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Ring-Opening Polymerization of 2-Methyloxetane: NMR Spectroscopy and Configurational and Dielectric Properties of the Polymer

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ABSTRACT: Poly(2-methyloxetane) was obtained by ring-opening polymerization of 2-methyloxetane using acetyl hexafluoroantimonate as initiator. Owing to the asymmetry of the monomer, head-to-head, head-to-tail (or tail-to-head), and tail-to-tail structures appear along the chains. The dyad composition was $P(\mathrm{ii}) = 0.40$, $P(\mathrm{ij}) = P(\mathrm{ji}) = 0.18$, and $P(\mathrm{jj}) = 0.24$, i and j representing the C–O bonds of the monomer ring where bond scission may occur and i being the less substituted C–O bond. It is shown, in contrast to earlier reports, that the tacticity of head-to-tail structures cannot be determined. Dielectric measurements were also carried out on solutions of the polymer in cyclohexane over the range 30–60 °C. The dipole moment ratio was 0.35 at 30 °C and showed a strong temperature dependence. The dielectric results were found to be in good agreement with the theoretical results based on a rotational isomeric state model, provided that gauche states about C–C skeletal bonds are much more favored than the alternative trans states.

Introduction

The analysis of the kinetics and mechanisms involved in the ring-opening polymerization of heterocycles has received considerable attention.[1-4] For oxetane and derivatives, investigations were first focused on the study of the correlation between the reactivity and the monomer ring substitution. Structural aspects have generally not been considered until recently when the tacticity of the polymers derived from the monosubstituted oxetanes 2-methyloxetane[5,6] and 3-methyloxetane[7] was studied. The analysis of the ^{13}C NMR spectrum of poly(3-methyloxetane) (P3MOx) showed that the methine carbons present three peaks which can be assigned to the iso-, syndio-, and heterotactic triads. The chemical shift differences of these signals (0.017 ppm) are much lower than those of similar triads corresponding to head-to-tail structures in poly(2-methyloxetane) (0.133 ppm), indicating that the proximity of the oxygen atom to the methine carbon enhances the splitting of these carbons.[7]

Owing to the asymmetry of 2-methyloxetane, the cationic polymerization of this monomer gives rise to head-to-head, tail-to-tail, and head-to-tail (or tail-to-head) structures. In the last case, the evidence at hand suggests random incorporation of the enantiomeric monomers.[5,6] The structural heterogeneity and the additional steric congestion engendered by the methyl groups can change dramatically some of the physical properties in comparison with those of symmetric oxetanes. For example, poly(oxetane) (POx) and poly(3,3-dimethyloxetane) (PDMOx) are crystalline, whereas P3MOx and poly(2-methyloxetane) (P2MOx) are amorphous.

One of the properties more affected by the substitution of methylene hydrogens of the repeating unit of POx for methyl groups is the polarity of the chains.[7-10] Other configuration-dependent properties such as the unperturbed dimensions[7] are not so sensitive to the substitution. The dipolar ratio $\langle\mu^2\rangle/nm^2$, 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 ca. twice larger in POx[11] than in PDMOx.[10,11] The cause of the change of this quantity is that in the latter polymer the skeletal C–O bonds are restricted to trans states whereas in the former gauche states about these bonds are permitted; consequently, the fraction of low-polarity $\mathrm{ttg^{\pm}g^{\pm}tt}$ conformations which place the dipoles corresponding to two consecutive COC groups in antiparallel direction decreases in POx and hence the polarity increases. Depending on the position d or l of the methyl group in P3MOx, $\mathrm{g^+}$ or $\mathrm{g^-}$ states in the skeletal C–O bonds are permitted, and hence the dipole moments of the chains are intermediate between those of PDMOx and POx.

It would be important to know how the location of the methyl group in the oxetanes affects the polarity of the polymers. For this purpose, the dipole moments of P2MOx were measured and the results were critically interpreted in terms of the rotational isomeric state model. Another goal of this work was a critical analysis of the microstructure of this polymer.

