1 + 2)^2 nm^2}\left\{\frac{d(\epsilon - \epsilon_1)}{dw} - \frac{d(\tilde{n}^2 - \tilde{n}_1^2)}{dw}\right\} \quad (1)$$

where k is the Boltzmann constant, T is the absolute temperature, M is the molecular weight of the solute, and ρ is the density of the solvent. The average m^2 of the skeletal bond dipole moments was calculated from $m^2 = (1/4)(2m_{C-O}^2 + 2m_{C-C}^2)$ using $m_{C-O} = 1.07$ D and $m_{C-C} = 0.00$ D.[5,22] The values of the dipole moment ratio thus obtained are listed in the last column of Table I. It should be pointed out that the values of $\langle\mu^2\rangle$[23-29] may be considered as the unperturbed values owing to the small excluded volume effects of such nearly symmetrical chains as PMOx. The temperature dependence of the dipole moments, obtained from the plot of the natural logarithm of the dipole moment ratio against temperature shown in Figure 5, amounted to 2.7×10^{-3} K^{-1}.

Theoretical Analysis of the Configurational Properties of Poly(3-methyloxetane). Values of the dipole moment ratio were calculated by standard matrix multiplication methods described elsewhere.[29,30] All the skeletal bond angles were assumed to have a value of 110°, and the rotational states were considered to be located at 0, +120, and −120°. Although the rotational angles corresponding to some skeletal bonds might depart somewhat from these values, the error introduced by assuming regularly staggered positions for the conformational states is not very important, in comparison with the errors introduced by the uncertainties involved in the determination of the conformational energies.

Before the theoretical calculations are performed, the values of the energies associated with the different rotational states of each skeletal bond of the repeating unit should be established. An isotactic dyad of PMOx in all-trans conformation is shown in Figure 6. Bond rotations about bonds of type i give rise to steric interactions between the methyl group associated with the asymmetric carbon $i + 1$ and the methylene group $i - 2$ that reduce the number of possible states to trans (t) and gauche positive (g$^+$); actually, a negative rotation of 120° about this skeletal bond places both groups at the intolerable distance of ca. 2.4 Å and, therefore, g$^-$ states should be totally disfavored with regard to the alternative trans states. The energy associated with g$^+$ states about bonds of type i was assumed to be 1.2 kcal mol^{-1} higher than that of the corresponding trans states.[5] The energy interactions arising from g$^-$ rotations about bonds of type $i + 1$ would be similar to those of the alternative trans states were it not for the Coulombic interactions between the positively charged $i + 2$ carbon atoms ($\delta_C = 0.155$ in electron units) and the negatively charged oxygen atom ($\delta_O = -0.31$ in the same units), which amounts to −1.83 kcal mol^{-1}, a value significantly lower than that corresponding to trans states, which is only −1.41 kcal mol^{-1}. In these calculations a value of 3 for the dielectric constant[8] was assumed. Therefore, the conformational energy E_β associated with g$^-$ states was considered to have, as a first approximation, a value 0.42 kcal mol^{-1} lower than that of the alternative trans states. Gauche states of positive sign about bonds of type $i + 2$ have an energy similar to that of g$^-$ states about bonds of type $i + 1$. Negative rotations about these bonds place the oxygen atom between a methylene and a methyl group; the value of the energy E_α associated with these states was determined, as indicated below, by comparing the theoretical and experimental values of the dipole moment ratio and its temperature coefficient. Finally, and for the reasons outlined above, only t and g$^+$ states are permitted about bonds of type $i + 3$.

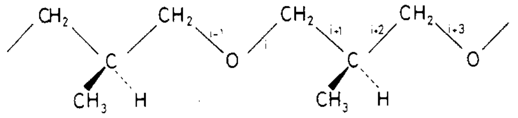


Figure 6. Isotactic dyad of poly(3-methyloxetane) in all-trans conformation.

Gauche rotations of different sign about pairs of skeletal bonds of the type $(i, i + 1)$ or $(i + 2, i + 3)$ cause overlap between two methylene groups separated by four bonds and, therefore, these conformations are not permitted. However, g$^\pm$g$^\mp$ rotations about $(i + 1, i + 2)$ bonds give rise to O···O interactions whose energy E_ω is ca.[9] 1.6 kcal mol^{-1}.

