# Phenyl Group Rotation in Polystyrene

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ABSTRACT: A semiempirical potential function is used to calculate nonbonded interactions encountered in the rotation ($\chi$) of a phenyl group about the C-$\varphi$ bond connecting it to the backbone of a polystyrene chain. The resistance to phenyl group rotation is evaluated as a function of the conformation of the polystyrene backbone. When all backbone bonds are required to be in one of the trans or gauche states, the phenyl group is restricted to the range ±20-30° about the positions ($\chi = 0$ and 180°) where the phenyl ring bisects the backbone valence angle at the asymmetric carbon atom to which it is attached. Furthermore, complete rotation of the phenyl group is permitted only when the backbone adopts sterically unfavorable conformations, *i.e.*, conformations expected to be present at equilibrium in amounts <1%. The barrier to complete rotation of the phenyl groups in these unlikely backbone conformations is 9-10 kcal/mol in agreement with the recent estimate of Reich and Eisenberg. Based on the vanishingly small probability of encountering polystyrene chain segments in backbone conformations which permit complete phenyl group rotation we suggest that both the $\delta$ and $\gamma$ subglass relaxations most probably owe their existence to molecular motions other than complete phenyl group rotation. In addition, phenyl group rotation in poly($\alpha$-methylstyrene) and poly($o$-methylstyrene) is also investigated.

Recently, efforts[1-7] have been made to interpret the subglass relaxations observed[1-12] in polystyrene and several of its substituted polymers in terms of the specific molecular motions thought to be responsible. In general, at low frequencies (~1 cps) two subglass relaxations are usually observed in polystyrene at *ca.* 40 and 100°K termed the $\delta$ and $\gamma$ relaxations, respectively. Both relaxations have usually been interpreted[1-5] as resulting from phenyl group motion, although Morgan[6] has implicated the presence of styrene monomer as the source of the $\gamma$ relaxation in polystyrene. More specifically, wagging, oscillation and rotation of the phenyl groups about the C-$\varphi$ bonds have been suggested as the source of the $\delta$ and $\gamma$ relaxations.

Using the formalism of O'Reilly and Tsang,[13] Reich and Eisenberg[5] have calculated the frequency of rotational or torsional oscillatory motion of a phenyl group about the C-$\varphi$ bond as a function of temperature and the barrier height hindering the rotation. By comparing the experimental temperature-frequency dependence of the $\delta$ and $\gamma$ relaxations with their calculations, Reich and Eisenberg[5] found that barrier heights, or activation energies, of 2 and 7-8 kcal per mol are necessary to produce the $\delta$ and $\gamma$ relaxations if the source of both relaxations is assumed to be rotation of the phenyl groups.

Next they proceeded to estimate the barrier to phenyl group rotation using a semiempirical potential function to account for certain of the nonbonded interactions involved in rotating a phenyl group in polystyrene. Their estimate of the lowest barrier to complete phenyl group rotation in polystyrene was 8.0 kcal/mol. Consequently, they ruled out phenyl group rotation as the source of the $\delta$ relaxation, but did suggest that phenyl group rotation could be the molecular motion underlying the $\gamma$ relaxation.

On the other hand, Abe, Tonelli, and Flory,[14] who accounted for nonbonded interactions longer in range than those considered by Reich and Eisenberg,[5] found the phenyl groups in polystyrene to be restricted to the range ±30° about the positions ($\chi = 0$ or 180°) where the plane of the phenyl ring bisects the backbone valence angle at the asymmetric carbon atom to which it is attached, regardless of the stereochemical configuration of the polystyrene chain. Their calculations, unlike Reich and Eisenberg's,[5] implied a large steric barrier to the complete rotation of phenyl groups in polystyrene. In the present work we briefly describe a more complete and detailed estimate of the barrier opposing the rotation of phenyl groups in polystyrene.

## Description of Calculations

The portion of a syndiotactic polystyrene chain in the all trans (t) or planar zigzag conformation, which serves as the model subject in the present calculations, is shown in Figure 1. As discussed by Abe, Tonelli, and Flory,[14] the steric hindrances to phenyl group rotation in polystyrene are minimized for the syndiotactic configuration. A 6-12 potential[15] is used to estimate the following nonbonded interactions encountered during phenyl group rotations $\chi$: $H_0$, $H_0'$, $C_0$, $C_0'$ with $H_0^{\alpha}$, $H_1^{\alpha}$, $H_2^{\alpha}$, $H_1$, $H_1'$, $H_2$, $H_2'$, and both $CH_2$ and $CH_3$ groups. Reich and Eisenberg[5] considered the interactions of $H_0$ and $H_0'$ with $H_0^{\alpha}$, $H_1$, $H_1'$, $H_2$ and $H_2'$, while Abe, Tonelli, and Flory[14] took into account the $H_0$, $H_0'$, $C_0$, $C_0'$ with $H_1$, $H_1'$, $H_2$ and $H_2'$ and the $C_0$, $C_0'$ with $H_1^{\alpha}$ and $H_2^{\alpha}$ interactions.