Experimental Section

Materials. 2-Methyloxetane was prepared from 3-chlorobutyl acetate according to the procedure described by Searles et al.[12] The monomer was purified by fractional distillation (bp 60–61

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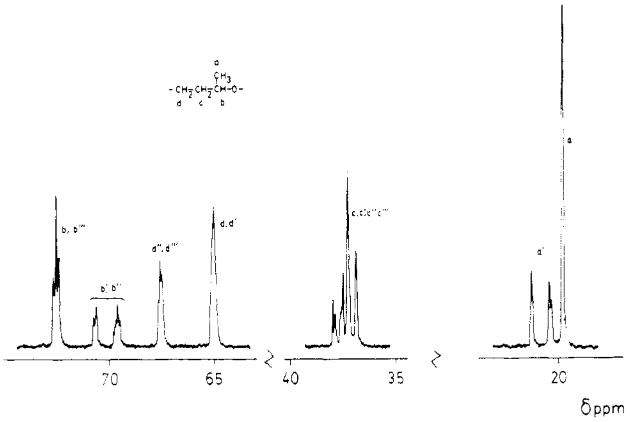


Figure 1. ^{13}C NMR spectrum of poly(2-methyloxetane).

°C (lit.[12] bp 60 °C)), dried over calcium hydride, and distilled onto sodium mirrors. Methylene chloride and silver hexafluoroantimonate were purified as described elsewhere.[13]

Ring-Opening Polymerization. The cationic polymerization of 2-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 1.2 and 0.4×10^{-3} mol L^{-1}, respectively. The reaction time was 96 h, although a relatively high viscosity was attained after 10 min and subsequently no increase in this quantity was observed. The polymer was precipitated twice in methanol, isolated at a low temperature, and finally dried in vacuo at room temperature.

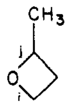
Characterization of the Polymer. The number-average molecular weight of the polymer, measured at 37 °C with a Knauer vapor pressure osmometer in chloroform solution, was 13 000.

The ^{13}C NMR spectra of the polymer were registered with a Bruker WM-360 at 90.55 MHz at the ambient temperature. Deuterated chloroform was used as solvent and tetramethylsilane as internal reference. Small flipping angles and long pulse delay times were used in order to avoid saturation and thus to obtain quantitative signals.

Dielectric Measurements. Dielectric constants of solutions of the polymer in cyclohexane were measured with a capacitance bridge (General Radio 1620 A), operating at 10 kHz, and a three-terminal cell (Foxboro 3HV35). Increments of the refractive indices of the solution with respect to the solvent were determined at 632.8 nm with a Chromatix KHX-16 laser differential refractometer.

Results and Discussion

NMR Spectroscopy of Poly(2-methyloxetane). The ^{13}C NMR spectrum of P2MOx, shown in Figure 1, presents several resonance signals corresponding to the carbons indicated in Scheme I, where the four possible triads are shown. These triads appear as a consequence of the ring-opening of 2-methyloxetane



through i or j bonds. The assignment of these signals was previously made by Kops et al.[5] and Oguni and Hyoda.[6] However, the assignment of the carbons c, c′, c″, and c‴ still remains confused owing to the complexity of the spectral pattern. In Figure 2 the expanded part of the spectrum from these carbons is shown. The complexity arises partly because of the different number of methyl groups in δ positions. Also tacticity splits certain peaks in iii, jjj, iji, and jij triads, presumably because in these the methyl carbons are closer to the analyzed carbon. The resonance signal at the higher field (36.9 ppm) may be attributed to the central c‴ carbons in the iij + ijj triads.