The statistical weight matrices required for evaluating the statistical properties for the polymer may be expressed in a 3 × 3 matrix scheme

$$\mathbf{U}_i = \begin{bmatrix} 1 & \sigma'' & 0 \\ 0 & 0 & 0 \\ 1 & 0 & 0 \end{bmatrix}; \quad \mathbf{U}_{i+1} = \begin{bmatrix} 1 & \alpha & \beta \\ 1 & 0 & 0 \\ 0 & 0 & \beta \end{bmatrix}$$

$$\mathbf{U}_{i+2} = \begin{bmatrix} 1 & \beta & \alpha \\ 1 & \beta & \alpha\omega \\ 1 & \beta\omega & \alpha \end{bmatrix}; \quad \mathbf{U}_{i+3} = \begin{bmatrix} 1 & 0 & \sigma'' \\ 1 & \sigma'' & 0 \\ 1 & 0 & 0 \end{bmatrix} \quad (2)$$

where subscripts i, $i + 1$, $i + 2$, and $i + 3$ denote the type of skeletal bonds, shown in Figure 6, to which each matrix should be applicable in an isotactic dyad. The corresponding matrices for mirror image or enantiomorphic structure can be obtained by pre- and postmultiplying each of the matrices $\mathbf{U}_i$, $\mathbf{U}_{i+1}$, $\mathbf{U}_{i+2}$, and $\mathbf{U}_{i+3}$ by the elementary matrix[29]

$$\mathbf{Q} = \begin{bmatrix} 1 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{bmatrix} \quad (3)$$

Since the NMR spectroscopic analysis of PMOx chains suggests that the chains are perfectly heterotactic, Monte Carlo techniques were used to generate chains in which the isotactic replication probability p_r was 0.50. Theoretical values of the dipole moment ratio and its temper-

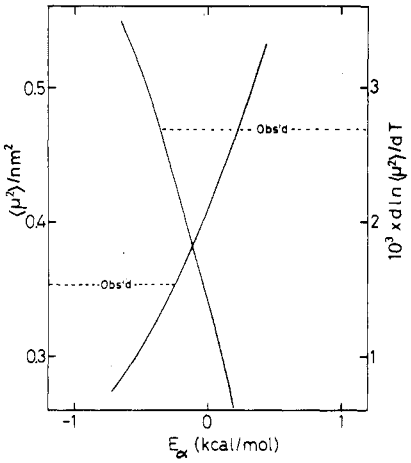


Figure 7. Dependence of the dipole moment ratio and its temperature coefficient on E_α.

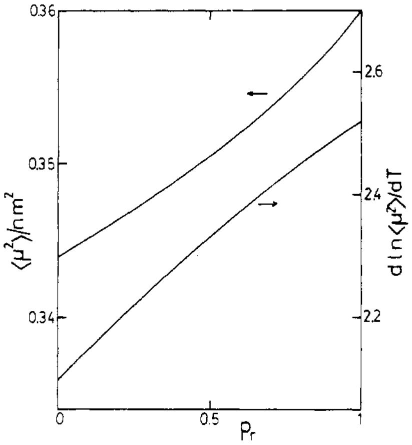


Figure 8. Variation of the dipole moment ratio and its temperature coefficient with the isotactic content of the chain.

