Intramolecular Flexibility of the Poly(2,6-disubstituted-1,4-phenylene oxides)

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ABSTRACT: The intramolecular flexibilities of poly(1,4-phenylene oxide) (H_2PPO), poly(2,6-dimethyl-1,4-phenylene oxide) (M_2PPO), poly(2-methyl-6-phenyl-1,4-phenylene oxide) (MPhPPO), and poly(2,6-diphenyl-1,4-phenylene oxide) (Ph_2PPO) are evaluated through estimation of the resistance to rotation about the $C_{1,4}$–O bonds in their backbones. A 6-12 potential is used to account for the van der Waals interactions between nonbonded atoms and groups encountered during the backbone rotations, while the twofold intrinsic potential to rotation about the $C_{1,4}$–O bonds resulting from π-electron delocalization is also included. For the Ph_2PPO and MPhPPO polymers the phenyl groups in the 2 and/or 6 positions are permitted to rotate, and the nonbonded interactions involving the rotating, pendant phenyl groups are considered. In general, all of the polymers are found to possess energetically allowed backbone conformations spanning the entire range of the rotation angle about the virtual bonds connecting neighboring ether oxygen atoms. Consequently, on an intramolecular basis each polymer is nearly truly freely rotating in both a statistical and a dynamical sense. The bulk and dilute solution properties of this class of polymers are discussed in terms of their intramolecular flexibilities as developed here.

Recently the physical properties of the poly(2,6-disubstituted-1,4-phenylene oxides) (PPO's) have been studied in dilute solution[1-3] and in the bulk.[4-18] Dilute solution intrinsic viscosity and light-scattering studies led[1-3] to the conclusion that these polymers obey freely rotating chain statistics[19] in terms of the net rotation permitted about the backbone virtual bonds spanning the phenyl groups and connecting neighboring ether oxygen atoms (see Figure 1). Their dimensions (mean-square end-to-end distance $\langle r^2 \rangle_0$) and the absence of a temperature dependence of the dimensions suggests[19] the existence of N symmetrically located rotational states φ of equal energy about the virtual bonds L.

With the exception of poly(2-methyl-6-phenyl-1,4-phenylene oxide) (MPhPPO), the twofold symmetry of these polymers, as had been noted,[1-3] ensures the presence of at least two φ-rotation energy minima of equal energy separated by 180°. In fact, using a detailed estimate (see below) of the resistance to rotations φ_1 and φ_2 about the $C_{1,4}$–O chemical bonds flanking the phenyl groups, which when summed lead to the net rotation φ about the virtual bond L, we[20] previously showed that in the case of poly(2,6-dimethyl-1,4-phenylene oxide) (M_2PPO) this net rotation is free of significant constraints. Thus, we concluded that M_2PPO is a nearly truly freely rotating polymer, with each rotational state appreciably populated, and not restricted to two symmetrically located rotational states of equal energy.[1-3] The impact strength[4] and fusion behavior[6,10,11,17] of M_2PPO were discussed[20] in terms of the nearly true free rotation nature of its backbone.

The present investigation is an extension of the study[20] performed on M_2PPO to those PPO's with hydrogen atoms (H_2PPO), or one methyl and one phenyl group (MPhPPO), or phenyl groups (Ph_2PPO) in the 2 and 6 positions, for the purpose of determining the effect of the nature of the substituents upon the intramolecular flexibility of the phenylene oxide backbone. Dynamic bulk properties, such as glass transition temperature, subglass mechanical and dielectric relaxations and impact strength, together with the static or equilibrium properties, such as the entropy of fusion and dilute solution dimensions, are discussed in terms of their backbone flexibilities.

Description of Calculations

The conformational energy of rotation $V(\varphi_1,\varphi_2,\theta)$ about a pair of $C_{1,4}$–O bonds attached to the same ether oxygen atom is independent[20] of the values of neighboring rotation ($\varphi_{1,2}$) and valence (θ) angles, because the atoms and groups whose interactions depend on more than a single set of ($\varphi_1,\varphi_2,\theta$) are separated by distances sufficiently large (at least the length of a phenyl group) to render their interactions negligibly small. Calculation of $V(\varphi_1,\varphi_2,\theta)$, thereby results in a complete description of the intramolecular conformational characteristics of the 2,6-disubstituted PPO's.