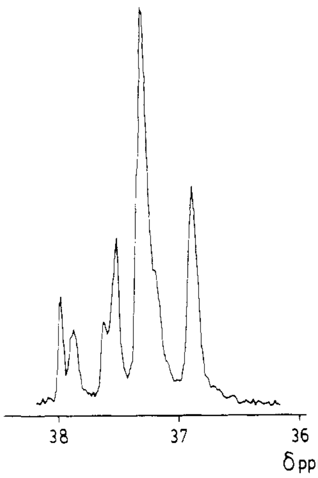
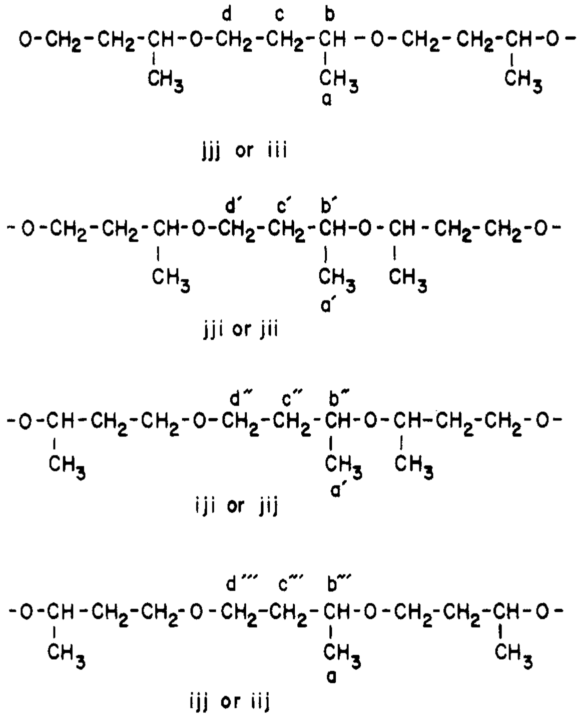


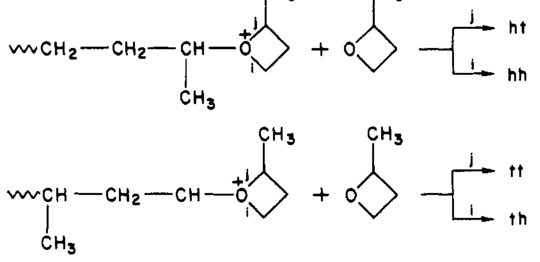
Figure 2. Expanded ^{13}C NMR spectrum of poly(2-methyloxetane) in the 36–38 ppm region.

Scheme I



In these triads tacticity effects may be expected to be negligible owing to the long distance between the c‴ carbons and the asymmetric carbons of the neighboring units. Thus no splitting is actually shown in the spectrum, in contrast to the signals of the other c carbons.

Mechanism of Polymerization. The ring-opening polymerization of 2-methyloxetane proceeds by nucleophilic attack of the monomer oxygen atom on the carbon atom in the α position relative to the oxonium ions, according to the mechanism shown in the following scheme:



Here, hh, ht (or th), and tt refer, respectively, to head-to-head, head-to-tail (or tail-to-head), and tail-to-tail units. The fraction of the different structures along the chains can be quantitatively estimated by ^{13}C NMR spectroscopy from the resonance signals corresponding to the methine, methyl, and oxymethylene carbons.[5,6] Dyad population alone does not express the influence of units penultimate to the oxonium ions on the ring opening through i or j bonds. But from the signals of the methylene carbons c‴ in the triads iij and ijj it is possible to know whether the ring opening is influenced by the methyl group in the β or δ position with respect to the oxonium ions. Thus it can be discovered whether the polymerization of 2-methyloxetane is an ideal random copolymerization in terms of ring opening through i and j bonds. The values obtained from NMR analysis for the different probabilities are $P(\text{ii}) + P(\text{jj}) = 0.64$ and $P(\text{ij}) = P(\text{ji}) = 0.18$ for the dyads and $P(\text{iij}) + P(\text{ijj}) = 0.23$ for the only triad that can accurately be assigned. From these values the conditional probabilities P_{ij}, P_{ji}, and P_{jj} can be obtained and, consequently, the ring-opening probabilities through i and j bonds (P(i) and P(j)) can also be determined. The values of P(i) and P(j) were found to be 0.58 and 0.42, respectively. Considering only dyads and assuming Bernoullian propagation, the values of these quantities would be 0.75 and 0.25, respectively. These results indicate, therefore, that the polymerization process of 2-methyloxetane is not Bernoullian; the ring opening through i and j bonds is affected by the unit vicinal to the oxonium ions.