The geometry employed by Abe, Tonelli, and Flory (see pp 299 and 300 in ref 14) is adopted, and each of the backbone rotation angles is restricted[18] to 0° (t) and ±120° ($g^{\pm}$). Rotation $\chi$ about the C-$\varphi$ bond proceeds in 10° increments beginning from $\chi = 0$ or 180°, where the plane of the phenyl ring is coincident with the C-$\varphi$ and C-$H_0^{\alpha}$ bonds. The phenyl groups which ordinarily flank the central phenyl group (see Figure 1) are replaced by methyl groups for purposes of calculation, because the van der Waals radius of a methyl group may be taken as the minimum steric requirement of a phenyl group without incurring the need to specify the rotation angles $\chi$ about the C-$\varphi$ bonds in these terminal repeat units. Replace-

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(14) Y. Abe, A. E. Tonelli, and P. J. Flory, *Macromolecules*, **3**, 294 (1970).

(15) The potential constants employed by Brant *et al.*[16,17] were used.

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(17) D. A. Brant, A. E. Tonelli, and P. J. Flory, *Macromolecules*, **2**, 228 (1969).

(18) Preliminary calculations performed with $\varphi_1 = \varphi_4 = 0°$ (t) and $\varphi_2$, $\varphi_3$ = 0-330° in 30° increments showed that the lowest barrier to phenyl group rotation occurred for ($\varphi_2$, $\varphi_3$) = $g^-g^+$.

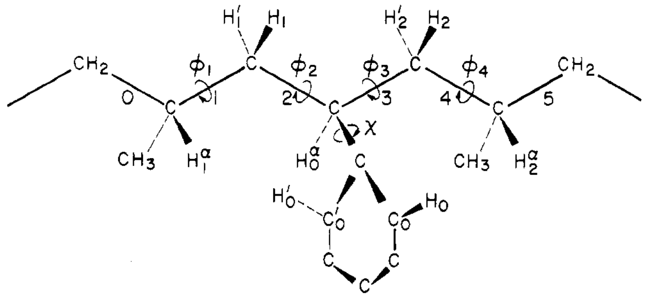

**Figure 1.** That portion of a syndiotactic polystyrene chain which serves as the model subject for the present calculations (note the replacement of the terminal phenyl groups by methyls). All backbone rotation angles ($\varphi_1$, $\varphi_2$, $\varphi_3$, $\varphi_4$) are 0° (all trans (t) or planar zigzag conformation), while the phenyl group is in the conformation corresponding to $\chi$ = 0 or 180°.

ment of the terminal phenyl groups by methyl groups in the polystyrene fragment under study (Figure 1) results in the neglect of possible phenyl–phenyl interactions which might occur due to small cooperative motions of the adjacent phenyl groups. However, it is believed that such cooperative phenyl–phenyl interactions are not sufficiently favorable to appreciably affect the magnitude of the barrier to complete phenyl group rotation as estimated here.

Identical calculations were performed for poly($\alpha$-methylstyrene) and poly(*o*-methylstyrene), where $H_0{}^\alpha$, $H_1{}^\alpha$ and $H_2{}^\alpha$ ($\alpha$-methyl), and $H_0{}'$ (*o*-methyl) are replaced by methyl groups.

## Results and Discussion

The barrier to phenyl group rotation in polystyrene and poly($\alpha$-methylstyrene) is high (>100 kcal/mol) except when the backbone of the polystyrene model in Figure 1 adopts the $tg^-g^+t$, $g^+g^-g^+t$, or $g^-g^-g^+t$ conformations. For these backbone conformations, the estimated energy of phenyl group rotation $\chi$ about the C–$\varphi$ bond is presented in Table I. Polystyrene and poly($\alpha$-methylstyrene) both possess estimated twofold barriers to complete phenyl group rotation of *ca.* 9.5 kcal/mol in these backbone conformations.

In agreement with Abe, Tonelli, and Flory,[14] C–$\varphi$ rotation in polystyrene is restricted to ±20-30° about $\chi$ = 0 or 180° for all likely backbone conformations (*cf. seq.*). However, the allowable range of phenyl group rotations increases to ±60° about $\chi$ = 0 or 180° (see Table I) when the backbone adopts the improbable conformations $tg^-g^+t$, $g^+g^-g^+t$, or $g^-g^-g^+t$. For poly($\alpha$-methylstyrene) in its most probable backbone conformations,[19] $\chi$ = (0 and 180°) or (90 and 270°) depending on the particular backbone conformation, *e.g.*, for the conformations tttt and $ttg^+g^+$ $\chi \approx$ 0 and 180° are favored, while for $tg^+tg^+$ and $tg^-tg^-$ $\chi \approx$ 90 and 270° are preferred.[23] In the less likely backbone conformations which permit complete phenyl group rotation (see Table I), C–$\varphi$ rotation is limited to ±10° about $\chi$ = 60, 120, 240, or 300°.

