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# Statistical Properties of Alternating Copolymers. 1. Dipole Moments of Poly(thiodiethylene glycol) Chains

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ABSTRACT: Mean-square dipole moments of poly(thiodiethylene glycol), an alternating copolymer of ethylene oxide and ethylene sulfide, were determined from dielectric constant measurements on dilute solutions of the polymer in benzene. Since the configuration-dependent properties of one of the parent homopolymers, poly(ethylene sulfide), are unknown, because of its insolubility in ordinary solvents, the results were preferably compared with those of poly(oxyethylene) chains. It was found that the dipole moments of poly(thiodiethylene glycol) are somewhat larger than those of poly(oxyethylene). The values of the dipole moments were also theoretically calculated using the rotational isomeric state model, in which the required energies of the bonds of the repeat unit, except those of the $CH_2—CH_2$ bonds, were obtained from previous configurational analysis of poly(oxyethylene) and polyethylene. Agreement between theory and experiment was obtained assuming that the energy from first-order interactions between S and O atoms is larger in gauche than in trans states.

Conformation-dependent properties of polyoxide chains have been intensively investigated in the framework of the rotational isomeric state approximation.[1-7] Rotational energies of the rotational states adopted by the skeletal bonds of the chains were determined through comparisons of calculated and experimental values of at least one configuration-dependent property.[3] The configurational energies thus determined for two or more relatively single chains were successfully used to predict the configuration-dependent properties of other more complicated polyethers such as the linear polyformals [$CH_2$-O-$(CH_2)_y$-O-], in which poly(oxymethylene) may also be considered the first member of the series.[8,9] The properties of the polyformals vary markedly with the number of methylene groups $y$ in the repeat unit. These polymers may be considered alternating copolymers of methylene oxide and alkylene oxide. However, in the polyformals as well as in other alternating copolymers, a particular configurational property cannot in general be obtained by simply averaging the values of the same property for the parent homopolymers. For example, poly(1,3-dioxepane), an alternating copolymer of methylene oxide and tetramethylene oxide, has possibly the lowest dipole moment ratio of any polymer reported up to date.[9]

It is desirable to extend the analysis to other polymers with sulfur atoms in their structure. The polyoxide chains may be converted schematically to any member of the polysulfide series [$(CH_2)_y$-S-] by simply substituting oxygen atoms for sulfur atoms. The polythioethers, with $y = 1$ and 2, have melting points higher than 200 °C and therefore are insoluble in most solvents. With the increase of the number of $CH_2$ groups in the repeat unit, the melting points of the polymers decrease abruptly, reaching a minimum value of about 70 °C for poly(trimethylene sulfide), and then increase gradually until they reach that of polyethylene.[10] Because of their relative low melting points, the polymers with $y > 2$ are soluble in ordinary solvents. Their configuration-dependent properties, however, have not been widely investigated. Information on some conformational states of the members of the series may be obtained from the configurational properties of poly(thiodiethylene glycol) (PTDG). This polymer, which may be considered an alternating copolymer of ethylene oxide and ethylene sulfide units, has a relatively low melting point and is readily soluble in a number of common organic solvents. Although the method of preparation of the polymer does not permit us to obtain high molecular weight samples (in fact molecular weight fractions higher than 13000 were not obtained), dielectric measurements can provide the necessary information to study the chains using the rotational isomeric state model. Actually, the corresponding dielectric property employed to characterize random coil conformations is the dipole moment ratio $\langle \mu^2 \rangle_0 / nm^2$, where $n$ is the number of bonds or group dipoles and $m^2$ is the average square of their magnitudes. This quantity is one of the most useful of the conformation-dependent properties since it can be determined for chains of any length, either in the bulk or in solution.[11]

The purpose of the present investigation is to determine the dipole moment ratio and its temperature dependence for PTDG chains. Of particular interest will be the molecular interpretation of the results in terms of the rotational isomeric state theory and the comparison of some configurational properties with those of poly(oxyethylene) (POE).