Oguni and Hyoda[6] and Kops et al.[5] suggested that the stereoregularity of the polymer in the case of ht arrangements can be obtained from the triplet centered at 72.5 ppm of the methine carbon b in the triads iii or jjj and iij or ijj. In our opinion, this assignment is not entirely correct, since the carbon b‴ in the triads iij or ijj is different from the carbon b in the triads iii or jjj. Actually, carbon b, when compared with the carbon b‴, has an additional methyl group in the ϵ position which increases the chemical shift by about 0.11 ppm.[14] Consequently, the resonance of the methine carbon in the triads iij or ijj will appear at higher field than the triads iii or jjj. Further, the triplet assigned to iso-, syndio-, and heterotactic structures presumably includes the resonances corresponding to meso and racemic dyads ii or jj in the triads iij or ijj. Therefore, the triplet centered at about 72.5 ppm does not allow the accurate determination of the tacticity of the head-to-tail structures.

Dielectric Results. Dielectric measurements were carried out at 30, 40, 50 and 60 °C on solutions of the polymer in cyclohexane. The dipole moments of the chains were determined by means of the method of Guggenheim and Smith,[15,16] which produced the equation

$$\langle \mu^2 \rangle = \frac{27kTM}{4\pi\rho N_A(\epsilon_1 + 2)^2}\left[\frac{d(\epsilon - \epsilon_1)}{dw} - \frac{d(n^2 - n_1^2)}{dw}\right]$$

where M is the molecular weight of the solute, k is the Boltzmann constant, T is the absolute temperature, N_A is Avogadro's number, and ρ is the density of the solvent; ϵ and n denote, respectively, the dielectric constant and refractive index of the solutions (the same quantities with subindex 1 refer to the solvent). Values of the derivatives $d(\epsilon - \epsilon_1)/dw$ and $d(n^2 - n_1^2)/dw$ were obtained from plots of the increments in dielectric constant ($\Delta\epsilon = \epsilon - \epsilon_1$) and squared index of refraction ($\Delta n^2 = n^2 - n_1^2$) against the weight fraction w of polymer. Illustrative plots of this kind are shown in Figure 3. The values of the derivatives at the temperatures of interest are given in the second and third columns of Table I, where it can be seen that the derivative $d(\epsilon - \epsilon_1)/dw$ does not show a noticeable temperature dependence. The dipole moments were expressed as the dipole moment ratio $\langle \mu^2 \rangle / nm^2$; the average m^2 in this quantity was calculated from $m^2 = (1/2)(m_{\text{C-O}}^2 + m_{\text{C-C}}^2)$, where the values of $m_{\text{C-C}}$ and $m_{\text{C-O}}$ were assumed to be 0.00 and 1.07 D,[8,17] respectively. Values of the dipole moment ratio are given in the last column of Table I. We estimate the uncertainty of these values to be approximately 10%. The temperature coefficient of the dipole moments, d ln $\langle \mu^2 \rangle / dT$, obtained by plotting the natural logarithm of the dipole moment ratio against temperature, was found to be 4.5×10^{-3} K^{-1}.

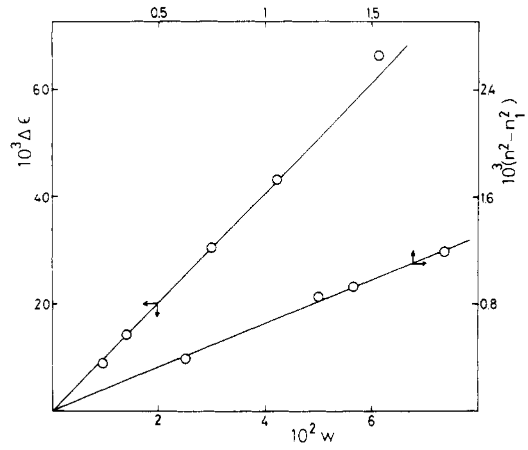


Figure 3. Increments in dielectric constant and squared index of refraction for solutions of poly(2-methyloxetane) in cyclohexane at 30 °C.