ature coefficient, obtained as a function of E_α, are shown in Figure 7. The other energy parameters ($E_{\sigma''} = 1.2$, $E_\beta = -0.42$, and $E_\omega = 1.3$, all in kcal mol^{-1}) were kept constant. In order to facilitate comparison between theory and experiment, the calculations were carried out at 30 °C. It can be observed that both $\langle\mu^2\rangle/nm^2$ and d ln $\langle\mu^2\rangle/\mathrm{d}T$ are quite sensitive to E_α. Variation of this conformational parameter from −0.67 to +0.5 kcal mol^{-1} raises the ratio from 0.281 to 0.525; the temperature coefficient, on the other hand, decreases from 3.5×10^{-3} to 8×10^{-5} K^{-1}. The values of E_α that reproduce the experimental quantities are quite restricted, a value of E_α in the vicinity of −0.3 kcal mol^{-1} being the best choice. The values of $\langle\mu^2\rangle/nm^2$ and d ln $\langle\mu^2\rangle/\mathrm{d}T$, calculated with the set of statistical weights ($\sigma'' = 0.138$, $\sigma_\beta = 2.0$, $\sigma_\alpha = 1.6$, and $\omega = 0.117$), are 0.34 and 2.3×10^{-3} K^{-1}, in very good agreement with the experimental results 0.353 and 2.7×10^{-3} K^{-1}, respectively.

Although the conditions used in the preparation of the polymer produce heterotactic chains, other conditions might be devised that presumably would produce polymers of variable stereochemical composition. It is important, therefore, to investigate how sensitive are the configuration-dependent properties to the stereoregularity of the chains. For this purpose, chains were generated with values of p_r ranging from 0 to 1. The results obtained, shown in Figure 8, indicate that the dipole moment ratio and its temperature coefficient of PMOx chains are not very sensitive to their stereochemical composition. For example, the values of $\langle\mu^2\rangle/nm^2$ for perfectly isotactic ($p_r = 1$) and syndiotactic ($p_r = 0$) chains are 0.353 and 0.336, respectively, whereas for heterotactic chains ($p_r = 0.5$), the value of this quantity is 0.344. The unperturbed dimensions are even less sensitive than the dipole moments to the stereochemical composition of the polymer. These results support previous ones,[31] according to which the configurational properties are not very sensitive to the stereoregularity of the chains when the asymmetric centers are separated by more than three skeletal bonds.

Table II
Configurational Characteristics of Poly(trimethylene oxide) (POx), Poly(3-methyloxetane) (PMOx), and Poly(3,3-dimethyloxetane) (PDMOx)

polymer	$\langle\mu^2\rangle/nm^2$	$\langle r^2\rangle_0/nl^2$	10^3d ln $\langle\mu^2\rangle/\mathrm{d}T$	10^3d ln $\langle r^2\rangle_0/\mathrm{d}T$	T_g, °C
POx[a]	0.42	3.9	1.8	0.1	−78[b]
PMOx	0.35	4.8[c]	2.7	0.4[c]	−62
PDMOx[d]	0.21–0.25	4.2[e]	2.5–4.1	1.1	−54[f]

[a] Reference 5. [b] References 34, 35, and 36. [c] Calculated by using the rotational isomeric state model. [d] References 7 and 8. [e] Reference 38. [f] Reference 37.

Table II compares experimental values of some configuration-dependent properties of the members of the polyoxetane series. In the cases in which a particular property was not measured, the theoretical value is given. It can be seen that PDMOx is the least polar of all of the members of the series. The reason is that in this polymer the C–O bonds are restricted to trans states and the C–C skeletal bonds have a strong preference for gauche states.[9] Therefore, there is a great incidence of $g^\pm g^\pm$ conformations about consecutive C–C skeletal bonds which place the dipoles corresponding to consecutive COC groups in antiparallel direction—hence the low polarity of these chains. When a methyl group in PDMOx is substituted for a hydrogen atom, the incidence of $ttg^\pm g^\pm tt$ conformations in the sequences CH_2-O-CH_2-CH(CH_3)-CH_2-O-CH_2 decreases, because g^+ or g^- states (depending on the stereoregularity of the triad) about C–O skeletal bonds are now permitted; consequently, the polarity of PMOx increases. This increase is higher in POx, where $g^\pm$ states about C–O bonds are equally permitted. In all cases an increase in temperature increases the fraction of tttttt conformations in the sequence indicated above, the dipole corresponding to the C–O–C groups becoming parallel, and, hence, the dipole moments of the chains increase. The changes in the dipole moments with temperature are, however, less important in the cases in which rotational states about C—O bonds are permitted because an increase in temperature increases the gauche population about these bonds, decreasing the incidence of tttttt conformations.

