Random-coil configurations of alicyclic polyformals

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A sample of poly (*trans*-1,4-cyclohexylene-dimethylene-oxymethylene oxide) (PTCDM) was synthesized by condensation of *trans*-1,4-cyclohexane dimethanol and paraformaldehyde using *p*-toluene sulphonic acid as catalyst. A fraction having $M_n = 6500$ and a melting point of 86°C was isolated and purified; its n.m.r. spectrum does not change with temperature in the range 20°–50°C which indicates a rigid distribution of methylene substituents in the cyclohexane ring; its dipole moment, measured in benzene solution at several temperatures between 20° and 60°C, yielded values of $D_n = \{\mu^2\}/\mathrm{nm}^2 = 0.17$–0.21 and a temperature coefficient $\mathrm{d}\ln\{\mu^2\}/\mathrm{d}T = 5.5 \times 10^{-3}\ \mathrm{K}^{-1}$, similar to those reported in the literature for acyclic polyformals. Agreement between experimental and calculated (using rotational isomeric states theory) values is satisfactory.

INTRODUCTION

Configuration-dependent properties of acyclic polyformal chains with the repeating unit $CH_2-O-(CH_2)_y$-O- have been investigated by Mark and one of the present authors[1-3]. Comparisons among dipole moments of the polyformals with $y = 1, 2, 4, 5$ and 6 were used to analyse the influence of the non-polar sequences on the angular correlations between the polar regions which they separate within the chains. An important conclusion which can be drawn from these studies is that the acyclic polyformals, which may be regarded as alternating copolymers of oxymethylene and oxyalkylene units, are similar to poly(oxymethylene) as far as their dipole moments are concerned. Their molecular dimensions, however, are similar to those of related poly(oxyalkylene) chains[4]. The manner in which the properties of polyformals vary with structure, especially when an alicyclic group is introduced into the repeating unit, is of particular interest.

Acyclic polyformals with $y > 1$ have relatively low melting points (<60°C [5,6]). However, the polyformals of the alicyclic diols in general have higher melting points than any previously reported for acyclic polyformals. For example, those of the tetramethyl cyclobutanediol polymers are unusually high (about 280° to 290°C under nitrogen[7]).

The present investigation focusses on the dipole moments of the polyformals synthesized from *trans*-1,4-cyclohexane dimethanol. The experimental results are interpreted in terms of the rotational isomeric state theory of chain configurations. They are compared with the corresponding results obtained on acyclic polyformals in order to determine whether the presence of an aliphatic ring in the structural unit causes a significant decrease in the angular correlation between the polar sequences in the chain.

EXPERIMENTAL

Materials

Trans-1,4-cyclohexane dimethanol (Eastman–Kodak) was purified by two successive crystallizations in diethyl ether. The melting point of the purified product was 65°C (literature value, 67°C [7]). The purity of the alicyclic diol was also checked by n.m.r. spectroscopy. Benzene (Merck) had a purity exceeding 99% as received; it was further purified by means of Linde 4A molecular sieves. Both paraformaldehyde and *p*-toluene sulphonic acid were used as received.

Polymerization

Poly(*trans*-1,4-cyclohexylene-dimethylene oxymethylene oxide) (PTCDM) was obtained by condensation polymerization of *trans*-1,4-cyclohexane dimethanol and paraformaldehyde. The reaction was carried out for 48 h under dry nitrogen in refluxing benzene, using *p*-toluene sulphonic acid (~1%) as catalyst. Water was removed in a Dean–Stark distillation trap. The polymer was precipitated into methanol, filtered and washed several times with distilled water to eliminate the catalyst. It was then dissolved in benzene, precipitated into methanol and dried in a high vacuum line at room temperature.

