Macromolecules **1985**, *18*, 2739–2743

Random-Coil Configurations of Alicyclic Poly(thioformals)

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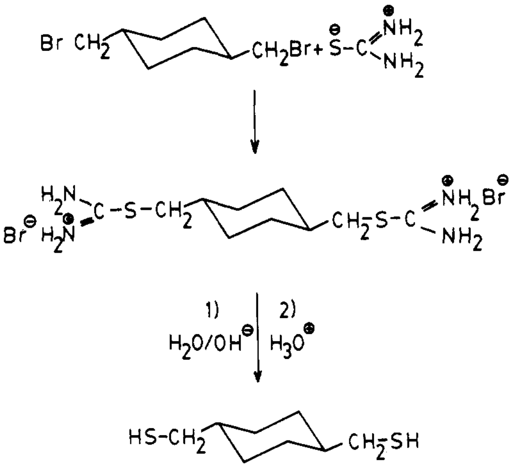
ABSTRACT: Poly(thiomethylene-1,4-*trans*-cyclohexylenemethylenethiomethylene) (PTCMT) was obtained by the condensation polymerization of *trans*-1,4-bis(mercaptomethyl)cyclohexane and paraformaldehyde using *p*-toluenesulfonic acid as the catalyst. The dielectric constants of the solutions of the polymer in benzene were, within experimental error, insensitive to temperature. The dipole moments of the chains, determined at several temperatures between 30 and 60 °C, yielded values of $D_n = \langle \mu^2 \rangle / nm^2 = 0.265–0.301$, significantly larger than the values of 0.176–0.207 obtained in the same interval of temperature for poly(oxymethylene-1,4-*trans*-cyclohexylenemethyleneoxymethylene) (POCMT), its homologous alicyclic polyformal. Also, the temperature coefficient $10^3(\mathrm{d} \ln \langle \mu^2 \rangle / \mathrm{d}T)$ of the dipole moments of the former polymer (4.3 K^{-1}) is somewhat lower than that of the latter (5.4 K^{-1}). Theoretical calculations, carried out with the rotational isomeric state model, showed that the dipole moments are extremely sensitive to the gauche population about the thioacetal skeletal bonds ($CH_2SCH_2SCH_2$). Comparison between theory and experiment suggests that the segment $SCH_2–SCH_2$ presents an attractive sulfur gauche effect of ca. 0.6 kcal mol^{-1}. The alicyclic poly(thioformal) has a melting point of 160 °C, a value significantly larger than that of the homologous polyformal (85 °C), in spite of the fact that the former polymer is more flexible than the latter.

Introduction

The schematic substitution of the oxygen atoms of polyethers and polyformals for sulfur atoms leads to the poly(thioethers) and poly(thioformals), respectively. Major changes occur in the properties of the resulting polymers as a consequence of the fact that the bond length C–S is longer than C–O by ca. 30%, while the bond angle CSC is smaller than COC by ca. 10°. Moreover, the values of the van der Waals radii more frequently used are in the range 1.8–1.9 Å for the sulfur atom and 1.4–1.6 Å for the oxygen atom.[1-3] These differences manifest themselves in the conformational characteristics of the chains; for example, CS–CC is quite flexible in contrast to the rigidity assigned to the CO–CC moiety of the polyoxide chains. Consequently, the structural characteristics of the poly(thioethers) and poly(thioformals) give rise to an increase in the flexibility of the chains with regard to that of the polyethers and polyformals, principally in the case of the homologous polymers in which the number of methylene groups in the repeating unit is three or lower. Taking the conformational entropy S_c as a measure of chain flexibility, one finds that the value of this parameter is 6.1 cal deg^{-1} per structural unit for poly(ethylene sulfide)[4] and 5.0 in the same units for poly(ethylene oxide);[5] these values are 4.8 and 4.0 cal deg^{-1} for poly(propylene sulfide)[3] and poly(propylene oxide),[6] respectively.

