$$\Delta\zeta(\mathbf{r}) = \zeta(\mathbf{r}) - \zeta^b \tag{A.5}$$

$$\zeta(\mathbf{r}) = \eta(\mathbf{r}) - \left[f(\{\rho_i(\mathbf{r})\}) - \sum_i^0 \rho_i(\mathbf{r}) \frac{\partial f}{\partial \rho_i(\mathbf{r})} \right] \tag{A.6}$$

It should be clear from eq A.2 to A.4 that the bulk value ζ^b of $\zeta(\mathbf{r})$ is independent of the choice of the bulk phase b.

Equation A.4 is identical with the corresponding equation in ref 11 and all the mathematical development in that paper can be taken over at once. Thus from eq 2.17 and A.4 we obtain[11]

$$F = \sum_i^0 N_i \hat{\mu}_i + \gamma A \tag{A.7}$$

with the following expression for the interfacial tension:

$$\gamma A = \int \mathrm{d}^3 r \left(\frac{1}{12} \sum_{ij} W_{ij} {\sigma_{ij}}^2 \vec{\nabla} \rho_i \cdot \vec{\nabla} \rho_j - \Delta\zeta \right) \tag{A.8}$$

Furthermore, for planar interfaces, we have the relations[11]

$$\Delta\zeta + \frac{1}{12} \sum_{ij} W_{ij} {\sigma_{ij}}^2 \left(2\rho_i \frac{\mathrm{d}^2 \rho_j}{\mathrm{d}x^2} - \frac{\mathrm{d}\rho_i}{\mathrm{d}x} \frac{\mathrm{d}\rho_j}{\mathrm{d}x} \right) - \sum_p \frac{\rho_p}{Z_p} + \sum_p \rho_p^* \left\{ \frac{1}{Z_p} q_p(x,1) + \int_0^1 \mathrm{d}t \, \frac{{b_p}^2}{6} \left(\frac{\partial q_p}{\partial x} - q_p \frac{\partial^2 {q_p}^\dagger}{\partial x^2} \right) \right\} = 0 \tag{A.9}$$

and

$$\Delta f + \frac{1}{12} \sum_{ij} W_{ij} {\sigma_{ij}}^2 \frac{\mathrm{d}\rho_i}{\mathrm{d}x} \frac{\mathrm{d}\rho_j}{\mathrm{d}x} - \sum_p \rho_p^* \left\{ \frac{1}{Z_p} q_p(x,1) + \int_0^1 \mathrm{d}t \left(\frac{{b_p}^2}{6} \frac{\partial q_p}{\partial x} \frac{\partial {q_p}^\dagger}{\partial x} + \frac{1}{Z_p} q_p \frac{\partial {q_p}^\dagger}{\partial t} \right) \right\} - \sum_p \frac{\rho_p}{Z_p} \left[\ln \left(\frac{\rho_p}{\rho_p^*} \right) - 1 \right] = 0 \tag{A.10}$$

where

$${q_p}^\dagger(x,t) \equiv q_p(x,1-t) \tag{A.11}$$

From these we obtain the following expressions for the interfacial tension:

$$\gamma = \sum_p \rho_p^* \frac{{b_p}^2}{3} \int \mathrm{d}x \int_0^1 \mathrm{d}t \, \frac{\partial q_p}{\partial x} \frac{\partial {q_p}^\dagger}{\partial x} - \frac{1}{6} \sum_{ij} W_{ij} {\sigma_{ij}}^2 \int \mathrm{d}x \, \frac{\mathrm{d}\rho_i}{\mathrm{d}x} \frac{\mathrm{d}\rho_i}{\mathrm{d}x} \tag{A.12}$$

and

$$\gamma = 2 \left\{ \int \mathrm{d}x \, \Delta f - \sum_p \frac{1}{Z_p} \int \mathrm{d}x \left[\rho_p \ln \left(\frac{\rho_p}{\rho_p^*} \right) + \rho_p^* \int_0^1 \mathrm{d}t \, q_p \frac{\partial {q_p}^\dagger}{\mathrm{d}t} \right] \right\} \tag{A.13}$$

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Experimental Study of the Conformational Energy Associated with Gauche States about CH_2–CH_2 Bonds in Poly(ethylene sulfide)

