Random coil configuration of the polyformals $(CH_2O(CH_2)_yO-)$: 4. Dipole moments of poly(1,3-dioxocane) (y =5) and poly(1,3-dioxonane) (y = 6)

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Samples of poly(1,3-dioxocane) $[CH_2O(CH_2)_5O-]$ and poly(1,3-dioxonane) $[CH_2O(CH_2)_6O-]$ were prepared by reacting paraformaldehyde with 1,5-pentanediol and 1,6-hexanediol, respectively. Fractions of both polymers, obtained by liquid-liquid precipitation separations, were studied in benzene solutions by means of dielectric constant measurements from 20 to 60°C. Mean-square dipole moments $\langle\mu^2\rangle_0$ thus obtained were compared with theoretical results based on rotational isomeric state models of the two chains. Very good agreement is obtained for the magnitudes of the dipole moments, and for their dependence on chain length and temperature. Values of the dipole moment ratio $\langle\mu^2\rangle_0/nm^2$, where n is the number of bond dipoles of moment m, are essentially the same for the polyformals corresponding to y = 2, 4, 5, and 6. This indicates that even the very short CH_2CH_2 non-polar sequences strongly suppress the correlations between the polar oxymethylene $CH_2OCH_2OCH_2$ sequences in this type of chain. The configurational analysis also identifies the lowest energy conformations of poly(1,3-dioxocane) and poly(1,3-dioxonane), and they are found to be the conformations adopted by the chains in crystalline state.

INTRODUCTION

The polyformals $[CH_2O(CH_2)_yO-]$ are an excellent class of chain molecules for characterizing the effect of structure on configuration-dependent properties. Experimental investigation is facilitated by the fact that most of the lower members of the series are readily soluble in common organic solvents.[1-4] In addition, theoretical calculations based on rotational isomeric state models are straightforward because of the relatively simple structure of the repeat units and the wealth of relevant information available on conformational energies from earlier studies of other polyethers[1-3,5,6] and of polyethylene.[5]

The present investigation focuses on the dipole moments of the fifth and sixth members of the series, viz. poly(1, 3-dioxocane) (PXC) $[CH_2O(CH_2)_5O-]$ and poly(1, 3-dioxonane) (PXN) $[CH_2O(CH_2)_6O-]$. The dipole moments are determined as a function of chain length and temperature, and the results are compared with theoretical results calculated from rotational isomeric state models of the two chains. Comparisons among dipole moments of the four polyformals corresponding to y = 1, 2, 4, 5, and 6[1,2,7,8] are then used to draw conclusions about the effect of the length of the non-polar sequences on the correlations between the polar regions which they separate along the chain. Finally, the (intramolecular) conformational preferences in PXC and PXN are used to predict the configurations of these chains in the crystalline state, and the predictions evaluated using the results of previously published X-ray diffraction studies of the polymers.

EXPERIMENTAL

The samples of PXC and PXN were obtained in condensation polymerizations of paraformaldehyde with 1,5-pentanediol and 1,6-hexanediol, respectively, as described elsewhere.[4] The chemicals were reagent grade and the polymerizations were carried out in refluxing benzene in the presence of sulphuric acid. Water was removed as an azeotrope in a Dean-Stark distillation trap. Both polymers were purified by precipitation from acetone solution. Their melting points were found to be 38 and 32°C, respectively, in exact agreement with the published values.[4]

Liquid-liquid fractional precipitations were carried out, using acetone as solvent and water as non-solvent. Three fractions of the PXC and two of the PXN were thus obtained for the dipole moment determinations. One of each was analysed for carbon and hydrogen, with the following satisfactory results: PXC (C, 61.3% found, 62,04% calculated from formula; H, 10.40, 10.41%), PXN (C, 63.91, 64.58%; H, 10.70, 10.84%). Number-average molecular weights M_n were determined for each of the five fractions using a Perkin-Elmer vapour phase osmometer, which had been calibrated using benzil. The results are given in the second column of *Table 1.*

The polymer fractions were studied in benzene solutions at 20, 30, 40, 50, and 60°C. Dielectric constants ϵ of the solutions were determined by a standard capacitance bridge operating at a fixed frequency of 10 kHz.[9,10] The three-terminal dielectric cell was calibrated at each of the above temperatures using benzene, toluene, and cyclohexane.