Included in $V(\varphi_1,\varphi_2,\theta)$ are the interactions of the 2 and 6 substituent groups (H, CH_3, or C_6H_5) 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 (see Figure 1). In addition, for MPhPPO and Ph_2PPO the interactions of the 2 and 6 hydrogen atoms and the 1, 2, and 6 carbon atoms of the pendant phenyl groups with the 1 and 3 or 5 carbon and 3 or 5 hydrogen

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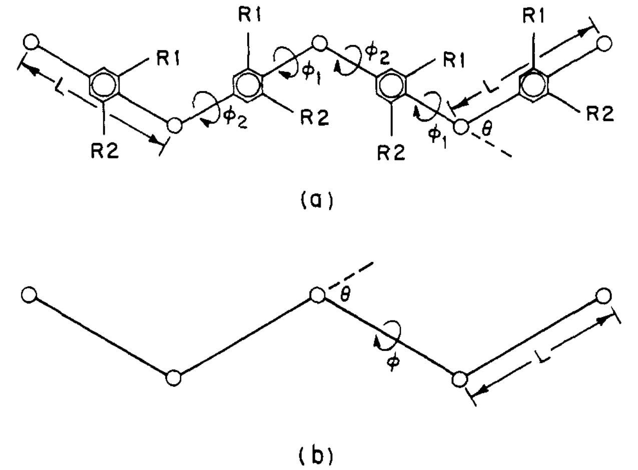

Figure 1. (a) A portion of a 2,6-disubstituted-1,4-phenylene oxide chain ($R_{1,2}$ = H or CH_3 or C_6H_5) in the planar zigzag conformation, where $\varphi_1 = \varphi_2 = 0°$. All phenyl rings are coplanar in this reference conformation, and φ_1, φ_2 assume positive values for right-handed rotations.[19] (b) A portion of the same chain where the phenyl rings are replaced by virtual bonds L linking the ether oxygen atoms. The virtual bond rotation angle φ is taken as 0° in this conformation and adopts positive values for right-handed rotations.[19]

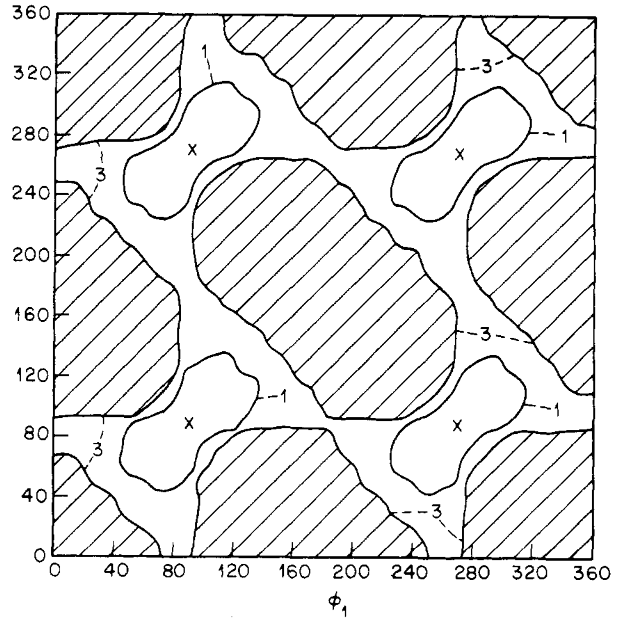

Figure 2. Nonbonded conformational energy $V(\varphi_1,\varphi_2,\theta)$ map for H_2PPO with $\theta = 61°$. Energy contours in kcal/mole of repeat unit are drawn relative to the minimum energy conformations denoted by X's.

