Preparation of 2,3-Benzo-5-phenyl-1,6,9-trioxa-4-thia-5-phospha(V)spiro[4.4]nona-2-ene (4).[10] Into an equimolar amount of *o*-hydroxybenzenethiol and 2-phenyl-1,3,2-dioxaphospholane (30 mmol each) in 100 mL of dry diethyl ether was dropwise added 30 mmol of diisopropylchloroamine in 50 mL of diethyl ether at −78 °C with stirring. On the addition, white precipitate was formed. After the addition the reaction system was allowed to warm to room temperature and stirred for 3 h. The solid salt was separated by filtration and washed with 30 mL of dry benzene. The filtrate was combined with benzene washing and solvents were evaporated in vacuo to give an oily residue. *n*-Hexane (50 mL) was added to the residue, and the mixture was stirred to form a white solid, which was separated. After recrystallization from a chloroform/diethyl ether mixed solvent, 4 was obtained in 70% yield: mp 96–97 °C (lit.[9] 96–97 °C); ^1H NMR ($CDCl_3$) δ 3.5–4.5 (m, OCH_2, 4 H), 6.6–8.2 (m, aromatic protons, 9 H); ^{31}P NMR (CH_3CN) δ +3.8.[3] Anal. Calcd for $C_{14}H_{13}O_3PS$: C, 57.53; H, 4.48; P, 10.60. Found: C, 57.61; H, 4.64; P, 10.09.

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Random-Coil Configurations of the Polyformals $[CH_2O(CH_2)_yO]$. 5. Dipole Moments, Unperturbed Dimensions, Optical Anisotropies, and Molar Kerr Constants for 1,3-Dioxolane Polymers Containing Structural Irregularities

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Experimental values of the dipole moments of poly(1,3-dioxolane) were recently reported[2] and successfully interpreted[2] in terms of the rotational isomeric state theory.[3] The theoretical values of the dipole moments had been calculated assuming all of the repeat units in the chain to be identical. This polymer, however, is generally prepared by ring-opening polymerization of the monomer $\overline{CH_2\text{–}O\text{–}(CH_2)_2O}$.[2,4] Bond scissions occurring exclusively at bonds of the first type shown or exclusively at bonds of the second type would yield the same, perfectly-regular polymer $[CH_2O(CH_2)_2O]$. Scissions occurring at both types of bonds, however, would introduce the irregular sequences CH_2OCH_2O and $(CH_2)_2O(CH_2)_2O$, arising from the presence of the two different repeat units $CH_2O(CH_2)_2O$ and $(CH_2)_2OCH_2O$. The fact that the experimental and theoretical values of the dipole moments were in good agreement[2] thus supported the regular structure for this polymer, but the sensitivity of the dipole moment to the structural irregularities was not known. Also, polymerization may be more complex in the case of other formals,[4-7] particularly those of more complicated structure. Additional calculations could therefore provide valuable guidance in the choice of configuration-dependent properties for characterizing this class of chain molecules.

Previous studies have shown that the dipole moment generally has a sensitivity to structure which is much larger than that shown by the unperturbed dimensions.[8,9] Specific examples are its sensitivity to chemical composition and sequence distribution in chemical copolymers and to stereochemical structure in vinyl polymers. This enhanced sensitivity is due to the fact that skeletal bonds or polymer repeat units can generally vary much more in polarity than they can in length. One would therefore expect the dipole moment (and also the optical anisotropy and the molar Kerr constant) to be particularly sensitive to structure in the case of asymmetric units in which the side chains contribute significantly to the property being measured.[10] This has been found to be the case.[8-16]

It is thus obviously of considerable interest to investigate a wide variety of configuration-dependent properties for polyformals having symmetrically substituted units which can be irregular with regard to the sequence of skeletal atoms and others having unsymmetrically substituted units which can be irregular with regard to stereochemical structure. Of particular interest will be the identification of those properties which should be most sensitive to a particular variation in structure and therefore most promising for experimental investigations. The present study is part of this general program. It focuses on poly(1,3-dioxolane) and how the irregular sequences CH_2OCH_2O and $(CH_2)_2O(CH_2)_2O$ affect the chain's dipole moments, unperturbed dimensions, optical anisotropies, and molar Kerr constants.

