Ordinarily the second term on the right-hand side may be ignored and the temperature coefficient of Δa may be identified with that of A. But when Γ is near zero, even minute changes in this term are magnified in $d \ln \Gamma/dT$ so that it may dominate $d \ln A/dT$. These changes may originate, for example, in correlations involving the methyl groups, which are themselves anisotropic. Such correlations may be diatropic (negative) as well as paratropic (positive).[50] The effect of temperature thereon, though normally of no importance, may become significant when $\Gamma \approx 0$.

According to a wealth of evidence,[10] the chain configuration in undiluted polymers, including especially PM and PDMS, differs little from that for the unperturbed chains when well separated from one another as in a dilute solution. The evidence comes largely from investigations of rubber elasticity including, in particular, the temperature coefficient of the stress.[10,51] It is supported also by cyclization equilibrium constants in the case of PDMS.[52] Such correlations as may be responsible for enhancement of the optical anisotropy evidently do not appreciably perturb the configuration.

It may be noteworthy in this connection that the range of intramolecular correlation for group optical anisotropies[33,53] is much shorter (*i.e.*, extends over a lesser number of skeletal bonds) than the correlation range for skeletal bond vectors,[54] the latter being pertinent to the average chain dimensions. Contributions from *intermolecular* effects will therefore be more readily evident in the optical anisotropy than in the chain dimensions. Such intermolecular correlations as exist in the undiluted polymer may suffice to enhance Δa without affecting significantly the mean dimensions measured by $\langle r^2 \rangle_0$. It may be important also to draw a distinction between intermolecular correlations and ordering of chains. Occurrence of the former does not necessarily imply the latter. We shall discuss this matter in greater detail elsewhere.

Acknowledgments. The authors are indebted to Dr. C. S. Munday of Raychem Corp. for irradiating the polymer samples. This work was supported by the Directorate of Chemical Sciences, U. S. Air Force Office of Scientific Research Grant No. 71-1960.

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Conformational Characteristics and Flexibility of Poly(2,6-disubstituted-1,4-phenylene oxides) and the Polycarbonate of Diphenylol-2,2′-propane

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ABSTRACT: The conformational energies per independent repeat unit of poly(2,6-dimethyl-1,4-phenylene oxide) and the polycarbonate of diphenylol-2,2′-propane are evaluated through use of a 6–12 potential to account for the van der Waals interactions between nonbonded atoms and groups which accompany rotations about the backbone bonds. Energetically allowed conformations are found to span the entire range of the rotation angle about the virtual bonds connecting neighboring ether oxygen atoms in the phenylene oxide polymer. Rotation about the virtual bonds in the polycarbonate chain is found to be similarly free of significant contraints. Consequently, both classes of polymers exhibit freely rotating chain statistics, as previously deduced by others from experimental chain dimension measurements and chain symmetry arguments. However, rotation about the virtual bonds in the phenylene oxide polymers and in polycarbonate is nearly truly free (each rotational state is appreciably populated) and not just restricted to two symmetrically located rotational states of equal energy at 90 and 270° as has been suggested. The flexibility of both classes of polymers, as manifested in their impact strength and fusion behavior, is discussed in light of the detailed conformational models (nearly true free rotation) developed here. The polysulfone chain is treated by analogy and is found to have a flexibility comparable to the poly(phenylene oxides) and polycarbonate.

The unperturbed chain dimensions have been measured[1-4] for the 2,6-dimethyl-, the 2,6-diphenyl-, and the 2-methyl-6-phenyl-1,4-phenylene oxide polymers and for the polycarbonate of diphenylol-2,2′-propane. Characteristic ratios of the mean-square end-to-end distance $\langle r^2 \rangle_0$ to the number n of backbone virtual bonds (see below) were found to be independent of temperature and equal to 85 Å^2 for the phenylene oxide polymers and 108 Å^2 for polycarbonate. Both ratios and their temperature independence can be predicted by assuming free rotation statistics[5] (N symmetrically located rotational states of equal energy) about the virtual bonds in both classes of polymers.