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Table 1. Some typical data and results

Polymer	$M_n \times 10^{-3}$ (g/mol)	T (°C)	$d(\epsilon - \epsilon_1)dw$	$-d(n^2 - n_1^2)/dw$	$\langle\mu^2\rangle_0/nm^2$
PXC	1.85	20	0.78	0.097	0.190
		30	0.80	0.085	0.199
		40	0.80	0.071	0.209
		50	0.81	0.058	0.218
		60	0.83	0.047	0.232
	2.56	20	0.74	0.090	0.183
		60	0.79	0.048	0.225
	3.70	20	0.65	0.103	0.168
		60	0.71	0.050	0.207
PXN	2.60	20	0.63	0.089	0.180
		30	0.64	0.077	0.187
		40	0.64	0.067	0.194
		50	0.66	0.056	0.208
		60	0.67	0.041	0.217
	4.02	20	0.68	0.089	0.190
		60	0.72	0.047	0.230

Values of the index of refraction n were measured at 546 nm, using a Brice–Phoenix differential refractometer.

RESULTS AND DISCUSSION

The dielectric constant and index of refraction for each PXC and PXN solution were expressed relative to the corresponding values for the pure solvent in the incremental quantities $(\epsilon - \epsilon_1)$ and $(n^2 - n_1^2)$. These quantities were then plotted against the weight fraction w of polymer in the solution, in order to obtain values of the derivatives $d(\epsilon - \epsilon_1)/dw$ and $d(n^2 - n_1^2)/dw$. Typical results are shown in *Figure 1*, with a more nearly complete set of values being given in columns four and five of *Table 1*. Values of the mean-square dipole moment $\langle\mu^2\rangle$ were then calculated from the standard equation of Guggenheim and Smith:[11]

$$\langle\mu^2\rangle = \frac{27kTM}{4\pi N_A \rho_1(\epsilon_1 + 2)^2}\left[\frac{d(\epsilon - \epsilon_1)}{dw} - \frac{d(n^2 - n_1^2)}{dw}\right] \quad (1)$$

in which k is the Boltzmann constant, T is the absolute temperature, N_A is Avodadro's number, and ρ_1 is the density of the solvent. Because of the absence of excluded volume effects on the dipole moments of symmetric chains such as PXC and PXN,[12,13] the values of $\langle\mu^2\rangle$ thus obtained may be written as the 'unperturbed' values $\langle\mu^2\rangle_0$.[5,12–14] These results are customarily expressed as the *dipole moment ratio* $\langle\mu^2\rangle_0/nm^2$, where n is the number of skeletal bonds (and is equal to $8M/M_0$ in the case of PXC, where M_0 = 116.2 g/mol is the molecular weight of the repeat unit, and $9M/M_0$ in the case of PXN, for which M_0 = 130.2 g/mol). The average m^2 of the squared moments of the skeletal bonds was calculated using $m_{C\text{-}O}$ = 1.07 D, $m_{C\text{-}C}$ = 0.00 D, and $m_{H\text{-}O}$ = 1.70 D.[6,15] The values of the dipole moment ratio thus obtained are given in the last column of *Table 1*; the values at the standard temperature of 25°C are also given in column three of *Table 2*. Values of the temperature coefficient $d\ln\langle\mu^2\rangle_0/dT$ were obtained by plotting the natural logarithm of the dipole moment ratio against temperature, as is shown by the typical data presented in *Figure 2*. The results are given in the fifth column of *Table 2*, and have an uncertainty the order of 10%.

Table 2. Comparisons between theory and experiment, at 25°C

Polymer	$M_n \times 10^{-3}$ (g/mol)	$\langle\mu^2\rangle_0/nm^2$		$d\ln\langle\mu^2\rangle_0/dT \times 10^3$	
		Exp.	Theor.	Exp.	Theor.
PXC	1.85	0.195	0.208	4.9	4.1
	2.56	0.189	0.193	5.1	4.2
	3.70	0.172	0.180	5.4	4.9
PXN	2.60	0.193	0.197	4.5	4.2
	4.02	0.184	0.181	4.8	4.9

The rotational isomeric state models adopted for PXC and PXN assumed rotational states located at 0° (trans, t), 120° (*gauche* positive, g^+), and −120° (*gauche* negative, g^-).[1,2,5,6] The required energies of the intramolecular interactions occurring in the PXC and PXN chains were the same as those used in previous analyses of other polyformals.[1,2] These energies and the above structural information were used in conjunction with standard matrix multiplication methods[5] to calculate $\langle\mu^2\rangle_0/nm^2$ and $d\ln\langle\mu^2\rangle_0/dT$ at the desired values of n. These results are given in columns four and six of *Table 2*. As can readily be seen, there is excellent agreement between the experimental and theoretical values of the magnitudes of these two quantities, and reasonably good agreement with regard to their dependence on molecular weight or chain length. More extensive calculated results, not recorded here, indicate that the dipole moment ratio reaches its asymptotic limit relatively rapidly (at approximately n = 300 skeletal bonds), as is generally found to be the case.[1,2,8]

