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Ring-Opening Polymerization of Heterocycles: Statistical Properties of the Polymer Derived from 1-Oxa-3-thiacyclopentane

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ABSTRACT: 1-Oxa-3-thiacyclopentane was polymerized in bulk with boron trifluoride etherate as initiator. Dielectric measurements were carried out on $\langle\mu^2\rangle/nm^2$ of the polymer in benzene at several temperatures in the interval 30–60 °C. The measurements yielded dipole moment ratios $\langle\mu^2\rangle/nm^2$ of 0.255–0.288 and a temperature coefficient d ln $\langle\mu^2\rangle/\mathrm{d}T$ of 4.2×10^{-3} K^{-1}. The experimental results were found to be in very good agreement with theoretical results based on a rotational isomeric state model which assumed perfect alternation of 1,3-dioxolane and 1,3-dithiolane, rather than a more irregular distribution which could conceivably occur in the type of ring-opening polymerization used to prepare the polymer.

Introduction

Ever-increasing emphasis is being placed in the cationic ring-opening polymerization of heterocycles.[1-4] The process involves an equilibrium between monomer and polymer, the equilibrium being governed by the ring size of the monomer, the nature of the heteroatoms, and the kind, number, and position of the substituents attached to the ring. The structure of the resulting polymer is determined by the place or places where bond scission occurs.

Recently, the ring-opening polymerization of 1-oxa-3-thiacyclopentane (OTC)[5,6] was reported. Although the polymerization seems to be initiated by quantitative formation of ethyl sulfonium, the propagation is not the simple repeating formation of sulfonium ions, as occurs

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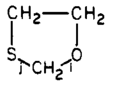
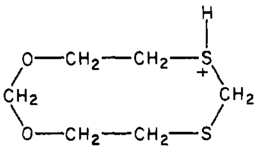


OTC

in the polymerization of thiiranes and thietanes.[7] In the analysis of the NMR spectrum of the polymer obtained with boron trifluoride etherate ($BF_3 \cdot Et_2O$) as initiator, the presence of $O-CH_2-S$ sequences was not detected.[6] The kinetic mechanism which might explain the absence of these sequences implies either that bond scission occurs in rigorously alternating order at i bonds and at j bonds on the monomer or that the polymerization proceeds by expansion of the cyclic sulfonium ion[6]



in a way similar to that proposed by Plesch and Westermann[8] for the polymerization of 1,3-dioxolane. According to this, the structure of the resulting polymer, POTC, is consistent with that of an ideally alternating copolymer of 1,3-dioxolane and 1,3-dithiolane.

The present investigation addresses the interesting question regarding the potentiality of the configuration-dependent properties to determine sequence monomer distribution in copolymers. Although high-resolution nuclear magnetic resonance is generally used for this purpose, situations may arise as in the case of vinyl copolymers with asymmetric units, in which stereoregularity effects are superimposed upon sequence distribution, and lead to complex NMR spectra with many overlapping resonances, which can preclude an unambiguous analysis of monomer sequence distribution. It is therefore desirable to test on simple models the usefulness of other techniques to study, in parallel with NMR, the sequence distribution of monomer units in copolymers as well as the structure of polymers in general. The use of molecular dimensions and dipole moments of chemical and stereochemical copolymers in dilute solutions, as a means of determining their monomer sequence distribution, has been successfully attempted in the past.[9-14] These studies have shown that the dipole moment generally is more sensitive to the structure than the molecular dimensions due to the fact that skeletal bonds or polymer repeat units often vary much more in polarity than they do in length. Therefore, the present investigation focuses on the dipole moments and their temperature dependence for the polymer chains synthesized from OTC via cationic polymerization. Of particular interest will be the molecular interpretation of the results in terms of rotational isomeric state theory. As is known, the dipole moment ratio $\langle \mu^2 \rangle / nm^2$, where $\langle \mu^2 \rangle$ is the mean-square dipole moment and nm^2 represents the mean-square dipole moment of the chain in the idealization that all skeletal bonds are freely jointed, is very sensitive to the presence of both oxymethylenic and thiomethylenic units along the chains.[15-17] As a consequence, for the reasons outlined above, it is of obvious importance to determine whether or not a model of the polymer chain POTC, which assumes perfect structural regularity (alternation of 1,3-dioxolane and 1,3-dithiolane units), will give theoretical results in good agreement with experiment.