## Experimental Section

**Preparation of the Samples.** Poly(thiodiethylene glycol) was prepared by refluxing thiodiethylene glycol reagent grade with *o*-xylene. The reaction was carried out at nitrogen atmosphere for 72 h, using *p*-toluene sulfonic acid (≈2%) as the catalyst. Water was removed as azeotrope in a Dean-Stark distillation trap. The polymer was precipitated from solution with a mixture of methanol–*n*-hexane. It was washed several times with distilled

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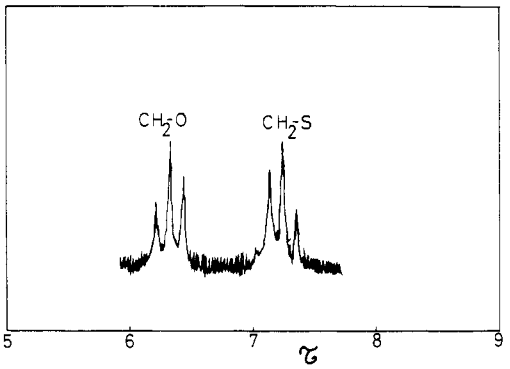

**Figure 1.** NMR spectrum of PTDG chains.

water to eliminate the residual catalyst. The polymer was further dissolved in chloroform, the solution was filtered, and the polymer was reprecipitated with *n*-hexane. It was finally dried under vacuum at room temperature and freeze dried to eliminate any remaining low molecular weight material.

**Characterization of the Samples.** The polymer was fractionated at 30 °C using chloroform–*n*-hexane as the solvent–nonsolvent system. Six fractions were obtained. The first fraction amounted to about 20% of the total polymer. The elemental analysis of this fraction gave the following results. Found: C, 46.1; H, 7.70. Calcd: C, 46.96; H, 7.94. The nuclear magnetic resonance spectrum, shown in Figure 1, was obtained by a Perkin-Elmer R-12 spectrometer at 60 MHz, using deutered chloroform as solvent and tetramethylsilane as reference. The analysis of the spectrum indicates the purity of the sample as well as its structure. Two triplets are observed at about $\tau$ 6.3 and 7.25 that correspond to the resonance of the adjacent protons to the ether and to the thioether groups, respectively. The melting points of the samples were visually determined at a heating rate of 1 °C/min in a Totoli type Büchi apparatus. It was found that their values lie in the interval 45–48 °C. The number average molecular weights of the fractions were measured in a Knauer vapor-pressure osmometer. Two fractions A and B of molecular weight 13 000 and 8 000, respectively, were used in the dielectric measurements.

**Dielectric Constants and Refractive Indices.** The dielectric measurements on solutions of the polymer in benzene were carried out using a capacitance bridge (General Radio, type 1620 A) at a frequency of 10 kHz. Previous tests on the frequency dependence of $\epsilon'$ showed that at 10 kHz the real part of the complex dielectric constant is to a good approximation the static value. A three-terminal platinum cell was used,[4,5] and the apparatus was calibrated at each temperature of interest using benzene (Merck, 99.5% pure), cyclohexane (Fisher, 99% pure), and toluene (Merck, 99.5% pure); precise values of their dielectric constants are available in the literature.[12,13] The refractive indices of the solutions were measured at 546 $\mu$m using a Brice-Phoenix differential refractometer.

## Results

The dielectric constant measurements were made at 20, 30, 40, 50, and 60 °C. It was found that both the dielectric increment ($\Delta\epsilon = \epsilon - \epsilon_1$) and the increment in squared index of refraction ($\Delta n^2 = n^2 - n_1^2$) are proportional to the weight fraction $w$ of the polymer, for values of $w$ lower than 0.02. Typical results are shown in Figure 2.

