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Calculated Intermolecular Energies Relevant to the Unusually High Melting Point of Poly(ethylene sulfide)

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ABSTRACT: Semiempirical potential energy functions were used to characterize interchain interactions in poly(ethylene sulfide) (PES) [CH_2CH_2S] and in poly(ethylene oxide) (PEO) [CH_2CH_2O], the primary purpose being to elucidate the very high melting point of PES (216 °C) relative to that of PEO (68 °C). In the case of the PEO chain, the partial charges on the atoms could be calculated by the CNDO/2 method. The charges thus obtained showed only a slight dependence on conformation, thus supporting the assumption of conformation-independent charges usually made in conformational analyses. They were also in good agreement with charges previously estimated from bond dipole moments. The total interchain interactions, significantly attractive in both polymers, were much larger in PES than in PEO, which is consistent with the interpretation of its unusually high melting point in terms of its enthalpy of fusion. The difference in intermolecular attractions is primarily due to van der Waals interactions, rather than to Coulombic (dipolar) effects. They are traceable to the fact that the S atom has twice as many electrons as the O atom, and thus a much higher polarizability. The stronger van der Waals attractions in PES are partly due to differences in crystalline state conformations, in that the S atoms in the PES (2/0) glide-plane conformation are much more exposed than the O atoms in the PEO (7/2) helix. Very approximate estimates of the crystalline state densities of the two polymers were found to be in satisfactory agreement with experiment.

The melting point T_m of any substance, including partially crystalline high molecular weight polymers, is given by the simple ratio $\Delta H_m/\Delta S_m$ of the enthalpy of fusion to the entropy of fusion.[1,2] Polymers, as might be expected, exhibit a wide range of melting points,[1-4] with those having unusually high melting points attracting particular attention because of their possible utilization as rigid materials in high-temperature applications. It is therefore of considerable interest and importance to interpret the melting point of a polymer, thermodynamically in terms of ΔH_m and ΔS_m, and molecularly in terms of the interchain interactions and chain flexibility on which these two thermodynamic qualities depend.

The polysulfides [$(CH_2)_yS$] are an unusually interesting series of molecules in this regard. They have melting points that are generally significantly higher than those of the corresponding polyoxides [$(CH_2)_yO$];[5-7] the differences are relatively large at small values of y but diminish as y increases in approaching the limiting case of polyethylene ($y = \infty$). The maximum difference occurs at $y = 2$, with poly(ethylene sulfide) (PES) [CH_2CH_2S] having a melting point of 215.6 °C[8,9] and poly(ethylene oxide) (PEO), 67.9 °C.[9,10] Elucidation of the molecular origin of this large difference in T_m, between these two structurally very similar polymers, is the major purpose of the present theoretical investigation.

A variety of information on PES and PEO of possible relevance to this problem is given in Table I. Rows three through five give some of the results, primarily theoretical, reported in two studies[9,11] of the intramolecular charac-

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Table I
Quantities Relevant to the Fusion Process in Crystalline Poly(ethylene sulfide) and Poly(ethylene oxide)

	PES	PEO
repeat unit	CH_2-CH_2-S-	CH_2-CH_2-O-
T_m, °C	216^a	68^b
z	10.2^c	4.3^c
S, eu mol^{-1}	6.1^c	5.0^c
$\langle r^2 \rangle_0/nl^2$	4.2^c	$5.2^{c,d}$
l(C-X), Å	$1.815^{c,e}$	$1.43^{c,e}$
θ(C-X-C), deg	$100^{c,e}$	$112^{c,e}$
R_{vdW}(X), Å	$1.8^{f,g}$	$1.5^{f,g}$
m(CH_2-X), D	$1.21^{c,h}$	$1.07^{d,h}$
ΔS_m, eu mol^{-1}	$6.9^{c,i}$	$6.5^{b,c}$
ΔH_m, kcal mol^{-1}	$3.4^{c,i}$	$2.2^{b,c}$
cryst state conform	(2/0) glide plane^{j,k}	(7/2) helix^{j,l}

[a] Reference 8. [b] Reference 10. [c] Reference 9. [d] Reference 11. [e] Reference 13. [f] Reference 14. [g] Reference 15. [h] Reference 16. [i] Reference 17. [j] Reference 7. [k] Reference 18. [l] Reference 19.

