changes remarkably with different r_0 values (see Figures 2 and 3). For small r_0 values, a minimum at $n = 6$–8 appears. With increasing r_0, the minimum disappears and the probability decreases monotonically with n. The same trend has been obtained in the αN-$(CH_2)_n$-αN system.[9] It should be pointed out that the intramolecular ring-closure reaction in the $X(CH_2)_nY$-type molecule is highly difficult at $n = 8$–13, and it becomes easy at longer chain lengths.[3] This is in accordance with the present study as the critical distance for ordinary ring closure reaction may be very small, being about 3 Å. Here, care must be taken when the results of the diffusion-controlled reactions and those of the ordinary reactions with a moderately high activation energy are discussed on the same ground. The chain length dependences of the two types of reactions can be compared only when the mean lifetime of the favorable conformations $\langle\tau\rangle_1$ is independent of the chain length (see eq 1).

The effect of different steric restrictions caused by the phthalimide and the α-naphthyl groups on the conformations of the methylene chain is apparent when the probability $W(r \leq r_0)$ obtained for $PI(CH_2)_nPI$ is compared with that for αN-$(CH_2)_n$-αN.[9] When $r_0 = 9$ Å, they reveal approximately the same values in both systems. On the other hand, when $r_0 = 7$ Å, a substitution of the phthalimide group by the naphthyl reduced the probability at $n = 6$ by a factor of 0.2 and shifted the minimum point from $n = 9$ to 6. If we adopt $r_0 = 6$ Å, the same substitution causes an even larger change in the chain length dependence of the probability for chains of $n \leq 8$. These findings indicate the importance of the steric structure of terminal groups in the conformational calculation of $X(CH_2)Y$-type molecules, especially when r_0 is small.

To conclude, the calculation of the chain length dependence of the frequency of intramolecular electron transfer in $PI(CH_2)_nPI$ with $n = 7$–14 or PI-$(CH_2CH_2O)_mCH_2CH_2PI$ with $m = 2$–4 reproduced the relevant experimental findings. The disagreement between calculated and observed results is found in short chains.

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Random-Coil Configurations of the Polyformals $[CH_2O(CH_2)_\gamma O-]$. 3. The Temperature Coefficient of the Unperturbed Dimensions of Poly(1,3-dioxolane) $[CH_2O(CH_2)_2O-]$

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The two properties which have been most extensively used to characterize the spatial configurations of polymer chains are the unperturbed dimension $\langle r^2\rangle_0$[1,2] and dipole moments $\langle\mu^2\rangle_0$.[3] The information obtained from these two properties is frequently supplementary since different properties generally have a different sensitivity to temperature, to chain length, and to the statistical weights used to characterize the various permitted conformations of the chain. The temperature coefficients of $\langle r^2\rangle_0$ and $\langle\mu^2\rangle_0$ are frequently also very different. For example, in the case of poly(oxymethylene) (POM) $[CH_2$–O–$]$, d ln $\langle r^2\rangle_0/dT$ is large and negative whereas d ln $\langle\mu^2\rangle_0/dT$ is large and positive.[3-5] This results from the fact that the low-energy conformation of the chain is the all-gauche 9_5 helix; it is of high spatial extension but of almost zero dipole moment so disruption of these helical sequences by increase in temperature decreases $\langle r^2\rangle_0$ but increases $\langle\mu^2\rangle_0$.[3-5]

Poly(1,3-dioxolane) (PXL) $[CH_2$–O–CH_2–CH_2–O–$]$ represents a very similar situation in some respects.[6] The coefficient d ln $\langle\mu^2\rangle_0/dT$ is large and positive, primarily because of the temperature-induced disruptions of the POM-type helical sequences; the experimental value of 6.0×10^{-3} K^{-1} is in fact well reproduced by rotational isomeric state calculations.[6] The unperturbed dimensions of PXL depend more strongly on all of the conformational transitions than do the dipole moments (nonpolar as well as polar skeletal bonds contribute to $\langle r^2\rangle_0$, and the fact that two of the five skeletal bonds in the repeat unit prefer trans states becomes more important).[7] As a result, calculations based on a rotational isomeric state model[6-8] of PXL predict that d ln $\langle r^2\rangle_0/dT$ should be positive and about an order of magnitude smaller than d ln $\langle\mu^2\rangle_0/dT$. Specifically, preliminary calculations predict 10^3 d ln $\langle r^2\rangle_0/dT \simeq 0.2$ K^{-1}.[7] This is puzzling since the only published experimental values[9] of this coefficient are -1.7 K^{-1} (in benzene) and -3.9 K^{-1} (in chloroform). These experimental results are highly suspect, however, since they were obtained by viscosity–molecular weight extrapolation methods which are of questionable reliability,[10] particularly when used to determine a relatively small quantity such as d ln $\langle r^2\rangle_0/dT$.[11] The present study was therefore undertaken in order to provide a more reliable estimate of this important quantity, using viscosity–temperature measurements in an athermal solvent.