Barrales-Rienda and Pepper,[1] Akers, Allen, and Bethell,[3] and Shultz[4] proposed the existence of two equally populated chain rotational states at rotation angles of 90 and 270° about the virtual bonds to explain the free rotation statistics exhibited by the phenylene oxide polymers. Williams and

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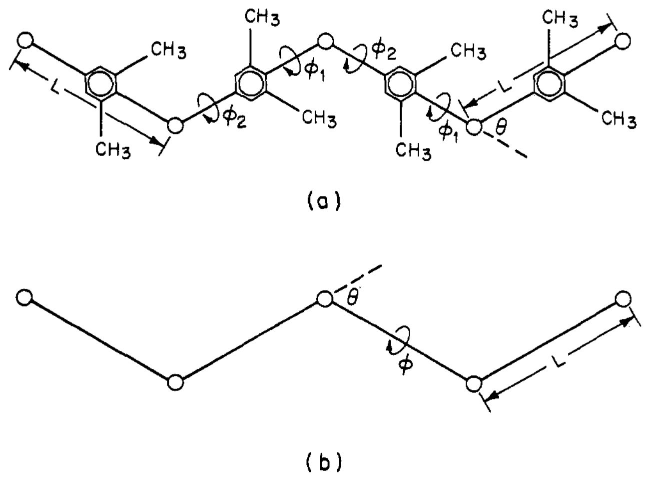

Figure 1. (a) A portion of the 2,6-dimethyl-1,4-phenylene oxide chain in the planar zigzag conformation, where $\varphi_1 = \varphi_2 = 0°$. All phenylene rings are coplanar in this reference rotational conformation, and φ_1 and φ_2 assume positive values for right-handed rotations.[5] (b) A portion of the backbone of the 1,4-phenylene oxide chain planar zigzag conformation, where neighboring ether oxygen atoms are connected by virtual bonds L. The virtual bond rotation angle φ is taken as 0° in this conformation and adopts positive values for right-handed rotations.[5]

Flory[6] discussed the chain statistics of polycarbonate and similarly concluded that free-rotation statistics must prevail owing to the symmetry of the polycarbonate chain.

The virtual bond rotation angles are a sum of two independent rotations (see below) about the real chemical bonds C_1–O, C_4–O, and C_1–C flanking the phenyl groups (see Figures 1 and 2). As an example, $\varphi = \varphi_1 + \varphi_2$. Inspection of the molecular models of both classes of polymers leads to the observation that rotation angles of 90 and 270° about the virtual bonds can be achieved with a variety of different pairs of the rotation angles about the real chemical bonds (see Figures 1 and 2). Thus the present investigation was undertaken for the purpose of determining the energetically allowed ranges in the rotations about the chemical bonds in the backbone, which in turn define the accessible ranges of rotation about the virtual bonds. Such a delineation of the allowed rotational states permits the level of understanding the conformational characteristics and flexibility of the phenylene oxide and polycarbonate polymers to be placed on more than the qualitative foundation laid previously by Barrales-Rienda and Pepper,[1] Akers, Allen, and Bethell,[3] Shultz,[4] and Williams and Flory.[6] This is achieved by calculating the conformational energies of rotation about adjacent pairs of C_1–O, C_1–C, and C_4–O bonds.

Description of Calculations

The interactions of the 2 and 6 methyl groups and the 1, 2, and 6 carbon atoms with the 3 and 5 hydrogen atoms and the 3, 4, and 5 carbon atoms belonging to adjacent phenyl rings in the phenylene oxide polymer are considered. In polycarbonate, where all carbonate groups are fixed[6] in the trans, trans conformation, the interactions of the 2 and 6 hydrogen atoms with the propyl groups and the 1, 2, and 6 carbon atoms with the methyl groups, together with their interactions with the adjacent phenyl 3 and 5 hydrogen atoms and the 3, 4, and 5 carbon atoms, are accounted for. In addition, the interactions of all the atoms of the carbonate group with the 2 and 6 hydrogen atoms and the 1, 2, and 6 carbon atoms of one phenyl group and with the 3 and 5 hydrogen atoms and the 3, 4, and 5 carbon atoms of the other adjacent phenyl group are considered, as well as the interaction of these adjacent phenyl group atoms with each other. All such interactions are evaluated using a 6–12 nonbonded van der Waals potential