teristics of these chains. The quantities are the configurational partition function z (per skeletal bond), the configurational entropy S (per mole of skeletal bonds), and the characteristic ratio $\langle r^2 \rangle_0/nl^2$ (of the unperturbed dimensions[12] divided by the number of skeletal bonds and the square of their lengths). The values of all three quantities indicate that PES is more flexible than PEO in the equilibrium sense of having a higher degree of randomness or compactness. These results thus argue against the high T_m of PES being due to a low entropy of fusion. The next four rows provide information relevant to the origin of this type of flexibility. The first three involve the van der Waals or steric contributions to the intramolecular interactions; they are the length l of the C–X bond (where the heteroatom is S or O),[9,13,14] the C–X–C bond angle θ,[9,13,14] and the van der Waals radius R_{vdW} of X.[14,15] The fourth quantity, the CH_2–X bond dipole moment m,[16] is relevant to the Coulombic or dipolar contribution to the intramolecular energy. (Although the C–S bond dipole is somewhat larger than the C–O one, the significantly smaller C–O bond length indicates that the partial charges in PES and PEO should be very similar.)[14] The most important of these four characteristics, which explains the high degree of flexibility of PES, is the unusually long C–S bond.[9,14] Experimental values of ΔS_m and ΔH_m are given in the next two rows.[9,10,17] The values of the former quantity support the conclusion that PES is the more flexible chain and those of the latter confirm that the unusually high melting point of PES is due to its relatively large enthalpy of fusion.[9,18]

The present study employs semiempirical potential energy functions to investigate interchain interactions in PES and PEO, specifically as they relate to the enthalpy of fusion for these two polymers. Questions of particular importance are whether or not these interactions are much stronger in PES and, if they are, whether the differences are due to van der Waals or to Coulombic interactions. Also, as is noted in the last row of Table I, the two chains have rather different conformations in the crystalline state.[7,18,19] The effect of this difference is established by including calculations on a (hypothetical) PEO chain forced to adopt the PES crystalline state conformation.

Theory

Structural Features of the Chains. The required structural information for the PES and PEO chains was obtained from previous studies carried out on these polymers and on related small molecules.[9,11-13,18-21] Bond lengths and bond angles employed which are not already given in Table I are l(C–C) = 1.53 Å, l(C–H) = 1.09 Å, θ(O–C–C) = 110°, θ(S–C–C) = 114°, and θ(H–C–H) = 109.5°. The PES chain in the (2/0) glide-plane configuration it has in the crystalline state has its three skeletal bonds [CH_2–CH_2–S–] in [$tg^{\pm}g^{\pm}$] conformations.[18] Since the structure of PES in the crystalline state has not been completely solved, these t and $g^{\pm}$ states were assumed to occur at their symmetric locations, which correspond to rotational angles ϕ of 0 and ±120°, respectively. The crystalline state configuration of the PEO chain is a (7/2) helix, in which the [CH_2–CH_2–O–] skeletal bonds are in [$g^{\pm}tt$] conformations. In this case, the values of ϕ for the t and $g^{\pm}$ states are known more precisely, corresponding to −6.0 and ±111.6°, respectively.[19]

The partial charges q on the chain atoms were obtained in two ways. In the case of PEO, they could be calculated by the quantum-mechanical CNDO/2 (complete neglect of differential overlap) method.[22] (It could not be used reliably for the PES chain, because of the number and types of electrons involved.) The calculations were carried out on sequences having increasing numbers of repeat units until constant values were obtained for the central unit in the sequence. In order to determine the extent to which the charges depend on conformation, both the actual (7/2) helix and the hypothetical (2/0) glide-plane conformation were included in the calculations. The charges in these two very different conformations were found to differ by only approximately 0.01 of the electronic charge e, which is consistent with the assumption that such changes in q can usually be ignored in conformational analyses. The charges on the C, O, and H atoms for the helix were $0.145e$, $-0.285e$, and $-0.004e$ to $+0.002e$, respectively. These results are in good agreement with values calculated from the bond dipole moment listed in Table I, which are $0.155e$ for the CH_2 group and $-0.31e$ for the O atom.[14] The bond dipole moment method was therefore used to obtain values of q for the PES chain (on the trivial assumption that the H atoms have the same charges they have in PEO in the (2/0) glide-plane conformation). The resulting values of q for C, S, and H atoms for PES in this conformation were $0.123e$, $-0.278e$, and $0.004e$ to $0.012e$, respectively.