Since for all-trans conformations $\lim_{n\to\infty} \langle r^2\rangle_0/nl^2 = \infty$, the dependence of the unperturbed dimensions on temperature will follow the same trend as the dipole moments. That is, PDMOx should have the higher value of d ln $\langle r^2\rangle_0/\mathrm{d}T$ and POx the lower, in agreement with the results given in Table II. Finally, it should be pointed out that all the polymers of Table II are conformationally rather random in the sense that two skeletal bonds of the repeating unit prefer trans states while the other two show preference for gauche states. Although the magnitudes of the rotational energy differences are obviously of importance, the fact that the fraction f_t of skeletal bonds showing preference for trans states is $^1/_2$ explains why the polyoxetanes are compact molecules with very small unperturbed dimensions. The data shown in Table II suggest that among all of the members of the polyoxetanes, PMOx seems to have the largest dimensions.

From the conformational analysis carried out above, it can be concluded that the flexibility of the polyoxetanes, as expressed for the configurational partition function, increases as the accessibility of the C–O skeletal bonds to gauche states increases, following the order POx > PMOx > PDOx. Assuming that the glass transition temperature of the polymers is closely related to the molecular flexibility such that the higher is the flexibility generally the lower is T_g,[32,33] the values of T_g should decrease in the order PDMOx > PMOx > POx. This prediction is confirmed in the last column of Table II, where it can be observed that the glass transition of PDMOx is higher than that of POx, the value of T_g corresponding to PMOx being intermediate.

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Registry No. Poly(3-methyloxetane), 87706-57-8; PMOx, 90697-51-1.

References and Notes

(1) Rose, J. B. *J. Chem. Soc.* **1956**, 546.
(2) Okamura, S. *Encycl. Polym. Sci. Technol.* **1968**, *9*, 668.
(3) Saegusa, T.; Fujii, H.; Kobayashi, H.; Ando, R. *Macromolecules* **1973**, *6*, 26.
(4) Bucquoye, M.; Goethals, E. J. *Makromol. Chem.* **1978**, *179*, 1681.
(5) Abe, A.; Mark, J. E. *J. Am. Chem. Soc.* **1976**, *98*, 6468.
(6) Takahashi, Y.; Mark, J. E. *Polymer* **1976**, *17*, 670.
(7) Garrido, L.; Riande, E.; Guzmân, J. *J. Polym. Sci., Polym. Phys. Ed.* **1982**, *20*, 1805.
(8) Saiz, E.; Riande, E.; Guzmân, J.; de Abajo, J. *J. Chem. Phys.* **1980**, *73*, 958.
(9) Chiu, D. S.; Mark, J. E. *J. Chem. Phys.* **1977**, *66*, 1901.
(10) Searles, S.; Pollart, K. A.; Lutz, E. F. *J. Am. Chem. Soc.* **1957**, *79*, 948.
(11) Garrido, L.; Guzmân, J.; Riande, E.; de Abajo, J. *J. Polym. Sci., Polym. Chem. Ed.* **1982**, *20*, 3378.
(12) Ledwith, A.; Sherrington, D. C. *Adv. Polym. Sci.* **1975**, *19*, 1.
(13) Matyjaszewski, K.; Slomkowski, S.; Penczek, S. *J. Polym. Sci., Polym. Chem. Ed.* **1979**, *17*, 2413.
(14) van Gurkon, M.; Hall, G. E. *Q. Rev. Chem. Soc.* **1968**, *22*, 14.
(15) Oguni, N.; Watanabe, S.; Maki, M.; Tani, H. *Macromolecules* **1973**, *6*, 195.
(16) Ivin, K. J.; Navratil, M. J. *J. Polym. Sci., Part A-1* **1971**, *9*, 1.
(17) Kops, J.; Hvilsted, S.; Spanggaard, H. *Macromolecules* **1980**, *13*, 1058.
(18) Oguni, N.; Hyoda, J. *Macromolecules* **1980**, *13*, 1687.
(19) Riande, E.; de la Campa, J. G.; Guzmân, J.; de Abajo, J. *Macromolecules*, in press.
(20) Guggenhein, E. *Trans. Faraday Soc.* **1949**, *45*, 714; **1951**, *47*, 573.
(21) Smith, J. W. *Trans. Faraday Soc.* **1950**, *46*, 394.
(22) McClellan, A. L. "Tables of Experimental Dipole Moments", Vol. I, W. H. Freeman: San Francisco, 1963; Vol. II, Rahara Enterprises: El Cerrito, CA, 1974.
(23) Riande, E.; Boileau, S.; Hemery, P.; Mark, J. E. *J. Chem. Phys.* **1979**, *71*, 4206.
(24) Riande, E.; Boileau, S.; Hemery, P.; Mark, J. E. *Macromolecules* **1979**, *12*, 702.
(25) Marchal, J.; Benoit, H. *J. Polym. Sci.* **1957**, *23*, 223.
(26) Nagai, K.; Ishikawa, T. *Polym. J.* **1971**, *2*, 416.
(27) Doi, M. *Polym. J.* **1972**, *3*, 352.
(28) Liao, S. C.; Mark, J. E. *J. Chem. Phys.* **1973**, *59*, 3825.
(29) Flory, P. J. "Statistical Mechanics of Chain Molecules"; Wiley: New York, 1969.
(30) Flory, P. J. *Macromolecules* **1974**, *7*, 381.
(31) Riande, E.; Garcia, M.; Mark, J. E. *J. Polym. Sci., Polym. Phys. Ed.* **1981**, *19*, 1739.
(32) Tonelli, A. E. *Macromolecules* **1974**, *7*, 632.
(33) Tonelli, A. E. *Macromolecules* **1977**, *10*, 633, 636.
(34) Willbourn, A. H. *Trans. Faraday Soc.* **1958**, *54*, 717.
(35) Saba, R. G.; Sauer, J. A.; Woodward, A. E. *J. Polym. Sci., Part A-1* **1963**, 1483.
(36) Faucher, J. A.; Koleske, J. V. *Polymer* **1968**, *9*, 44.
(37) Garrido, L.; Guzmân, J.; Riande, E. *Makromol. Chem., Rapid Comm.* **1983**, *4*, 725.
(38) Pêrez, E. Doctoral Thesis, University of Madrid, 1982.