$$V_{ij} = \frac{A_{ij}}{r_{ij}^{12}} - \frac{C_{ij}}{r_{ij}^{6}} \tag{1}$$

where A_{ij} and C_{ij} are taken from Brant, *et al.*[7,8] The distances r_{ij} between atoms or groups i and j in the phenylene oxide chain are calculated as a function of the rotation angles φ_1 and φ_2 and the supplement θ of the C_1–O–C_4 valence angle (see Figure 1), while the rotation angles φ_1', φ_2', φ_3, φ_4, and the supplement θ' of the C_1–C–C_1 valence angle are varied in the polycarbonate energy calculations (see Figure 2). Because the torsional barriers to rotation about C_1–O, C_4–O, and C_1–C single bonds are low,[8] the intrinsic torsional potentials associated with the rotations φ_1, φ_2, φ_1', φ_2', φ_3, and φ_4 are neglected. (The potential associated with valence angle bending is also ignored.) All rotation angles are varied in 20° increments over their entire range, while θ and θ' in the ranges $46° \leq \theta \leq 66°$ and $66° \leq \theta' \leq 70°$ are both varied in 2° increments. θ'' is fixed at 68° and standard bond lengths[9] ($l_{C_1-C_2} = 1.39$ Å, $l_{C_4-O} = 1.36$ Å, $l_{C-H} = 1.08$ Å, $l_{C_1-C} = 1.53$ Å, $l_{C=O} = 1.22$ Å, and $l_{C-O} = 1.34$ Å) and phenyl ring geometry ($<_{C_1-C_2-C_3} = 120°$) are adopted. Owing to the paucity of structural data on the carbonate group,[6] ester group geometry[10] is assumed for the carbonate group.

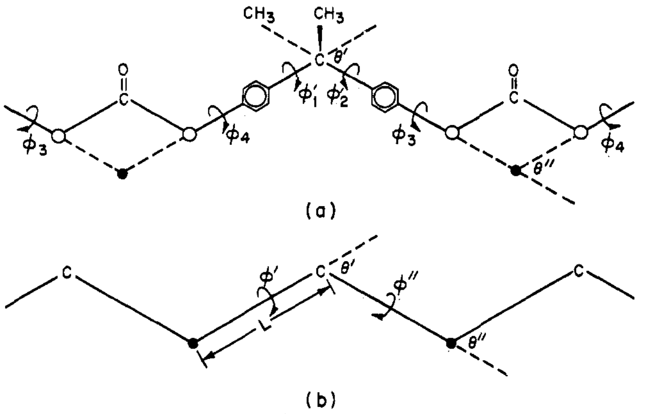

Figure 2. (a) A portion of the polycarbonate chain in the planar zigzag conformation, where $\varphi_1' = \varphi_2' = \varphi_3 = \varphi_4 = 0°$. All phenylene rings are coplanar in this reference conformation, and φ_1', φ_2' φ_3, and φ_4 adopt positive values for right-handed rotations.[5] (b) A portion of the backbone of polycarbonate in the planar zigzag conformation, where the virtual bond L extends from C to the intersection of the extensions of the C_1–O bonds. The virtual bond rotation angles φ' and φ'' are taken as 0° in this conformation and adopt positive values for right-hand rotations.[5]

The conformational energies of rotation $V(\varphi_1, \varphi_2, \theta)$ (poly(phenylene oxide)), $V(\varphi_1', \varphi_2', \theta')$, and $V(\varphi_3, \varphi_4, \theta'')$ (for the polycarbonate chain) are independent of the values of neigh-

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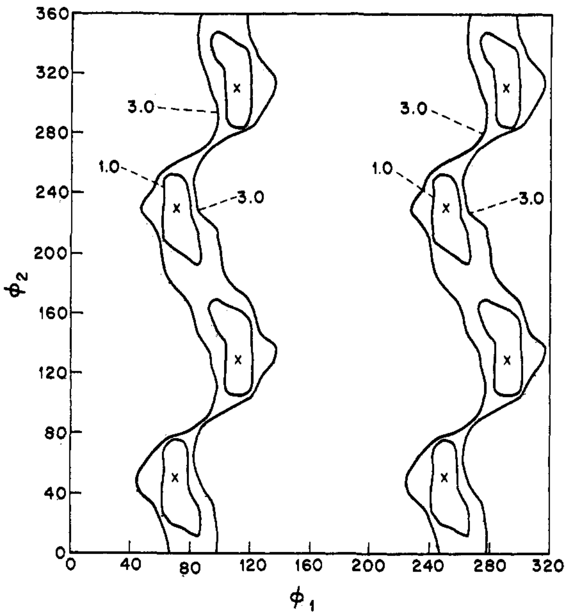

Figure 3. The conformational energy $V(\varphi_1, \varphi_2, \theta)$ map for poly(2,6-dimethyl-1,4-phenylene oxide) with $\angle C_1\text{–O–}C_4$ = 119° (θ = 61°, the value of the valence angle which leads to the correct dimensions[4]). Energy contours in kcal/mol of repeat unit are drawn relative to the minimum energy conformations which are denoted by X's. The energy maps for $\theta < 61°$ are very similar to the map in this figure except for a small increase in the number of allowed conformations.