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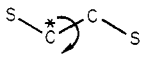
ABSTRACT: The conformational energy E_{σ_p} associated with gauche states about CH_2–CH_2 bonds in poly(ethylene sulfide) (PSE) was estimated from rotational isomeric state analysis of experimental dipole moments and their temperature coefficients corresponding to the alternating copolymer of pentamethylene sulfide and ethylene sulfide (PXS) as well as to 1,2-bis(butylthio)ethane (BBT). For both molecular chains, reasonable agreement between theoretical and experimental values of the dipole moments was found for values of E_{σ_p} lying in the range 0.4–0.7 kcal mol^{-1}. The values of E_{σ_p} thus determined are also in fair agreement with those calculated with semiempirical potential functions.

Introduction

The conformation-dependent properties of poly(ethylene sulfide) (PSE) have not been thoroughly investigated because of the intrinsic difficulties that the polymer presents; PSE is a highly crystalline polymer which melts at temperatures above 200 °C and is unstable above the melting temperature.[1] Recently, Abe[2] reported a theoretical study on the conformational properties of PSE and found that the flexibility of the polymer, as expressed by the partition function z, is significantly higher than that of poly(oxyethylene) (POE). Thus the value of z per monomer residue is 10.2 for PSE and 4.3 for POE. The high flexibility of PSE seems to promote the packing efficiency of the chains and, therefore, may contribute to strong molecular interactions that enhance the enthalpy of fusion of the polymer and its melting point. The conformational energies used in the calculations were obtained by using semiempirical potential functions.[2] It was found that the calculated values agree satisfactorily with known values of conformational energies of various simple alkyl sulfides bearing somewhat related structures. However, the reliability of the values calculated for the conformational energy associated with gauche states about CH_2–CH_2 bonds, in which first-order S···S interactions occur, was not tested due to the lack of suitable experimental data.

The experimental value of the first-order interaction involved in the gauche conformation of the moiety



in poly(propylene sulfide) was estimated from a rotational isomeric state analysis of the experimental values of the unperturbed dimensions, dipole moment, and their temperature coefficients observed for atactic samples of the polymer.[3] The value obtained for the gauche conformation (α) with the articulated methyl group trans to the preceding sulfur atom was $E_\alpha = 0.33$ kcal mol^{-1}, which is in fair agreement with the calculated value of 0.2 kcal mol^{-1} obtained by using Buckingham potential functions. On the contrary, the configurational properties indicated above are not sensitive to the energy associated with the gauche conformation (β), where the preceding sulfur atom is syn to both the following sulfur and the methyl group. The calculated value of this energy was 1.3 kcal mol^{-1}. In any case, the results seem to suggest that the gauche effect due to the first-order S···S interactions is slightly repulsive, in sharp contrast with the oxygen effect, which is attractive and has a value of 1 kcal mol^{-1} for POE[4] and 0.7 kcal mol^{-1} for poly(oxypropylene).[5]

The main purpose of this study is to estimate the S···S interaction energies involved in the gauche conformations about the skeletal C–C bonds in PSE from the rotational isomeric state analysis of the experimental dipole moment and its temperature coefficient corresponding to the alternating copolymer of ethylene sulfide and pentamethylene sulfide (PXS). The same treatment applied to 1,2-bis(butylthio)ethane will give additional information. These results should provide a quantitative estimate of the conformational energy associated with the SC–CS moiety, provided that the dipole moments are sensitive enough to this interaction energy. The conformational energy thus obtained will be compared with that calculated with semiempirical potential functions.

Experimental Section

Preparation of 1,2-Bis(butylthio)ethane (BBT). 1,2-Bis(butylthio)ethane was prepared by reaction of the sodium salt of butylthiol (2 mol) and 1,2-ethylene dibromide (1 mol) at room temperature, using absolute alcohol–dry benzene as solvent. The sodium bromide obtained in the reaction was eliminated by filtration. The product (BBT) was separated by fractional distillation and purified by successive distillations under vacuum ($n^{20}{}_D$ 1.4974). The molecular weight of the purified compound, determined in a Knauer vapor pressure osmometer, was 207, in very good agreement with the theoretical value (206).