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Experimental Section

The polymer was obtained in a cationic, ring-opening polymerization of 1,3-dioxolane, as was described earlier.[6] Its viscosity-average molecular weight M was approximately 40 × 10^3 g mol^{-1}.[12] Dilatometric measurements[13] indicated that the amorphous polymer had a specific volume v of 0.823 $\mathrm{cm}^3\ \mathrm{g}^{-1}$ at 35 °C and a thermal expansion coefficient $\mathrm{d}\ln v/\mathrm{d}T$ of 0.929 × $10^{-3}\ \mathrm{K}^{-1}$.

The solvent employed in the viscosity measurements was reagent-grade ethylene glycol dimethyl ether ($CH_3OCH_2CH_2OCH_3$), so chosen as to give essentially athermal solutions with the PXL polymer. According to pycnometry measurements, it has a molar volume V_1 of 105.8 $\mathrm{cm}^3\ \mathrm{mol}^{-1}$ at 35 °C and a thermal expansion coefficient of 1.37 × $10^{-3}\ \mathrm{K}^{-1}$. The viscosities of the PXL solutions were measured in the usual manner,[14,15] at 20, 30, 40, and 50 °C, using a Cannon–Ubbelohde capillary viscometer. Concentrations c ranged from 1.2 to 2.0 g dL^{-1}, and specific viscosities η_{sp} ranged from 0.32 to 0.59. Values of the reduced specific viscosity η_{sp}/c were extrapolated to infinite dilution to obtain the values of the intrinsic viscosity $[\eta]$[16] of the PXL sample at the chosen temperatures.

Results and Discussion

The values of $[\eta]$ are shown semilogarithmically as a function of temperature in Figure 1. The slope of the line, which was located by least-squares analysis, is $10^3\ \mathrm{d}\ln[\eta]/\mathrm{d}T = 0.69\ \mathrm{K}^{-1}$. Since the polymer and solvent were of nearly identical chemical structure, it was assumed that the PXL solutions were athermal, thus permitting calculation of the temperature coefficient of the unperturbed dimensions $\langle r^2\rangle_0$ from the equation[17]

$$\mathrm{d}\ln\langle r^2\rangle_0/\mathrm{d}T = (5/3 - \alpha^{-2})\ \mathrm{d}\ln[\eta]/\mathrm{d}T - (1 - \alpha^{-2})\ \mathrm{d}\ln(v^2/V_1)/\mathrm{d}T \quad (1)$$

The chain expansion factor α was calculated from the standard relationship[16,17]

$$\alpha^5 - \alpha^3 = 27(2\pi)^{-3/2}(v^2/N_{\mathrm{A}}V_1)[\langle r^2\rangle_0/M]^{-3/2}M^{1/2}\psi_1 \quad (2)$$

in which N_{A} is Avogadro's number. The value[9] 5.24 × 10^{-25} $\mathrm{cm}^3\ (\mathrm{g/mol})^{-3/2}$ was used for $[\langle r^2\rangle_0/M]^{3/2}$, and the entropy of mixing parameter ψ_1 was assigned the value of 0.2.[14,18] The value of α thus calculated was found to be 1.29. (As was observed in similar studies,[14,18] ψ_1 and α need not be known very accurately.) The resulting value of $10^3\ \mathrm{d}\ln\langle r^2\rangle_0/\mathrm{d}T$ is 0.54 K^{-1}, with an uncertainty of approximately 0.2, which is definitely in satisfactory agreement with theory.[7-9] This resolves a puzzling discrepancy in the configurational analysis of the PXL chain and thus strengthens confidence in the use of rotational isomeric state theory in the prediction and interpretation of the properties of the polyethers in general.

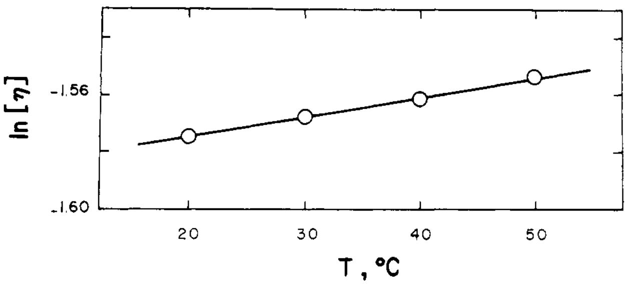

Figure 1. The natural logarithm of the intrinsic viscosity shown as a function of temperature for poly(1,3-dioxolane) in the athermal solvent ethylene glycol dimethyl ether.

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