Macromolecules 1981, 14, 608–613

ΔH_{bb} and ΔH_{sc}, depend upon the tacticity of the polymer. Conformational energies derived from spectroscopic measurements are compared with energies derived from rotational isomeric state calculations and from changes in specific heat at the glass temperature. Reasonable agreement is obtained when all the uncertainties are considered. Improvements in analysis and experiments will provide further tests of these concepts. The predictions of the Gibbs–DiMarzio theory are not supported by the observation that $\Delta H/RT_g$ is not constant (1.1–2.6 for isotactic and syndiotactic PMMA's). Side-chain conformations are identified as an important factor in the glass temperature behavior of isotactic PMMA. The utility and value of precise spectroscopic measurements in testing and extending polymer theory have been demonstrated.

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Conformational Properties of Poly(3,3-dimethylthietane)

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ABSTRACT: A sample of poly(3,3-dimethylthietane) (PDS) was obtained by cationic polymerization of 3,3-dimethylthietane, using acetyl hexafluoroantimonate as initiator. A fraction having $M_n = 8200$ was isolated and purified; dipole moment measurements carried out in benzene solutions in the temperature range 30–60 °C yielded values of $\langle \mu^2 \rangle / xm^2 = 0.616$–$0.627$ and a temperature coefficient $d \ln \langle \mu^2 \rangle / dT = 0.6 \times 10^{-3}\ K^{-1}$ at 30 °C. The rotational isomeric state model was used to compute theoretical values of these quantities by utilizing calculated values of conformational energies. Agreement between theory and experiment is achieved if extra stabilization energies associated with gauche conformations about skeletal C–C bonds are postulated. Comparisons between several conformational properties of PDS, PDO [poly(3,3-dimethyloxetane)], and PTS [poly(trimethylene sulfide)] are presented.

Introduction

Conformational analysis of poly(3,3-dimethyloxetane) (PDO) has been reported in a previous paper.[1] It was found that this polymer is similar to poly(trimethylene oxide) (PTO) in molecular dimensions and flexibility but that the polymers differ vastly in their dipole moments. Rotational isomeric state computations carried out by utilizing calculated conformational energies gave a good account of the PDO dipole moments and their temperature coefficient without the need of postulating noticeable extra stabilization energies associated with the gauche conformations about the C–C bonds.

A similar treatment can be applied to poly(3,3-dimethylthietane) (PDS), the sulfur analogue of PDO. PDS differs considerably from PDO in its structural features; thus the C–S bond length is ca. 30% longer than the C–O bond length,[2-4] the CSC bond angle is about 10° smaller than the COC bond angle,[2-4] and the van der Waals radius of the S atom is about 20% larger than that of the O atom.[5] It should be interesting to investigate whether these differences manifest themselves in the conformational characteristics.

Another important purpose of the present investigation was to compare the configuration-dependent properties of PDS, mainly its dipole moments, with those of poly(trimethylene sulfide) (PTS). It has been suggested from spectroscopic studies on various simple alkyl sulfides that the bond sequence CS–CC is quite flexible, in contrast with the rigidity assigned to the CO–CC moiety of polyoxide chains.[6,7] For example, whereas gauche conformations about the former bonds seem to be slightly more stable than the trans conformations, these conformations about the latter bonds have an energy 0.9 kcal mol^{-1} higher than the corresponding trans states.[8-10] Moreover, recent calculations on the conformational energies of gauche states about SC–CC bonds in PTS indicate that these states have a slightly higher energy than the trans states.[11,12] It should therefore be interesting to investigate the influence of the

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Table I
Summary of Dielectric Results

T, °C	$d(\epsilon - \epsilon_1)/dw$	$d(n^2 - n_1^2)/dw$	$\langle\mu^2\rangle/xm^2$
30	1.99	0.12	0.616
40	1.90	0.12	0.619
50	1.82	0.12	0.624
60	1.74	0.12	0.627

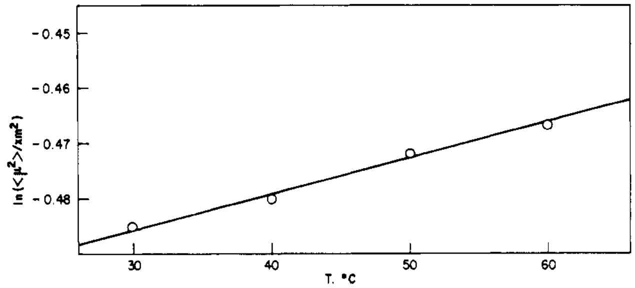

Figure 1. Natural logarithm of the dipole moment ratio as a function of temperature.

methyl groups on the conformational energies about CC–SC and CC–CS bonds since, as a result of this influence, some of the configuration-dependent properties of PDS may differ from those of PTS.