Most of the work dealing with the study of the conformational properties of polyethers, polyformals, poly(thioethers), and poly(thioformals) were carried out on symmetric chains.[4,5,7-18] In the case of the polyformals these investigations were extended to chains with cyclohexane rings incorporated in the main chain. Owing to the conformational wealth of the cyclohexane ring,[19] these studies are important to obtain a deeper knowledge of the relationship between structure and properties in polymers. In this context, the dipole moments and the configurational optical parameter Δa of poly(oxymethylene-1,4-*trans*-cyclohexylenemethyleneoxymethylene) were measured[20] and the results theoretically interpreted in terms of the rotational isomeric state (RIS) model.

Scheme I



This work focuses on the analysis of the configurational properties of poly(thiomethylene-1,4-*trans*-cyclohexylenemethylenethiomethylene) (PTCMT) the poly(cyclohexylene sulfide) homologue of poly(oxymethylene-1,4-*trans*-cyclohexylenemethyleneoxymethylene) (POCMT). The dipole moments and their temperature coefficient were measured and the results compared with those reported for POCMT in order to investigate how the presence of the sulfur atom affects the polarity and the melting behavior of the chains.

Experimental Section

Materials. *trans*-1,4-Bis(hydroxymethyl)cyclohexane (*trans*-cyclohexanedimethanol) (Eastman Kodak) was purified by two successive crystallizations in diethyl ether. The melting point of the purified product was 65 °C (lit.[21] mp 67 °C). The purity of the alicyclic diol was also checked by ^{1}H NMR spectroscopy. Thiourea, *p*-toluenesulfonic acid, hydrobromic acid, and paraformaldehyde were used as received. Benzene was purified by methods described elsewhere.[22]

Synthesis of *trans*-1,4-Bis(bromoethyl)cyclohexane. This compound was obtained by the reaction of *trans*-1,4-bis(hydroxymethyl)cyclohexane with hydrobromic acid and concentrated sulfuric acid.[23] The crystallization of the crude product yields colorless crystals of melting point 55 °C.

Synthesis of *trans*-1,4-Bis(mercaptomethyl)cyclohexane. The preparation of this compound was carried out by the reaction of *trans*-1,4-bis(bromomethyl)cyclohexane and thiourea, followed by hydrolysis of the resulting thiouronium salt according to Scheme I.[24]

Polymerization. Poly(thiomethylene-1,4-*trans*-cyclohexylenemethylenethiomethylene) (PTCMT) was obtained by

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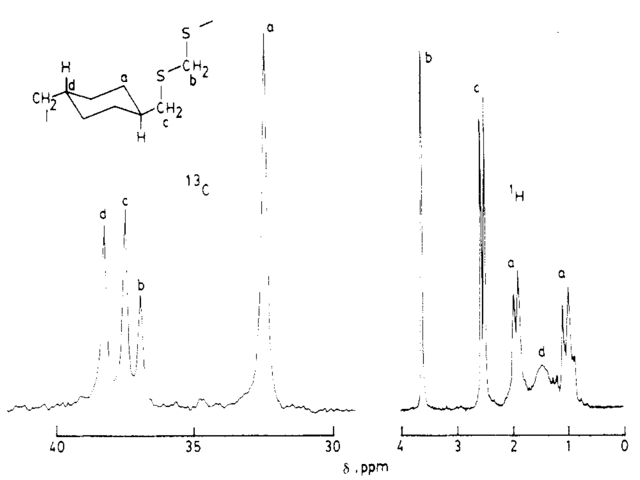

Figure 1. ^{1}H and ^{13}C NMR spectra of PTCMT.

the condensation polymerization of *trans*-1,4-bis(mercaptomethyl)cyclohexane and paraformaldehyde. The reaction was carried out under a nitrogen atmosphere in refluxing benzene for 24 h, using *p*-toluenesulfonic acid (1%) as the 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 further dissolved in benzene, precipitated into methanol, and dried under high vacuum at room temperature.

Characterization of the Polymer. The polymer was fractionated at 25 °C with chloroform–methanol as the solvent–nonsolvent system. Only the first fraction, which amounted to 30% of the total polymer, was used in the dielectric measurements. The number-average molecular weight of the fraction, measured with a Knauer vapor pressure osmometer, was 6000. The melting point of the polymer was determined with a Tottoli type Büchi apparatus at a heating rate of 2 °C/min; a value of 160 °C was found for the melting temperature.