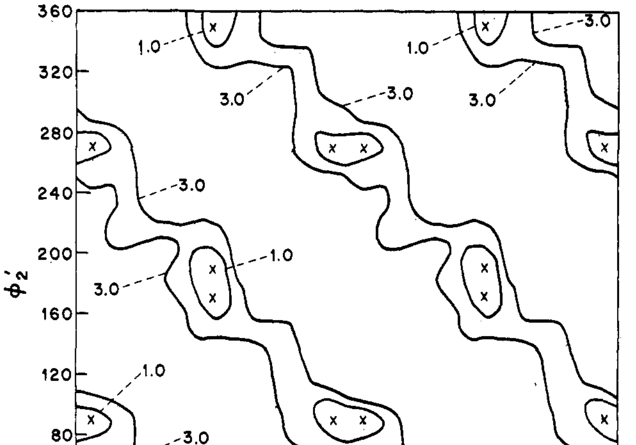

Figure 4. The conformational energy $V(\varphi_1', \varphi_2', \theta')$ map of rotations about the C_1–C bonds in polycarbonate with $\angle C_1\text{–C–}C_1$ = 112° (θ' = 68°). Energy contours in kcal/mol of virtual bonds are drawn relative to the minimum energy conformations which are each denoted by an X. The energy maps corresponding to θ' = 66° and 70° are virtually identical with the map presented in this figure.

boring rotation and valence angles, because the atoms or groups whose interactions depends on more than one set of (φ_1, φ_2, θ) in poly(phenylene oxide) or on more than the two adjacent rotation angles (φ_1', φ_2') or (φ_3, φ_4) in polycarbonate are separated by distances sufficiently large[6] (at least the length of a phenyl group) to render them negligible.

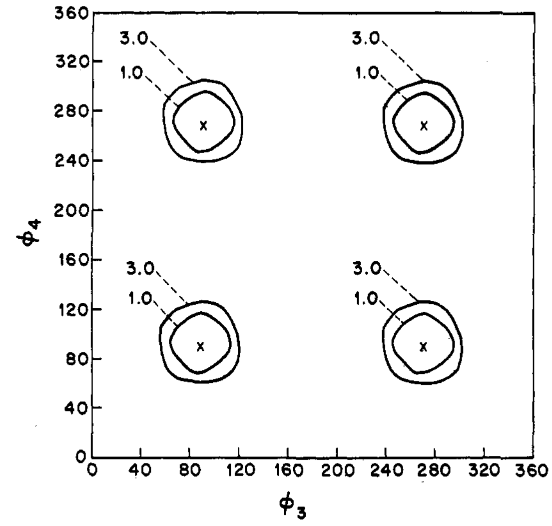

Figure 5. The conformational energy $V(\varphi_3, \varphi_4, \theta'')$ map of rotations about the C_4–O bonds in polycarbonate with θ'' = 68°. Energy contours in kcal/mol of virtual bonds are drawn relative to the minimum energy conformations which are each denoted by an X.

Results and Discussion

The conformational energy maps for the repeat units in poly(2,6-dimethyl-1,4-phenylene oxide) and the polycarbonate of diphenylol-2,2′-propane are presented in Figures 3, 4, and 5. φ_1 rotation in the phenylene oxide is restricted to the ranges 50° ≤ φ_1 ≤ 130° and 230° ≤ φ_1 ≤ 310° primarily as a result of the steric interaction of the 2 and 6 methyl groups with the 3 and 5 hydrogen atoms on the adjacent phenyl ring.

Steric interference of the 2 and 6 and the 3 and 5 hydrogen atoms of the adjacent phenyl rings with the propyl methyl groups and with each other results in a relatively limited number of conformations (φ_1', φ_2') about the propyl group (the energy map in Figure 4 is virtually independent of θ' in the range 66–70° considered here). The inaccessible areas of the φ_3, φ_4 conformation space about the carbonate group (see Figure 5) are the result of overlaps involving the carbonyl oxygen and the 2 and 6 and the 3 and 5 hydrogen atoms of the adjacent phenyl rings.