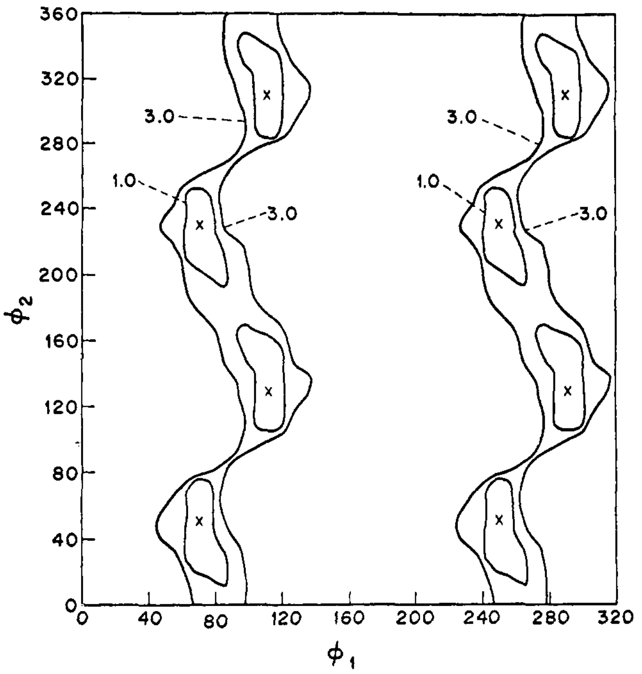

Figure 3. Nonbonded conformational energy $V(\varphi_1,\varphi_2,\theta)$ map for M_2PPO with $\theta = 61°$. Energy contours in kcal/mole of repeat unit are drawn relative to the minimum energy conformations denoted by X's.

atoms of the backbone phenyl group to which it is attached, and with the ester oxygen atom ortho to the pendant phenyl groups, and with the 3, 4, and 5 carbon atoms and 3 and 5 hydrogen atoms of the adjacent backbone phenyl group attached to the ortho ester oxygen atom are considered. A 6–12 van der Waals potential

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

where A_{ij} and C_{ij} are taken from Brant *et al.*,[21,22] is used to evaluate these nonbonded interactions. From the microwave spectrum of phenol[23] the intrinsic twofold torsional barrier about bonds of the type $C_{1,4}$–O, due to the delocalization of π electrons, is estimated to be *ca.* 3.2 kcal/mol. Thus, the twofold intrinsic rotation potential

$$V_\pi = (3.2/2)(1 - \cos 2\varphi_{1,2}) \qquad (2)$$

is added to the nonbonded interactions to give an estimate of the total resistance to rotations $\varphi_{1,2}$. The contribution made by V_π to the rotational resistance about the $C_{1,4}$–O bonds was ignored in the previous study[20] of M_2PPO. (The potential resisting valence angle deformation is ignored in the case of H_2PPO below.)

For Ph_2PPO and MPhPPO the conformational energy $V(\varphi_1,\varphi_2,\theta)$ is also a function of χ_1 and/or χ_2, the angles of rotation about the $C_{2,6}$–C_1 bonds connecting the pendant and backbone phenyl groups. All rotation angles φ_1, φ_2, χ_1, and χ_2 are varied in 20° increments over their entire ranges, and $\theta = 61°$ is adopted for all PPO's except H_2PPO whose θ is taken as either 56 or 61°. (The dilute solution dimension measurements[1-3] lead to $\theta = 61 \pm 1°$ for M_2PPO, MPhPPO, and Ph_2PPO, while X-ray studies[12] of drawn H_2PPO and Ph_2PPO films lead to θ = 56 and 53°, respectively.) The geometry[24] employed in the previous study[20] of M_2PPO is also adopted here.

Results and Disucssion

Conformational energy maps[25] for the independent repeat units in H_2PPO, M_2PPO, MPhPPO, and Ph_2PPO are presented in Figures 2–5. The energies $V(\varphi_1,\varphi_2,\theta = 61°)$ appropriate to MPhPPO and Ph_2PPO in Figures 4 and 5 correspond to the lowest energy rotational states (χ_1,χ_2) of the pendant phenyl groups for each backbone conformation (φ_1,φ_2). (The reader is referred to the discussion in the previous investigation[20] of M_2PPO and is

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(25) The energy contours plotted in the maps of Figures 2–5 are nonbonded energies as evaluated from eq 1 and do not include the twofold intrinsic π-electron overlap barrier (eq 2). Inclusion of V_π does not produce any significant qualitative changes in the contours.