^{1}H and ^{13}C NMR spectra of the polymer were obtained with a Bruker WP 80SV spectrometer working at 80 and 20.1 MHz, respectively. Deuterated chloroform was used as the solvent and tetramethylsilane as the internal standard. The spectra obtained are shown in Figure 1. The doublet centered at 2.55 ppm corresponds to the resonance of the thiomethylene protons. The resonance of the thioacetal protons appears as a singlet at 3.63 ppm. The other signals belong to the resonance of the axial and equatorial protons in the cyclohexane ring. The ^{13}C NMR spectrum presents four resonance signals corresponding to the four different carbons of the polymer. Both NMR spectra clearly show the purity of the polymer and the absence of 1,4-*cis*-cyclohexylene units in the polymer chain.

Dielectric Measurements. Values of the dielectric constant ϵ of solutions of the polymer in benzene were obtained at 30, 40, 50, and 60 °C, using a capacitance bridge (General Radio, Type 1620 A) operating at 10 kHz and a three-terminal cell.[8,9] Values of $n^2 - n_1^2$, where n and n_1 represent the refractive indices of the solutions and solvent, respectively, were measured at 633 nm with a Chromatix KHX laser differential refractometer.

Experimental Results

The dielectric constants of the solutions were, within experimental error, insensitive to temperature in the range 30–60 °C. A plot showing the concentration dependence of the increments of the dielectric constant of the solutions with respect to that of the solvent ($\Delta\epsilon = \epsilon - \epsilon_1$) at 30 °C is given in Figure 2. The increments in squared indices of refraction of the solutions ($\Delta n^2 = n^2 - n_1^2$) showed a slight increase with increasing temperature. In Figure 2 are also plotted the experimental values of Δn^2 at 30 °C against the weight fraction w of the polymer in the solution; values of $\mathrm{d}(n^2 - n_1^2)/\mathrm{d}w$, obtained from these plots at the temperature of interest, are also shown in Table I.

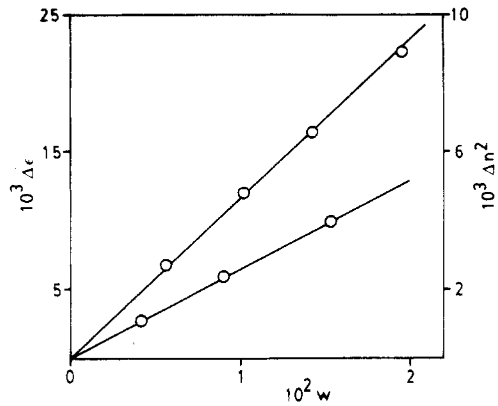

Figure 2. Increments in dielectric constant and squared index of refraction for solutions of PTCMT in benzene at 30 °C.

Table I
Summary of Dielectric Results for PTCMT and Comparison of the Dipole Moment Ratio of This Polymer with That of POCMT

T, °C	$\mathrm{d}(\epsilon - \epsilon_1)/\mathrm{d}w$	$\mathrm{d}(n^2 - n_1^2)/\mathrm{d}w$	$(\langle\mu^2\rangle/nm^2)_{\mathrm{PTCMT}}$	$(\langle\mu^2\rangle/nm^2)_{\mathrm{POCMT}}$[a]
30	1.137	0.258	0.265	0.176
40	1.137	0.265	0.277	0.186
50	1.137	0.276	0.289	0.197
60	1.137	0.285	0.301	0.207

[a] Reference 20.