Theory

General Features of the Rotational Isomeric State Model. As in the previous study[2] of poly(1,3-dioxolane), skeletal bond angles were assumed to be tetrahedral, and rotational states were located at dihedral angles of 0, 120, and −120°. The two alternative repeat units $CH_2O(CH_2)_2O$ and $(CH_2)_2OCH_2O$ were designated types 1 and 2, respectively. The chains investigated had $n = 200$ skeletal bonds and, in the case of those having structural irregularities, Monte-Carlo methods were used to generate 15 representative chains having Bernoullian placements of the structures 1 and 2.[3] The conformational energies employed were those presented and discussed elsewhere.[2] Standard matrix methods[3,17] were used to generate the values of the statistical properties of interest, at 25 °C.

Dipole Moments. The calculated values of the mean-square dipole moment $\langle \mu^2 \rangle$ were expressed as the dipole moment ratio $\langle \mu^2 \rangle / n\mu_0^2$, where μ_0^2 is the average square of the bond moments. The required bond moments, μ_{CO} and μ_{CC}, were assigned the values 1.07 and 0.00 D, respectively.[2]

Unperturbed Dimensions. The values calculated for the mean-square end-to-end distance pertain only to the chains in the absence of excluded volume interactions and are thus designated as the unperturbed values $\langle r^2 \rangle_0$. These results are expressed as the characteristic ratio $\langle r^2 \rangle_0 / nl^2$,

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Table I
The Effect of Structural Irregularities on the Dipole Moments, Unperturbed Dimensions, Optical Anisotropies, and Molar Kerr Constants of Poly(1,3-dioxolane)

	w_2[a] (irregularities)		
property	0.00	0.50	variation, %
$\langle \mu^2 \rangle / n\mu_0^2$	0.156	0.250	60.3
$\langle r^2 \rangle_0 / nl^2$	3.69	3.68	−0.27
$\langle \gamma^2 \rangle / n$, Å^6	0.070	0.090	28.6
$\langle {}_{\mathrm{m}}K \rangle / n$, 10^{-12} cm^5 statvolt^{-2} mol^{-1}	0.667	0.636	−4.6

[a] Fraction of repeat units having the structure $(CH_2)_2$-OCH_2O rather than $CH_2O(CH_2)_2O$.

where l^2 is the average of the squares of the bond lengths l_{CC} = 1.53 Å and l_{CO} = 1.43 Å.[3]

Optical Anisotropies. The mean-square optical anisotropy was calculated from[17]

$$\langle \gamma^2 \rangle = (3/2)\langle \mathrm{Tr}(\hat{\alpha}\hat{\alpha}) \rangle \tag{1}$$

where Tr represents the trace and $\hat{\alpha}$ is the anisotropic part of the polarizability tensor. This tensor may be evaluated by the addition of contributions from all of the bonds in the chain. Its value for any of the (single) skeletal bonds is given by[18]

$$\hat{\alpha} = \Delta\alpha \ \mathrm{Diag}(\tfrac{2}{3}, -\tfrac{1}{3}, -\tfrac{1}{3}) \tag{2}$$

where $\Delta\alpha$ is the optical anisotropy of the bond and Diag$(^2/_3, -^1/_3, -^1/_3)$ represents a 3 × 3 matrix with all the elements equal to zero except those along the main diagonal. Taking into account that for a tetrahedral geometry $\Delta\alpha_{CH_3} = -\Delta\alpha_{CH}$, the contributions for bonds of the types a through e in the sequence CH_2-O-CH_2-CH_2-O- are given by

$$\Delta\alpha_a = \Delta\alpha_{CO} + \Delta\alpha_{CH_3} = \Delta\alpha_{CO} - \Delta\alpha_{CH}$$
$$\Delta\alpha_b = \Delta\alpha_{CO} - \Delta\alpha_{CH}$$
$$\Delta\alpha_c = \Delta\alpha_{CC} + \Delta\alpha_{CH_3} - \Delta\alpha_{CH} = \Delta\alpha_{CC} - 2\Delta\alpha_{CH}$$
$$\Delta\alpha_d = \Delta\alpha_{CO} + \Delta\alpha_{CH_3} = \Delta\alpha_{CO} - \Delta\alpha_{CH}$$
$$\Delta\alpha_e = \Delta\alpha_{CO} - \Delta\alpha_{CH} \tag{3}$$

According to Patterson and Flory,[19] $\Delta\alpha_{CC}$ = 0.95 Å^3, $\Delta\alpha_{CO}$ = 0.58 Å^3, and $\Delta\alpha_{CH}$ = 0.21 Å^3. Thus,

$$\hat{\alpha}_a = \hat{\alpha}_b = \hat{\alpha}_d = \hat{\alpha}_e = 0.37 \ \mathrm{Diag}(\tfrac{2}{3}, -\tfrac{1}{3}, -\tfrac{1}{3}) \tag{4}$$
$$\hat{\alpha}_c = 0.53 \ \mathrm{Diag}(\tfrac{2}{3}, -\tfrac{1}{3}, -\tfrac{1}{3})$$

The results were expressed as the anisotropy ratio $\langle \gamma^2 \rangle / n$.