Synthesis of the Polymer Sample. An alternating copolymer of pentamethylene sulfide and ethylene sulfide (PXS) was synthesized by condensation polymerization of the disodium salt of 1,5-pentamethylenedithiol with 1,2-ethylene dibromide in absolute alcohol–dry benzene. In order to obtain chains with CH_2Br end groups, an excess of ethylene dibromide was added in the reaction medium at the end of the synthesis process. The fraction insoluble in the medium at room temperature was separated and washed with alcohol and with distilled water until free of sodium bromide. A fraction of number-average molecular weight 3800, which amounted to 24% of the total polymer, was obtained by precipitation from benzene solution, using ethanol as precipitant. The sample was further freeze-dried from benzene.

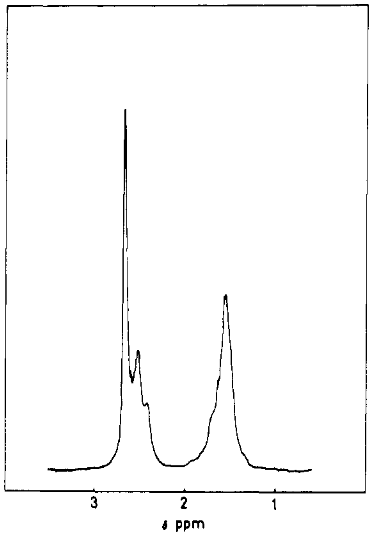


Figure 1. ^{1}H NMR spectrum of the alternating copolymer of pentamethylene sulfide and ethylene sulfide (PXS).

Characterization of the Polymer. The ^{1}H NMR spectrum of the polymer, shown in Figure 1, was recorded with a Perkin-Elmer spectrometer at 60 MHz, using deuterated chloroform as solvent and Me_4Si as internal reference. The analysis of the spectrum indicates the purity of the sample as well as its structure. Two multiplets at δ 2.55 and 1.55 are observed which correspond, respectively, to the resonance of the protons adjacent to the sulfur atoms and to the rest of the methylenic protons with two adjacent carbon atoms. The polymer is crystalline and the value of its melting point, determined at 1 °C/min in a Totoli-type Büchi apparatus, lies in the interval 64–66 °C.

Dielectric Measurements. Dielectric measurements were made at different temperatures on solutions of the polymer and of BBT in benzene, using a capacitance bridge and a three-terminal cell (Foxboro Model 3HV35) operating at a frequency of 10 kHz.[6,7] The apparatus was calibrated at each temperature of interest with reagent grade benzene, cyclohexane, and carbon tetrachloride, all being substances of known dielectric constant. Refractive indices were determined at 540 nm with a Brice-Phoenix differential refractometer.

Results and Discussion

The values of the dipole moment ratio $D_x = \langle\mu^2\rangle/nm^2$ were evaluated by means of the equation of Guggenheim and Smith[8,9]

$$D_x = \frac{27kTM}{4\pi\rho N_A(\epsilon_1 + 2)^2 nm^2}\left[\frac{d(\epsilon - \epsilon_1)}{dw} - \frac{d(\bar{n}^2 - \bar{n}_1^2)}{dw}\right] \quad (1)$$

where k is the Boltzmann constant, T is the absolute temperature, M is the molecular weight of the solute, and N_A is Avogrado's number. The value of nm^2, which represents the mean-square dipole moment of the chain in the idealization that all skeletal bonds are freely jointed, was calculated by assuming that the dipole moments associated with the skeletal bonds are $m_{C-S} = 1.21$ D,[2,10] $m_{C-Br} = 1.96$ D,[11] and $m_{C-C} = 0.00$ D.[4] Values of the limiting derivatives $d(\epsilon - \epsilon_1)/dw$ and $d(\bar{n}^2 - \bar{n}_1^2)/dw$ were obtained, as usual, from plots of the dielectric increments ($\Delta\epsilon = \epsilon - \epsilon_1$) and