Potential Energy Functions. The total intermolecular interaction energy was taken to be the sum

$$E = \sum_{i<j} E_{ij} \tag{1}$$

of the interaction energies between pairs of atoms i and j located on different chains and separated by the distance r_{ij}. Each separate contribution was calculated from the equation[12,23]

$$E_{ij} = a_{ij} \exp(-b_{ij}r_{ij}) - c_{ij}/r_{ij}^6 + kq_iq_j/\epsilon r_{ij} \tag{2}$$

in which the first two terms (the "Buckingham potential function") represent the van der Waals or steric interactions and the last term represents the Coulombic interactions. The parameters a, b, and c in the Buckingham potential function differ, of course, for different atom pairs. The parameter c in the attractive term was calculated from atomic polarizabilities[24] by application of the Slater–Kirkwood equation.[25] The value of b for a like atom pair was taken from Scott and Scheraga,[26] while the value for an unlike pair was given by the geometric mean $b_{ij} = (b_{ii}b_{jj})^{1/2}$. The values of b and c thus obtained are essentially those used in a number of previous studies of conformational energies.[9,11,12,14] The corresponding values of the parameter a were then determined by minimizing the first two terms of eq 2 at $r = R_{min} \equiv R_i + R_j$, where R_i and

Table II
Parameters for the Buckingham Potential Functions

atom pair	$R_{\min}$	$10^{-3}a^a$	b^a	c^a
C· · ·C	3.4	541.4	4.59	363.0
C· · ·H	2.9	55.08	4.57	127.0
H· · ·H	2.4	7.03	4.54	45.2
S· · ·S	3.6	906.3	3.90	3688
S· · ·C	3.5	733.0	4.25	1158
S· · ·H	3.0	83.32	4.22	407.0
O· · ·O	3.0	139.9	4.59	245.0
O· · ·C	3.2	267.6	4.59	294.0
O· · ·H	2.7	27.67	4.57	96.5

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

Table III
Minimum Values of the Intermolecular Energy

polymer	crystalline state conformation	$E_{\min}$, kcal mol^{-1}
PES	(2/0) glide plane	−10.3
PEO	(7/2) helix	−4.11
PEO	(2/0) glide plane	−6.33

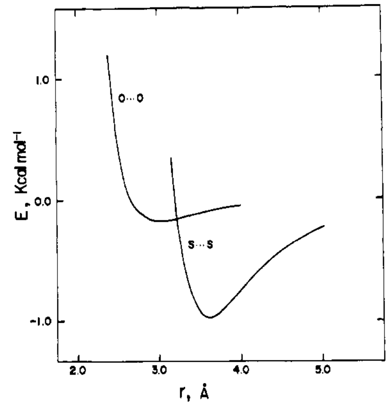

Figure 1. Typical curves showing the van der Waals energy of interaction between two atoms as a function of their distance of separation. The parameters of the two curves, which are for a pair of sulfur atoms and a pair of oxygen atoms, are given in Table II. The much stronger maximum attraction between the S atoms is due to their higher polarizability and is apparently the primary reason for the unusually high melting point of poly(ethylene sulfide).

R_j are the van der Waals radii[15] of the interacting atoms. The resulting values of $R_{\min}$, a, b, and c are given in Table II.

The Coulombic contributions were calculated from the last term of eq 2, in which $k = 332.1$ is a conversion factor giving energies in kcal mol^{-1} when q_i and q_j are in fractional parts of the electronic charge. The dielectric constant ϵ was taken to be 3.0, as is generally done in calculations of conformational energies.[12,23]

Calculations of Intermolecular Energies. As is known from previous studies,[7,23,27-30] calculations of intermolecular interaction energies rapidly become impracticable as the number of atoms increases, particularly when this increase is due to an increase in the number of chains (since this increases both the number of interactions and the number of relative chain locations to be investigated). In addition, calculations of this type in their present state are really only semiquantitative. The model employed here, however, although necessarily rather simple for the above reasons, should nonetheless be very useful for elucidating the very large difference in melting point between PES and PEO.

The calculations were based on a pair of PES chains or a pair of PEO chains in their crystalline state conformations and maintained parallel to one another. The shorter chain in the pair was one fiber repeat unit long (two monomer units and 6.7 Å for the PES (2/0) glide-plane configuration, seven monomer units and 19.3 Å for the PEO (7/2) helix, and two monomer units and 5.3 Å for the PEO (2/0) glide-plane conformation). The second chain was made considerably longer so as to minimize end effects; it was six fiber periods long in the case of the glide-plane configurations and four periods long in the case of the helix. The shorter chain was moved relative to the longer in increments of 0.5 Å in the three directions (x,y,z) of a Cartesian coordinate system and also rotated in increments of 10° about its axis. Intermolecular energies in kcal mol^{-1} were calculated as described above for each of the relative locations. The ones for the POE (7/2) helix were divided by 3.5 so that all of the energies refer to the interaction between a relatively long chain and a short chain consisting of two monomer units.