Characterization

The polymer was fractionated at 25°C using chloroform–methanol as the solvent–non-solvent system. Only the first fraction, which amounted to about 30% of the total polymer, was used in the dielectric measurements. The number-average molecular weight of the fraction, determined with a Knauer vapour pressure osmometer, was 6500. The melting point of the fraction was determined in a Perkin–Elmer calorimeter model

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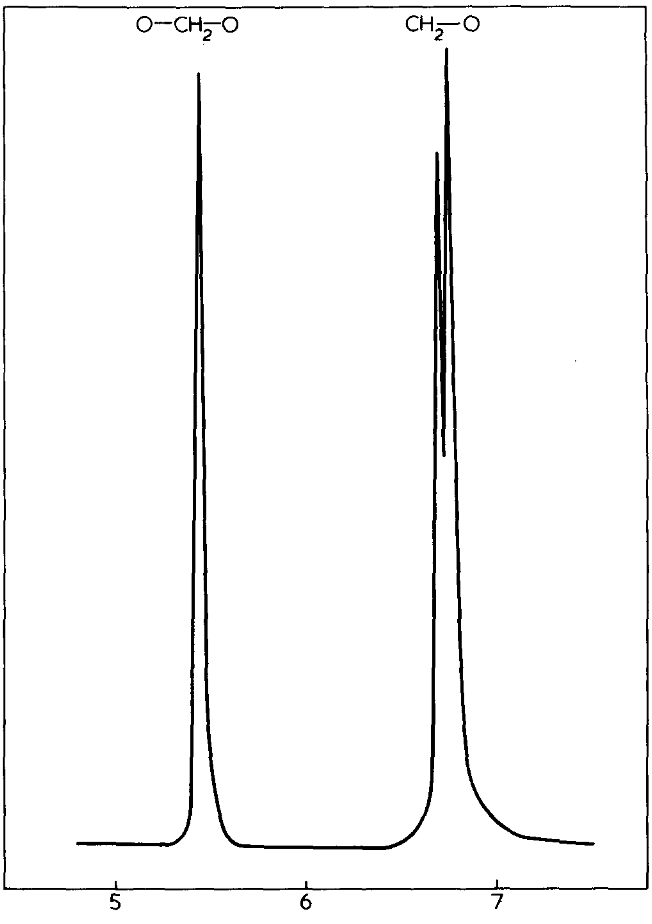

Figure 1 N.m.r. spectrum of the PTCDM chain in deuterated chloroform, T = 20°–50°C, see text

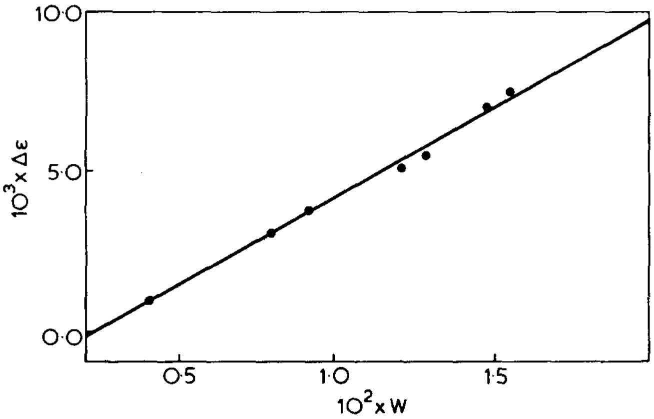

Figure 2 Dielectric constant increment against *w*, the weight fraction of polymer, T = 20°C

DSC-1B, at a heating rate of 8°C min^{-1}; a value of 86°C was found (literature value, 83°–86°C[7]).

Nuclear magnetic resonance spectra of the fraction were obtained using a Varian XL-100 A spectrometer at 20°, 40° and 50°C, using deuterated chloroform as solvent. The spectrum of the polymer (*Figure 1*) is the same for all temperatures in the range 20° to 50°C, indicating that the spatial distribution of methylene substituents in the cyclohexane is rigid, at least over the range of temperature studied. *Figure 1* shows a doublet resonance peak (τ = 6.7–6.8) of the protons of the 1,4-substituent methylene groups and the single resonance peak ($\tau \sim 5.5$) of the protons of the acetal groups.