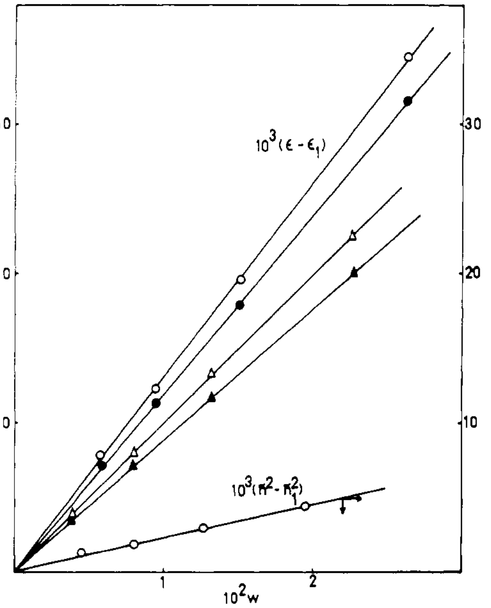


Figure 2. Typical data showing the concentration dependence of the increments in dielectric constant for PXS [(○) 20 °C; (●) 60 °C] and for BBT [(△) 20 °C; (▲) 60 °C]. The increments in squared index of refraction correspond to PXS at 30 °C.

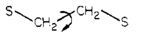
Table I
Dielectric Results for the Alternating Copolymer of Pentamethylene Sulfide and Ethylene Sulfide (PXS) and for 1,2-Bis(butylthio)ethane (BBT)

	T, °C			
	30	40	50	60
		PXS		
$d(\epsilon-\epsilon_1)/dw$	2.61_5	2.53_8	2.46_2	2.38_4
$d(\tilde{n}^2-\tilde{n}_1^2)/dw$	0.22_6	0.22_6	0.22_8	0.23_0
$\langle\mu^2\rangle/nm^2$	0.635	0.649	0.661	0.672
		BBT		
$d(\epsilon-\epsilon_1)/dw$	2.00_0	1.92_0	1.84_6	1.76_9
$d(\tilde{n}^2-\tilde{n}_1^2)/dw$	~0.00	~0.00	~0.00	~0.00
$\langle\mu^2\rangle/nm^2$	0.656	0.664	0.674	0.677

Table II
Dipole Moment Results for Poly(pentamethylene sulfide) (P5MS), Poly(ethylene sulfide) (PSE), the Alternating Copolymer of P5MS and PSE (PXS), and 1,2-Bis(butylthio)ethane (BBT) at 30 °C

polymer	$(\langle\mu^2\rangle/nm^2)_{exptl}$	$(d\ln\langle\mu^2\rangle/dT)_{exptl}$	$(\langle\mu^2\rangle/nm^2)_{theor}$	$(d\ln\langle\mu^2\rangle/dT)_{theor}$[c]
P5MS[a]	0.762	1.2×10^{-3}		
PSE[b]			0.43	2.8×10^{-3}
PXS	0.635	1.7×10^{-3}	0.604	9.4×10^{-4}
BBT	0.656	1.2×10^{-3}	0.696	6.6×10^{-4}

[a] Reference 12. [b] Reference 2. [c] The theoretical values were obtained by assuming that the energy involved in gauche states about the CH_2–CH_2 bonds in the moiety



is 0.55 kcal mol^{-1} over that of the alternative trans states.

the squared index of refraction increments ($\Delta\tilde{n}^2 = \tilde{n}^2 - \tilde{n}_1^2$) against the weight fraction of solute, w. Typical plots of this kind are shown in Figure 2 for PXS and BBT. In the case of BBT, the experimental values of $\Delta\tilde{n}^2$ are negligible in the temperature range studied. Values of the dipole moment ratio for PXS and BBT, in the temperature interval 30–60 °C, are given in the second and fifth rows of Table I, respectively. In Table II and for comparative purposes, the values of $\langle\mu^2\rangle/nm^2$ for poly(pentamethylene sulfide) (P5MS) and PSE are indicated. It can be observed that the value of the dipole moment ratio at 30 °C for PXS is intermediate to the values of this parameter for PSE[2] and P5MS,[12] the parent homopolymers of the alternating copolymer, PXS.

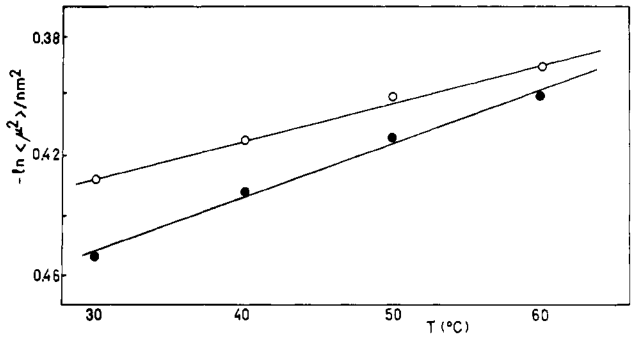


Figure 3. Temperature dependence of the natural logarithm of the dipole moment ratio for PXS (●) and BBT (○).