Experimental Procedures

1-Oxa-3-thiacyclopentane, prepared by condensation of paraformaldehyde and 2-mercaptoethanol, was refluxed with sodium for 2 days and distilled in vacuo into a sodium mirror. Polymerization of the monomer thus purified was carried out in evacuated sealed ampules at 70 °C, using boron trifluoride etherate as initiator. The reaction was terminated with methanol and the solution of the polymer in chloroform was precipitated several times with methanol. The polymer, which is a viscous liquid, was washed with n-hexane and finally dried under high vacuum at room temperature. The number-average molecular weight of the polymer was 5200. The ^1H NMR spectrum of POTC is described elsewhere.[6] Essentially, it shows two triplets and one singlet; the signals of the peaks are present in a 2:4:6 intensity ratio, corresponding, respectively, to the singlet (δ 4.68) and the two triplets (δ 2.85 and 3.77). As was shown in ref 6, the structure of the polymer corresponds to that of a regularly alternating copolymer of 1,3-dioxolane and 1,3-dithiolane units.

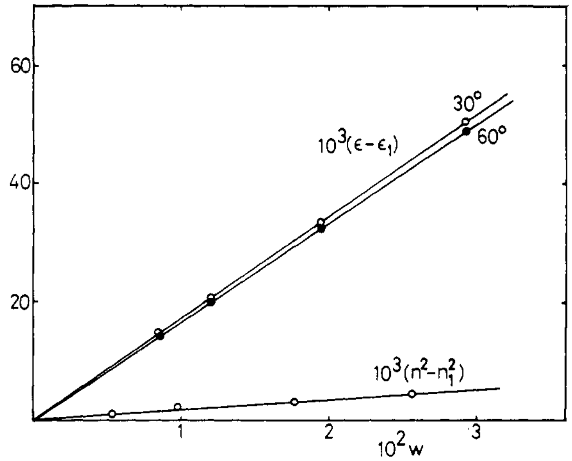


Figure 1. Concentration dependence of the increments in dielectric constant and squared index of refraction for POTC at 30 and 60 °C.

Table I
Dielectric Results for POTC Chains in Benzene

T, °C	$d(\epsilon - \epsilon_1)/dw$	$d(n^2 - n_1^2)/dw$	$\langle \mu^2 \rangle / nm^2$
30	1.73	0.167	0.255
40	1.71	0.167	0.266
50	1.68	0.167	0.275
60	1.67	0.167	0.288

The dielectric constants ϵ of the solutions were measured with a capacitance bridge (General Radio Type 1620 A) operating at a frequency of 10 kHz. A three-terminal cell (Foxboro Model 3HV35) was used. Values of the index of refraction of the solutions were measured at 546 nm with a Brice-Phoenix differential refractometer.[18]

Experimental Results

The dielectric constants of the solutions of POTC in benzene were slightly dependent on temperature. In order to obtain the value of $d(\epsilon - \epsilon_1)/dw$ in the limit $w \rightarrow 0$, values of the dielectric increments $\Delta\epsilon = \epsilon - \epsilon_1$ at each temperature of interest were plotted as a function of the weight fraction of polymer, w. Illustrative plots of this kind are shown in Figure 1. In the same way, differences between the squared refraction index of the solutions, n^2, and that of the solvent, n_1^2, are plotted as a function of w in the same figure. It was found that $d(n^2 - n_1^2)/dw$ is, within experimental error, independent of temperature. Values of $d(\epsilon - \epsilon_1)/dw$ and $d(n^2 - n_1^2)/dw$ are gathered in the second and third columns of Table I. Values of the dipole moment ratio at 30, 40, 50, and 60 °C were evaluated by means of the equation of Guggenheim[19] and Smith.[20] The average square of the bond dipole moments was calculated by assuming that $m_{C-O} = 1.07$ D,[21] $m_{C-C} = 0.00$ D,[21] and $m_{C-S} = 1.21$ D.[22,23] Values of $\langle \mu^2 \rangle / nm^2$ are given in the fourth column of Table I.