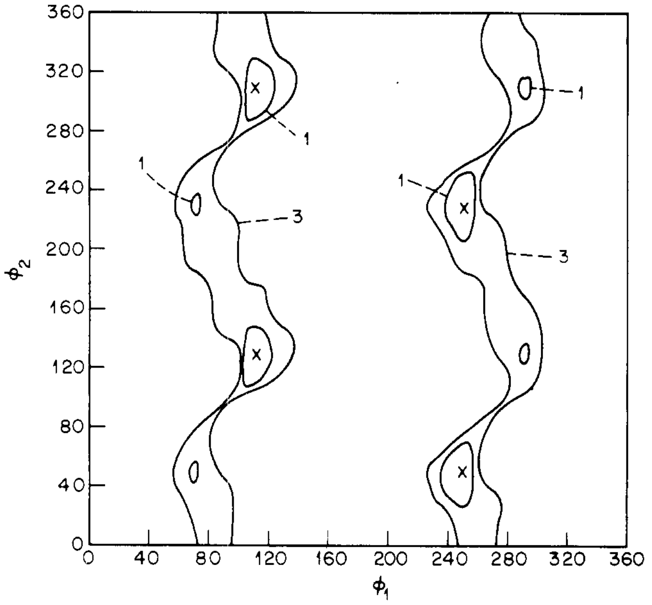

Figure 4. Nonbonded conformational energy $V(\varphi_1,\varphi_2,\chi_1,\theta)$ map for MPhPPO with θ = 61°. Energy contours in kcal/mole of repeat unit are drawn relative to the minimum energy conformations denoted by X's. Each $V(\varphi_1,\varphi_2,\chi_1,\theta)$ corresponds to the lowest energy rotational state χ_1 of the pendant phenyl group.

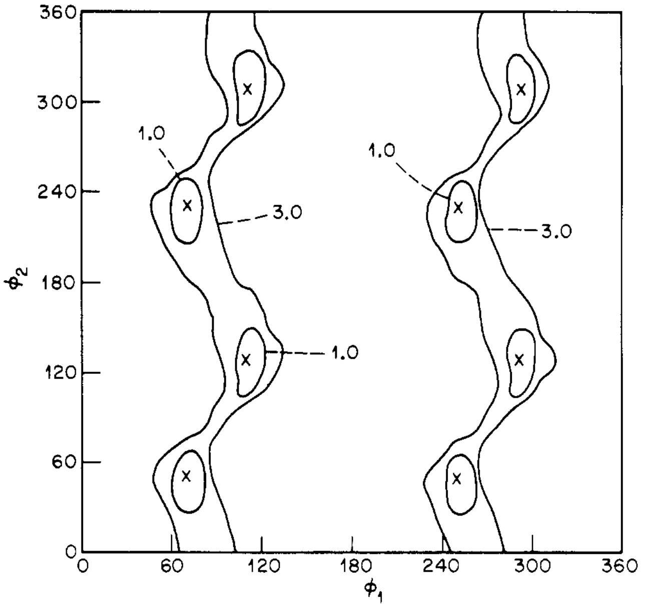

Figure 5. Nonbonded conformational energy $V(\varphi_1,\varphi_2,\chi_1,\chi_2,\theta)$ map for Ph$_2$PPO with θ = 61°. Energy contours in kcal/mole of repeat unit are drawn relative to the minimum energy conformations denoted by X's. Each $V(\varphi_1,\varphi_2,\chi_1,\chi_2,\theta)$ corresponds to the lowest energy rotational states χ_1 and χ_2 of the pendant phenyl groups.

also urged to build space-filling molecular models in order to visualize which of the interactions between nonbonded groups are primarily responsible for the shape and symmetry of the energy contours in Figures 2-5.) If the angle of rotation $\chi_{1,2}$ about the bonds connecting the pendant and backbone phenyl groups in MPhPPO and Ph$_2$PPO is defined as 0° when both phenyl rings are coplanar, then in the preferred backbone conformations it is found that $\chi_{1,2}$ may adopt values of 90 ± 50° and 270 ± 50° for the energetic price of <5.0 kcal/mol ($\chi_{1,2}$ = 90 or 270° corresponds to a perpendicular arrangement of phenyl rings). This perpendicular arrangement of pendant to backbone phenyl rings is also found[12] in the crystal. On the other hand, the coplanar arrangements of pendant and backbone phenyl groups are strongly disfavored for all backbone conformations.