Molar Kerr Constants. The molar Kerr constant, characterizing the electrical birefringence, was calculated from[13]

$$\langle {}_{\mathrm{m}}K \rangle = (2\pi N/15kT)[\langle \mu^{\mathrm{T}}\hat{\alpha}\mu \rangle / kT + (\epsilon - 1)\langle \mathrm{Tr}\hat{\alpha}\hat{\alpha} \rangle / (\tilde{n}^2 - 1)] \tag{5}$$

where N is Avogadro's number, k the Boltzmann constant, μ the permanent dipole moment and μ^{T} its transpose, ϵ the static dielectric constant of the medium, and $\tilde{n}$ the refractive index of the medium at the wavelength used in the measurements. The results were expressed as the ratio $\langle {}_{\mathrm{m}}K \rangle / n$.

Results and Discussion

The values calculated for the dipole moment ratio are shown in Figure 1 as a function of the fraction w_2 of units having the structure $(CH_2)_2OCH_2O$. The curve increases monotonically to the composition w_2 = 0.50, about which it is symmetrical. The sensitivity of the dipole moment ratio to this type of structural irregularity was therefore gauged by the difference between the values of the ratio at the limiting compositions w_2 = 0.00 and 0.50. The results are given in the first row of Table I. The observed difference of 60% is quite large and thus supports the previous use[2] of this property in the characterization of the poly(1,3-dioxolane) chain.[20]

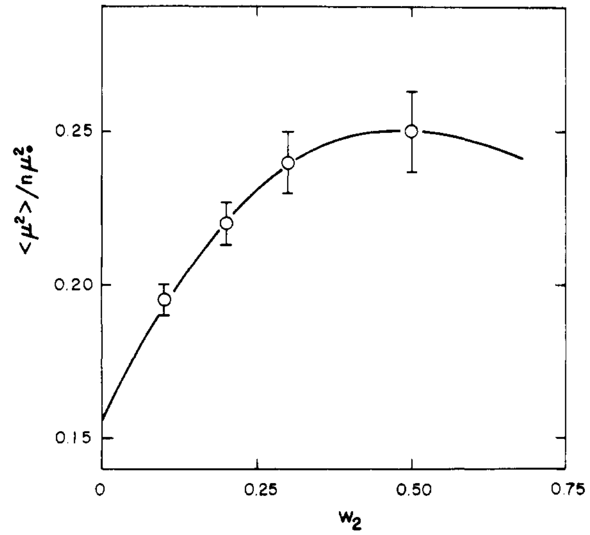

Figure 1. The dipole moment ratio of poly(1,3-dioxolane) at 25 °C shown as a function of the fraction of units having the structure $(CH_2)_2OCH_2O$ rather than $CH_2O(CH_2)_2O$. The results for the irregular chains ($w_2 > 0$) were calculated for 15 chains, each having n = 200 skeletal bonds, and the vertical bars represent standard deviations.

The corresponding curves obtained for the other three properties have the same general shape as that shown in Figure 1 and are therefore not shown here. Their sensitivities to the irregularities are presented in the last three rows of Table I. As can be seen, the optical anisotropy should also be useful for characterizing the structure of this polymer. The very low sensitivity in the case of the characteristic ratio was perhaps to be expected on the basis of the preceding comments, but the low sensitivity exhibited by the molar Kerr constants is surprising.[20] The use of Kerr constants is further discouraged by the observation[21] that calculated values of these constants for poly(oxyethylene) $[(CH_2)_2O]$ are in poor agreement with experimental values. In any case, the present study clearly demonstrates the utility of carrying out preliminary theoretical calculations on a polymer prior to initiation of the corresponding experimental investigations.

In the earlier, experimental study of dipole moments,[2] it was concluded that poly(1,3-dioxolane) does not have a significant number of irregular chemical sequences. This is consistent with the fact that the ^{13}C NMR spectrum[22] of a particular sample of this polymer clearly demonstrates the absence of such irregularities.