Values of the mean-square dipole moment $\langle\mu^2\rangle$ were obtained using the method of Guggenheim[14] and Smith[15] which results in the equation

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

in which $N_A$ is the Avogadro number, $k$ is the Boltzmann constant, $M$ is the molecular weight of the polymer, $T$ is the absolute temperature, $\rho$ is the density of the solvent, and $\epsilon_1$ and $n_1$ are respectively the dielectric constant and the index of refraction of the solvent. The values of the limiting derivatives were obtained from plots similar to those shown in Figure 2. The complete set of values of the two derivatives is given in columns four and five of Table I. Equation 1 assumes that $\epsilon_\infty$ can be approximated by $n^2$. Since in the case of PTDG chains the concentration dependence of $\epsilon'$ is sensibly larger than that of $n^2$, the error thus introduced should be relatively small. The dipole moments of chains as symmetric as PTDG,[16-18] measured in good solvents, are unaffected by long-range perturbations of the molecular configurations, so that their values may be compared with the unperturbed values $\langle\mu^2\rangle_0$.[1,16-19] In keeping with the usual way of expressing the results, the values of $\langle\mu^2\rangle_0$ were divided by $nm^2$, the mean-square dipole moment of the chains, in the idealization that the skeleton bonds are freely jointed. The bond dipole moments pertaining to the chains lie along the skeleton bonds and their values are: $m_{\text{H-O}}$ = 1.7 D,[20] $m_{\text{C-C}}$ = 0.00 D,[3,21] $m_{\text{C-O}}$ = 1.07 D,[3,21] and $m_{\text{C-S}}$ = 1.21 D.[21,22]

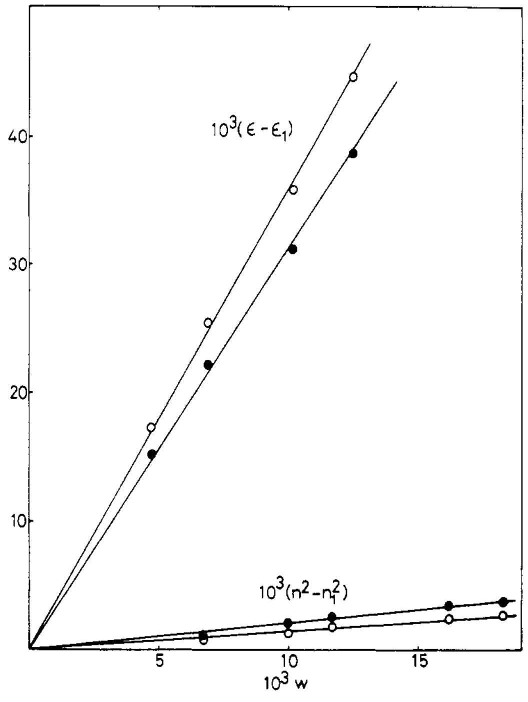

**Figure 2.** Concentration dependence of the increments in dielectric constant and squared index of refraction for PTDG A sample at 20 and 60 °C.

**Table I**
**Summary of Experimental Results Obtained from Solutions of PTDG in Benzene**

| sample | $10^{-3}M_n$ | $T$, °C | $\mathrm{d}(\epsilon - \epsilon_1)/\mathrm{d}w$ | $\mathrm{d}(n^2 - n_1^2)/\mathrm{d}w$[a] | $\langle\mu^2\rangle_0/nm^2$ |
|---|---|---|---|---|---|
| A | 13 | 20 | 3.58 | 0.140 | 0.607 |
| | | 30 | 3.46 | 0.160 | 0.615 |
| | | 40 | 3.35 | 0.175 | 0.625 |
| | | 50 | 3.26 | 0.185 | 0.640 |
| | | 60 | 3.16 | 0.200 | 0.648 |
| B | 8 | 20 | 3.70 | 0.140 | 0.627 |
| | | 30 | 3.60 | 0.160 | 0.640 |
| | | 40 | 3.46 | 0.175 | 0.646 |
| | | 50 | 3.36 | 0.185 | 0.659 |
| | | 60 | 3.26 | 0.200 | 0.669 |

[a] The values were obtained on sample A and were also assumed to apply to sample B.