Values of the dipole moment ratio $D_n = \langle\mu^2\rangle/nm^2$, where nm^2 is the mean-square dipole moment of a chain with n skeletal bonds, each of them having a dipole moment m, were obtained by means of the Guggenheim[25] and Smith[26] method, which results in the equation

$$D_n = \frac{27kTM}{4\pi\rho nm^2 N_{\mathrm{A}}(\epsilon_1 + 2)^2}\left\{\frac{\mathrm{d}(\epsilon - \epsilon_1)}{\mathrm{d}w} - \frac{\mathrm{d}(n^2 - n_1^2)}{\mathrm{d}w}\right\}$$

where k is the Boltzmann constant, N_{A} is Avogadro's number, ρ is the density of the solvent, M is the molecular weight of the solute, T is the absolute temperature. The average m^2 of the skeletal bond moments was calculated from $m^2 = (1/7)(4m_{\mathrm{CS}}^2 + 2m_{\mathrm{CC}}^2 + m_{\mathrm{CyCy}}^2)$. The values used for the bond dipole moments were $m_{\mathrm{CS}} = 1.21$ D, $m_{\mathrm{CC}} = 0.00$ D and $m_{\mathrm{CyCy}} = 0.00$ D,[3,20,27] where m_{CyCy} represents the bond dipole moment associated with the virtual bond joining the carbon atoms located in the 1,4 position of the cyclohexane ring. The uncertainty involved in the experimental values of D_n listed in the fourth column of Table I was estimated to be ca. ±5%. In the last column of the table and for comparative purposes the experimental values of the homologous polyether are also shown. It can be seen that the experimental value of D_n at 30 °C corresponding to PTCMT is almost 55% above that of POCMT. The temperature coefficient of the dipole moments $\mathrm{d}\ln\langle\mu^2\rangle/\mathrm{d}T$ was obtained by plotting the natural logarithm of the dipole moment ratio against temperature. The experimental value of this quantity for PTCMT was found to be 4.3×10^{-3} K^{-1}.

Theoretical Results

Conformational Energies. In order to interpret the differences observed in the conformational characteristics and melting behavior of PTCMT and POCMT, the conformational energies of these polymers were calculated with semiempirical potential functions. The repeating unit of these compounds in the planar all-trans conformation is shown in Figure 3, where X represents oxygen and sulfur atoms for POCMT and PTCMT, respectively. Appro-

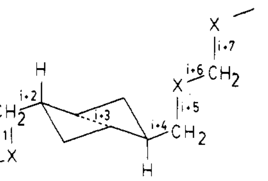

Figure 3. Structural unit of PTCMT in its all-trans conformation.

Table II
Parameters for the Lennard-Jones Potential[a]

atom pair	$R_{\min} = r_i + r_j$, Å	c	$10^3 a$
H...H	2.6	76.0	11.74
H...C	3.1	127.4	56.53
H...O	2.9	123.9	36.849
H...S	3.2	290.0	155.8
C...C	3.6	372.5	405.4
C...O	3.4	367.2	283.6
C...S	3.7	845.9	1085.2

[a] Units are such as to give E in kcal mol^{-1} when r is in Å.

priate values of the bond lengths and bond angles were obtained in most cases from studies of structurally related small molecules.[1-3,10] Briefly, bond lengths for C–S, C–O, C–C, and C–H are 1.815, 1.43, 1.53, and 1.09 Å, respectively. Values of the CSC, COC, CCS, CCO, CCC, and CCH bond angles are 100, 110, 114, 111.5, 111.5, and 110°, respectively.[2,3,10]

Conformational energies were calculated as a function of rotational angles for bonds of type $i + 4$ and $i + 5$ in Figure 3. The conformational energies for the other bonds are given elsewhere.[10,12] Two contributions to the conformational energies were computed: Torsional energies were evaluated with three-fold intrinsic potentials with barriers of 2.8, 1.76, and 1.80 for rotations around C–C, C–S, and C–O, respectively.[2,3,10] Nonbonded interactions between atoms separated by more than two bonds were calculated with the Lennard-Jones potential $V_{ij} = (a_{ij}/r_{ij}^{12}) - (c_{ij}/r_{ij}^{6})$. The London dispersion parameters c_{ij} were taken from ref 28; the values of the repulsive term a_{ij} were obtained by minimizing the potential V_{ij} for a given pair of atoms when their distance is set equal to the sum of the corresponding van der Waals radii. The parameters used in the computation of V_{ij} are given in Table II.