Results and Discussion

The lowest values of the energy (maximum attraction) for the PES and PEO chains in their crystalline state configurations are given in the first two rows of Table III. The much larger favorable interaction energy for the PES is consistent with, and is clearly the origin of, its significantly higher melting point. Only a small fraction (approximately 4%) of the PES interaction energy is due to Coulombic interactions,[31] in contradiction to what had generally been thought to be the case. The major source of the difference in attraction is the van der Waals interactions involving the S or O atoms. A S atom has twice as many electrons as an O atom (or CH_2 group) and therefore has much higher polarizability and interatomic attractions. This can be seen from the values of the van der Waals c parameter given in Table II. It is also illustrated very strikingly in Figure 1, which shows that the maximum attraction between a pair of S atoms is approximately 6 times the maximum attraction between a pair of O atoms.

It would be extremely difficult to relate these calculated energies to the experimentally observed heat of fusion. In this regard, it is important to note that the volume change upon fusion is somewhat different for the two polymers. In the vicinity of 25 °C, the change in volume per mole of repeat units is approximately 3.8 cm^3 in the case of the PES[17] and 3.4 cm^3 in the case of the PEO.[10,32] This would increase the difference between values of ΔH_m predicted on the basis of calculations such as those reported here. Also important would be changes in intramolecular energy as the chains randomize their configurations in the melting process. The difference between the lowest and the higher energy rotational states is lower in PES than it is in PEO,[14] and incorporation of intramolecular energies would therefore be expected to decrease the difference between predicted values of ΔH_m.

The extent to which chain configuration affects the intermolecular interactions can be seen from the last entry in Table III, which is the maximum energy between two PEO chains arbitrarily placed in the PES crystalline state configuration. The intermolecular attractions are now significantly larger since, as can be seen from Figures 2 and 3, the S or O atoms are much more accessible for strong intermolecular interactions in the (2/0) glide-plane configuration. Although it is difficult to attach quantitative significance to these results, it appears that approximately one-third of the difference in attraction energy between PES and PEO is due to the difference in crystalline state configuration.

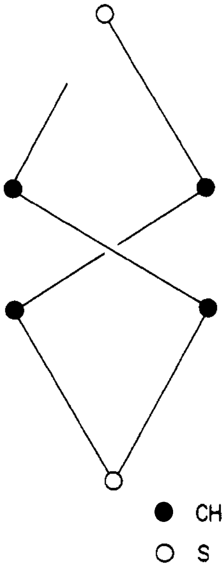

Figure 2. Projection of the PES chain in the (2/0) glide-plane conformation it adopts in the crystalline state.[18] Of particular importance is the high degree of exposure of the S atoms.

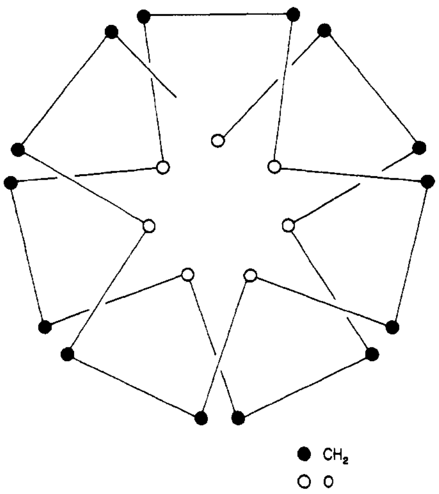

Figure 3. Projection of the PEO chain in the (7/2) helical conformation it adopts in the crystalline state.[19] Comparison with Figure 2 shows that the O atoms are much less exposed than the S atoms in the crystalline state conformation of PES.

The specific volumes of PES and PEO in the crystalline state are 0.71[18] and 0.81 cm^3 g^{-1},[10,20] respectively. Predictions of these qualities would really require much more elaborate calculations on a significantly larger number of chains. Estimates based on the present calculations are 0.61 and 0.91 cm^3 g^{-1}, which are in the correct order and in fair agreement with the experimental values.

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