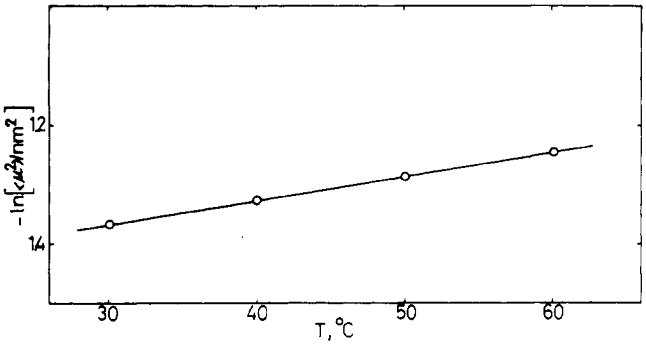


Figure 2. Temperature dependence of the natural logarithm of the dipole moment ratio.

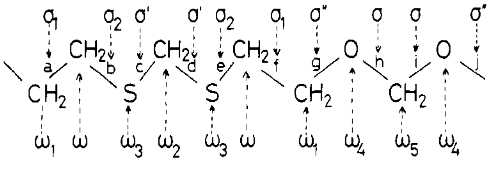


Figure 3. Repeat unit of POTC in the all-trans conformation.

The temperature coefficient d ln $\langle\mu^2\rangle/\mathrm{d}T$ of the dipole moments, calculated from the plots of Figure 2, is 4.2×10^{-3} K^{-1}, an unusually high value for a temperature coefficient of any configuration-dependent property.

Theoretical Results

The rotational isomeric state model adopted for the calculations of the dipole moments of the polymer assumed perfect alternation between $OCH_2OCH_2CH_2$ and $SCH_2SCH_2CH_2$ units along the chains. Values of the CSC and CCS bond angles are 100 and 114°, respectively.[22] There does not seem to be a reliable value for the SCS bond angle. It was assumed that it has a value very close to that of CCS,[24] as the OCO angle (112°) is close to that of CCO (111.5°). A value of 114° was assigned in the present investigation. Conformational energy calculations reported elsewhere[24] indicate that the trans states are located at 0° and the location of the $g^{\pm}$ states differ ca. 10° from the usual values of ±120°. Specifically, gauche states about skeletal bonds of types a, c, d, f, h, and i are located at ±114°, and the rotational angles associated with gauche states about the remaining skeletal bonds are ±110°.

According to earlier calculations,[17] the two thiomethylenic skeletal bonds (c and d in Figure 3) should have energies in the gauche states approximately 0.3 kcal mol^{-1} below the alternative trans states. It should be mentioned, however, that the observed value of the conformational energy for these types of bonds in poly(1,3-dithiocane)[17] is in the vicinity of −1.1 kcal mol^{-1}. This difference is called a gauche effect, and a similar discrepancy occurs in the case of oxymethylenic bonds in poly(1,3-dioxolane).[15] Therefore, $E_\sigma = -1.1$ kcal mol^{-1} was used in the calculations. Gauche states about skeletal bonds of types h and i in Figure 3 brings CH_2 groups and O atoms separated by three bonds into proximity; these states have an energy approximately 1.2 kcal mol^{-1} lower than the trans states.[15,16] Bonds of types g and j have gauche states approximately 0.9 kcal mol^{-1} higher than the corresponding trans states,[21] bonds of types a and f have gauche states approximately 0.3–0.4 kcal mol^{-1} higher than trans states,[25,26] and bonds of types b and e have gauche states approximately 0.1 kcal mol^{-1} lower than the trans states.[27,28]