The molecule $C_6H_{11}CH_2XCH_3$ with equatorial substitution was used as a model compound to evaluate energies associated with rotations around $i + 4$ and $i + 5$ skeletal bonds, respectively. Distances r_{ij} between atom pairs separated by 3–6 bonds were calculated for the model with geometric transformation matrices defined about the chain bonds. Rotational angles about particular skeletal bonds were varied by intervals of 5°. The results as a function of the rotation angle ϕ are shown in Figures 4 and 5 for the ether and thioether model compounds, respectively. It can be observed that both curves are symmetrical around the $\phi = 180°$ line.

As can be seen in Figures 4 and 5 the energy associated with rotations about $i + 4$ bonds, which give rise to CH_2...S and CH_2...O interactions, respectively, presents three minima located at $\phi = 0$ and $\phi = \pm 120°$. The energy of the gauche states with respect to the alternative trans states is lower for the thioformal than for the formal; for example, the value of $E_\sigma = E(g^\pm) - E(t)$ is −0.4 kcal/mol in the former case and −0.15 kcal/mol in the latter. As for the rotation about the $i + 5$ bond, the energy increases as ϕ departs from 0° and reaches a small minimum at $\phi = \pm 80°$; then the energy steeply increases owing to the dramatic increase in the repulsive interactions between the hydrogen atoms corresponding respectively to the methyl and methylene groups of the cyclohexane ring (see Figure 4 and 5).

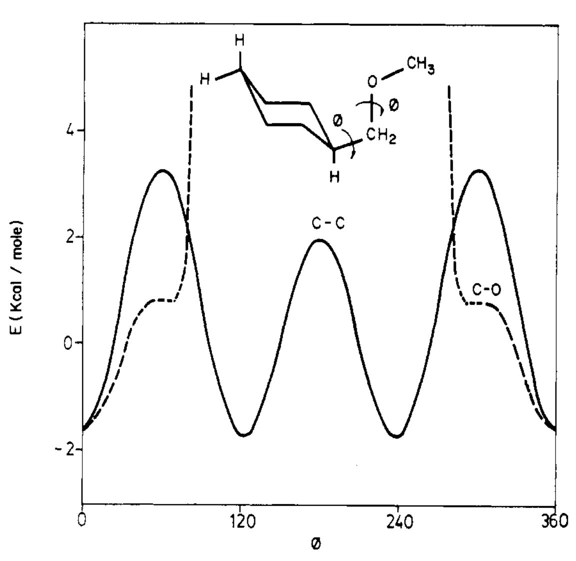

Figure 4. Calculated conformational energies as a function of rotational angles ϕ over C–C ($\phi_{C-O} = 0°$) and C–O ($\phi_{C-C} = 0°$) bonds.

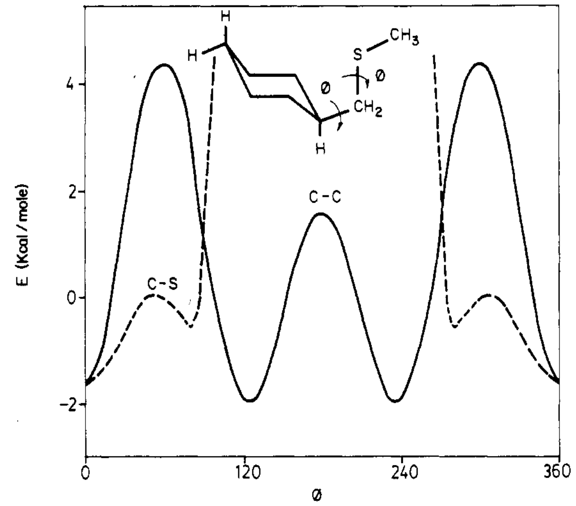

Figure 5. Calculated conformational energies as a function of rotational angles ϕ over C–C ($\phi_{C-S} = 0°$) and C–S ($\phi_{C-C} = 0°$) bonds.