The values of the dipole moment ratio $\langle\mu^2\rangle_0/nm^2$ are indicated in the last column of Table I. Since the error involved in the estimation of the derivatives of the dielectric increments is about ±2%, the dipole moment ratio is 0.62 ± 0.01 in the vicinity of 25 °C, somewhat larger than

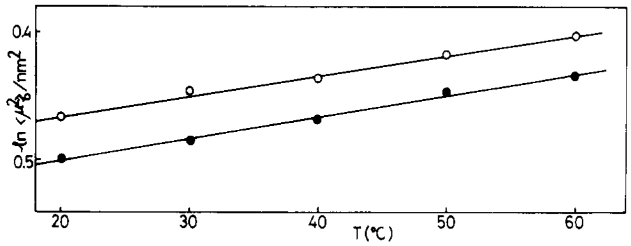

**Figure 3.** Dependence of the natural logarithm of the dipole moment ratio on temperature for two PTDG samples.

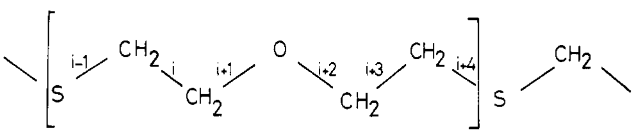

**Figure 4.** The PTDG chain in the all-trans conformation, with brackets used to set off the repeat unit.

that reported for POE which is 0.52.[1,4] 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 shown in Figure 3, the samples exhibited very nearly the same slope, which corresponds to $1.6 \times 10^{-3}$ deg$^{-1}$, a value which is close to that reported for POE chains.[1,4]

## Comparison of Theoretical and Experimental Results

Values of the mean-square dipole-moment ratio were calculated as a function of the degree of polymerization using the rotational isomeric state approximation.[1] The calculations were carried out assuming that the rotational states are located at 0° (trans, *t*), 120° (gauche positive, $g^+$), and −120° (gauche negative, $g^-$). All the bond-angle supplements were considered to be equal to 70°, except those corresponding to the ∠CSC and ∠SCC angles which were taken to be equal to 80°[22] and 66°,[22] respectively. The statistical weight matrices required in the conformational analysis were constructed in the usual way, utilizing as distances between nonbonded atoms and groups in the assignment of rotational statistical weights those indicated in Table II. A brief summary of this information follows.

Gauche states about skeletal bonds such as $S-CH_2$ and $CH_2-S$ of Figure 4 decrease the distance between $CH_2$ groups separated by three bonds from a center to center distance of 4.21 to 3.20 Å. These states should be lower in energy than the corresponding states about $CH_2-O$ and $O-CH_2$ bonds in POE, where two $CH_2$ groups are only 2.81 Å apart. Reference to the conformational analysis of polyethylene might provide an indication of the interactions from the transition trans to gauche about $S-CH_2$ bonds. A gauche rotation about any skeletal bond in polyethylene places $CH_2$ groups at a distance of 3.03 A,[1] and the energy associated with this rotation is 400 ± 100 cal mol$^{-1}$. On the basis of this comparison, it should be reasonable to assume for the $g^{\pm}$ states of bonds $i-1$ and $i+4$ an energy of approximately 400 cal mol$^{-1}$ higher than the alternative trans states. However, in the analysis of the crystalline structure of poly(ethylene sulfie) (PES), Takahashi et al.[23] have found that the conformation of this polymer is just opposite to that of POE. That is, $CH_2-CH_2$ bonds take the trans form, and $CH_2-S$ bonds take the gauche form. Moreover, Raman and infrared spectra[24] of molecules with $CH_2-S$ bonds in their structure such as ethyl methyl sulfide show that the gauche conformation is slightly more stable than the trans. The preference for gauche states of $CH_2-S$ bonds is striking. According to literature,[24,25] a value of $E_\sigma = -0.1$ kcal mol$^{-1}$ seems to be a reasonable choice, and it will be used in the theoretical calculations. In the case of gauche rotations of the same sign about bond pairs such as $i-2$ and $i-1$, no significant interactions between $CH_2$ groups separated by four bonds are expected since they are at a distance of 3.73 Å. The same occurs for pairs of bonds such as $i+3$ and $i+4$ where the distance between $CH_2$ groups is 3.78 Å. In both cases, $g^{\pm}g^{\pm}$ states also receive statistical weights of $\sigma \approx \exp(100/RT)$. Pairs of gauche states of opposite sign $g^{\pm}g^{\mp}$ corresponding to bonds $i-2$ and $i-1$ place the $CH_2$ groups at a distance of 2.84 Å. Since the van der Waals radius of $CH_2$ groups is approximately 2 Å,[1] steric repulsions must exclude such conformations. The distance of separation of negatively charged O atoms from positively charged $CH_2$ groups in $g^{\pm}g^{\mp}$ states of $CH_2-CH_2-S$ bonds is 2.67 Å. The energy contribution from these groups was taken to be equal to that of similar states in $CH_2-CH_2-O$ bonds pertaining to POE chains; therefore, a factor $\omega \approx \exp(-300/RT)$ is required for the above states in PTDG chains.