Dielectric constants and refractive indices

The sample used in the dielectric measurements was freeze-dried in benzene to eliminate any remaining low molecular weight material. Measurements of dielectric constant in benzene solution were carried out using a capacitance bridge (General Radio, type 1620A) and a three terminal platinum cell[8,9]. All the measurements were made at a frequency of 10 kHz. At this frequency, the real part of the complex dielectric permittivity is to a good approximation the static value. The refractive indices of the solutions were measured at 546 nm using a Brice–Phoenix differential refractometer.

RESULTS

The dipole moments of the PTCDM chains were obtained by means of the Guggenheim–Smith equation[10]:

$$\langle\mu^2\rangle=\frac{27kTM}{4\pi N_A\rho_1(\varepsilon_1+2)^2}\left[\frac{\mathrm{d}(\varepsilon-\varepsilon_1)}{\mathrm{d}w}-\frac{\mathrm{d}(n^2-n_1^2)}{\mathrm{d}w}\right] \quad (1)$$

in which $\langle\mu^2\rangle$ is the mean-square dipole moment, N_A is the Avogadro number, k is the Boltzmann constant, M is the molecular weight of the polymer, ρ_1 is the density of the solvent and ε_1 and n_1 are the low-frequency dielectric permittivity and the refractive index of the solvent, respectively. The experimental derivatives $\mathrm{d}(\varepsilon-\varepsilon_1)/\mathrm{d}w$ were, within experimental error, insensitive to temperature in the range 20° to 60°C. A plot showing the concentration dependence of the increment in dielectric constant is indicated in *Figure 2*. The experimental values of $\Delta n^2=n^2-n_1^2$ are negligible in the temperature interval studied. The molecular weight of the repeating unit (M_0 = 156 g mol^{-1}) was used instead of M in equation (1); and therefore the dipole moment per repeating unit ($\mu_{\mathrm{eff}}=\langle\mu^2\rangle/x$, where x is the number of repeating units in the chain) was obtained; these results were expressed as the dipole moment ratio $D_n=\langle\mu^2\rangle/nm^2(=\mu_{\mathrm{eff}}/7m^2)$ where $n=7x$ is the number of skeletal bonds (we take the repeating unit as having 6 real bonds and a virtual bond connecting positions 1,4 in the cyclohexane ring as shown in *Figure 3*). The average m^2 of the skeletal bond moments was calculated from $m^2=(1/7)(4m_{\mathrm{CO}}^2+2m_{\mathrm{CC}}^2+m_{\mathrm{C}_y\mathrm{C}_y}^2)$. The following values of the bond dipole moments were used $m_{\mathrm{CO}}=1.07$ D[11,12], $m_{\mathrm{CC}}=0.00$ D[11,12] and $m_{\mathrm{C}_y\mathrm{C}_y}=0.00$ D[12] where $\mathrm{C}_y\mathrm{C}_y$ represents the virtual bond. Given the low polarity of the solutions, the uncertainty in the dielectric permittivity increment derivative is moderately high (about ±5%). Therefore, the values of D_n listed in *Table 1* have also an uncertainty of ±5%. In any case, the value of the experimental dipole moment ratio, $\langle\hat{\mu}^2\rangle/\mathrm{nm}^2$, of the polymer at 25°C seems to be comparable to those of acyclic polyformals which in most cases are lower than 0.2[1-3].