As noted previously[1,3–5], the symmetry of the 2,6-dimethyl-1,4-phenylene oxide and polycarbonate chains is such that the values of the cosine and sine of the rotation angles φ, φ', and φ'' about the virtual bonds in these chains must average[11] to zero. This symmetry is reflected in the energy maps pre-

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[11] The virtual bond rotation angles φ, φ', and φ'' and the rotation angles φ_1, φ_2, φ_1', φ_2', φ_3, and φ_4 about the C_1–O, C_4–O, and C_1–C bonds, as defined in Figures 1 and 2, are related by $\varphi = \varphi_1 + \varphi_2$, $\varphi' = \varphi_1' + \varphi_4$, and $\varphi'' = \varphi_2' + \varphi_3$. Each of the virtual bond rotation angles is a sum of two independent rotations about real chemical bonds. As an example, the probabilities of rotations φ_1' and φ_4 are independent, so the probability, $f_{\varphi'}$ of a virtual bond rotational state φ' is simply the product of the independent probabilities of rotational states φ_1' and φ_4

$$\varphi' = (SW\varphi_1')(SW\varphi_4) \Big/ \sum_{\varphi_1', \varphi_4} (SW\varphi_1')(SW\varphi_4)$$

where, for example, the statistical weight of conformations with φ_1' is given by

$$SW\varphi_1' = \left\{\sum_{\varphi_2'} \exp[-V(\varphi_1', \varphi_2')/RT]\right\} \Big/ \left\{\sum_{\varphi_1', \varphi_2'} \exp[-V(\varphi_1', \varphi_2')/RT]\right\}$$

TABLE I
PROBABILITIES OF ROTATIONAL STATES IN POLY(2,6-DIMETHYL-1,4-PHENYLENE OXIDE) ($\theta = 61°$) AND IN THE POLYCARBONATE OF DIPHENYLOL-2,2′-PROPANE ($\theta' = \theta'' = 68°$.)

φ, φ', and φ''	f_{φ}[a]	$f_{\varphi'}$ or $_{\varphi''}$[a]
0	0.036	0.129
20	0.063	0.055
40	0.060	0.006
60	0.073	0.032
80	0.036	0.093
100	0.036	0.093
120	0.073	0.032
140	0.060	0.006
160	0.063	0.055
180	0.036	0.129
200	0.063	0.055
220	0.060	0.006
240	0.073	0.032
260	0.036	0.093
280	0.036	0.093
300	0.073	0.032
320	0.060	0.006
340	0.063	0.055

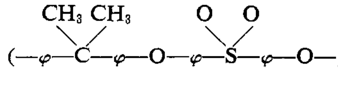
[a] $f_{\varphi,\varphi', \text{ or } \varphi''}$ = fractional probability of rotational state φ, φ', or φ''.

sented in Figures 3–5 and clearly illustrates the reasons why both chains obey freely rotating chain statistics.[5]

The calculated distributions and probabilities of the virtual bond rotational states for both classes of polymers are presented in Table I. It is apparent that the entire range of the virtual bond rotation angle φ in the phenylene oxide polymer is accessible and not just values immediately surrounding φ = 90 and 270° as suggested in ref 1, 3, and 4. Similar, though somewhat more restricted, freedom of rotation is possible for the virtual bond rotation angles φ' and φ'' in the polycarbonate chain.

Thus, unlike the earlier qualitative treatments[1,3,4] of the conformational characteristics of the phenylene oxide polymers, which predicted two symmetrically located rotational minima of equal energy to explain the observed freely rotating chain statistics, the present study finds the virtual bond rotations to be almost unimpeded, or nearly truly freely rotating, over the whole range of φ. Each of the polycarbonate virtual bond rotational states is appreciably populated, although the distribution of virtual bond rotation angles (φ' or φ'') in polycarbonate is not as uniform as that calculated for the phenylene oxide polymer. (The maximum energy differences between virtual bond rotational states in the phenylene oxide polymer are 0.40 (25°) and 0.23 (−100°) kcal/mol, 1.8 (25°) and 1.0 (−100°) kcal/mol separate the highest and lowest energy rotational states in polycarbonate.) Consequently, the phenylene oxide polymer would appear to be relatively more flexible than the polycarbonate chain.