Table II
**Distances between Nonbonded Atoms and Groups and Statistical Weights for the Structural Unit of PTDG Chains**

| conform | interactions of atoms or groups | no. of bonds apart | distance,[a] Å | statistical wt |
|---|---|---|---|---|
| $t_{i-1}$ | $CH_2\cdots CH_2$ | 3 | 4.21 | 1 |
| $g^{\pm}_{i-1}$ | | 3 | 3.20 | $\sigma$ |
| $g^{\pm}_{i-2}g^{\pm}_{i-1}$ | $CH_2\cdots CH_2$ | 4 | 3.73 | $\sigma$ |
| $g^{\pm}_{i-2}g^{\mp}_{i-1}$ | | 4 | 2.84 | 0 |
| $t_i$ | $S\cdots O$ | 3 | 4.08 | 1 |
| $g^{\pm}_i$ | | 3 | 3.15 | $\sigma'$ |
| $g^{\pm}_{i-1}g^{\pm}_i$ | $O\cdots CH_2$ | 4 | 3.78 | $\sigma'$ |
| $g^{\pm}_{i-1}g^{\mp}_i$ | | 4 | 2.67 | $\omega\sigma'$ |
| $t_{i+1}$ | $CH_2\cdots CH_2$ | 3 | 3.70 | 1 |
| $g^{\pm}_{i+1}$ | | 3 | 2.81 | $\sigma''$ |
| $g^{\pm}_i g^{\pm}_{i+1}$ | $CH_2\cdots S$ | 4 | 3.67 | $\sigma''$ |
| $g^{\pm}_i g^{\mp}_{i+1}$ | | 4 | 2.60 | $\omega'\sigma''$ |
| $t_{i+2}$ | $CH_2\cdots CH_2$ | 3 | 3.7 | 1 |
| $g^{\pm}_{i+2}$ | | 3 | 2.81 | $\sigma''$ |
| $g^{\pm}_{i+1}g^{\pm}_{i+2}$ | $CH_2\cdots CH_2$ | 4 | 3.44 | $\sigma''$ |
| $g^{\pm}_{i+1}g^{\mp}_{i+2}$ | | 4 | 2.38 | 0 |
| $t_{i+3}$ | $O\cdots S$ | 3 | 4.08 | 1 |
| $g^{\pm}_{i+3}$ | | 3 | 3.15 | $\sigma'$ |
| $g^{\pm}_{i+2}g^{\pm}_{i+3}$ | $CH_2\cdots S$ | 4 | 3.67 | $\sigma'$ |
| $g^{\pm}_{i+2}g^{\mp}_{i+3}$ | | 4 | 2.60 | $\omega'\sigma'$ |
| $t_{i+4}$ | $CH_2\cdots CH_2$ | 3 | 4.21 | 1 |
| $g^{\pm}_{i+4}$ | | 3 | 3.20 | $\sigma$ |
| $g^{\pm}_{i+3}g^{\pm}_{i+4}$ | $CH_2\cdots O$ | 4 | 3.78 | $\sigma$ |
| $g^{\pm}_{i+3}g^{\mp}_{i+4}$ | | 4 | 2.67 | $\omega\sigma$ |