Table I
Summary of Dielectric Results

T, °C	$d(n^2 - n_1^2)/dw$	$d(\epsilon - \epsilon_1)/dw$	$\langle \mu^2 \rangle / nm^2$
30	0.066	1.01	0.355
40	0.070	1.01	0.373
50	0.076	1.01	0.390
60	0.082	1.01	0.408

Table II
Experimental Dipole Moment Ratios and Their Temperature Coefficients for Different Members of the Polyoxetane Series

polymer	$\langle \mu^2 \rangle / nm^2$	10^3d ln $\langle \mu^2 \rangle / dT$
POx[a]	0.42	0.1
P3MOx[b]	0.35	2.7
P2MOx	0.35	4.5
PDMOx[c]	0.21–0.25	2.4–4.1

[a] References 8 and 11. [b] Reference 7. [c] References 9 and 10.

In Table II and for comparative purposes the experimental values of $\langle \mu^2 \rangle / nm^2$ and d ln $\langle \mu^2 \rangle / dT$ for the members of the polyoxetane series are shown. It can be seen that POx exhibits the higher dipole moment ratio and PDMOx the lower; the dipole moments of asymmetric polyoxetanes are intermediate to those of POx and PDMOx and they do not show a noticeable dependence on the location of the methyl group.

Theoretical Analysis of the Dipole Moments. Whenever the molecular chains present centers of symmetry (planes, axis, or points), the dipole moments determined in nonpolar thermodynamically good solvents coincide with the unperturbed values.[18-22] However, the dipole moments associated with each COC group of P2MOx forms a small angle with the line bisecting the skeletal COC angle owing to inductive effects of the methyl group and, consequently, the dipole moments of the chains should present excluded volume effects that presumably are smaller than in poly(oxypropylene) (POP).[18] Studies

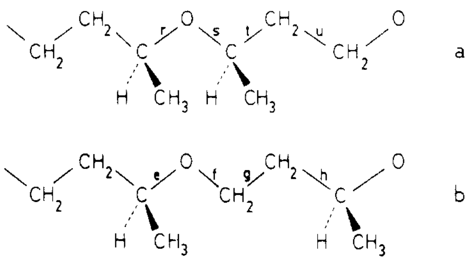


Figure 4. Isotactic head-to-head (a) and head-to-tail (b) dyads.

carried out in the latter polymer have shown that these effects as well as local solvent effects are relatively small when the dielectric measurements are carried out in nonaromatic solvents.[18,23] We have assumed that the dipole moments of P2MOx determined in cyclohexane do not differ significantly from the unperturbed values and have ignored any contribution from the methyl dipole.

As was stated above, the ring-opening polymerization of 2-methyloxetane gives rise to hh, ht (or th), and tt dyads. The number of skeletal bonds separating two consecutive asymmetric carbons is an even number that ranges from two skeletal bonds for hh dyads to six for tt dyads. If the chain is placed in an all-trans configuration for isotactic P2MOx, the methyl groups are thus located on the same side of the plane, whereas for the syndiotactic configuration they are located alternatively above and below the plane. For hh dyads the methyl groups suffer conformational congestions that severely reduce the conformational phase space. As can be observed in Figure 4a, where an isotactic dyad of this kind is shown, bonds of type r are restricted to g^+ conformations, whereas skeletal bonds of type s can only be in trans conformation provided that the preceding skeletal bond is in g^+ conformation. Gauche rotations of positive sign about skeletal bonds of type t cause interactions between CH_2 groups and O atoms separated by three skeletal bonds. The energy E_β of these interactions in POx may be -0.4 kcal mol^{-1} (with respect to the trans), which is similar to that found for P3MOx and somewhat higher than that reported for PDMOx.[10] As for g^- rotations that place an oxygen atom between a methylene and a methyl group, earlier studies carried out in P3MOx[7] suggest that the energy E_α of these states should be somewhat higher than that for the alternative gauche states. In view of the uncertainties of these energies, the calculations were carried out for different sets of values of E_α and E_β. Gauche states of positive sign about skeletal bonds of type u gives rise to pentane-type interferences between an oxygen atom and a methyl group; the energy E_ω of the second-order interactions was considered to be[8] 0.47 kcal mol^{-1}. A pair of gauche rotations of different sign about bonds of type tu cause O···O interactions, the energy $E_{\omega'}$ of which was considered to be[10] 2.1 kcal mol^{-1}.