Bond rotations of the same sign about pairs of bonds of type $i + 4$ and $i + 5$ are not permitted; however, bond rotations of different sign are allowed, and the energy associated with $g^\pm g^\mp$ conformations is 0.4 kcal mol^{-1} below that of the tt conformations in the case of the thioformal. The energy of this conformation is ca. 0.9 kcal mol^{-1} above that of the tt states in the case of the formal compound.

Earlier calculations carried out on the conformational energy associated with gauche states in the thiomethylene and oxymethylene sequences suggest that gauche states are preferred over the alternative trans states;[2,10,14] values of $E_{\sigma'} = -0.60$ and -0.30 kcal mol^{-1} were reported for gauche states about the skeletal bonds of the former and latter sequences, respectively. In considering interactions between atoms separated by four skeletal bonds the $g^\pm g^\mp$ conformations give rise to pentane-like interferences. For bond pairs in which CH_2...S interactions are involved, the energy is so high as to permit them to be ignored in the calculations of the dipole moments.[10] In the case of CH_2...O second-order interactions the energy is of the order[2] of 0.6 kcal mol^{-1}.

Statistical Weight Matrices. According to the results given above, the statistical weight matrices for the bonds

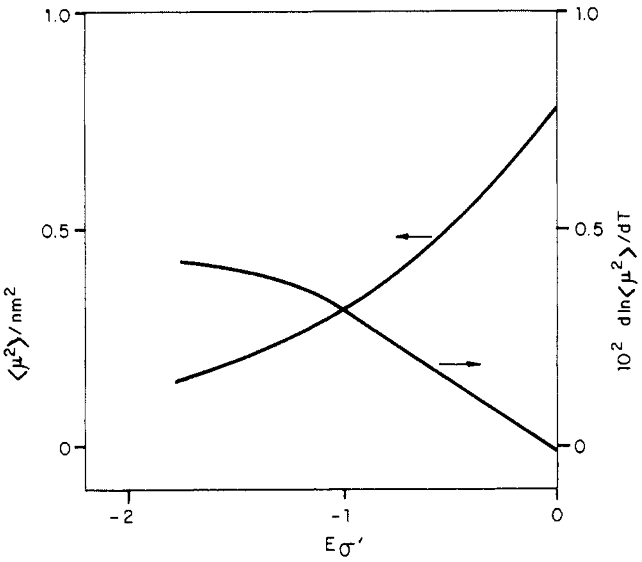

Figure 6. Theoretical dependence of the dipole moment ratio and its temperature coefficient on the conformational energy $E_{\sigma'}$.

included in the repeating unit of PTCDM (Figure 3) may be written in a first approximation as

$$U_{i+1} = U_{i+5} = \begin{bmatrix} 1 & 0 & 0 \\ 1 & 0 & \sigma \\ 1 & \sigma & 0 \end{bmatrix} \qquad U_{i+2} = \begin{bmatrix} 1 & \sigma & \sigma \\ 0 & 0 & \sigma \\ 0 & \sigma & 0 \end{bmatrix}$$

$$U_{i+3} = \begin{bmatrix} 1 & 0 & 0 \\ 1 & 0 & 0 \\ 1 & 0 & 0 \end{bmatrix} \qquad U_{i+4} = \begin{bmatrix} 1 & \sigma & \sigma \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$$

$$U_{i+6} = U_{i+7} = \begin{bmatrix} 1 & \sigma' & \sigma' \\ 1 & \sigma' & 0 \\ 1 & 0 & \sigma' \end{bmatrix}$$