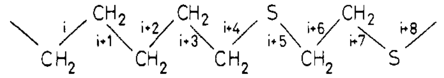
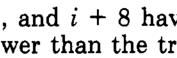


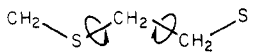
Figure 4. Repeat unit of the PXS chain in the all-trans conformation.

Values of the temperature coefficient d ln $\langle\mu^2\rangle/dT$ for both BBT and PXS were obtained from plots of the natural logarithm of the dipole moment ratio against temperature. As shown in Figure 3, both samples exhibited very nearly the same slope, which corresponds to 1.2×10^{-3} and 1.7×10^{-3} K^{-1}, respectively.

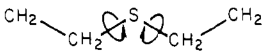
The experimental results were interpreted in terms of the rotational isomeric state model. The PXS chain in its all-trans conformation is shown in Figure 4. Values of the CSC, CCS, and CCC bond angles were taken to be 100, 114, and 110°, respectively.[2,3,13] Conformational energies about bonds i to $i + 8$ in Figure 4 were obtained from spectroscopic studies of model compounds, by comparison between theoretical and experimental values of some configuration-dependent properties, or by calculations of these energies using standard semiempirical potential energy functions. A brief summary of this information follows. The energy associated with gauche states about bonds of types i and $i + 3$ should be identical with that of similar bonds in P5MS. Recent calculations[14] carried out by using Buckingham potential functions show that the conformational energy parameter $E_{\sigma'}$ assigned to gauche states about these bonds may be in the vicinity of 0.4 kcal mol^{-1}, a value very close to that obtained from the comparison of the theoretical and the experimental dipole moment ratio corresponding to P5MS,[12] which is 0.3 kcal mol^{-1}. Abe[2,3] used semiempirical potential functions to examine the relative stability of gauche states about



bonds in methyl ethyl sulfide. He found $E_{\sigma''} = -0.1$ kcal mol^{-1}, which is in reasonable agreement with the value obtained from Raman and infrared spectra on the same compound ($E_{\sigma''} = 0$ to -0.2 kcal mol^{-1}).[15,16] According to this, we shall assume in the calculations that bonds of types $i + 4$, $i + 5$, $i + 7$, and $i + 8$ have gauche states with energies slightly lower than the trans states.[14] Gauche states about bonds of type $i - 1$ are 0.5 kcal mol^{-1} higher in energy than the alternative trans states.[4,13] As for the conformational energy associated with gauche states about bonds of type $i + 6$, recent calculations[2,14] on the conformational energy of gauche states about C–C bonds in PSE suggest that the trans states should definitely be preferred, the value of the energy difference $[E(g^{\pm}) - E(t)]_{S\cdots S}$ lying in the vicinity[17] of 0.4 kcal mol^{-1}. The magnitude of the gauche sulfur effect associated with the $SCH_2CH(CH_3)S$ moiety was estimated by Abe[3] in poly(propylene sulfide) (PPS) from rotational isomeric state analysis of the experimental values of several configuration-dependent properties. He found that in contrast with what occurs in poly(oxypropylene), the gauche effect is somewhat repulsive and should be only of the order of 0.1 kcal mol^{-1}. Therefore, he used a value of 0.5 kcal mol^{-1} for the energy of gauche states about CH_2–CH_2 bonds in PSE. Given the relatively low molecular weight of the PXS sample studied, it is necessary to take into account the terminal groups of the molecular chains. In this case, they are two CH_2–Br bonds which have a dipole moment of 1.96 D. Gauche states about bonds 2 and $n - 1$ give rise to S···Br interactions. The energy associated with these conformations is not known and we have assumed, as a first approximation, that it is 0.5–2 kcal mol^{-1} higher than that corresponding to the alternative trans conformations. The $g^{\pm}g^{\mp}$ conformations about pairs of bonds $(i, i - 1)$, $(i - 1, i - 2)$, and $(i + 2, i + 3)$ were considered to be excluded; in any case, the dipole moment ratio is not at all sensitive to the energy of these conformations. In accordance with earlier calculations[2] on the second-order interactions involved in the sequences



and



it was assumed that the corresponding conformational energies are $E_{\omega'} = 1.1$ and $E_{\omega''} = 0.4$ kcal mol^{-1}, respectively.

