Conformational Studies on Cycloaliphatic Polyethers Obtained by Ring-Opening of Bicyclic Ethers

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Received January 3, 1990

ABSTRACT: Poly(*trans*-7-oxabicyclo[4.3.0]nonane) (PTOXN) was synthesized by cationic polymerization of *trans*-7-oxabicyclo[4.3.0]nonane) (TOXN). The analysis of the ^1H and ^{13}C NMR spectra of the polymer suggests that the scission of the monomer ring occurs at the O–CH$_2$ bond. The values of the dipole moment ratio $\langle \mu^2 \rangle / nm^2$ and its temperature coefficient amount to 0.63 and 1.52×10^{-3} K^{-1}, respectively, at 30 °C. Rotations about the C_{Cy}–O and C_{Cy}–CH$_2$ bonds, flanking the cyclohexylene group, give rise to severe interactions between neighbor methylene groups. Semiempirical potential calculations indicate that the C_{Cy}–O bond is restricted to a single rotational state (either g^- or g^+), this rotational state being dependent on the location of the neighbor C_{Cy}–CH$_2$ bond. In general, the rotational isomeric state model gives a good account of the dielectric conformation-dependent properties of the polymer.

Introduction

Owing to the simple structure of linear polyethers with the structural unit $(CH_2)_m$–O–, the study of the conformation-dependent properties of these chains as a function of the number of methylene groups in the repeat unit has been important to obtain quantitative information on the conformational energies associated with different rotational states in polyoxides in general.[1–6] The introduction of cyclohexane rings in these chains gives rise to the family of cycloaliphatic polyoxides whose physical properties may not only depend on the chain length separating two consecutive cycloaliphatic groups but also may be conditioned by the type of hydrogen atoms substituted (equatorial–equatorial or equatorial–axial) in the cyclohexane rings. For example, the physical properties of the cis (eq–ax substitution) and trans (eq–eq substitution) isomers of poly(1,4-cyclohexanedimethanol-*alt*-formaldehyde) are significantly different.[7] Thus poly(*trans*-1,4-cyclohexanedimethanol-*alt*-formaldehyde) (PCCDO) is a crystalline polymer with a melting point in the vicinity of 80 °C, whereas poly(*cis*-cyclohexanedimethanol-*alt*-formaldehyde) (PTCDO) is amorphous. However, the polarity of the chains is low for both isomers as a consequence of the fact that a high preference for $g^{\pm}g^{\pm}$ conformations is exhibited for the CH$_2$O–CH$_2$–OCH$_2$ oxymethylene sequences, which place the dipole moments in an almost antiparallel direction.[8]

Conformational interactions among the atoms of the two moieties attached to the cyclohexane ring are not important for polymers in which the substitution takes place in the 1,4 positions. However, this may not be the case for polyethers in which the attachment of the chains to the cyclohexane ring occurs in neighboring positions. This work addresses the investigation of these interactions by studying the dependence of the polarity of poly(*trans*-7-oxabicyclo[4.3.0]nonane) (PTOXN) on the relative population of conformational states around the C_{Cy}–CH$_2$ and C_{Cy}–O bonds flanking the cyclohexylene groups.

Experimental Section

Materials. *trans*-7-Oxabicyclo[4.3.0]nonane (TOXN) was prepared by following the synthetic route indicated in Scheme I as described by Kops et al.[9] The monomer was purified by fractional distillation, dried over calcium hydride, and distilled several times onto sodium mirrors. Acetyl chloride was distilled in an inert atmosphere immediately before use. Silver hexafluoroantimonate was purified by the method described elsewhere.[5]

Ring-Opening Polymerization. The bulk cationic polymerization of TOXN was carried out at –30 °C under vacuum by using acetyl hexafluoroantimonate as initiator. The initiator was prepared in situ by reaction of equimolar amounts of silver hexafluoroantimonate and acetyl chloride. The initiator concentration was 2.6×10^{-2} mol L^{-1}. In order to eliminate the low molecular weight species, the polymer was precipitated several times with methanol and finally dried in vacuo at 25 °C.

Characterization of the Polymer. The number-average molecular weight of PTOXN was measured in chloroform at 30 °C with a Knauer vapor pressure osmometer, and its value was 9500. The ^1H and ^{13}C NMR spectra were registered on a Varian XL-300 operating at 300 (^1H) and 75.4 MHz (^{13}C), using deuterated chloroform and *o*-dichlorobenzene as solvents and Me$_4$Si as internal standard.