Comparison between Theoretical and Experimental Dipole Moments. The 3 × 3 rotational state scheme adopted for PTCMT chains was based upon the conformational energies discussed above. The rotational states were assumed to be located at 0 and ±120°. Standard matrix multiplication methods[29,30] were used to calculate the dipole moment ratio and its temperature coefficient for chains of number-average molecular weight 6000; the atypical S–H dipolar end groups were properly taken into account. In order to facilitate the calculations, the cyclohexane ring was substituted by a virtual bond connecting the atoms in the 1,4 positions. The length of the virtual bond is 2.97 Å, and its direction makes an angle of 148.5° with the equatorial substitution.[20] By the standard convention concerning Cartesian coordinate systems,[29] the **T** matrix required to transform the coordinates from the reference frame $i + 5$ to $i + 4$ or $i + 3$ to $i + 2$ in Figure 3 will require adding 180° to the ϕ rotation angles of $i + 4$ and $i - 2$ skeletal bonds. By the use of the set of conformational energies $E_\sigma = -0.4$ and $E_{\sigma'} = -0.6$, all of them in kcal mol^{-1}, the values of $\langle\mu^2\rangle/nm^2$ and $10^3(\mathrm{d}\ln\langle\mu^2\rangle/\mathrm{d}T)$ were found to be 0.47 and 1.8 K^{-1}, respectively, in poor agreement with the experimental results of 0.265 and 4.3 K^{-1}. The discrepancy between theory and experiment may be caused by important sulfur gauche effects that probably occur for S...CH$_2$ interactions in the SCH$_2$–SCH$_2$ segment. Sulfur gauche effects were previously reported for these segments in the analysis of the dipole moments of poly(1,3-dithiocane).[12] In order to confirm these earlier results, the dipole moment ratio and its temperature coefficient were calculated as a function of $E_{\sigma'}$. The results obtained are plotted in Figure 6. It can be seen that satisfactory agreement between theory and experiment is found for $E_{\sigma'} = -1.2$ kcal mol^{-1}. Good agreement between the theoretical and experiment values of the temperature coefficient is also found for this value of $E_{\sigma'}$; for example, $10^3(\mathrm{d}\ln\langle\mu^2\rangle/\mathrm{d}T)_{\mathrm{th}} = 3.7$ K^{-1} whereas $10^3(\mathrm{d}\ln\langle\mu^2\rangle/\mathrm{d}T)_{\mathrm{exptl}} = 4.3$ K^{-1}. The value of $E_{\sigma'}$ found in this analysis is in very good agreement with the values of −1.1 and −1.2 kcal mol^{-1} obtained for this quantity from the critical analysis of the dipole moments of poly(1,3-dithiocane)[12] and poly(1-oxa-3-thiacyclopentane),[31] respectively. These results reveal that in the analysis of the dipole moments of symmetric polymers with SCH$_2$–SCH$_2$ segments in their chains, an extra stabilization energy of about 0.6 kcal mol^{-1} must be applied to gauche states relative to the alternative trans in order to achieve agreement between theory and experiment. This large attractive gauche effect in such linkages is somewhat lower than that found (0.9 kcal mol^{-1}) for the OCH$_2$–OCH$_2$ segments in POCMT as well as in the members of the aliphatic polyformals with repeating unit[14,15,18] (CH$_2$)$_z$OCH$_2$O. The great preference for gauche states about SCH$_2$S bonds gives rise to a high fraction of g$^\pm$g$^\pm$ conformations which place the dipoles corresponding to the CH$_2$SCH$_2$ groups in almost antiparallel direction—hence the relatively low polarity of these chains. An increase in temperature also increases the fraction of trans conformations in which the dipoles are in parallel direction, and consequently the dipole moments of these chains exhibit a strong dependence on temperature. Finally, it should be pointed out that the dipole moment ratio of the PTCMT chains is only slightly sensitive to E_σ. Thus $\langle\mu^2\rangle/nm^2 = 0.253$ for $E_\sigma = -0.58$ kcal mol^{-1}, and this value reduces to 0.242 for $E_\sigma = 0.3$ kcal mol^{-1}.

Conformational flexibility around the skeletal bonds may be expressed in terms of the conformations allowed to the bonds. The configurational partition function per skeletal bond z, related to the molecular configurational partition function Z by[5,7]

$$z = Z^{1/n}$$

where n is the number of skeletal bonds in the chain, should be useful to express the molecular flexibility of polymer chains. Since Z is dependent on the reference state, each element of the statistical weight matrices corresponding to the bonds should be taken relative to the most preferred state in the calculations. On the other hand, the configurational entropy related to z by the equation[5,7]

$$S_c = R(\ln z + (T/z)(\mathrm{d}z/\mathrm{d}T))$$

is independent on the reference states used to calculate z and consequently is also a very useful parameter to compare the flexibility of the chains. The results obtained for the values of S_c at 30 °C were 1.13 and 1.02 cal deg^{-1} per mol skeletal bond for PTCMT and POCMT, respectively. According to these calculations, the substitution of the oxygen atoms of alicyclic polyformals for sulfur atoms increases the flexibility of the chains.