Following standard matrix multiplication methods,[13,18] values of the dipole moment ratio were calculated at 30 °C for a chain of PXS consisting of $x = 21$ units ($n = 201$ bonds), as well as for the BBT compound. Since the results of the conformational energy calculations in PSE[2,14] suggest that the displacements $\Delta\phi$ of the rotational minima from the regularly staggered gauche position are in the range of 5–10°, for both C–S and C–C bonds, the rotational minima for similar bonds in PXS were assumed to be located at 0 and ±110°. For the other bonds it was assumed that they occur at 0 and ±120°.

As stated above, the value of the calculated conformational energy involved in gauche conformations about bonds of type $i + 6$ has not been tested due to the lack of suitable experimental results. Therefore, the dipole moment ratio corresponding to PXS and BBT was evaluated in both cases as a function of the rotational state energy $E_{\sigma_p} = [E(g^{\pm}) - E(t)]_{S\cdots S}$. Values of E_{σ_p} used in the calculations are indicated in Figure 5. The other conformational parameters were kept constant: $E_{\sigma'} = 0.3$, $E_{\sigma''} = -0.1$, $E_{\sigma} = 0.5$, $E_{\omega'} = 1.7$, and $E_{\omega''} = 0.4$, all in kcal mol^{-1}. The observed values of $\langle\mu^2\rangle/nm^2$ for PXS and BBT are shown by the dotted lines in Figure 5. The calculations show that the dipole moment ratio decreases markedly as the trans conformation tends to be more stabilized around the C–C bond of the thioethylene unit. The negative value of $\langle\mu^2\rangle/nm^2$ vs. E_{σ_p} may be explained on the basis of the fact that the value of the dipole moment ratio should be nil for the all-trans conformation of the chain. For both PXS and BBT chains, agreement between the calculated and the experimental value of $\langle\mu^2\rangle/nm^2$ is obtained for values of E_{σ_p} lying in the range 0.4–0.7 kcal mol^{-1}. For $E_{\sigma_p} = 0.55$ kcal mol^{-1} the results at 30 °C are as follows: PXS, $\langle\mu^2\rangle/nm^2 = 0.604$, i.e., 5% lower than the experimental result; BBT, $\langle\mu^2\rangle/nm^2 = 0.697$, i.e., 6% higher than the experimental value. All theoretical results (Figure 5) related to the dipole moment ratio of PXS chains were carried out by assuming that the energy associated with gauche states about bonds 2 and $n - 1$ have an energy 0.5 kcal mol^{-1} higher than the trans states. If we assume that both bonds are restricted to the trans state, then the values of $\langle\mu^2\rangle/nm^2$ decrease about 3%. It can be observed in Figure 5 that the value of E_{σ_p} necessary to match the experimental results for BBT is somewhat larger than that for PXS. In both cases, however, the agreement is reasonable within the uncertainties involved in the experimental error as well as in the rotational isomeric state approximation.

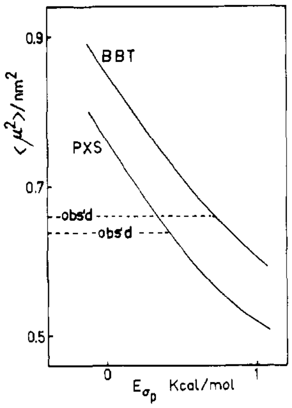
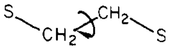


Figure 5. Results of rotational isomeric state analysis calculations showing the dependence of the dipole moment ratio on $E_{\sigma_p} = [E(g^{\pm}) - E(t)]_{S\cdots S}$ for both BBT and PXS.