The polysulfone chain



$$(\text{—}\varphi\text{—}\overset{\text{CH}_3\ \text{CH}_3}{\text{C}}\text{—}\varphi\text{—O—}\varphi\text{—}\overset{\text{O}\ \ \text{O}}{\text{S}}\text{—}\varphi\text{—O—})$$

is very similar in its molecular structure to both the poly(phenylene oxides) and polycarbonate. In fact, the energy maps for rotation about the C_1–C bonds and, in the first approximation, about the C_1–S bonds should be the same as the map in Figure 4 for polycarbonate, because the sulfone group is similar in geometry and size to the propyl group. Owing to the severity of the nonbonded interactions (see Figure 4), the as yet unmeasured barrier to rotation about the C_1–S bond resulting from π-electron delocalization into the aromatic rings is neglected. On the other hand, the energy map describing the rotations about the C_4–O bonds should be similar and with identical symmetry to the energy map for the phenylene oxide polymer in Figure 3. In the first approximation then, rotation about the C_1–C and C_1–S bonds should be the same. Thus, there are just two different types of virtual bonds in polysulfone, those beginning at O and terminating at C or S (L1) and those beginning at C or S and ending at O (L2). When the rotation angles about these virtual bonds φ''' (L1) and φ'''' (L2) are averaged over the energy maps in Figures 3 and 4, φ''' and φ'''' are found to be nearly truly freely rotating, with distributions of rotational states less uniform than those of the phenylene oxide polymer, but more uniform than the distribution of polycarbonate virtual bond rotational states. Consequently, the polysulfone chain should also obey freely rotating chain statistics and should be somewhere between polycarbonate and the poly(phenylene oxides) in its flexibility (see Table I). (The end-to-end distance of polysulfone and its temperature coefficient, as determined from a dilute-solution viscosity study,[12] are consistent with the predicted free rotation statistics of this polymer.)

The ability of these polymers to adopt conformations spanning the entire range of the virtual bond rotation angle may explain their excellent impact strength properties.[13] Especially significant in this connection is the fact that the phenylene oxide and polycarbonate polymers exhibit[13,14] high impact strengths down to −200°, or more than 300° below their glass-transition temperatures. This unusual behavior may have its origin in the ability of both polymers to rotate about their virtual bonds without encountering intramolecular rotation barriers or rotational states of high energy. (It is assumed that impact strength is related to the ability of a polymer chain to undergo a reversible conformational transformation without bond rupture.) The greater relative freedom of rotation in the poly(phenylene oxide) chain may explain the observation[13,14] that its impact strength is greater than that of polycarbonate over the temperature range −200 to 100° (well below the glass-transition temperature), where large-scale motions of substantial portions of the polymer backbone have been assumed[14] to be absent.

Nearly free rotation about the virtual bonds in the phenylene oxides and polycarbonate is also consistent with the low-temperature heat capacity behavior of both polymers. Neither polymer shows[15] any heat capacity anomalies between −200 and 100°. Since the rotation is nearly truly free (each rotational state is almost equally probable, or has nearly the same energy and there are no significant barriers between virtual bond rotational states), this rotation approximates a constant conformational energy mode of motion which would not be expected to cause a heat capacity anomaly.

The melting temperatures and heats of fusion of the 2,6-dimethyl- and 2,6-diphenyl-1,4-phenylene oxide polymers and of polycarbonate are presented in Table II together with

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TABLE II
FUSION DATA FOR THE 2,6-DISUBSTITUTED 1,4-PHENYLENE OXIDE POLYMERS AND POLYCARBONATE

Polymer	T_m, °C	ΔH_u,[a] calcd	ΔS_u,[a] cal °C^{-1}
2,6-Dimethylphenylene oxide[c]	262	1230–1440	2.36–2.69
2,6-Diphenylphenylene oxide[d]	484	2800–3040	3.70–4.02
Polycarbonate[e]	253	4060–4320	7.97 (4.94)[b]

[a] Per mole of virtual bonds. [b] $(\Delta S_u)_v = \Delta S_{conf}$. [c] Reference 15 and A. R. Schultz and C. R. McCullough, *J. Polym. Sci., Part A-2*, **7**, 1577 (1969); **10**, 307 (1972). [d] W. Wrasidlo, *Macromolecules*, **4**, 642 (1971). [e] L. D. Jones and F. E. Karasz, *J. Polym. Sci., Part B*, **4**, 803 (1966).