The statistical weight matrices associated with the skeletal bonds r to u can be expressed in a 3 × 3 rotational state scheme by

$$\mathbf{U}_r = \begin{bmatrix} 0 & 1 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 0 \end{bmatrix}, \quad \mathbf{U}_s = \begin{bmatrix} 0 & 0 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$$

$$\mathbf{U}_t = \begin{bmatrix} 1 & \beta & \alpha \\ 0 & 0 & 0 \\ 1 & 0 & \alpha \end{bmatrix}, \quad \mathbf{U}_u = \begin{bmatrix} 1 & \beta\omega & \beta \\ 1 & \beta & \beta\omega' \\ 1 & \beta\omega' & \beta\omega \end{bmatrix}$$

For illustrative purposes the conformational energies associated with the different states of each skeletal bond of the isotactic ht dyad, shown in Figure 4b, are briefly described. Gauche states of positive sign about skeletal bonds of type e have an energy[8] $E_{\sigma''} = 1.2$ kcal mol^{-1} above the alternative trans states; g^- rotations about these bonds that would place a CH_2 group between a methyl and a methylene group should be completely disfavored with respect to the alternative gauche rotation. Gauche rotations of positive sign about bonds of type f give rise to pentane-type interferences between a methyl and a methylene group and, therefore, were considered to be suppressed; however, g^- states about these bonds have the same energy that g^+ states about skeletal bonds of type e. The energies for the other conformational states of the other skeletal bonds of the dyad can easily be derived from the information given above for the hh dyad. Accordingly, the statistical weight matrices for the skeletal bonds e to h of the ht dyads are

$$\mathbf{U}_e = \begin{bmatrix} 1 & \sigma'' & 0 \\ 1 & \sigma'' & 0 \\ 1 & 0 & 0 \end{bmatrix}, \quad \mathbf{U}_f = \begin{bmatrix} 1 & 0 & \sigma'' \\ 1 & \sigma'' & 0 \\ 1 & 0 & 0 \end{bmatrix}$$

$$\mathbf{U}_g = \begin{bmatrix} 1 & \beta & \beta\omega \\ 0 & 0 & 0 \\ 1 & 0 & \beta\omega \end{bmatrix}, \quad \mathbf{U}_h = \begin{bmatrix} 1 & \alpha & \beta \\ 1 & \alpha\omega & \beta\omega' \\ 1 & \alpha\omega' & \beta \end{bmatrix}$$

Table III
Influence of the Conformational Energies E_α and E_β[a] on the Dipole Moment Ratio and Its Temperature Coefficient at 30 °C

$-E_\alpha$	$-E_\beta$	$\langle\mu^2\rangle/nm^2$	$10^3 d \ln \langle\mu^2\rangle/dT$
0.42	0.66	0.35	2.3
0.42	0.56	0.38	1.9
0.32	0.56	0.39	1.8
0.42	0.42	0.41	1.5
0.36	0.42	0.42	1.4

[a] E_α and E_β are expressed in kcal mol^{-1}.

Values of the dipole moment ratio were theoretically calculated at 30 °C by the usual methods.[24,25] For simplicity, the skeletal bond angles were assumed to have a value of 110° and the rotational states were assumed to be located in perfectly staggered positions. Monte Carlo techniques were used to generate chains representative with regard to both bond scissions of the monomer ring and stereoregularity of the chains. Preliminary calculations showed that the dipole moments are not very sensitive to the atomic configuration *d* or *l* of the asymmetric carbon, in concordance with what occurs in other asymmetric polymers in which the asymmetric carbons are separated by more than three skeletal bonds.[26] In any case, the calculations were performed for perfectly heterotactic polymers, assuming that bond scissions on the monomer ring take place preferentially through the C–O bond (bond i) located farther away from the methyl group. Monte Carlo methods were used to generate chains in which the dyad composition was similar to that obtained by ^{13}C NMR spectroscopy (P(ii) = 0.40, P(ij) = P(ji) = 0.18, P(jj) = 0.24). Values of the dipole moment ratio, shown in the third column of Table III, were obtained by using the set of values of E_α and E_β given, respectively, in the first and second columns of the table. The calculations show that the polarity of these chains is only moderately dependent on the values of E_α and E_β, in sharp contrast with P3MOx, where a great dependence was found.[7] Thus for $E_\alpha = -0.42$ and $E_\beta = -0.66$ (both in kcal mol^{-1}), $\langle\mu^2\rangle/nm^2 = 0.35$; this value only changes to 0.42 when the values of E_α and E_β

increase to –0.36 and –0.42 kcal mol^{-1}, respectively.