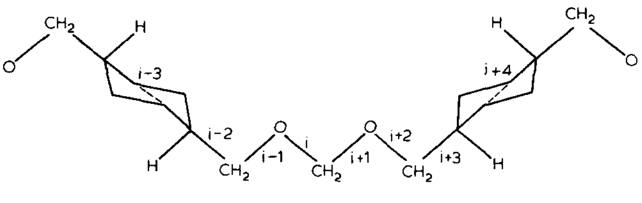

Figure 3 PTCDM chain shown in the all-*trans* conformation. Virtual bonds (i – 3 and i + 4) connecting positions 1,4 of the cyclohexane ring are shown by broken lines

Table 1 Dielectric results for PTCDM chains

T (°C)	$10^{-3} \times \rho_1$ (kg m^{-3})	ϵ_1	$d(\epsilon - \epsilon_1)/dw$	D_n
20	0.8790	2.2836	0.548	0.167
30	0.8683	2.2633	0.548	0.176
40	0.8576	2.2438	0.548	0.186
50	0.8468	2.2232	0.548	0.197
60	0.8360	2.2036	0.548	0.207

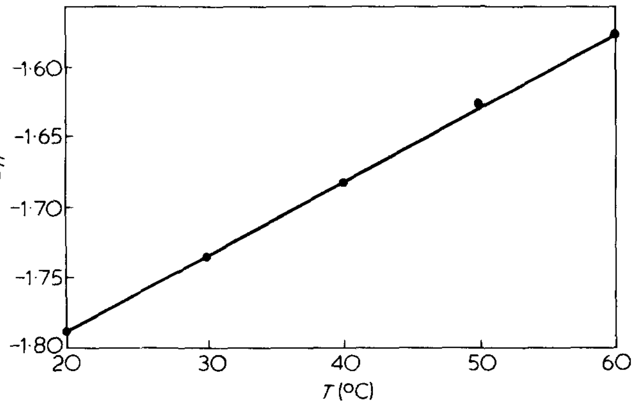

Figure 4 Temperature dependence of the natural logarithm of the dipole moment ratio for the PTCDM polymer

The dipole moment of PTCDM chains increases with increasing temperature. The value of the temperature coefficient $d \ln\langle\mu^2\rangle/dT$ was obtained by plotting the natural logarithm of the dipole moment ratio against temperature. The resulting plot, shown in *Figure 4*, exhibits a high slope, as in the case of the acyclic polyformals[1-3], which corresponds to $d \ln\langle\mu^2\rangle/dT = 5.5 \times 10^{-3}$ K^{-1}.

COMPARISON OF THEORETICAL AND EXPERIMENTAL RESULTS

Given the low molecular weight of the sample studied as well as its symmetry, the experimental values of $\langle\mu^2\rangle$ should coincide satisfactorily with the unperturbed dipole moment[13-15]. The experimental data may therefore be used to study the configurational properties of alicyclic polyformals using the rotational isomeric state model[16]. Certain structural features must be established in order to carry out the calculations. The cyclohexane possesses two favourable conformations which correspond to the two chair forms[17,18]. These two forms can interconvert at relatively high energy (about 11 kcal mol^{-1}), passing through an energy minimum ($\sim$5.0 kcal mol^{-1}), known as the twist (or skew) form; however, this is considerably above the energy of the two chair forms[17,18]. Moreover, since the energy of the boat form is 5.5 kcal mol^{-1} above the chair form[17-19], it is clear that the chair conformation is the only one we should consider in further calculations, since the proportions of the boat and twist conformations are negligible at room temperature.

Two types of protons can be distinguished in the cyclohexane ring; axial protons which are perpendicular to the plane of the ring and equatorial protons which are parallel to the plane of the ring. Cyclohexane rings containing bulky substituents are known to favour conformations which enable the substituents to occupy the equatorial positions. For *trans*-1,4-cyclohexane dimethanol the fraction of axial–axial conformations is expected to be less than 0.3%[17]. Thus, the equatorial–equatorial conformation should be most favoured in *trans*-1,4-cyclohexane dimethanol.