The number of backbone conformation within the 1-kcal/mol contours decreases in the order H$_2$PPO > M$_2$PPO > Ph$_2$PPO > MPhPPO, while for the 3-kcal/mol contours the order is identical except for M$_2$PPO ≈ Ph$_2$PPO. An alternative measure of backbone flexibility is the calculated conformational entropy[21] S_{conf}.

$$S_{\text{conf}} = R\left[\ln Z + \frac{T}{Z}(\mathrm{d}Z/\mathrm{d}T)\right] \quad (3)$$

where, as an example

$$Z = \sum_{\varphi_1}\sum_{\varphi_2}\sum_{\chi_1}\sum_{\chi_2} \exp[-V(\varphi_1,\varphi_2,\chi_1,\chi_2)/RT] \quad (4)$$

for Ph$_2$PPO. In addition, the average conformational energy $\bar{E}_{\text{conf}}$ of Ph$_2$PPO may be obtained[21] from

$$\bar{E}_{\text{conf}} = \frac{\sum_{\varphi_1}\sum_{\varphi_2}\sum_{\chi_1}\sum_{\chi_2}[V(\varphi_1,\varphi_2,\chi_1,\chi_2)] \exp\left[\frac{-V(\varphi_1,\varphi_2,\chi_1,\chi_2)}{RT}\right]}{Z} \quad (5)$$

The conformational entropies S_{conf} and average conformational energies $\bar{E}_{\text{conf}}$ calculated according to eq 3-5 using 20° increments in all rotation angles and including the π-electron overlap energy V_π (eq 2) are listed in Table I as a function of temperature, along with the conformational free energies A_{conf}

$$A_{\text{conf}} = \bar{E}_{\text{conf}} - TS_{\text{conf}} \quad (6)$$

The order of decreasing conformational entropy is Ph$_2$PPO > H$_2$PPO > MPhPPO > M$_2$PPO for −200° ≤ T ≤ 100° and Ph$_2$PPO > MPhPPO > H$_2$PPO > M$_2$PPO for 100° ≤ T ≤ 200°. Obviously the additional degrees of rotational freedom (χ_1 and/or χ_2) possessed by Ph$_2$PPO and MPhPPO results in a reversal in the order of decreasing backbone flexibility as determined from the energy maps, which are limited to just two degrees of rotational freedom (φ_1,φ_2).

The net rotation φ about a virtual bond L is the sum of two independent rotations φ_1 and φ_2 about the real C$_{1,4}$–O chemical bonds which terminate L.[20] Since the probabilities of the rotational states of φ_1 and φ_2 are independent (provided they are separated by a phenyl ring), the probability f_φ of a virtual bond rotational state $\varphi = \varphi_1 + \varphi_2$ is just the product of the independent probabilities of rotational states φ_1 and φ_2.

$$f_\varphi = (SW_{\varphi_1})(SW_{\varphi_2})/\sum_{\varphi_1,\varphi_2}(SW_{\varphi_1})(SW_{\varphi_2}) \quad (7)$$

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

$$SW_{\varphi_1} = \left\{\sum_{\varphi_2} \exp[-V(\varphi_1,\varphi_2)/RT]\right\}\Big/\left\{\sum_{\varphi_1,\varphi_2} \exp[-V(\varphi_1,\varphi_2)/RT]\right\} \quad (8)$$

The probabilities of the virtual bond rotational states φ calculated in this manner with inclusion of the π-electron overlap energy V_π are presented in Table II.

It is clear from the symmetry of the calculated distributions of virtual bond rotational states shown in Table II that $\langle\sin\varphi\rangle = 0$ and $\langle\cos\varphi\rangle = 0$ leading to free rotation chain statistics[19] $[\langle r^2\rangle_0/nL^2) = (1 + \cos\theta)/(1 - \cos\theta)]$ for each of the polymers. Of greater significance is the uniformity in the distributions of f_φ which means that

Table I
Average Conformational Entropy, Energy, and Free Energy Calculated for Isolated Poly(2,6-disubstituted-1,4-phenylene oxides)