[a] Distances were calculated using the following bond lengths: $l_{C-C} = 1.53$ Å,[1] $l_{C-O} = 1.43$ Å,[1] $l_{C-S} = 1.815$ Å.[22]

By comparing gauche states about bonds of type $i+1$ and $i+2$ with those from rotations about $CH_2-O$ bonds in POE,[1,3,20] it may be concluded that these states are 900 cal mol$^{-1}$ higher in energy than the corresponding trans states. As it occurs in POE chains, a pair of bond rotations of the same sign about $CH_2-CH_2-O$ bonds as well as $CH_2-O-CH_2$ bonds give rise to no significant interactions between groups separated by four bonds, and in both cases a statistical weight of $\sigma'' = \exp(-900/RT)$ was assigned to $g^{\pm}g^{\pm}$ states. The conformations $g^{\pm}g^{\mp}$ in $CH_2-O-CH_2$ bonds are completely excluded. These states in $CH_2-CH_2-O$ bonds, however, cause interactions between negatively charged S atoms and positively charged $CH_2$ groups at a distance of 2.60 Å. The repulsions should be larger than those of similar states in $CH_2-CH_2-S$ bonds owing to the fact that the van der Waals radius of S atoms (1.8 Å) is higher than that of O atoms (1.4 Å).[1] Therefore, a statistical weight $\omega' \approx 0.20$ was used at 25 °C, as first approximation, for the $g^{\pm}g^{\mp}$ conformations.

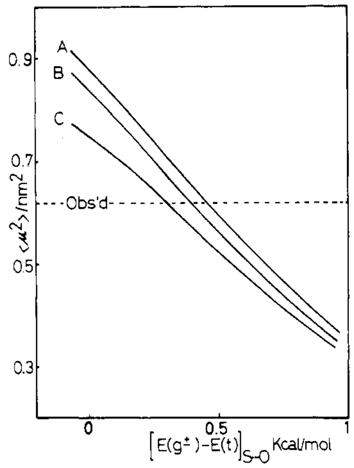

**Figure 5.** Theoretical calculations showing the dependence of the dipole moment ratio of PTDG on the energy difference between gauche and trans states in which the interacting species are S and O atoms. Curves A and B were obtained assuming $\varphi_g = \pm 120°$ and $\varphi_g = \pm 115°$, respectively. In both cases, the values used for the skeletal bond angles were: ∠CSC = 100°; ∠SCC = 114° and ∠OCC = ∠COC = 110°. Curve C was calculated assuming $\varphi_g = \pm 120°$ and all the skeletal bond angles were equal to 110°.

Rotations of ±120° about skeletal bonds of the type $i$ and $i + 3$ in Figure 4 reduce the distance between S and O atoms, separated by three bonds, from 4.08 to 3.15 Å. Similar rotations about $CH_2$–$CH_2$ bonds in POE bring O atoms separated by three bonds to a distance of 2.84 Å, being that the energy associated with these states is approximately 400 cal $mol^{-1}$ lower than the corresponding trans energy.[3,20] It should then be reasonable to expect that the energy associated with the gauche states of the PTDG chains is not far from that of the alternative trans states.[26] Given the uncertainty of the value of the energy involved in the transition trans to gauche, the calculations were carried out as a function of the rotational state energy $E_\sigma' = [E(g^\pm) - E(t)]_{S\cdots O}$. Because of the reasons outlined above, the statistical weights associated with the $g^\pm g^\mp$ states of the bonds S-$CH_2$-$CH_2$ and O-$CH_2$-$CH_2$ were considered to be $\omega$ and $\omega'$, respectively.