This work focuses on the dipole moments of PDS, an interesting configuration-dependent property which can be determined for chains of any length either in the bulk state or in solution.[13] Possible sulfur gauche effects were also investigated by comparison of theoretical and experimental (i.e., adjusted) energies.

Experimental Section

The monomer 3,3-dimethylthietane was prepared from 2,2-dimethyl-1,3-dibromopropane and potassium hydrosulfide in alcoholic medium; bp 115–117 °C (lit.[14] bp 120 °C). Final purification of the monomer was accomplished by treatment with calcium hydride for 24 h under high vacuum. The cationic polymerization of the monomer was carried out in bulk at room temperature, using acetyl hexafluoroantimonate as initiator. The polymer was precipitated in an aqueous solution of sodium carbonate, extracted with benzene, reprecipitated in methanol, and finally freeze-dried from benzene.

The number-average molecular weight of the polymer, measured with a Knauer vapor pressure osmometer, was 8200. The NMR spectrum, registered on a Perkin-Elmer 60-MHz spectrometer, is similar to that reported elsewhere[15] and shows two singlets at $\delta = 1$ and $\delta = 2.6$ from Me_4Si, corresponding to the methyl and methylene protons, respectively.

Dielectric constants of solutions of the polymer in benzene were measured with a capacitance bridge operating at a fixed frequency of 10 kHz. The three-terminal cell (Foxbord Model 3HV35) was calibrated with suitable purified solvents at each temperature of interest.[16,17] The refractive indices of the solutions were measured at 546 nm, using a Brice-Phoenix differential refractometer.

Values of the derivatives $d(\epsilon - \epsilon_1)/dw$ and $d(n^2 - n_1^2)/dw$ for the polymer solutions were measured in the temperature range 30–60 °C and the results obtained are given in the second and third columns of Table I. The dipole moments of the chains were then determined by using the equation of Guggenheim and Smith.[18,19] The value of the dipole moment ratio $\langle\mu^2\rangle/xm^2$ (where x is the number of repeat units of the chain, each one having a dipole moment m) at each temperature of interest is shown in the fourth column of Table I.

The value of the temperature coefficient was obtained by plotting the natural logarithm of the dipole moment ratio against temperature. As shown in Figure 1, the resulting plot exhibits quite a low slope, corresponding to $10^3[d \ln \langle\mu^2\rangle/dT] = 0.6\ K^{-1}$.

Conformational Energies

The structural parameters and dipole moments used in the calculations of the conformational energies were obtained from studies of structurally related small molecules. Bond lengths for C–S,[2] C–C,[20] and C–H[20] bonds are 1.815, 1.53, and 1.10 Å, respectively. Values of the CSC,[2-4] CCC,[20] CCS,[4] and CCH[20] bond angles are 100, 110, 114, and 110°, respectively. The CH_2–S bond dipole moment[21] is 1.21 D, and this value, in conjunction with the C–S bond length, indicates that partial electron charges of −0.28 and 0.14 must be assigned respectively to the sulfur and carbon atoms joined by the C–S bond.

Table II
Parameters Used for Nonbonded Interactions

atom or group	van der Waals radius, Å	eff no. of electrons	polarizability, Å³
C	1.8	5	0.93
S	1.9	13.5	2.39
H	1.3	0.9	0.42
CH_3	2.0	7	1.77

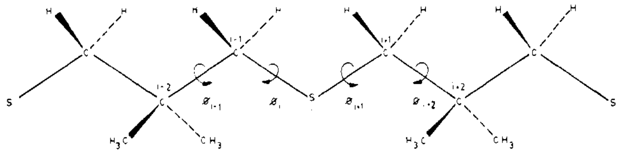

Figure 2. A segment of the PDS chain shown in its planar all-trans ($\phi = 0$) conformation.

The intramolecular energy associated with a given conformation was taken to be the sum of nonbonded, torsional, and Coulombic contributions. Nonbonded interaction energies between atoms i and j separated by more than two bonds were calculated by using the Lennard-Jones potential $V_{ij} = a_{ij}/r_{ij}^{12} - C_{ij}/r_{ij}^{6}$. The attractive parameters C_{ij} were evaluated from atomic polarizabilities and the number of effective electrons by application of the Slater–Kirkwood equation[22,23] and the repulsive term a_{ij} was determined by minimizing the energy V_{ij} at $r_{ij} = r_m = r_i^0 + r_j^0$, where r_i^0 and r_j^0 are the adjusted van der Waals radii of atoms i and j, respectively. Methyl groups were treated as spherical domains.[23] The parameters used to compute a_{ij} and C_{ij} are given in Table II.