The present results confirm those reported earlier by Abe,[2] according to which trans states about the moiety



in PSE should be clearly preferred to the alternative gauche states, in sharp contrast with what occurs in POE, where CH_2–CH_2 bonds have gauche states with an energy 0.5 kcal mol^{-1} lower than the trans states. It should also be stressed that the value of the conformational energy associated with gauche states about CH_2–CH_2 bonds in PSE is quite in line with that corresponding to gauche states about similar bonds in poly(thiodiethylene glycol) ($E = +0.4$ kcal mol^{-1}), where S···O interactions occur.[19]

The dipole moments of PXS and BBT exhibit a positive temperature coefficient due to the strong dependence of $\langle\mu^2\rangle$ on the gauche population about bonds of type $i + 6$. An increase in temperature causes an increase in gauche states about these bonds and, for the reasons outlined above, the dipole moments of the chains also increase. Hence the temperature coefficient becomes positive. The contribution of C–S bonds to the temperature coefficient is insignificant due to the fact that these bonds are almost freely rotating.[2,3,14] In brief, agreement between theory and experiment is satisfactory, as can be seen in Table II, where experimental and theoretical values of $d \ln \langle\mu^2\rangle/dT$ for both PXS and BBT are shown.

The PXS repeat unit has nine skeletal bonds and the C–S bonds have gauche and trans states of essentially the same energy. Since the rest of the bonds show a clear preference for trans states, the crystalline state configuration of PXS should correspond to an all-trans conformation.

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Evolution and Stability of Polypeptide Chain Conformation: A Simulation Study[1]

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ABSTRACT: The evolution of the conformations of short polypeptide chains has been studied by using a variant of the Monte Carlo method. A detailed molecular model is used in which the atoms and bonds are represented in full; short- and long-range interactions, hydrogen bonding, and bond torsional energies are incorporated by means of the empirical ECEPP scheme. Partial and complete folding of the chains from initially open conformations was observed, and simulations begun in a helical state were observed to remain in the same conformation throughout the run. The computations made use of a high-speed array processor; this permitted simulation runs of lengths barely attainable on the fastest of large scientific computers currently available.

I. Introduction

It is well established that the amino acid sequence and the surrounding solvent dictate the unique structural form in which a globular protein exists in its native state in solution.[3,4] A considerable degree of effort has been invested in attempting to determine the nature of the interactions within the molecule that are responsible for this three-dimensional structure and for the folding pathways by which the molecule evolves from the denatured coiled state to the well-structured native state, but, despite limited success,[4] a great deal of work remains to be done.

A related, but somewhat more tractable problem involves the conformational properties of shorter polypeptide chains containing some 10 residues, as opposed to proteins which generally consist of more than 100 residues. The two problems are connected by the fact that the same structural units and interactions are present in each; the simplification results from the fact that, in any attempt to simulate these molecules numerically, the shorter the chain the fewer the number of degrees of freedom, and hence the greater the chance of sampling a significant proportion of the conformational space of the molecule.

In this paper we report on a series of numerical simulations of peptide chains using a Monte Carlo type approach. The chain is placed in a particular initial state and its conformation is allowed to evolve by means of small random changes of the internal coordinates; whether or not a particular change is accepted is determined by a Monte Carlo procedure which examines the energy differences involved. The simulation follows the conformation of the chain over a great many such changes, as many as 5×10^6. A variety of different kinds of behavior are found to occur; these will be detailed subsequently, but several of the runs lead to the formation of apparently stable right- or left-handed α-helices from initially extended chain conformations, whereas others did not succeed in producing persistent, recognizable structures.

The simulations described here are considerably more extensive than those of previous Monte Carlo work,[5-10] both in regard to the nature and extent of the sampling involved and also in the fact that the often drastic simplifications of the underlying model necessary to reduce the computational requirements in some of the earlier studies[5-8] have been obviated (see below). The key to the ability to carry out lengthy computations of the kind required in this study lies in the use of an array processor. This device will be described in greater detail below, but briefly, it is a small high-speed processor, supervised (in our case) by a minicomputer, which, if carefully programmed, can exhibit a performance comparable to, or even exceeding, most of the large-scale scientific computers currently in use. More significantly, this performance is achieved at a small fraction (less than 5%) of the cost of the large machines.

The earliest simulations[5] employed hard-sphere models; such systems lack the attractive forces which are essential for the appearance of ordered three-dimensional chain structure. A later Monte Carlo study[6] using a more detailed residue model failed to include the interactions between residues; effects arising from excluded volume and long-range interactions could not, therefore, be observed. Several subsequent studies[7-10] included all interresidue interactions. In some,[7-9] the sampling scheme permitted individual residue conformations corresponding only to low-energy states of the terminally blocked single residue; this approach excluded those low-energy conformations of the full polypeptide in which attractive long-range interactions compensate for any residues not in states com-