Values of the dipole moment ratio were calculated at 25 °C for PTDG chains containing $n = 398$ bonds, using the rotational isomeric state theory. The calculations show that the dipole moment ratio varies markedly with $E_\sigma'$. The results are plotted in Figure 5. Curve A in the figure was obtained assuming that the rotational isomeric states occur at $\varphi_t = 0°$ and $\varphi_g = \pm 120°$. Agreement between theory and experiment is found for $E_\sigma' = 450 \pm 20$ cal $mol^{-1}$. The theoretical value of $\langle\mu^2\rangle_0/nm^2$ is slightly sensitive to $\varphi_g$ as can be seen in curve B that was calculated using $\varphi_g = \pm 115°$. Here coincidence between theoretical and experimental results is found for $E_\sigma' = 400 \pm 20$ cal $mol^{-1}$. Moreover, the theoretical dipole moment ratio is moderately dependent on the skeletal bond angle values (in the vicinity of 110°) as is shown in curve C that was calculated assuming that all these angles were equal to 110°. The dipole moment ratio is very sensitive to the gauche population about $i$ and $i + 3$ bonds as is indicated in Table III where the partial derivatives of $\langle\mu^2\rangle_0$ with respect to the first-order statistical weights are given. The dependence of $\langle\mu^2\rangle_0/nm^2$ on the second-order parameters $\omega$ and $\omega'$ is negligible. The theoretical value of d ln $\langle\mu^2\rangle_0/dT$ was calculated to be $1.0 \times 10^{-3}$ $deg^{-1}$, in fair agreement with the experimental result.

The dependence of the dipole moment ratio on molecular weight follows the same trend as that in the family of polyoxides[1] and polyformals[8,9] in the sense that this quantity decreases as the chain length increases, reaching an asymptotic limit at relatively low molecular weight, well below the minimum value employed in the present study.

**Table III**
**Coefficients Calculated Using the Set of Parameters Indicated in the Text**

| coefficient | value |
|---|---|
| $\partial \ln \langle\mu^2\rangle_0/\partial \ln \sigma$ | 0.08 |
| $\partial \ln \langle\mu^2\rangle_0/\partial \ln \sigma'$ | 0.54 |
| $\partial \ln \langle\mu^2\rangle_0/\partial \ln \sigma''$ | −0.05 |

**Table IV**
**Dipole Moment Results on Poly(oxyethylene), Poly(thioethylene), and Their Alternating Copolymer Poly(thiodiethylene glycol)**

| | POE | PSE | PTDG |
|---|---|---|---|
| repeat unit | $(CH_2)_2O$- | $(CH_2)_2S$- | $(CH_2)_2O(CH_2)_2S$- |
| $\langle\mu^2\rangle_0/nm^2$ | 0.52[a] | 0.49[b] | 0.62 |
| $10^3$ d ln $\langle\mu^2\rangle_0/dT$ | 1.5[a] | | 1.6 |

[a] References 1 and 4. [b] Calculated using the RIS model (ref 22).

## Discussion

The theoretical analysis indicates that the energy corresponding to gauche states of bonds $i$ and $i + 3$ of the repeat unit of Figure 4 should be somewhat larger than that of trans states. Actually, agreement between theory and experiment is found for values of $E_\sigma'$ in the vicinity of 450 cal $mol^{-1}$, almost 0.9 kcal $mol^{-1}$ higher than that corresponding to gauche states about similar bonds in POE. This result is surprising in view of the fact that gauche states about $CH_2$–$CH_2$ bonds in POE and PTDG place a pair of adjoining O atoms in the former case and S and O atoms in the latter at distances that almost coincide with the sum of their respective van der Waals radius in each case. The value of $E_\sigma'$ is apparently similar to that found for gauche states about CH–$CH_2$ bonds in poly(propylene sulfide), where S atoms interact.[22]

Since PTDG may be considered a perfectly alternating copolymer of $CH_2$–$CH_2$–O and $CH_2$–$CH_2$–S units, it would be important to compare its configuration-dependent properties with those of POE and PSE. Unfortunately, experimental results relating to the configurational statistics of PES are meager, so that reliable comparisons can only be made with POE chains. The comparisons for the dipole moment results are given in Table IV, where the estimated value of $\langle\mu^2\rangle_0/nm^2$ for PES is also shown. It can be observed that the value of this particular property seems to be higher for the copolymer than for the homopolymers. The comparison once more demonstrates that very large errors may be introduced by use indiscriminate of the assumption that an alternating copolymer should have statistical properties intermediate with those of its parent homopolymers.[27]