The conformations $g^{\pm}g^{\mp}$ give rise to pentane-type interactions between groups and atoms separated by four bonds. For bond pairs aj, bc, cd, de, and fg in Figure 3 the interacting species are either two CH_2 groups or a CH_2 group and a sulfur atom; in both cases their steric overlaps cause complete exclusion of these conformations.[17,29] For the other bond pairs in the repeat unit, the participating species are a CH_2 group and a relatively small oxygen atom. When the $g^{\pm}g^{\mp}$ states occur about C–O–C bond pairs such as gh and ij, the shortness of the C–O bond causes sufficient CH_2···O overlap to exclude these states as well.[16] Finally, in the case of bond pairs ab and ef, the CH_2···O interactions give rise to a repulsive energy of only approximately[25,26] 0.4 kcal mol^{-1}.

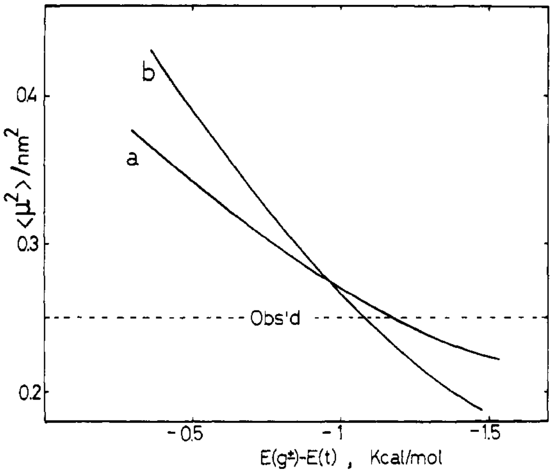


Figure 4. Theoretical results showing the dependence of the dipole moment ratio of POTC on the energy difference between gauche and trans states in which the interacting species are CH_2 groups and O atoms (curve a) and CH_2 groups and S atoms (curve b).

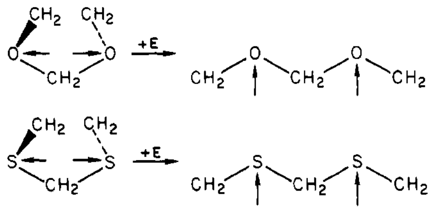
Table II
Coefficients Calculated Using the Set of Boltzmann Factors Indicated in the Text

coefficient	value	coefficient	value
$\partial \ln \langle\mu^2\rangle/\partial \ln \sigma_1$	0.045	$\partial \ln \langle\mu^2\rangle/\partial \ln \sigma''$	<0.01
$\partial \ln \langle\mu^2\rangle/\partial \ln \sigma_2$	0.125	$\partial \ln \langle\mu^2\rangle/\partial \ln \sigma$	−0.265
$\partial \ln \langle\mu^2\rangle/\partial \ln \sigma'$	−0.487	$\partial \ln \langle\mu^2\rangle/\partial \ln \omega$	0.012

Standard matrix multiplication methods of rotational isomeric state theory[29,30] were used to calculate the dipole moment ratio at 30 °C for chains containing 480 skeletal bonds. The statistical weight parameters assigned to each of the states of each skeletal bond of the structural unit are represented in Figure 3. First-order parameters are indicated above the formula, and second-order parameters are shown below. From the information given above it can be expected that the Boltzmann factors are $\sigma_1 = 0.56$, $\sigma'' = 0.22$, $\sigma_2 = 1.18$, $\sigma' = 6.13$, $\sigma = 7.23$, $\omega = 0.61$, $\omega_1 = \omega_2 = \omega_3 = \omega_4 = \omega_5 = 0$.