Dielectric Measurements. Values of the dielectric constant ϵ of solutions of PTOXN in benzene were measured at several temperatures with a capacitance bridge (General Radio, Type 1620 A) and a three-terminal cell at 10 kHz. The dielectric results were expressed in terms of the increments in dielectric constant of the solution with respect to that of the solvent ($\Delta\epsilon = \epsilon - \epsilon_1$) and plotted as a function of the weight fraction w of polymer. $\Delta\epsilon$ was, within experimental error, a linear function of w, and from the slope of the plots in the limit $w \rightarrow 0$, the values of $d\epsilon/dw$ indicated in the third column of Table I were determined. Values of the increments in refractive index n of the solutions with respect to that of the solvent ($\Delta n = n - n_1$) were also plotted as a function of w. From the slopes of the plots the values of $2n_1\, dn/dw$ presented in the second column of Table I were obtained.

Results and Discussion

The ^1H NMR spectrum of PTOXN presents a complex spectral pattern due not only to the normal couplings among the different protons of the structural unit but also to the stereoregularity of the polymer and to the magnetic nonequivalence of the aliphatic methylene protons. In fact, the OCH$_2$–CH$_2$–cyclohexane residue can be considered like 1,2-disubstituted ethanes and therefore gives rise to an AA′BB′ resonance system. As can be seen in Figure 1, the resonance signals of the oxymethylene protons appear as multiplets in the range 3.2–3.8 ppm. The multiplets must be attributed to the two stereostructures shown in Figure 2. The equivalence of the areas of both multiplets suggests

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0024-9297/90/2223-3573$02.50/0

Scheme I

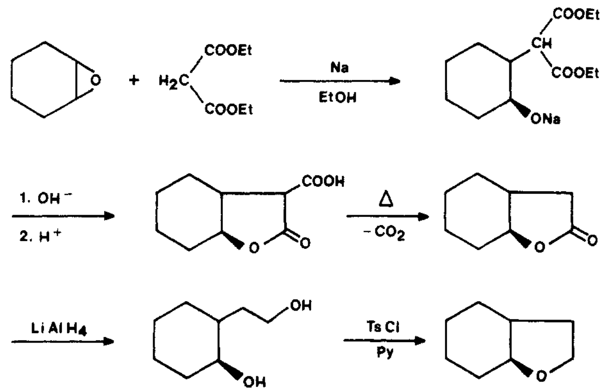

Table I
Summary of Experimental Dielectric Results

T, °C	$2n_1\,dn/dw$	$d\epsilon/dw$	$\langle\mu^2\rangle/nm^2$
30	0.021	1.228	0.632
40	0.029	1.169	0.636
50	0.027	1.132	0.646
60	0.026	1.098	0.660

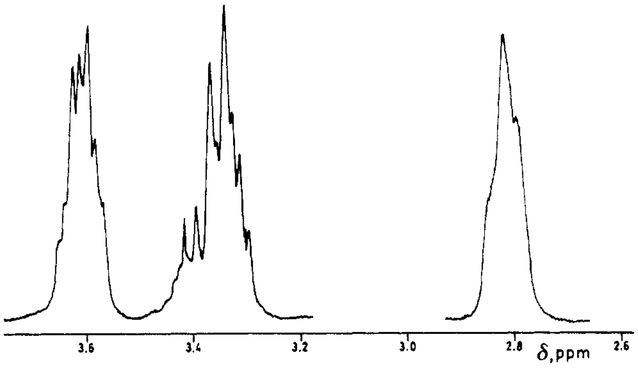

Figure 1. ^1H NMR spectrum of poly(*trans*-7-oxabicyclo[4.3.0]-nonane) (PTOXN).

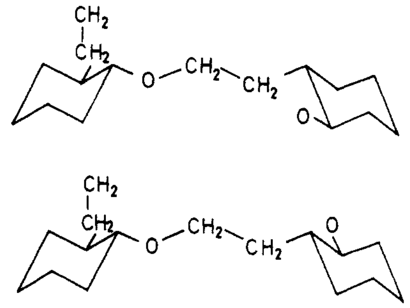

Figure 2. Stereostructures of poly(*trans*-7-oxabicyclo[4.3.0]-nonane) (PTOXN).

that there is not stereochemical preference in the propagation reaction. However, this result should not lead to the conclusion that an ideal atactic polymer will be obtained at any temperature; in fact, the low ceiling temperature of PTOXN (T_c = 12 °C)[9] limits the polymerization to a very narrow interval of temperature, thus precluding the possibility of reaching any reliable conclusion regarding the influence of temperature on the stereoregularity of the polymer.