An increase in temperature causes a decrease in the $g^{\pm}g^{\pm}$ conformations about two consecutive C–C skeletal bonds and, consequently, the dipole moments of the chains increase. Values of the temperature coefficient as a function of E_α and E_β are given in the fourth column of Table III. It can be seen that in increasing E_α and E_β from –0.42 and –0.66, respectively, to –0.36 and –0.42, the value of $10^3 d \ln \langle \mu^2 \rangle / dT$ decreases from 2.3 to 1.4.

The best agreement between the calculated values of both the dipole moment ratio and its temperature coefficient with the experimental ones ($\langle \mu^2 \rangle / nm^2 = 0.35$ and $10^3 d \ln \langle \mu^2 \rangle / dT = 4.5$ at 30 °C) is obtained for the values of E_α and E_β given in the first row of Table III. The relatively low values of these conformational energies suggest that in this polymer, as in the other members of the polyoxetane series, particular effects stabilizing gauche conformations about C–C skeletal bonds are important.

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Registry No. 2-Methyloxetane, 2167-39-7; poly(2-methyloxetane) (homopolymer), 26100-60-7.

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Ring-Opening Reactions of a Bicyclic Aziridine in Polymeric Medium

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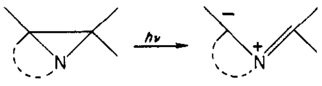
ABSTRACT: Upon irradiation above 290 nm, bicyclic aziridines give an ylide intermediate whose stability depends on the structure of the aziridine. The photolysis of 2,2-dimethyl-4-phenyl-6-(*p*-nitrophenyl)-1,3-diazabicyclo[3.1.0]hex-3-ene (DNBH) has been studied in solution and in a polymer matrix. In solution the quantum yield of enediimine formation, Φ_I, increases with temperature ($\Phi_I \cong 0.3$ at 35 °C). In poly(methyl methacrylate), $\Phi_I = 0.75$ above its T_g, while $\Phi_I = 0.3$ below T_g. Ylide fading, i.e., ylide cyclization into bicyclic aziridine and/or ylide isomerization into enediimine, is about 10 times slower in polymeric medium as compared to the solution and does not obey first-order kinetics. Consequently, the behavior in polymeric medium differs considerably from that in solution with respect to the rate of reaction and the relative importance of enediimine formation.

It has been shown by Trozzolo and co-workers[1] that the photolysis of bicyclic aziridines involves a C–C bond scission with the formation of a colored azomethine ylide intermediate[2]



In this respect the bicyclic aziridine 2,2-dimethyl-4-phenyl-6-(*p*-nitrophenyl)-1,3-diazabicyclo[3.1.0]hex-3-ene (DNBH) is particularly attractive.[3] On irradiation above 290 nm in the crystalline state and in the glassy state, it develops a transient blue color due to ylide formation; this color change is reversible. On the basis of trapping experiments with dimethyl acetylenedicarboxylate and tetracyanoethylene as dipolarophiles, Trozzolo showed[4] that the ylide resulting from the photolytic disrotative ring cleavage first isomerizes into the syn-4-ylide, which may then give a cycloadduct and either return back to the initial compound or isomerize into enediimine. Moreover, the formation of two isomeric ylides was easily shown by the presence of two absorption maxima in the visible spectrum after photolysis at low temperature.[5] This enediimine formation is similar to that described by Padwa and Glazer[6] in the case of the 2,4,6-triphenyl-1,3-diazabicyclo[3.1.0]hex-3-ene.

The scheme shown in Figure 1 summarizes this photolytic and thermal behavior of DNBH.[7] Although a thermal

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