the entropies of fusion derived from them ($\Delta S_u = \Delta H_u T_m$). The total entropy of fusion ΔS_u can be separated[16–18] into two independent contributions, the constant-volume intramolecular or conformational contribution $(\Delta S_u)_v = \Delta S_{conf}$ and the volume expansion or intermolecular contribution ΔS_V. A lower limit[19] of $R \ln 4$ and $R \ln 2 = 2.75$ (phenylene oxide) and 1.40 (polycarbonate) eu/mol of virtual bonds can be placed on the conformational entropy change accompanying fusion if both polymer chains are assumed to possess perfect conformational order in the crystal ($S_c = 0$), because $(\Delta S_u)_v = \Delta S_{conf} = S_a - S_c = S_a$ (conformational entropy of a chain in the melt).

Comparison of the measured entropies of fusion in Table II with the lower limits of the conformational contributions leads to the observation that $\Delta S_{conf}(\text{calcd}) \approx (\Delta S_u)_v > \Delta S_u$ (exptl) for the 2,6-dimethyl-1,4-phenylene oxide polymer and approaches the total entropy of fusion for the diphenyl derivative. This implies that the volume expansion or intermolecular contribution to the entropy of fusion ΔS_V must be less than or equal to zero, because $\Delta S_u = (\Delta S_u)_v$ or $\Delta S_{conf} + \Delta S_V$. We believe[9,10,13] the existence of substantial conformational disorder in the crystals of both phenylene oxide polymers, which would lower $(\Delta S_u)_v = \Delta S_{conf}$, rather than chain ordering in the melt,[20a,b] to be the most probable explanation for their low observed entropies of fusion. Since $\varphi = \varphi_1 + \varphi_2$, the phenyl group flanked by φ_1 and φ_2 may adopt many different orientations, with respect to the plane defined by adjacent virtual bonds, for the same value of φ. Hence, we suggest partial disorientation of backbone phenyl groups as a likely source of disorder in the poly(phenylene oxide) crystals.

Measurement of the frequency dependence of the shear modulus or viscosity of dilute solutions of the phenylene oxide, carbonate, and sulfone polymers in solvents of widely varying viscosities should serve as an experimental means of testing the validity or degree of applicability of the presently proposed nearly true free rotation nature of these polymers. Peterlin[21] has recently demonstrated that the internal viscosity of a polymer chain is a consequence of two distinct molecular phenomena opposing its rate of shape change.

The first is an intramolecular contribution attributable to the potential barriers between the various possible chain conformations. This contribution constitutes the only resistance to rate of shape change envisioned in the original[22] concept of internal viscosity and is independent of solvent viscosity.

Resistance to the rate of polymer chain shape change resulting from the lateral displacements of chain elements through the viscous medium (solvent), which accompany a conformational transition, is the intermolecular source of internal viscosity advanced by Peterlin.[21] This intermolecular source (polymer–solvent interaction) of polymer chain internal viscosity is directly proportional to the solvent viscosity.

If the presently developed models (nearly true free rotation) of the phenylene oxide, carbonate, and sulfone polymers are valid, then their high-frequency dynamic intrinsic viscosities should vanish or be significantly reduced in comparison to other polymers. This prediction follows from the absence of significant intramolecular potential barriers to internal rotation about each of the virtual bonds in these polymers.

Another experimental consequence of the lack of substantial intramolecular rotation barriers is the predicted dependence of their internal viscosities upon solvent viscosity even in very fluid solvents. Since these polymers possess only minor intramolecular sources of internal viscosity (rotation barriers), the intermolecular source, which depends directly upon solvent viscosity, should dominate even in solvents of low viscosity. This prediction receives further support from the realization that it is the bulky backbone phenyl groups, some of which are substituted, which must be displaced through the solvent during the course of conformational transitions.

Acknowledgment. The author is grateful to the referees of this paper for their helpful comments and suggestions.

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(19) $S = R \ln z$, where $z = \Sigma_\varphi \exp[-V(\varphi)/RT]$ and the $\mathrm{d} \ln z/\mathrm{d}T$ term is neglected. Since there are four equal energy minima in the φ conformation space (φ = 60, 120, 240, and 300°; see Table I) and two equal energy minima in the φ' and φ'' spaces ($\varphi' = \varphi'' = 0$ and 180°; see Table I), a lower limit on z would be 4 for the phenylene oxide polymers and 2 for the polycarbonate virtual bonds.

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