The methine proton produces a multiplet centered at ca. 2.8 ppm, which confirms the results obtained at Kops et al.[9] in the sense that the spectrum is consistent with a polymer structure originated by polymerization of the monomer without inversion of configuration, indicating that the scission of the ring occurs at the O–CH_2 bond.

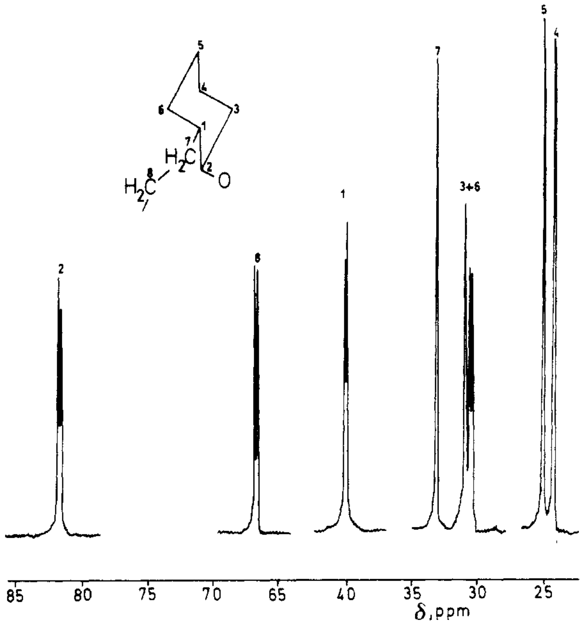

Figure 3. ^{13}C NMR spectrum of poly(*trans*-7-oxabicyclo[4.3.0]-nonane) (PTOXN).

The assignment of the ^{13}C NMR signals corresponding to the different carbons of the TOXN structural unit is indicated in Figure 3, where the spectrum obtained in *o*-dichlorobenzene solution at room temperature is shown. The methylene carbons labeled as 5, 4, 3, and 7 appear as singlets, whereas the other carbons give rise to two resonance signals of approximately the same intensity, assigned to the resonance of the corresponding carbons in the two stereodiads. The splitting in the resonance signals cannot be attributed to configurational changes in the cyclohexane ring because the differences in chemical shifts are very small. In conclusion, the cationic polymerization of TOXN occurs without inversion of configuration of the substituents in the cyclohexane ring and the polymer obtained seems to be ideally atactic.

Values of the mean-square dipole moment $\langle\mu^2\rangle$ were obtained as usual from the equation of Guggenheim[10] and Smith[11]

$$\langle\mu^2\rangle = \frac{27kTM}{4\pi\rho N_A(\epsilon + 1)^2}\left(\frac{d\epsilon}{dw} - 2n_1\frac{dn}{dw}\right)$$

where k is the Boltzmann constant, N_A is Avogadro's number, T is the absolute temperature, M is the molecular weight of the solute, and ρ is the density of the solvent. The experimental results were expressed in terms of the dipole moment ratio $\langle\mu^2\rangle/nm^2$, where n is the number of skeletal bonds of the chains and m is the average value of the dipole moment associated with each skeletal bond. In the evaluation of m it was assumed that m_{C-O} = 1.07 D and m_{C-C} = 0 D.[2,12] Values of the dipole moment ratio at different temperatures are given in the fourth column of Table I. The uncertainty of these quantities was estimated to be ±5%. As can be seen in Table II the values of $\langle\mu^2\rangle/nm^2$ and its temperature coefficient for PTOXN chains are somewhat larger than those obtained for other polyoxides such as poly(ethylene oxide) (POE),[1] poly(tetramethylene oxide) (PTMO),[13] and poly(hexamethylene oxide) (PHMO).[3]

A portion of the chain in an arbitrary conformation of reference is shown in Figure 4. An analysis of molecular models suggests that rotations about bonds of type a and c should give rise to strong interactions between the atoms of the moieties flanking the cyclohexylene group. Con-

Table II
Experimental Values of the Dipole Moment Ratio and Its Temperature Coefficient for Poly(oxyethylene) (POE),[1] Poly(oxytetramethylene) (PTMO),[3] Poly(oxyhexamethylene) (PHMO),[3] and Poly(*trans*-7-oxabicyclo[4.3.0]nonane) (PTOXN) at 30 °C

polymer	$\langle\mu^2\rangle/nm^2$	10^3 d ln $\langle\mu^2\rangle$/dT, K^{-1}
POE	0.53	1.7
PTMO	0.51	1.8
PHMO	0.54	1.2
PTOXN	0.63	1.5