According to the results, the form of the PTDG chains of minimum intramolecular energy has the rotational states $g^\pm ttttg^\pm$ for bonds $i - 1$ to $i + 4$ in Figure 4. The chains should be conformationally rather random, and the value of the characteristic ratio $\langle r^2\rangle_0/nl^2$ should not be far from that of POE. Actually, although the preference for gauche states about $CH_2$–$CH_2$ bonds in thioethylene units is lower than in similar bonds of POE, this preference may be compensated for by a higher population of such rotational states about $CH_2$–S bonds than about $CH_2$–O bonds.

Other physical properties such as melting points may also be compared. PES exhibits a high melting point, larger than 200 °C,[10] while POE melts at temperatures lying in the range 60–70 °C.[28] Since PTDG chains have melting points in the vicinity of 48 °C, the polymer is also similar to POE in its melting behavior.

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# Time-Resolved Emission Study of the Poly(*N*-vinylcarbazole)–Dimethyl Terephthalate and Poly(1-vinylnaphthalene)–Dicyanobenzene Interactions

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ABSTRACT: Both steady-state and time-resolved emission studies have been made for solutions containing poly(*N*-vinylcarbazole) and dimethyl terephthalate. Fluorescence spectra clearly reveal the presence of both an exciplex and an "exterplex" consisting of two carbazole chromophores and one molecule of dimethyl terephthalate. Similar results were obtained for solutions containing poly(1-vinylnaphthalene) and dicyanobenzene.

Exciplexes formed between an excited aromatic molecule and an electron donor or acceptor molecule have recently received considerable attention.[2] Caldwell et al. found that these highly polar exciplexes can be quenched by an additional electron donor or acceptor molecule to give an excited triplex or "exterplex" made up of three molecules.[3] The exterplex receives its stability from the distribution or separation of charge over three molecules. The exterplex, once it is formed, can reversibly reform the exciplex, or it may return to the ground state of each molecule by nonradiative or radiative decay. In particular, the exterplex formed between two naphthalene molecules and 1,4-dicyanobenzene (DCNB) has been studied throughly by Mimura and Itoh.[4] They found that in a concentrated solution of 2-methylnaphthalene, addition of DCNB quenched the naphthalene monomer and excimer emission with the appearance of both an exciplex emission ($\lambda_{max} \sim 420$ nm) and an exterplex emission ($\lambda_{max} \sim 490$ nm). The two peaks responsible for the exciplex and exterplex emission were fully resolved by decay and time resolved fluorescence measurements. In additon, they found that the exterplex formed between the two naphthalene chromophores of 1,3-dinaphthylpropane and DCNB was identical with the exterplex formed between two separated naphthalene molecules and DCNB. In order to extend these results to polymers and understand the exterplex formation between excited pendant aromatic chromophores on various polymers and small molecule ground state electron donor or acceptor molecules, it is first necessary to consider briefly the photophysical properties of polymers with repeating aromatic chromophores.

The emission spectra of several polymers in dilute solution, such as poly(1-vinylnaphthalene) (PVN) and poly(*N*-vinylcarbazole) (PVCz), are characterized by emission from excimers formed from two neighboring pendant aromatic groups on the same polymer chain.[5] The low-energy sandwich-type excimers of PVN ($\lambda_{max} \sim 400$ nm) and PVCz ($\lambda_{max} \sim 420$ nm) are accompanied by emission from a monomer state ($\lambda_{max} \sim 355$)[6] and a higher-energy excimer state ($\lambda_{max} \sim 370$ nm),[7] respectively.

The fluorescence emissions of both PVN and PVCz are readily quenched in the presence of small-molecule electron acceptors. For instance, the fluorescence of PVCz is greatly diminished when dimethyl terephthalate (DMTP) is added to either a solution or film of PVCz.[8] The quenching process is accompanied by the appearance

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