The torsional contributions were taken to be[23] $E_{tor} = (E_0/2)(1 - \cos 3\phi)$, where ϕ is the skeletal bond rotation angle and E_0 is the intrinsic barrier height, whose value was taken as[4] 2.8 and 1.82 kcal mol^{-1} for rotations about C–C and C–S, respectively.

The Coulombic contributions were calculated as[23] $E_{Coul} = kq_iq_j/\epsilon r_{ij}$, where $k = 332.1$ is a conversion factor giving E_{Coul} in kcal mol^{-1} when q_i and q_j are in fractional parts of electron charge and r_{ij} is in Å. A value of $\epsilon = 3$ was assigned for the effective dielectric constant, as is generally done in calculations of this kind.[1]

A portion of the poly(3,3-dimethylthietane) chain in its planar all-trans conformation is shown in Figure 2. Two kinds of skeletal bonds have to be considered according to their conformational energies: the C–S or S–C bonds (like i and $i + 1$ in Figure 2) and the C–C bonds (like $i - 1$ and $i + 2$ in Figure 2). The molecule $(CH_3)_3CCH_2SCH_2CH_3$ and the molecular fragment $SCH_2C(CH_3)_2CH_2SCH_3$ were used as models for evaluating energies associated with rotations around S–C and C–C bonds, respectively. The results are shown in Figure 3 as a function of rotation angle ϕ; all the remaining skeletal bonds were kept trans. Each curve was normalized with respect to the energy of its trans ($\phi = 0$) conformation; the figure is symmetrical around the $\phi = 180°$ line, and the second part is not shown.

As can be seen in Figure 3, the energy associated with rotation ϕ around C–S bonds increases as ϕ departs from 0°. In the region $0 \le \phi \le 75°$, the variation of energy with

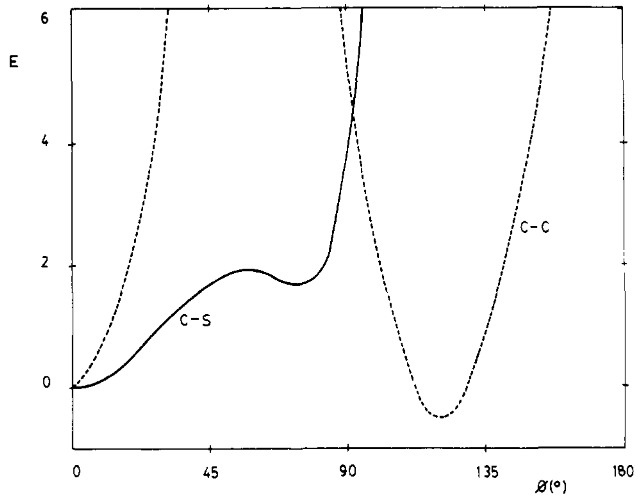

Figure 3. Calculated conformational energies (in kcal mol^{-1}) as functions of rotational angle ϕ over C–S (solid line) and C–C (broken line) bonds. See text for details.

ϕ is mainly due to the rotational barrier over the C–S bond since all the interacting groups are placed far apart because of the length of the C–S bond, and, therefore, nonbonded and electrostatic interactions are negligible. However, when $\phi > 75°$, the energy rises steeply as ϕ increases because the distance between the methylene group $i + 1$ and the methyl groups attached to C_{i-2} decreases; for instance, when $\phi = 95°$, the distance between these groups is 3.08 Å and the conformational energy is ca. 5 kcal mol^{-1} and remains above this value for the interval $95 \leq \phi \leq 265°$. Therefore, as a consequence of this interaction, gauche states around C–S bonds were considered to be located at ±75°. Figure 3 shows that $g^{\pm}$ states corresponding to C–S bonds should have an energy of 1.8 kcal mol^{-1} higher than the trans states.