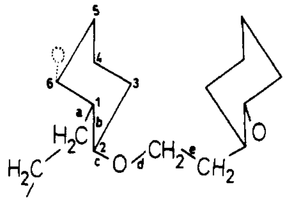

Figure 4. A fragment of poly(*trans*-7-oxabicyclo[4.3.0]nonane) (PTOXN) in an arbitrary reference conformation.

formational energies were calculated as a function of the rotational angles associated with bonds of type a (Ψ_a) and c (Ψ_c) by assuming that the potential energy involves three contributions: (a) torsional energies, which were evaluated by using threefold intrinsic potentials with barrier heights[2,5] of 2.8 and 1.8 kcal mol^{-1}, respectively; (b) van der Waals interactions, which were calculated by means of the Lennard-Jones potential $V_{ij} = (a_{ij}/r_{ij}^{12}) - (c_{ij}/r_{ij}^{6})$, where the London dispersion parameter c_{ij} was obtained from the Slater–Kirkwood[13,14] equation by utilizing the van der Waals radii, effective number of electrons, and polarizabilities given elsewhere[5] (the repulsive term a_{ij} was assigned as to minimize the potential V_{ij} for a given pair of atoms when the distance r_{ij} is set equal to the sum of the corresponding van der Waals radii); (c) Coulombic interactions which were obtained by assigning partial charges to the oxygen ($\delta_O = -0.31$) and carbon ($\delta_C = 0.155$) atoms joined to the C–O bond.

The molecular fragment indicated in Figure 4 was used to evaluate energies associated with rotations around the a and c skeletal bonds. The calculations were performed by keeping the rest of the bonds in a trans conformation. Interactions between atoms were obtained by assuming that the bond angles all have values of 110° and the bond lengths are 1.53, 1.43, and 1.09 Å for C–C, C–O, and C–H, respectively. As can be seen in Figure 5, a minimum is reached for values of $\Psi_{a(g^+)} = 140°$ and $\Psi_{c(g^-)} = 210°$ which is more than 2 kcal mol^{-1} below the energies corresponding to the alternative conformational states. Consequently, it was assumed that bonds of type c are restricted to the g$^-$ conformation, whereas bonds of type a are in the t, g$^+$, and g$^-$ conformations, the energies of the g$^+$ and g$^-$ conformational states, E_{σ_α} and $_{\sigma_\beta}$ being expected to be negative and positive, respectively, with respect to that of the alternative trans state. In fact, the semiempirical potential calculations suggest that the values of E_{σ_α} and E_{σ_β} should be about 2 and 1 kcal mol^{-1} below and above, respectively, the energy of the trans states. Bonds of type d are restricted to t and g$^+$ states, because rotations of the same sign about two consecutive c,d bonds give rise to strong interactions between aliphatic and cycloaliphatic methylene groups, and consequently, these conformations were considered to be forbidden; in any case, semiempirical potential calculations suggest that g$^\pm$g$^\mp$ should have an energy E_γ ca. 1–2 kcal mol^{-1} above that of the corresponding tg$^+$ conformation. Finally, gauche states about bonds of type e were considered to have the same energy as the alternative trans states. It should be pointed out that for bonds of type d and e the rotational states were assumed to be located at 0, ±110°. If the substitution were 1,6 instead of 1,2 in Figure 4, the minimum potential would correspond to $\Psi_{a(g^-)} = -140°$ and $\Psi_{c(g^+)} = 150°$ for a and c bonds, respectively; consequently, the conformations preferred for the rest of the skeletal bonds would change accordingly.

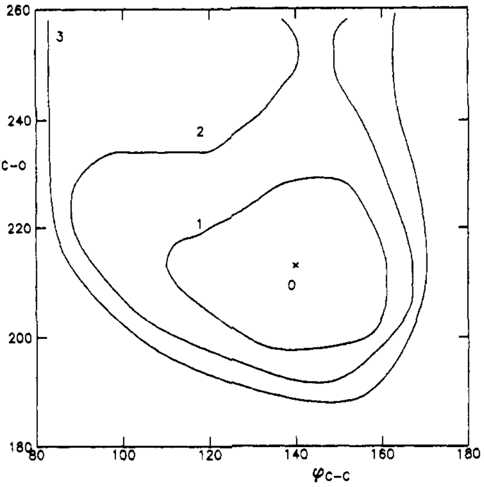

Figure 5. Calculated energy contours as a function of rotation over bonds like a and c in Figure 4. Energies are labeled in kcal mol^{-1} and referred to the local minimum of the g$^\pm$g$^\mp$ conformation.