In spite of the higher flexibility of PTCMT, this polymer melts at 162 °C, whereas its homologous polyformal POCMT has a melting point of 85 °C. One of the principal contributions to the melting entropy ΔS_m is the entropy of fusion at constant volume $(\Delta S_m)_V$. The configurational entropy, evaluated at the melting temperature of the polymer, was found to be in reasonable agreement with $(\Delta S_m)_V$ in some cases.[4,5] The values of S_c for PTCMT and POCMT, obtained at their respective melting temperatures, were 1.21 and 1.08, respectively, in the units given above. These results suggest that the large differences observed in the melting temperatures of these polymers should be attributed to the enthalpy rather than the entropy. It should be pointed out that since the sulfur atom has a much higher polarizability and interatomic attraction than the oxygen atom, the enthalpy of fusion of PTCMT should be higher than that of POCMT.[32] Molecular packing of the chains in the crystal that enhances S...S interactions would greatly increase the enthalpy of fusion of the alicyclic poly(thioformal).

Registry No. PTCMT (SRU), 99113-59-4; (*trans*-1,4-bis(mercaptomethyl)cyclohexane)·(paraformaldehyde) (copolymer), 99113-61-8.

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Remarks on A_2, Hydrodynamic Coil Expansion, and Concentration Dependence of the Diffusion Coefficient for Polystyrene in Toluene

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ABSTRACT: The approximation of the second virial coefficient by its expression for a hard sphere with a radius equal to the hydrodynamic radius R_H is investigated and shown to hold even for low molecular weights. The experimentally observed hydrodynamic expansion factor $\alpha_H^{\text{exptl}} \equiv R_H(T)/R_H(\Theta)$, where $R_H(T)$ and $R_H(\Theta)$ are the hydrodynamic effective radii in toluene (T) and cyclohexane (Θ), is found to decrease below unity at low molecular weight. This effect is interpreted by the theory of Yamakawa and Fujii as being due to the difference in the characteristic parameters of the linear mass density m_L, the Kuhn length l_K, and the effective chain thickness d. The concentration dependence of the diffusion coefficient is in the high molecular weight region satisfactorily expressed by the parameter X in the theories of Akcasu and Benmouna and of Yamakawa. The theory of Pyun and Fixman is also considered and shown to give good agreement if the function $\kappa(A)$ is interpreted properly.

Relation between A_2 and Hydrodynamic Volume

It is often convenient to investigate the molecular weight and temperature dependence of the second virial coefficient A_2 in terms of reduced variables. A commonly used example is the interpenetration function $\psi(\bar{z})$ defined by

$$A_2 = 4N_A\pi^{3/2}(\langle S^2\rangle^{3/2}/M^2)\psi(\bar{z}) \qquad (1)$$

where the symbols have their usual meaning. Another example is the effective hard-sphere radius r defined by[1,2]

$$A_2M^2/N_A = 16\pi r^3/3 \qquad (2)$$

In the study of the concentration dependence of the diffusion coefficient, it is often convenient to introduce the ratio $X = r/R_H$, with R_H the hydrodynamic radius of an isolated chain, by the following equation:[3,4]

$$(A_2M^2/N_A)/V_H = 4X^3 \qquad (3)$$

with $V_H = (4\pi/3)R_H^3$ the hydrodynamic volume. The dimensionless variables $\psi(\bar{z})$ and X are then related to each other through

$$X = (3\pi^{1/2}/4)^{1/3}\rho(\psi(\bar{z}))^{1/3} \qquad (4)$$

where

$$\rho = \langle S^2\rangle^{1/2}/R_H \qquad (5)$$

In these equations R_H is measured via D_z by quasi-elastic

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0024-9297/85/2218-2743$01.50/0