There are two major differences between trans (t, ϕ = 0) and gauche ($g^{\pm}$, $\phi = \pm 120°$) states around the C–C bonds. First, the t conformation places S atom i between the two methyl groups attached to the C atom $i - 2$, whereas the $g^{\pm}$ conformations place that sulfur atom between a methyl and a methylene (number $i - 3$) group; this difference stabilizes the $g^{\pm}$ states vs. the t states. On the other hand, electrostatic interactions between S atom i and C atom $i - 3$ are higher in $g^{\pm}$ than in t conformations; this effect also stabilizes $g^{\pm}$ states. Figure 3 shows that as a result of these two differences, $g^{\pm}$ states should have an energy about 0.5 kcal mol^{-1} lower than the trans state (E_σ = −0.5 kcal mol^{-1}). Let us examine now the second-order interactions (i.e., those depending on rotations over two consecutive skeletal bonds). For bond pairs like $(i, i + 1)$, $(i + 1, i + 2)$, and $(i + 3, i + 4)$, the second-order interactions corresponding to each pair of states of each pair of bonds should be similar. Bond pairs like $(i + 2, i + 3)$ (or $i - 2, i - 1$) require a closer examination. Some energy calculations were carried out allowing for simultaneous rotational freedom over these two bonds; the results are shown in Figure 4 as contours of conformational energies for rotations ϕ_{i-2} and ϕ_{i-1}; only six out of nine existing minima are shown in Figure 4, since those for g^-t and $g^-g^{\pm}$ are identical with g^+t and $g^+g^{\pm}$, respectively. Partition functions and average energies were evaluated at 20 °C for regions of ±40° over each minimum at intervals of 5° in both angles; the results of that calculation gave averaged energies (normalized to tt) of 0, -0.6_9, -0.4_9, and 1.4_1 kcal mol^{-1} for conformations tt, tg, gg, and gg^-, respectively; these results agree[24] with the conclusion drawn from Figure 3, i.e., that the gauche states about C–C bonds have an energy about 0.5 kcal mol^{-1} lower than the alternative trans conformation. No significant second-order interactions appear in $g^{\pm}g^{\pm}$ conformations. However, the energy of the $g^{\pm}g^{\mp}$ states is about 1.9 kcal mol^{-1} higher than that of $g^{\pm}g^{\pm}$; therefore, there is a second-order energy $E_\omega \cong 1.9$ kcal mol^{-1} due to interactions between sulfur atoms $i - 4$ and i, separated by 2.76 Å in these conformations.

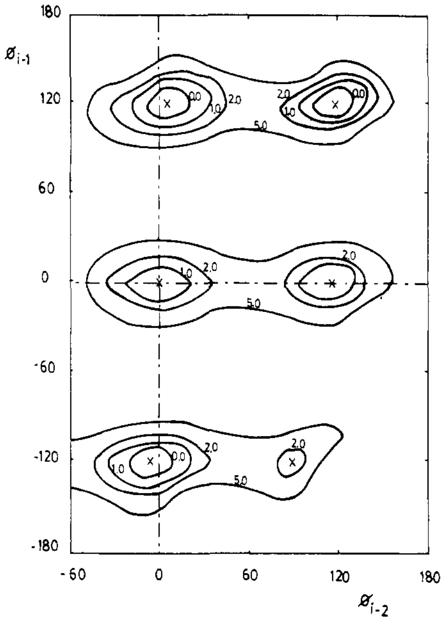

Figure 4. Calculated energy contours as functions of rotations over bonds like ϕ_{i-2} and ϕ_{i-1} in Figure 2. Energies are labeled in kcal mol^{-1} and refered to the local minimum of tt conformation. See text for details.

Theoretical Dipole Moments and Comparison with Experimental Data

According to the above analysis, the statistical weights required for evaluating the configurational properties of PDS may be expressed in a 3 × 3 matrix scheme as

$$\mathbf{U}_{i+1} = \begin{bmatrix} 1 & \tau & \tau \\ 1 & \tau & \tau \\ 1 & \tau & \tau \end{bmatrix} \qquad \mathbf{U}_{i+2} = \begin{bmatrix} 1 & \sigma & \sigma \\ 1 & \sigma & \sigma \\ 1 & \sigma & \sigma \end{bmatrix}$$

$$\mathbf{U}_{i+3} = \begin{bmatrix} 1 & \sigma & \sigma \\ 1 & \sigma & \sigma\omega \\ 1 & \sigma\omega & \sigma \end{bmatrix} \qquad \mathbf{U}_{i+4} = \begin{bmatrix} 1 & \tau & \tau \\ 1 & \tau & \tau \\ 1 & \tau & \tau \end{bmatrix}$$

where the subscripts $i + 1$ to $i + 4$ denote the type of bond to which each matrix should be applicable. As usual, the states are written in the order t, g^+, g^- and rows and columns in the $\mathbf{U}_j$ matrix are associated with the rotational states of bonds $j - 1$ and j, respectively. The statistical weights τ, σ, and ω are taken to be simple Boltzmann factors of E_τ, E_σ and E_ω, respectively. Values of the dipole moment ratio $D_x = \langle \mu^2 \rangle / x m^2$ were computed for chains with $x = 100$ (n = 400 skeletal bonds) according to the conventional procedure.[8,25] Preliminary calculations showed D_x to reach an asymptotic value for x = 50–60. For C–C and C–S bonds, trans states were located in both cases at 0°, whereas gauche states were located at ±120° for the former bonds and at ±75° for the latter. Results of D_{100} are shown in Figure 5 as a function of E_σ and E_τ; as can be seen in this figure, D_{100} strongly depends on the value of E_σ (the energy associated with gauche states about the $i + 2$ or $i + 3$ bonds); the sensitivity of D_{100} to E_τ decreases as E_σ increases. Moreover, the results shown in Figure 6 indicate that the sensitivity of D_{100} to E_ω (the energy as-