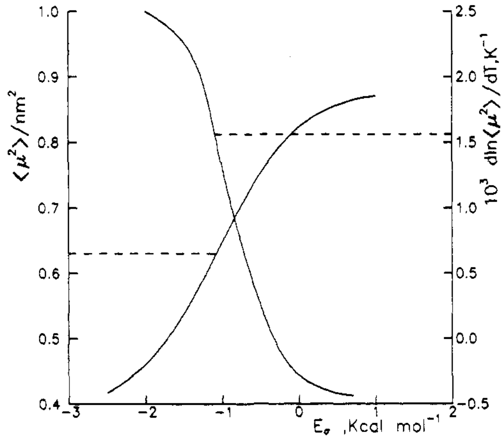

Figure 6. Dependence of the dipole moment ratio and its temperature coefficient at 30 °C on E_{σ_α} for poly(*trans*-7-oxabicyclo[4.3.0]nonane) (PTOXN). See text for details.

With the standard conventions concerning Cartesian coordinate systems, the matrix required to transform the coordinate systems from reference frame b to a for the 1,2 substitution will require adding 120° to the rotational angles of a and c whereas $\Psi = 120°$ for the b bond; if the substitution is 1,6, the angle to add would be −120° and the angle Ψ corresponding to the b bond would be −120°. Theoretical calculations of the dipole moment were carried out by using standard matrix multiplication methods described in detail elsewhere.[1] In addition, it was considered that 50% of the substitutions are in 1,2 positions and another 50% in 1,6 positions, randomly distributed. Values of the dipole moment ratio as a function of E_{σ_α} are shown in Figure 6, where it can be seen that $\langle\mu^2\rangle/nm^2$ decreases as E_{σ_α} decreases; these results were computed assuming E_{σ_β} = 2 kcal mol^{-1} and E_γ = 1 kcal mol^{-1}. Agreement between the theoretical and experimental values of the dipole moment ratio are found for $E_{\sigma_\alpha} \approx -1$ kcal mol^{-1}. The theoretical calculations also suggest that the temperature coefficient should be positive, though its value (0.3×10^{-3} K^{-1}) for $E_{\sigma_\alpha} \approx -1$ kcal mol^{-1} is somewhat lower than the experimental result (1.52×10^{-3} K^{-1}, presumably as a consequence of small errors in the measurements of $\langle \mu^2 \rangle / nm^2$ that can affect in a significant way the value of the temperature coefficient.

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Registry No. PTOXN, 75995-49-2.

High-Resolution Solid-State Carbon-13 Nuclear Magnetic Resonance Study of Chitin

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Received September 27, 1989

ABSTRACT: High-resolution ^{13}C cross-polarization magic-angle spinning (CPMAS) NMR spectra have been acquired from a variety of solid chitin samples. Spectra of highly crystalline β-chitin contain peaks that have remarkably narrow line widths. Single lines can be assigned to all the chemically distinct carbon atoms of the chitin repeat, except for the carbonyl and the C2, which give rise to asymmetric doublets. These doublets arise from the failure of magic-angle spinning (MAS) to remove the dipolar interactions occurring between these carbon atoms and the directly bonded quadrupolar ^{14}N nucleus. The single lines, assigned to the remaining carbon atoms, are consistent with a proposed crystal structure of the β polymorph. Spectra from at least three different forms of β-chitin have been identified. The differences between these three forms are a consequence of the differing states of hydration of the β polymorph. Spectra of several highly crystalline forms of β-chitin serve as reference spectra when interpreting the more complex spectra acquired from less ordered samples. The spectra of α-chitin, presented here, contain broad lines and show distinct peak asymmetries. This makes it difficult to interpret spectra, to measure accurate values of chemical shifts, and to make useful comparisons between spectra of the α- and β-chitin polymorphs. ^{13}C relaxation rates for the C6 carbon are large relative to the other chemically distinct carbon atoms in chitin of low crystallinity. This difference in relaxation rate is particularly marked in α-chitin.

Introduction

^{13}C cross-polarization magic-angle spinning (CPMAS) NMR has proved useful in studies of the structure and packing of molecules in the solid state.[1-5] A good example of the use of these techniques is provided by two crystalline native cellulose samples, *Valonia* and tunicin, which gave distinct NMR spectra.[6,7] ^{13}C CPMAS spectra are also useful in studying samples that are either heterogeneous or poorly crystalline since NMR signals can be observed from both crystalline and amorphous domains. The appearance of starch spectra, for example, depends on the degree of sample crystallinity and on the nature of the starch polymorph.[8] In this study we have used ^{13}C CP-MAS spectroscopy together with X-ray diffraction to investigate the structure of a number of chitin samples of

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0024-9297/90/2223-3576$02.50/0