	$\bar{E}_{conf}$ (kcal/mol)					S_{conf} (cal/(°C-mol))					$A = \bar{E}_{conf} - TS_{conf}$ (kcal/mol)				
Temp (°C)	H_2PPO (θ = 56°)	H_2PPO (θ = 61°)	M_2PPO	MPhPPO	Ph_2PPO	H_2PPO (θ = 56°)	H_2PPO (θ = 61°)	M_2PPO	MPhPPO	Ph_2PPO	H_2PPO (θ = 56°)	H_2PPO (θ = 61°)	M_2PPO	MPhPPO	Ph_2PPO
−200	0.09	0.09	0.06	0.10	0.14	4.45	7.11	5.19	4.95	7.65	−0.23	−0.43	−0.32	−0.27	−0.42
−150	0.29	0.18	0.15	0.25	0.27	6.54	7.97	6.18	6.46	9.08	−0.51	−0.80	−0.61	−0.55	−0.85
−100	0.50	0.27	0.22	0.41	0.41	7.91	8.37	6.68	7.61	10.1	−0.87	−1.2	−0.95	−0.91	−1.3
−50	0.66	0.35	0.27	0.55	0.55	8.76	8.98	6.96	8.33	10.8	−1.3	−1.7	−1.3	−1.3	−1.9
0	0.78	0.42	0.32	0.68	0.67	9.26	9.26	7.19	8.88	11.3	−1.8	−2.1	−1.6	−1.7	−2.4
50	0.87	0.47	0.37	0.78	0.78	9.60	9.46	7.35	9.24	11.7	−2.2	−2.6	−2.0	−2.2	−3.0
100	0.95	0.51	0.42	0.87	0.88	9.80	9.52	7.47	9.44	11.9	−2.7	−3.0	−2.4	−2.7	−3.6
150	1.0	0.54	0.47	0.95	0.97	9.94	9.62	7.59	9.70	12.1	−3.2	−3.5	−2.7	−3.2	−4.2
200	1.1	0.57	0.52	1.0	1.1	10.1	9.72	7.77	9.84	12.4	−3.7	−4.0	−3.2	−3.6	−4.8

Table II
Probabilities of Virtual Bond Rotational States in Poly(2,6-disubstituted-1,4-phenylene oxides)

	f_ϕ[a]				
ϕ	H_2PPO (θ = 56°)	H_2PPO (θ = 61°)	M_2PPO	MPhPPO	Ph_2PPO
0	0.089	0.062	0.003	0.010,[b] 0.007[c]	0.011,[b] 0.009[c]
20	0.080	0.056	0.019	0.031, 0.029	0.035, 0.031
40	0.056	0.051	0.051	0.054, 0.053	0.061, 0.053
60	0.040	0.054	0.075	0.067, 0.069	0.069, 0.066
80	0.025	0.059	0.104	0.092, 0.095	0.091, 0.096
100	0.025	0.059	0.104	0.091, 0.094	0.097, 0.096
120	0.040	0.054	0.075	0.048, 0.068	0.060, 0.066
140	0.056	0.051	0.051	0.054, 0.056	0.050, 0.053
160	0.080	0.056	0.019	0.032, 0.029	0.026, 0.031
180	0.089	0.062	0.003	0.010, 0.007	0.011, 0.009
200	0.080	0.056	0.019	0.031, 0.029	0.035, 0.031
220	0.056	0.051	0.051	0.054, 0.053	0.061, 0.053
240	0.040	0.054	0.075	0.067, 0.069	0.069, 0.066
260	0.025	0.059	0.104	0.092, 0.095	0.091, 0.096
280	0.025	0.059	0.104	0.091, 0.094	0.097, 0.096
300	0.040	0.054	0.075	0.048, 0.068	0.060, 0.066
320	0.056	0.051	0.051	0.054, 0.056	0.050, 0.053
340	0.080	0.056	0.019	0.032, 0.029	0.026, 0.031

[a] f_ϕ = fractional probability of rotational state ϕ. [b] Calculated using eq 1 and 2, where $V(\phi_1, \phi_2, \theta = 61°)$ corresponds to lowest energy pendant phenyl ring conformation(s). [c] Calculated from complete conformational energy, *i.e.*, from $V(\phi_1, \phi_2, \chi_1, \theta = 61°)$ for MPhPPO and $V(\phi_1, \phi_2, \chi_1, \chi_2, \theta = 61°)$ for Ph_2PPO.

every virtual bond rotational state φ is appreciably accessible. In fact the maximum energy differences in kcal/mole between the virtual bond rotational states at 25 and −100° are 0.11–0.75 and 0.07–0.44 (H_2PPO),[26] 2.1 and 1.2 (M_2PPO), 1.3–1.5 and 0.80–0.90 (MPhPPO),[26] and 1.3 and 0.7 (Ph_2PPO). Not only are these polymers free rotators in the statistical or equilibrium sense,[19] but on an intramolecular basis they should also behave as dynamically freely rotating chains when isolated from other polymer molecules as in dilute solution.