**Table I**
**Estimated Energy $E_\chi$ of Phenyl Group Rotation in Polystyrene and Poly($\alpha$-methylstyrene)**

| $\chi$ (deg) | $E_\chi{}^a$ (kcal/mol)<br>Polystyrene | $E_\chi{}^a$ (kcal/mol)<br>Poly($\alpha$-methylstyrene) |
|---|---|---|
| 0, 180 | 0.0 | 9.6 |
| 10, 170, 190, 350 | 0.3 | 8.8 |
| 20, 160, 200, 340 | 1.4 | 7.2 |
| 30, 150, 210, 330 | 2.8 | 5.8 |
| 40, 140, 220, 320 | 3.1 | 3.8 |
| 50, 130, 230, 310 | 2.1 | 1.3 |
| 60, 120, 240, 300 | 1.7 | 0.0 |
| 70, 110, 250, 290 | 3.6 | 1.4 |
| 80, 100, 260, 280 | 7.4 | 4.9 |
| 90, 270 | 9.4 | 6.9 |

[a] Nonbonded energy of phenyl group rotation for the backbone conformations (see Figure 1) $tg^-g^+t$, $g^+g^-g^+t$, and $g^-g^-g^+t$.

Unlike polystyrene and poly($\alpha$-methylstyrene), polymers with unsubstituted phenyl rings, no backbone conformations were found for poly(*o*-methylstyrene) which permitted complete phenyl group rotation without surmounting high barriers (>100 kcal/mol). As the inspection of molecular models confirms, however, methyl substitution in the meta or para positions should not result in any significant increase in the nonbonded steric interactions over those encountered when rotating unsubstituted phenyl groups in polystyrene.

As mentioned previously, Reich and Eisenberg,[5] by considering only the nonbonded interactions of $H_0$ and $H_0{}'$ with $H_0{}^\alpha$, $H_1$, $H_1{}'$, $H_2$ and $H_2{}'$, found the lowest barrier hindering the complete rotation of a phenyl group in polystyrene to be 8.0 kcal/mol. This lowest phenyl group rotation barrier occurs for the backbone conformations ($\varphi_2$, $\varphi_3$) = $g^\pm g^\mp$ (see Figure 1). Since the activation energy of the subglass $\gamma$ relaxation in polystyrene is 7.0–8.0 kcal/mol, they concluded that complete rotation of phenyl groups in those portions of the chain in the $g^\pm g^\mp$ conformations may be the molecular motion underlying the $\gamma$ relaxation.

In further support of this proposal, Reich and Eisenberg[5] cited the consistency between the very low peak intensity observed for the $\gamma$ relaxation and the relatively low probability of encountering a polystyrene chain segment in the $g^\pm g^\mp$ conformations. In fact, from the work of Flory and Fujiwara[24] it can be seen that the probability of encountering the $g^\pm g^\mp$ conformations is <5%.

This investigation has shown that consideration of nonbonded interactions longer in range than those accounted for by Reich and Eisenberg[5] requires the backbone to adopt conformations ($\varphi_1$, $\varphi_2$, $\varphi_3$, $\varphi_4$) = $tg^-g^+t$, $g^-g^-g^+t$, or $g^-g^-g^+t$ before complete phenyl group rotation can be accomplished for <10 kcal/mol. The probability of finding the syndiotactic polystyrene chain segment shown in Figure 1 in any of these backbone conformations can be estimated[24] to be <1%. Based on the vanishingly small probability of encountering polystyrene chain segments in backbone conformations which permit complete phenyl group rotation we suggest that both the $\delta$ and $\gamma$ subglass relaxations most probably owe their existence to molecular motions other than complete phenyl group rotation.

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(19) Assuming the preferred backbone conformations of poly($\alpha$-methylstyrene) and poly(isobutylene) are the same, the results of conformational studies[20-22] performed on poly(isobutylene) were adopted for poly($\alpha$-methylstyrene).

(20) P. J. Flory, "Statistical Mechanics of Chain Molecules," Interscience, New York, N. Y., 1969, Chapter V.

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(23) Interactions between $H_0{}^\alpha$ and $H_0$, $H_0{}'$, $C_0$ and $C_0{}'$ favor $\chi$ = 90 and 270° over 0 and 180°. For $<\varphi$–C–$H_0{}^\alpha$ = 106.8° the value thought[14] to be appropriate for polystyrene, $\Delta E_\chi = E_{\chi=0,180°} - E_{\chi=90,270°}$ = 13 kcal/mol. If one increases this valence angle to conform with the geometry expected[20-22] for poly($\alpha$-methylstyrene), then this energy difference decreases, but does not become insignificant. For example, $\Delta E_\chi$ = 5 kcal/mol when this valence angle is increased by 9° to 115.8°. This difference in the average orientation of the phenyl rings with respect to the backbone in polystyrene ($\chi \approx$ 0 or 180°) and poly($\alpha$-methylstyrene) ($\chi \approx$ 0, 180° or 90, 270°) may be manifested in differences between those properties which depend on the optical anisotropy[14] of both polymers.

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