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Thermotropic Anthraquinone Polymers: Structure and Enthalpic Relaxation

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The existence of a mesogenic state for certain low molecular weight species has been recognized for decades. Only recently, however, have a variety of polymers that melt to an ordered liquid been developed. In a previous publication, the author reported on the crystallization kinetics of aromatic polyesters from ordered melts.[1] Not all thermotropic polymers crystallize, however, particularly those that contain bulky side groups or bulky or asymmetric backbone entities or lack a regular backbone sequence. These polymers typically lack three-dimensional order in the solid state, lack a strong melting endotherm, have a strong glass transition (T_g) and flow with stress above T_g. Hence, they may be more closely modeled as amorphous polymers than as semicrystalline polymers.

The phenomenon of enthalpic relaxation in glassy polymers is well documented and it is generally accepted that it is due to a loss in free volume rather than to an increase in the local ordering.[2,3] Enthalpic relaxation can be easily detected by using differential scanning calorimetry (DSC), but it also parallels changes in mechanical properties, density, etc.[3]

Theoretically, enthalpic relaxation may occur in amorphous or semicrystalline thermotropic polymers even though they possess two-dimensional order. Petrie, indeed, has shown that enthalpic relaxations can be observed for glassy, nonpolymeric mesogens.[3]

It is generally accepted that the rate of enthalpic relaxation is determined by the self-diffusion coefficient and, hence, is dependent on the reduced temperature and the departure from equilibrium.[2,3] Consequently, small changes in experimental conditions (viz., temperature) can produce dramatic changes in the rate of diffusive transport.

The diffusion tensor of an amorphous unoriented polymer is isotropic. With oriented vitreous or liquid crystalline polymers, however, the diffusion coefficients are not independent of direction. Moreover, and particularly in the case of polymers with stiff molecules in a frozen-in nematic texture, a large number of atoms must move cooperatively for effective long-range self-diffusion. Motion on a scale of ångstroms, however, should not be much more difficult in the anisotropic glass as compared with that in the isotropic glass. Motion associated with enthalpic or volume relaxation is expected to be short range and, hence, ought not be affected by orientation.

Several difficulties are encountered when one attempts to study relaxation in oriented amorphous polymers: (1) The density of the material may change significantly with drawing. (2) Strong shrinkage forces may develop during low-temperature annealing. (3) Orientation changes the glass transition temperature.

Despite these difficulties some authors have succeeded in producing some data which suggest that the rate of relaxation is not changed dramatically by orientation once corrected for density and glass transition temperature.[4,5]

As described in this paper, the aforegiven problems have been circumvented by the use of liquid crystal polymers and it has been found that the rate and magnitude of enthalpic relaxation is comparable to that of conventional (flexible) amorphous or semicrystalline polymers.

Experimental Section

The polymers utilized in this study were prepared by the usual melt polymerization techniques, using 1,4-acetoxybenzoic acid, 2,6-dihydroxyanthraquinone, terepthalic acid, and isophthalic acid, and will be described in detail in a subsequent paper.[6,7] A variety of compositions were synthesized and all the polymers investigated show qualitatively the same behavior. The data in this paper are derived from a single polymer with the nominal composition being 50/25/12.5/12.5 mol %, respectively, and the intrinsic viscosity in 0.1% pentafluorophenol being 1.91 dL/g. Samples employed were fibrous, having been spun with the use of a micromelt unit at about 360 °C to a denier of 3.7 and a birefringence of 0.367. The details of spinning will be presented in a subsequent paper.[7]

Annealing was generally conducted in a circulating air oven at 125 °C for various times. Fibers were mounted free to shrink to accomodate the negative thermal expansion coefficient. There is virtually no entropic shrinkage.

When samples were to be analyzed by thermal analysis, they were annealed directly in the differential scanning calorimeter, Perkin-Elmer DSC 2.

X-ray diffraction patterns were obtained with a Rigaku-Denki rotating anode unit, Ni-filtered Cu radiation, and recorded by using a Unicam S27. A Joyce-Loeb microdensitometer was employed when semiquantitative data were needed; aluminum powder was used for calibration purposes.

Glass transition temperatures (T_g) were determined with the use of a DuPont 990 Thermal Analyzer (DTA) and specific heats obtained with the use of a sapphire standard.[7] The DSC was calibrated by using indium and used at 20 °C/min. The purge gas was nitrogen. Excess enthalpy was determined by the method of Petrie.[3]

Density measurements were achieved by the use of columns filled with calcium nitrate and water. Because of slight porosity in the fibers, the accuracy provided by the columns could not be fully utilized.

Mechanical properties were determined with the use of an Instron Testing Machine. A gauge length of 2.54 cm and a strain rate of 20%/min were employed. The data have not been corrected for gauge length (i.e., uncorrected for compliance or grip effects) which typically results in an incremental increase in modulus of about 20%, no change in tenacity, and only a minor