A summary of the transition (fusion and glass) and relaxation (subglass) temperatures experimentally observed for the poly(2,6-disubstituted-1,4-phenylene oxides) in the bulk is presented in Table III. We have just presented evidence that the intramolecular barriers hindering internal rotations in these polymers are low, yet their T_g's range from 90 to 220°. By elimination then, it would appear that intermolecular interactions, which hinder the chain motions, must be the source of the high glass transition temperature in PPO's. Acceptance of intermolecular interactions as the principle source of their high T_g's leads one to the qualitative prediction, based mainly on the bulkiness of the pendant groups, that the order of decreasing T_g for these polymers should be Ph_2PPO > MPhPPO > M_2PPO > H_2PPO. Obviously the T_g of MPhPPO does not conform to this simple qualitative correlation.

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(26) The range in values of the maximum energy difference between virtual bond rotational states for H_2PPO stems from the two different values (56 and 61°) adopted[3,12] for the supplement θ of the valence angle. For all the polymers except MPhPPO, f_φ calculated for $0° < \varphi_1 < 180°$, for $180° < \varphi_1 < 360°$, and for $0° \leq \varphi_1 \leq 360°$ are identical. However, for the unsymmetrically substituted MPhPPO, f $(0° < \varphi_1 < 180°) \neq f_\varphi(180° < \varphi_1 < 360°) \neq f_\varphi(0° \leq \varphi_1 \leq 360°)$, because of the absence of twofold symmetry in the interactions dependent upon φ_1 rotation (see Figure 4). Only in H_2PPO (see Figure 2) can all values of φ_1 be assumed with less than a 3.0-kcal/mol expenditure of energy. Since we are primarily interested in the dynamic aspects of chain flexibility, the f_φ's for MPhPPO should be calculated separately over the ranges $0° < \varphi_1 < 180°$ and $180° < \varphi_1 < 360°$. The f_φ values presented in Table II for MPhPPO are averages over both of the ranges in φ_1 rotation.

Table III
Experimental Transition and Relaxation Temperatures Observed for the Poly(2,6-disubstituted-1,4-phenylene oxides)

Transition or Relaxation	Temperature (°C)			
	H_2PPO	M_2PPO	MPhPPO	PH_2PPO
Fusion (T_m)[6,10,11,17,27]	260	260–290		480
Glass (T_g)[16,17]	90	205	160–180	220
$\beta(T_\beta)$[16]	−115	−55		80
$\gamma(T_\gamma)$[16]			−130	−140
$\delta(T_\delta)$[16]			−210	−180

Furthermore, MPhPPO does not exhibit[16] a subglass β relaxation usually attributed to hindered rotation of phenylene backbone segments. Eisenberg and Cayrol[16] have shown, by comparing estimated and measured activation energies, that the barriers to the β relaxation are intermolecular in origin. They cite a chain packing effect (an intermolecular effect) as the source of the anomalous behavior of MPhPPO. Although we are unable to envision the details of such a chain packing effect, we do agree, since the intramolecular barriers to phenylene segment motion are low for all the PPO's under study, that regardless of the specifics the absence of a β relaxation in MPhPPO most probably has an intermolecular origin.

The γ and δ relaxations,[16] which appear only in the polymers with pendant phenyl groups, most likely involve motion of the substituent phenyl groups. Activation energies of *ca.* 12 and *ca.* 4 kcal per mol, respectively, characterize these relaxations. As noted earlier, the intramolecular barrier to the complete rotation of pendant phenyl groups is high, certainly higher than the 12 and 4 kcal per mol observed for the activation energies of the γ and δ relaxations. However, oscillations of *ca.* ±50° about the substituent conformations where pendant and backbone phenyl groups are perpendicular is possible for less than 5 kcal/mol.