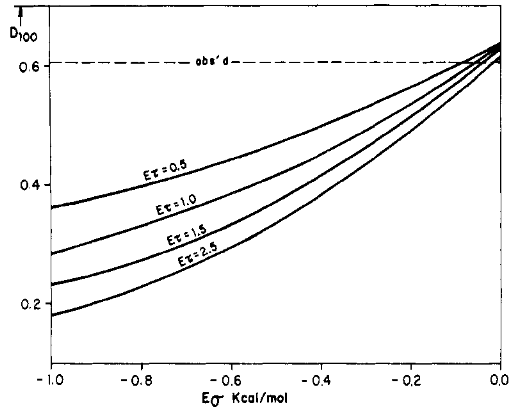

Figure 5. Calculated values of the dipole moment ratio at 30 °C as a function of E_σ for several values of E_τ (in kcal mol^{-1}). In the calculations it was assumed E_ω = 1.8 kcal mol^{-1}.

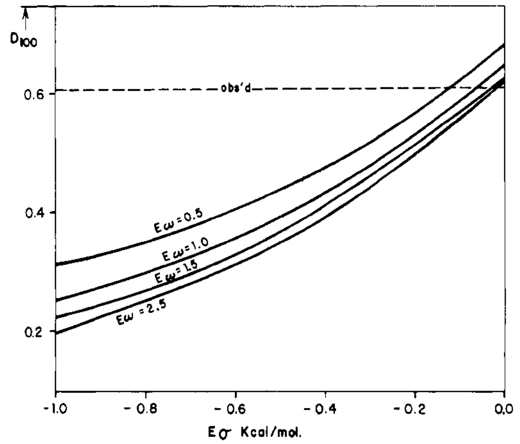

Figure 6. Calculated values of the dipole moment ratio at 30 °C as a function of E_σ for several values of E_ω (in kcal mol^{-1}). It was assumed E_τ = 1.8 kcal mol^{-1}.

sociated with $g^\pm g^\mp$ conformations about bond pairs like ($i + 2, i + 3$)) is almost the same for all the values of E_σ lying in the range -1 to 0 kcal mol^{-1}. Reasonable agreement between theory and experiment is found for E_σ = 0 to -0.1 kcal mol^{-1} and for values of both E_τ and E_ω lying in the interval $0.5 \leq E \leq 2.5$ kcal mol^{-1}.

The temperature coefficient of $\langle\mu^2\rangle$ was estimated by the equation

$$\mathrm{d}\ln\langle\mu^2\rangle/\mathrm{d}T = -(1/T)\sum_k \ln\xi_k(\partial\ln\langle\mu^2\rangle/\partial\ln\xi_k)$$

where ξ_k refers to the statistical weights or Boltzmann factors. The calculated values decrease as E_σ increases. This quantity, however, is not sensitive to the values of E_τ and E_ω in the range of interest (0.6×10^{-3} K^{-1}), as can be seen, for example, in Figure 7, where d ln D_{100}/dT is plotted as a function of E_τ. Since an error of 10% may be involved in the experimental determination of $\langle\mu^2\rangle$, the set of values E_σ = -0.1 kcal mol^{-1} and $E_\tau = E_\omega$ = 1.5 kcal mol^{-1} seems to be a reasonable choice, since the calculated value (D_{100} = 0.57 at 30 °C) is in fair agreement with the experimental result (0.61_5 at the same temperature) and the theoretical temperature coefficient (0.86×10^{-3}) reproduces the experimental result.

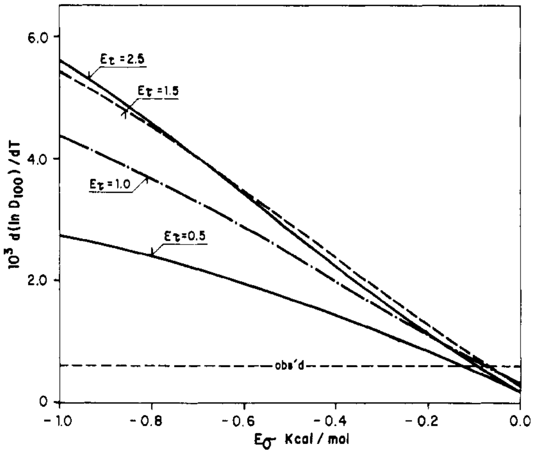

Figure 7. Temperature coefficient of the dipole moment ratio as a function of E_σ for several values of E_τ (in kcal mol^{-1}). The value of E_ω was taken to be 1.8 kcal mol^{-1}.