A geometric study of the cyclohexane ring in which the values 0.154 nm[20,21] and 111.5°[20] were used for the C–C bond lengths and for the CCC bond angles, respectively, indicated that bonds i-4 and i-2 (or $i+3$ and $i+5$) in *Figure 3* are parallel for the same kind of substitution (axial–axial or equatorial–equatorial), and therefore, the same value of D_n is obtained whether the two substitutions are axial or equatorial.

The theoretical calculations were carried out assuming that the rotational states are located at 0° (*trans*, t), 120° (*gauche* positive, g^+) and $-120°$ (*gauche* negative, g^-) for bonds i-2 to $i+3$ in *Figure 3*. Virtual bonds (bonds $i-3$ and $i+4$) were fixed at the positions shown in *Figure 3* without allowing rotational freedom; as a consequence of this rigid position of bond $i-3$ and of the fact that bonds $i-2$ and $i-4$ are parallel, any vector expressed in reference frame $i-2$ may be transformed into its representation[15] in reference frame $i-4$ using a transformation matrix $T(0, \varphi+180)$ for any rotational state φ of bond $i-2$.

Some exploratory calculations of the energy interactions for the three rotational states of bonds $i-2$ or $i+3$ in *Figure 3* were carried out using semi-empirical Lennard-Jones potentials. The results of these calculations show that the *gauche* states have an energy approximately 0.4 kcal mol^{-1} higher than the *trans* state. We are aware of the low accuracy of these kinds of energy calculations; however, an exact value of this particular energy is not needed, since it scarcely modifies the results of D_n (see *Table 2*); we have used $E_\sigma = 0.4$ kcal mol^{-1} for this type of bond in all our calculations.

Gauche states about skeletal bonds $i-1$ and $i+2$ in *Figure 3*, have an energy approximately 0.9 kcal mol^{-1} higher than the alternative *trans* states[1,11]. Bonds of type i and $i+1$ have a decisive preference for *gauche* over the *trans* states the energy associated with these states being ~ -1.2 kcal mol^{-1} (ref 1).

Pairs of *gauche* states of opposite sign $g^{\pm}g^{\mp}$ give rise to pentane-type interferences between groups and atoms separated by four bonds. In the case of bond pairs of type $i-4, i-2$ or $i+3, i+5$, the second order interaction energy is zero because these bonds are separated by the cyclohexane ring; as a consequence their bond rotations must be independent. For the bond pairs $i-2, i-1$; $i, i+1$ and $i+2, i+3$, the interacting species are two CH_2 groups and their steric overlaps cause the complete exclusion of these conformations[11]. Finally, for the bond pairs $i-1$, i and $i+1$, $i+2$ the participating species are a CH_2 group and an O atom, giving rise to a repulsive energy[11] of $E_\omega \simeq 0.4$ kcal mol^{-1}. Accordingly the statistical weight matrices used for bonds $i-2$ to $i+3$ have the form[16]:

Table 2 Influence of the rotational energy on the dipole moment of PTCDM chains, T = 25°C

E (kcal mol^{-1})	$d\ln\langle\mu^2\rangle/dE$
$E_\sigma(i-2) = E_\sigma(i+3) = 0.4$	-2.375×10^{-2}
$E_\sigma(i-1) = E_\sigma(i+2) = 0.4$	-1.361×10^{-1}
$E_\sigma(i) = E_\sigma(i+1) = -0.9$	1.210
$E_\sigma(i) = E_\sigma(i+1) = -1.2$	1.389
$E^*_\omega = 0.4$	9.469×10^{-2}

* Only for bond pairs $i-1, i$ and $i+1, i+2$ (see text)

$$U_j = \begin{bmatrix} 1 & \sigma & \sigma \\ 1 & \xi\sigma & \omega\sigma \\ 1 & \omega\sigma & \xi\sigma \end{bmatrix}_j \qquad (2)$$

where the rows and columns are indexed in the order t, g^+ and g^-. Following conventional procedures, σ_j, ξ_j and ω_j are taken to be simple Boltzmann factors of the corresponding conformational energies. Since for pair rotations $g^\pm g^\pm$ of the same sign, no significant interactions between groups or atoms separated by four bonds are expected the value of ξ_j was taken to be the unity in the calculations.