Measurement of the Kinetics of Chain Polymerization of Single Poly(vinyl acetate) Molecules in a Cloud Chamber

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ABSTRACT: The gas-phase, photoinduced, free radical polymerization of vinyl acetate is studied, using drop formation in supersaturated vinyl acetate vapor in a diffusion cloud chamber as a detector. A detailed kinetic mechanism involving initiation, propagation, termination, and chain transfer is postulated, and the corresponding rate equations are solved. We are able to achieve conditions such that growing polymer molecules cannot encounter one another. Thus the arrival, by growth, of individual polymer molecules is detected. The system can be "tuned" to detect polymer molecules of a given size by adjusting the supersaturation and therefore constitutes a technique of high resolution. In view of the "extreme" nature of the measurement, no alternative method exists that allows a comparative confirmation of the assumed fundamental process. Therefore, confirmation is a "bootstrap" operation in which the harmonious register of many quantitative and qualitative observations, with each other and with theory, must be used to prove-out the technique. The demonstration of this observational consistency, and *not* the measurement of particular kinetic parameters, forms the main purpose of this paper. Almost all the features of the assumed kinetic mechanism are dramatically confirmed. Detected polymer molecules have degrees of polymerization of the order of 50, and the activation energy for propagation is of the order of 4000 cal mol^{-1}, in agreement with independent studies on bulk polymerization. The "noise" in the polymerization reaction is actually sensed.

I. Introduction

In a recent paper[1] we developed a theory for the nucleation of supersaturated vapors of monomers, by polymers formed from them. Using this theory, we made quantitative estimates of the various associated phenomena for the case of vinyl acetate. The results indicated that it should be possible to achieve experimental conditions under which a single poly(vinyl acetate) molecule could nucleate the condensation of supersaturated vinyl acetate vapor. Indeed, it appeared that conditions could be

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