Table III
Dipole Moments and Dimensions of the Possible Conformations of an Eight-Bond Segment of the PDS Chain

conformation	μ^2, D^2	r^2, Å^2
tttttt	9.44	119.4
tttg$^+$tt	4.75	91.4
ttg$^+$g$^+$tt	0.13	63.3
ttg$^+$g$^-$tt	5.99	45.6
ttg$^+$ttt	4.75	91.4
g$^+$ttttt	9.44	105.2
g$^+$ttg$^+$tt	4.75	82.1
g$^+$tg$^+$g$^+$tt	0.13	45.2
g$^+$tg$^+$g$^-$tt	5.99	40.6
g$^+$tg$^+$ttt	4.75	79.8
g$^+$g$^+$tttt	6.89	102.2
g$^+$g$^+$tg$^+$tt	3.11	68.6
g$^+$g$^+$g$^+$g$^+$tt	3.06	78.9
g$^+$g$^+$g$^+$g$^-$tt	4.63	59.3
g$^+$g$^+$g$^+$ttt	1.18	96.5
g$^+$g$^+$ttg$^+$t	2.43	101.6
g$^+$g$^+$tg$^+$g$^+$t	3.12	59.7
g$^+$g$^+$g$^+$g$^+$g$^+$t	6.90	86.4
g$^+$g$^+$g$^+$g$^-$g$^+$t	5.53	34.3
g$^+$g$^+$g$^+$tg$^+$t	3.12	80.6
g$^+$g$^+$ttg$^+$g$^+$	2.43	94.2
g$^+$g$^+$tg$^+$g$^+$g$^+$	3.12	72.76
g$^+$g$^+$g$^+$g$^+$g$^+$g$^+$	6.90	87.0
g$^+$g$^+$g$^+$g$^-$g$^+$g$^+$	5.53	49.1
g$^+$g$^+$g$^+$tg$^+$t	3.12	72.8

Discussion

The experimental value of E_σ (-0.1 kcal mol^{-1}) derived from the critical analysis of the experimental data suggests that the CH_2···S interaction in the gauche conformation is more positive than that obtained from the conformational energy calculations (-0.5 kcal mol^{-1}). This result indicates that the gauche sulfur effect, defined as $\Delta E = (E_\sigma)_{\mathrm{exptl}} - (E_\sigma)_{\mathrm{theor}}$, may be somewhat repulsive, in contrast to the decisively attractive gauche oxygen effect for CH_2···O interactions of most of the polyoxides.[9] In this context, Abe has also found a positive gauche effect for S···S interactions in the case of poly(propylene sulfide).[26]

The influence of the different rotational states on the dipole moments and molecular dimensions is shown in Table III, where the values of μ^2 and r^2 are gathered for various conformations of the segment of eight bonds comprised between atoms $i - 4$ and $i + 4$ of Figure 2. It can be observed that the maximum value of μ^2 is obtained for the case in which all of the bonds are in the trans state and the minimum value corresponds to those conformations in which the pair of central bonds are in $g^\pm g^\pm$ states, the remaining bonds being trans. In the latter conformation, the dipole moments of the two CSC groups nearly cancel each other and the whole segment has 0.13 D^2. This value rises to μ^2 = 9.44 D^2 if the central bonds are in a tt conformation because in this case the pair of bond dipoles is in a parallel orientation. The values of the dipole moments

Table IV
Comparison between Conformational Properties of Poly(trimethylene sulfide) (PTS), Poly(3,3-dimethylthietane) (PDS), and Poly(3,3-dimethyloxetane) (PDO)

polymer	$\langle\mu^2\rangle/xm^2$	$10^3[\mathrm{d}\ln\langle\mu^2\rangle/\mathrm{d}T]$	Z	T_m, °C	$\langle r^2\rangle_0/nl^2$
PTS	0.60[a]	1.3		75[b]	
PDS	0.61	0.8	1.59	120[c]	5.1[d]
PDO	0.26[e]	4.9[e]	2.17[e]	45[e]	4.2[e]

[a] Reference 11. [b] Reference 31. [c] Reference 30.
[d] Calculated with the rotational isomeric state model.
[e] Reference 1.

of the remaining conformations are intermediate to those found for tttttt and ttg$^{\pm}$g$^{\pm}$tt conformations. It can also be observed that, in comparison with the dimensions, the dipole moments are extremely sensitive to the conformation due to the fact that, as usual, the skeletal bonds can vary much more in polarity than they can in length.