The theoretical calculations show that the dipole moment ratio of POTC is extremely sensitive to the gauche states associated with both the thiomethylenic and the oxymethylenic bonds. It can be observed in Figure 4 that $\langle\mu^2\rangle/nm^2$ decreases as the gauche population about these bonds increases, the coefficients $\partial \ln \langle\mu^2\rangle/\partial \ln \sigma'$ and $\partial \ln \langle\mu^2\rangle/\partial \ln \sigma$ being −0.487 and −0.265, respectively. However, it can be observed in Table II that the dipole moments are not so sensitive to the conformations of the other skeletal bonds. Coincidence between theoretical and experimental values of the dipole moment ratio is found for values of $[E(g^{\pm}) - E(t)]_{CH_2-O}$ and $[E(g^{\pm}) - E(t)]_{CH_2-S}$ of −1.2 and −1.1 kcal mol^{-1}, respectively, in agreement with results obtained for similar bonds in the theoretical analysis of the con-

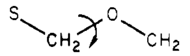
Scheme I



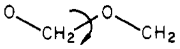
formational properties of poly(1,3-dioxolane)[15] and poly(1,3-dithiocane).[17]

Due to the strong preference of bonds of types c, d, h, and i for gauche states, the dipole moments of the chains have an unusually high temperature coefficient. The calculated value for d ln $\langle\mu^2\rangle/\mathrm{d}T$ at 30 °C is 4.7×10^{-3} K^{-1}, in excellent agreement with the experimental result (4.2×10^{-3}). The reason for this high value is that as the temperature increases, the occurrence of $g^{\pm}g^{\pm}$ conformations about consecutive O–C–O bonds and S–C–S bonds decreases. Since pairs of gauche states $g^{\pm}g^{\pm}$ corresponding to both oxymethylenic[16] and thiomethylenic[17] bonds place pairs of bond dipoles in very nearly antiparallel orientations, an increase in temperature causes an increase in the number of the higher energy trans states which have a much higher dipole moment, as is illustrated in Scheme I.

The theoretical analysis indicates that the dipole moment ratio at 30 °C of a chain with a repeat unit similar to that shown in Figure 3 has a value of 0.248, in excellent agreement with the experimental result (0.255). There is also good agreement between theoretical and experimental temperature coefficients. These facts support, therefore, the regular alternation of 1,3-dioxolane and 1,3-dithiolane along the molecular chains, so that ring-opening mechanisms which might cause disruption of this alternation should be disregarded. It could be argued that the dipole moments might not be sensitive enough to the presence of other structures, such as those that would arise if bond scissions had occurred at random at i and j bonds on the monomer ring. In this case the resulting polymer would be made up of $CH_2SCH_2CH_2O$ and $CH_2OCH_2CH_2S$ units randomly distributed and therefore $CH_2OCH_2SCH_2$ sequences would also appear in the molecular chains. Although the energy associated with gauche states about



bonds is not known, it is reasonable to assume that its value will be similar to that corresponding to the same states about



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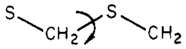
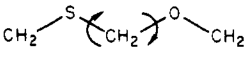
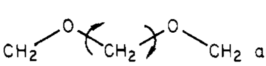


bonds; that is, gauche states will be strongly preferred over the alternative trans states. However, the value of the dipole moment associated with $g^{\pm}g^{\pm}$ states about



bonds is significantly larger than that corresponding to similar states about



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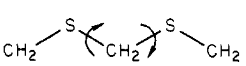

bonds; as a consequence, the dipole moments should be sensitive to the presence of S–CH_2–O sequences along the POTC chains. Therefore, the good agreement between theory and experiment for a polymer chain with the structural unit of Figure 3 rules out the random scission of the monomer at i and at j bonds. It can be concluded that the present investigation supports earlier findings,[9-14] according to which the rotational isomeric state analysis of the experimental configurational properties of molecular chains may be an important tool for determining molecular structures.

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