It is also of interest to compare values of the dipole moment ratio for the various polyformals that have been characterized in this regard.[1,2,6–8] The pertinent information has been gathered in *Table 3*. The value for polyoxymethy-

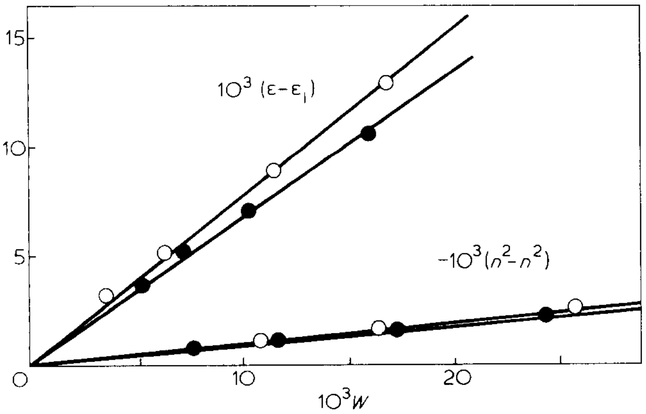

Figure 1 Typical data, showing the concentration dependence of the increments in dielectric constant and squared index of refraction for the lowest molecular weight fractions of poly(1, 3-dioxocane) (○) and poly(1, 3-dioxonane) (●) at 20°C

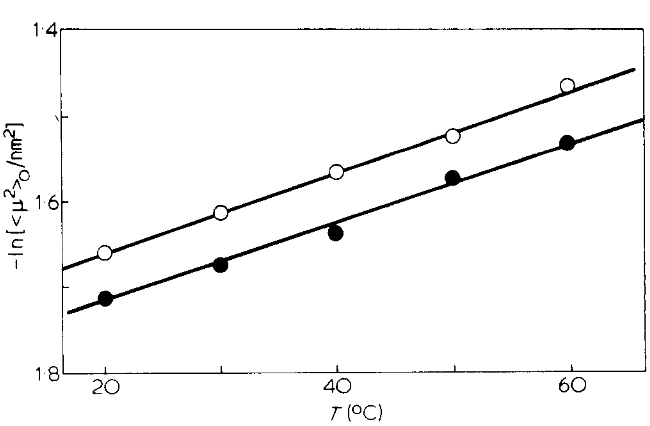

Figure 2 The temperature dependence of the natural logarithm of the dipole moment ratio for the lowest molecular weight fractions of PXC (○) and PXN (●)

Table 3. Comparisons between experimental values of the dipole moment ratio for the polyformals $[CH_2O(CH_2)_yO-]$

Polymer	y	$\langle\mu^2\rangle_0/nm^2$
Polyoxymethylene	1	0.2–0.3[a]
Poly(1, 3-dioxolane)	2	0.17[b]
Poly(1, 3-dioxepane)	4	0.16[c]
Poly(1, 3-dioxocane)	5	0.17
Poly(1, 3-dioxonane)	6	0.18

[a] Refs 6–8
[b] Ref 1
[c] Ref 2

lene (POM) is very approximate,[6–8] unfortunately, because the high melting point of this polymer greatly complicates its experimental characterization. The most striking result of the comparison is the observation that the dipole moment ratio is essentially independent of the length y of the non-polar $-(CH_2)_y-$ sequences separating the polar POM-type sequences $-CH_2-O-CH_2-O-CH_2-$. Apparently even the $-CH_2CH_2-$ sequence of minimum length in poly(1,3-dioxolane) is sufficient to suppress the correlations between the polar sequences. This is consistent with the fact that the C–C bond in the sequence $-O-CH_2-CH_2-O-$ is nearly freely rotating[14] in that its rotational states are not very different in energy.[5,6,16]

The above type of configurational analysis identifies of course the chain conformation of minimum intramolecular energy, and this is of importance since it is generally the form adopted by the chain upon crystallization.[5,17] These conformations are . . . *g*[*gtgttgtg*] *g* . . . for the PXC sequence $-[CH_2OCH_2CH_2CH_2CH_2CH_2O]CH_2-$, and . . . *g*[*gtgtttgtg*] *g* . . . for the PXN sequence $-[CH_2OCH_2CH_2CH_2CH_2CH_2CH_2O]CH_2-$. In both cases, pairs of adjacent *gauche* states are necessarily of the same sign in order to avoid severe pentane-type interferences.[2,5] The results[4] of X-ray diffraction analyses confirm that the above chain conformations are indeed the ones adopted by the PXC and PXN chains in the crystalline state.

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