Poly(3,3-dimethylthietane) can be schematically derived from PTS by substituting the two hydrogen atoms of the central CH_2 group in the repeat unit by two methyl groups. Therefore, it may be interesting to compare their configuration-dependent properties. A comparison of this kind concerning the dipole moments and temperature coefficients is shown in Table IV. It can be observed that the value of $\langle\mu^2\rangle/xm^2$ is similar to that found for PTS. This similarity can be explained on conformational grounds by closely analyzing the conformational features of the C–C and C–S bonds in both polymers. Thus, while gauche states about C–C bonds in PTS have an energy E_σ lying in the range[11-12] 0.1–0.3 kcal mol^{-1} over the trans state, the same bonds have a slight preference for gauche states in the case of PDS chains. Raman and infrared spectra of molecules with CH_2–S bonds, such as methyl ethyl sulfide,[6,7] show that gauche states about CH_2–S bonds are slightly more stable than the alternative trans states. A value[6,7,27] of $E_{\sigma'} = -0.1$ kcal mol^{-1} seems to be a reasonable choice for gauche conformations about CH_2–S bonds in PTS. On the contrary, the energy associated with gauche states about C–S bonds is 1.5 kcal mol^{-1} higher than that associated with the corresponding trans states in PDS. In both cases, however, the conformations of the maximum and minimum values of $\langle\mu^2\rangle$ are not favored with respect to the remaining conformations and hence the dipole moments are similar for both polymers.

Another polymer closely related to PDS is PDO. Actually the former polymer can also be schematically derived from the latter by substituting O atoms in PDO by sulfur atoms. Both polymers, however, are different in their structural features. Thus the C–S bond length is 1.815 Å whereas $l_{\mathrm{C-O}} = 1.43$ Å; bond angles COC and CSC are 110 and 100°, respectively; finally, the van der Waals radii of oxygen and sulfur atoms are 1.6 and 1.9 Å, respectively. The result of these differences is that whereas CH_2–O bonds in PDO are restricted to trans states, gauche states about CH_2–S bonds in PDS are permitted. Moreover, the presence of sulfur gauche effects in PDS causes gauche states about C–C bonds in this polymer to have almost the same energy as the corresponding trans states. However, gauche states about these bonds in PDO have an energy 0.5 kcal mol^{-1} lower than the trans state. As a consequence, the fraction of ttg$^{\pm}$g$^{\pm}$tt conformations is much lower in PDS than it is in PDO and hence the polarity of the chains of the former polymer is higher than that of the latter.

The flexibility of a molecule, as measured by its characteristic ratio $\langle r^2\rangle_0/nl^2$, may be characterized by a thermodynamic contribution, expressed by the partition function Z, which involves conformational preferences as exemplified by the energy difference between the rotational states, and by a geometric structural contribution, which determines the relative extent of the competing conformational alternatives.[27] As can be seen in Table IV, the values of Z for PDO and PDS are 2.18 and 1.85 per bond, respectively. According to this and taking into account the compensating effects of the CSC and COC bond angles in the molecular dimensions, the value of the characteristic ratio of PDS should be only slightly higher than that of PDO in spite of the fact that $l_{\mathrm{C-S}} > l_{\mathrm{C-O}}$. Actually, the calculated values of $\langle r^2\rangle_0/nl^2$, shown in Table II, are in agreement with this conclusion.

The theoretical analysis shows that the PDS conformation of minimum intramolecular energy has the rotational states ttg$^{\pm}$g$^{\pm}$ for bonds i to $i + 3$ in Figure 2. Since the difference in energy between this form and the planar zigzag form is small and possibly zero, crystalline modifications [tttt], [tt gt], and [ttg$^{\pm}$g$^{\pm}$] might occur for this polymer. As far as the melting temperatures of PDS and PDO are concerned, some previous considerations should be made. The melting behavior of crystalline polymers is strongly dependent on the molecular flexibility, as expressed by the configurational entropy ΔS_f. This thermodynamic parameter is related to the partition function by the standard expression[28,29]

$$\Delta S_f = R[\ln Z - \sum_k \ln \xi_k(\partial \ln Z/\partial \ln \xi_k)]$$

where ξ_k represents the statistical weights or Boltzmann factors. The configurational entropy is an essential component of the fusion entropy at constant volume ΔS_V and Tonelli[28] has shown that in some cases $\Delta S_f \simeq \Delta S_V$. Since PDS has a configurational entropy (1.59 cal K^{-1} per mole of skeletal bond) somewhat lower than that of PDO (2.16), the melting temperature of the former polymer should be higher than that of the latter, provided, of course, that the value of the melting enthalpy ΔH for PDO is not well above the value of ΔH for PDS. As can be seen in Table IV, this conclusion is in agreement with the experimental results. Actually PDO[1] and PDS[30] melt at 45 and 120 °C, respectively.

It can be observed in Table IV that PDS also melts at a higher temperature than PTS.[31] This behavior may be due to the fact that whereas rotational states about C–S bonds in PDS have a strong preference for trans states, similar skeletal bonds in PTS are almost freely rotating. Therefore, PDS should be less flexible than PTS and hence it should melt at a higher temperature.