In a recent study[18] of the dynamic mechanical properties of several poly(2-methyl-6-(secondary alkyl)-1,4-phenylene oxides), which like MPhPPO do not exhibit a subglass β relaxation, Cayrol *et al.*[18] concluded that their γ relaxations (hindered torsional oscillations of planar zigzag, alkyl side chains) are uncoupled from their glass transitions. The same uncoupling is not observed in other series of polymers with alkyl side chains. We feel that it is possible to explain the uncoupling of side chain (γ relaxation) and large-scale backbone (glass transition) motions in these PPO's on the basis of the calculations performed here.

As the length of the alkyl side chain increases, T_g decreases and T_γ increases in this series of PPO's, *i.e.*, increasing the alkyl side-chain length decreases the intermolecular barrier to large-scale backbone motions, while increasing the barrier to rigid side-chain rotation. An increase in the distance between the backbones of neighboring chains must accompany an increase in the side-chain length and facilitate backbone motion. If backbone motions were coupled to side-chain oscillations, then T_γ would also decrease with increasing side-chain length.

Rotation about the methine to methylene C–C bond in the side chain, which appears according to Cayrol *et al.*[18] to be the mode of motion involved in the γ relaxation, should have no intramolecular effect on the rotation of the backbone phenyl groups, because that portion of the alkyl side chain which is rotating is too distant from the 1 and 5 positions of the backbone phenyl ring to interact very strongly (see Description of Calculations). Hence, the side-chain oscillations occurring in the γ relaxation should be independent or uncoupled from the backbone phenyl group motion resulting in glass transitions and γ relaxations which are not coupled.

The heats and entropies of fusion measured for H_2PPO,[17] M_2PPO,[6,10,11,27] and Ph_2PPO,[17] are 1770–1970 cal/mol and 3.3–3.7 eu/mol, 1230–2400 cal/mol and 2.3–4.3 eu/mol, and 2800–3040 cal/mol and 3.7–4.0 eu/mol, respectively. Conformational entropies calculated at the melting temperatures, according to eq 3 and 4 from the virtual bond rotational state distributions in Table II, are 16.1 eu/mol (H_2PPO), 9.6 eu/mol (M_2PPO), and 10.5 eu/mol (Ph_2PPO). In all three cases the calculated conformational entropy greatly exceeds the total entropy of fusion, which consists[28,29] of the increase in conformational entropy upon melting (intramolecular) and the increase in entropy due to the accompanying volume expansion (intermolecular). The source of this disparity must lie in the existence of conformational disorder[20] in the crystal and, or partial ordering[17] of the polymer chains in the melt. As noted in the previous study,[20] a backbone phenyl group flanked by the rotatable $C_{1,4}$–O bonds (φ_1, φ_2) may adopt many different orientations, with respect to the plane defined by adjacent virtual bonds, for the same value of φ, since $\varphi = \varphi_1 + \varphi_2$. A likely source of disorder in the poly(2,6-disubstituted-1,4-phenylene oxide) crystals would be just such a partial disorientation of backbone phenyl groups (see ref 12).

A final comment on the relative roles of intramolecular and intermolecular forces or barriers to motion in bulk PPO's may be worthwhile. The high impact strength and ductility observed[4] for these polymers well below their glass transitions, considered in conjunction with their high T_g's, appears puzzling. However, if it is assumed[20] that impact strength is related to the ability of a polymer chain to undergo a rapid, reversible conformational transition without bond rupture, then the nearly true free rotation nature of the PPO's may be the source of their substantial impact strengths in the glassy state. By eliminating substantial intramolecular barriers to chain motion as a source, it would appear[16] that the intermolecular interactions between these bulky chains lead to their high glass transition temperatures. We believe, therefore, that at least for polymers similar[20] to the PPO's, such as polycarbonate, polysulfone, etc., those bulk mechanical properties dependent upon high-frequency chain motions (impact strength) are primarily governed by the intramolecular barriers to polymer motion, while mechanical processes involving lower frequency motions (glass transition) are predominantly controlled by the intermolecular barriers opposing these motions.

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