Following standard matrix multiplication methods[16,22], values of the dipole moment ratio were calculated for a chain consisting of $x = 100$ repeating units ($n = 700$ bonds) using $m_{OC} = -m_{CO} = 1.07$ D[11,17] and $m_{CC} = 0.00$ D[11,17]. Preliminary calculations had shown that the asymptotic limit of D_n is reached rapidly for values of x well below 100 (i.e. $x \simeq 40$).

The results of D_n proved to be highly sensitive to the value of the rotational energy about bonds i and $i+1$ of the repeating unit, as indicated in *Table 2*, where the derivatives of the natural logarithm of the dipole moment with respect to the conformational energy of the different bonds are shown. The reason for the high sensitivity of the dipole moment ratio to $E_\sigma(i)$ and to $E_\sigma(i+1)$ is that $g^\pm g^\pm$ combinations for bonds i and $i+1$ place pairs of bond dipole moments in nearly antiparallel orientations; i.e. $\mu^2 = 0.00$ D^2 for the repeating unit. However, if both bonds are in t conformation, the bond dipole moments of the CH_2–O–CH_2 groups are parallel and a value of $\mu^2 = 6.03$ D^2 is obtained. Finally, for conformations $tg^\pm$ or $g^\pm t$ the situation is intermediate, and a value of $\mu^2 = 3.00$ D^2 is obtained. Thus the value of the dipole moment ratio increases rapidly with increasing stability of the t isomer; i.e. as the value of $E_\sigma(i) = E_\sigma(i+1)$ increases. Agreement between theory and experiment was found for values of $E_\sigma(i) = E_\sigma(i+1) = -1.10 \pm 0.05$ kcal mol^{-1} ($D_n = 0.17 \pm 0.01$ calculated at 20°C with this range of E_i and the above mentioned values of all the other energies), in accordance with that of -1.2 kcal mol^{-1} reported for similar bonds in acyclic formals[1–3].

It is interesting to compare values of the dipole moment ratio of this polymer with those of acyclic polyformals. Poly(oxymethylene)[11] (POM), poly(1,3-dioxolane)[1] (PXL) and poly(1,3-dioxonane)[3] (PXM) have been studied for comparison. The most striking result of this comparison is that the dipole moment ratio is essentially independent of the non-polar $(CH_2)_y$ sequences separating the polar fragments –O–CH_2–O–, ($D_n = 0.20$; 0.17 and 0.18 for POM ($y=1$), PCL ($y=2$) and PXM ($y=6$), respectively at 25°C), and that it it is also independent of the presence of an aliphatic ring, ($D_n = 0.17$ for PTCDM). It seems then that the alicyclic group also suppresses the angular correlations between the polar sequences.

Temperature coefficients of the dipole moments were computed for the PTCDM chains using the equation:

$$\frac{d \ln \langle \mu^2 \rangle}{dT} = -(1/T) \sum_k \ln \xi_k \frac{\delta \ln \langle \mu^2 \rangle}{d \ln \xi_k}$$

The value of the temperature coefficient calculated at 25°C using the statistical weight parameters ξ_k derived from the conformational energies listed in *Table 2* is 5.0×10^{-3} K^{-1} which is in fair agreement with the experimental results. It is interesting to note that these chains have a high temperature coefficient (6.0; 6.0; 4.8 and 5.5 in 10^{-3} K^{-1} for POM, PXL, PXM and PTCDM, respectively), owing to the high sensitivity of the dipole moments to the conformations of the oxymethylenic bonds. An increase in temperature evidently increases the fraction of *trans* conformers about bonds i and $i+1$ and hence, the value of the dipole moment ratio also increases.

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