References and Notes

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Further Study on Peptides Having the L-Alanyl-L-leucylglycyl Repeating Unit. Syntheses and Conformations of the Peptides up to the Hexatriacontapeptide Level

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ABSTRACT: A series of peptides having the L-alanyl-L-leucylglycyl repeating unit, Nps-(L-Ala-L-Leu-Gly)$_n$-OEt (n = 7–10 and 12), has been synthesized by the fragment condensation method, using the active ester Nps-(L-Ala-L-Leu-Gly)$_2$-ONSu. Conformations of these peptides as well as those of the lower homologues with n = 1–6, which had been prepared in an earlier study, were studied by X-ray powder diffraction measurement and IR spectroscopy for the solid state and CD spectroscopy for solutions. The 15-peptide (n = 5) takes two different conformations, an α helix or a β structure, depending upon the casting procedure from a solution in trifluoroethanol. The β structure was found in the solid sample obtained by evaporation of the solvent, a slow phase transformation from the solution to the solid state, and the α helix was found in the sample obtained by reprecipitation, a rapid phase transformation. The conformations of the peptides obtained by the slow phase transformation were the β structure for the peptides with n = 1–5 and the α helix for the peptide with n = 7. The 18-peptide (n = 6) was in a transition area from the β structure to the α helix. The CD study demonstrated that the onset of helicity begins at the 12-peptide (n = 4) for these peptides in TFE. The intensity of the CD bands at 207 and 222 nm and the total molar optical rotation were found to be related to the conformations of these peptides in the solid state.

Oligopeptides consisting of L-alanyl-L-leucylglycyl repeating units begin forming α helices at the 15-peptide in the solid state when the peptide samples are reprecipitated from solution by addition of diethyl ether.[1] We have examined the solid-state conformations of these peptides when obtained by another casting procedure involving slow evaporation of the solvent from solutions. The observed conformations of the samples thus obtained are different from those of the samples obtained by reprecipitation. The 15-peptide takes the β structure and the 18-peptide has a conformation similar to the α helix. This experimental fact shows that the solid-state conformations of the oligopeptides can vary with the casting procedure. An analogous phenomenon has been observed for homooligo(L-methionine) bound with poly(ethylene glycol).[2] This variation of conformation should be prominent for oligopeptides having rather short peptide chain lengths which cannot form enough hydrogen bonds to stabilize a specific conformation, and there should be a critical peptide chain length for the formation of the α helix which is independent of the casting procedure. Thus we have prepared peptides having longer peptide chain lengths, Nps-(L-Ala-L-Leu-Gly)$_n$-OEt (n = 7–10 and 12), and studied the conformation of the solid samples obtained by slow evaporation of the solvent. The conformation of the peptides with n = 1–10 and 12 in solution was also studied since it may be related to the solid-state conformation and since we were seeking information concerning its variation with solid-state conformation.

Experimental Section

Syntheses of Peptides. Nps-L-Ala-L-Leu-Gly-ONSu and Nps-(L-Ala-L-Leu-Gly)$_2$-ONSu. These active esters were prepared by the procedure reported in our earlier study.[3]

Nps-(L-Ala-L-Leu-Gly)$_8$-OEt as an Example for the Fragment Condensation. The 18-peptide Nps-(L-Ala-L-Leu-Gly)$_6$-OEt[3] (1.65 g, 1 mmol) was dissolved in 5 mL of 1,1,1,3,3,3-hexafluoropropan-2-ol (HFIP), and to the solution was added 0.5 mL of 4 N hydrochloric acid in ethanol to precipitate the 18-peptide ethyl ester hydrochloride. The precipitate was collected on a glass filter and washed with diethyl ether until the yellow color of the solid disappeared. The white solid was reprecipitated from HFIP. The product was dissolved in 100 mL of dimethyl sulfoxide (Me$_2$SO), and triethylamine (0.154 mL, 1.1 mmol) and Nps-(L-Ala-L-Leu-Gly)$_2$-ONSu (0.75 g, 1 mmol) were added with stirring at room temperature. The reaction was monitored by thin-layer chromatography as will be mentioned in the text. After 5 h, the active ester (0.23 g, 0.3 mmol) was added to the solution, and stirring was continued for an additional 5 h. After the reaction, the reaction system was diluted with 500 mL of water to precipitate the product. The product was collected on a glass filter and washed with methanol until the filtrate did not show the yellow color. Then the product was washed with diethyl ether and dried. The crude product was dissolved in warm Me$_2$SO, and the solution was diluted with water to give a precipitate. The product was collected on a glass filter, washed with methanol, tetrahydrofuran (THF), and diethyl ether, and dried over P$_2$O$_5$ to give 1.96 g (92% yield) of pure Nps-(L-Ala-L-Leu-Glu)$_8$-OEt (5).

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