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Effect of Articulated Side Groups on the Main-Chain Flexibility of Polycarbonates

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ABSTRACT: Conformational energies were calculated for a series of polycarbonates with articulated side groups attached to the central C_α atom. In all the cases considered here, the placement of a CH_2 spacer for the articulated side chain increases the main-chain rigidity as compared to that of Bisphenol-A polycarbonate (BPAPC) although the energies of the segment at the minima are lowered. The minima also become localized, thus impeding the synchronous rotation of the phenyls within a low energy barrier. A new steric factor σ_s based on the conformational partition function is used for comparing the chain flexibilities. The cases of the articulated side chains deviate from the correlation between the conformational entropy and T_g which applies for the homologous series of polycarbonates with nonarticulated side groups.

Following the early work of Williams and Flory[1] and Tonelli,[2] a number of authors[3-15] have recently examined the conformational characteristics of the Bisphenol-A polycarbonate (BPAPC) chain. These studies were aimed at one or more of the following: calculating the minimum-energy conformations, calculating the energy barrier to the phenyl motion and π flip, estimating the flexibility of the segment by constructing the energy diagrams in terms of rotations ϕ and ψ of the contiguous phenyls (see Figure 1), and simulating the conformations of the chain in the bulk by constructing energy-minimized amorphous structures. In terms of the flexibility of the BPAPC chain, the energy contour maps indicate that the segment can assume a number of conformations within a low energy barrier by the synchronous rotation of the contiguous phenyls about the central C–C bonds.[2-6,13,15] The rotations ϕ and ψ of the various pairs of contiguous phenyl groups of the chain in the amorphous structure[15] fall within the band of low-energy conformations calculated for the single chain.

Calculations on the effect of different types of substitutions at the central carbon atom on the conformational flexibility of the polycarbonate chains have been reported,[13] and the influence of these substituents on the conformational energy surface in terms of enabling or impeding the synchronous rotation of the contiguous phenyl moieties has been discussed. With (H,H), (H,CH_3), or CCl_2 substitutions, the minima become localized and the synchronous rotation of the phenyls is impeded. The high energy of ≥ 10 kcal·mol^{-1} between the energy minima in the case of the CCl_2 substitution accounts for the NMR observation[16,17] that the phenyl motion and the π flip are more restricted compared to that in BPAPC. The differences in the conformational attribute of the phenyl rotation in BPAPC and cyclohexyl polycarbonate were qualitatively related to the differences in the T_1 relaxation times derived from the NMR studies.[18] On the basis of these calculations for a homologous series of polycarbonates with different types of substituents, a linear correlation was shown to exist between the conformational entropy of the segment and the T_g of these polycarbonates.[19]

It is known that articulated side chains (e.g., methyl vs ethyl) invariably reduce the glass transition temperature of polymers. For example, whereas the T_g of BPAPC (with (CH_3,CH_3) substitution) is 145–150 °C, it reduces to 137 °C with (CH_3,$CH_2CH_2CH_3$) substitution. This can generally be attributed to the increased flexibility of the chain segment. It is to be expected, however, that the increased side-chain length would also influence the flexibility of the main chain. In the case of vinyl polymers with articulated substituents, e.g., polyacrylates with ethyl, butyl, etc. side groups, the skeletal bond rotations are expected to be significantly hindered since the substituents form part of the segment affected by the rotation about the skeletal C–CH_2 bond, and the "volume" of the side group would contribute to the hindrance to the rotation. However, in the case of polycarbonates discussed above, the C_α atom, to which the substituents are attached, is the center of rotation of the skeletal phenyl groups. It would then be of interest to explore the extent to which the rotations of contiguous skeletal phenyls are affected in the case of polycarbonates with articulated side groups at the C_α atom. The effect of such articulated side chains at the central carbon atom on the main-chain flexibility of polycarbonates is discussed in this paper.

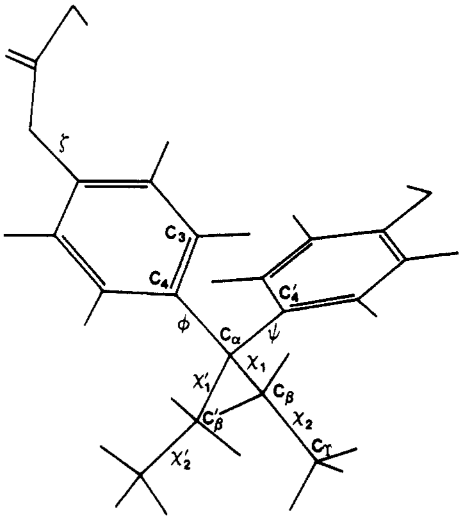

Figure 1. Schematic of the segment of a polycarbonate chain with (CH_2CH_3,CH_2CH_3) substitution.

Details of the Calculations

Calculations were performed on polycarbonate segments with the following substitutions at the C_α atom: (i) (CH_3,CH_2CH_3), (ii) (CH_2CH_3,CH_2CH_3), (iii) (CH_3,$CH_2C_6H_5$), (iv) ($CH_2C_6H_5$,$CH_2C_6H_5$), (v) (H,CH_2CH_3), and (vi)

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$(H,CH_2C_6H_5)$. For each of the skeletal bond rotational states denoted by ϕ and ψ, all the rotational states of the side groups were varied in order to locate the side-group atoms in their minimum-energy position and calculate the energy corresponding to that (ϕ,ψ) state. For the (ethyl,ethyl) substitution, for example, this requires four interdependent side-group rotations for each of the skeletal rotational states. All the rotations were varied at intervals of 10°. Together with the skeletal bond rotations ϕ and ψ, the summation from 0 to 350° under this scheme entails scanning more than 2.1×10^9 conformational states. The magnitude of the problem is reduced by varying ϕ and ψ from 0 to 170° each and transposing the results for ϕ or $\psi \geq 180°$ using the symmetry. Further reduction in the number of states is achieved by eliminating the need for the side group rotations for those states which are of high energy due to backbone interactions. With these strategies, the number of states for the (ethyl,ethyl) substitution reduced to 3.4×10^8. If one is interested in the flexibility of only the backbone, the contribution to the number of states from the side groups will be reduced by using the threefold symmetry of the terminal methyl group or the twofold symmetry of the terminal phenyl moiety. However, in the present calculations for the evaluation and comparison of the entropies of the whole segment for the cases of different substitutions, the symmetry of the side group is ignored.

The cis conformation of the C_4–C_3 and C_α–$C_{4'}$ bonds defines $\phi = 0$. Likewise, $\psi = 0$ when the C_4–C_α and C_4'–C_3 bonds are cis to each other. For the side-group conformations of, e.g., the (ethyl,ethyl) substitution, the trans conformation of $C_{\beta'}$–C_α–C_β–C_γ corresponds to $\chi_1 = 0$, and one of the hydrogens of the methyl group being trans to the C_β–C_α bond defines $\chi_2 = 0$ (see Figure 1). Similarly, for the $(CH_3,CH_2C_6H_5)$ substitution, $\chi_2 = 0$ when the plane of the phenyl group bisects the plane formed by C_β and the corresponding methylene hydrogens. As in the previous calculations,[13] a value of 60° was assigned to the torsion angle ζ. Any small variation from this conformation for the carbonate group would not affect the results due to the large distance of separation between this group and the substituents at the C_α atom.

The geometrical and energy parameters used here are the same as described before.[13] The Lennard-Jones function was used for calculating the nonbonded interaction energies. A threefold torsional potential with a barrier of 3 kcal·mol^{-1} was used for the rotations around the C–CH_2, C–CH_3, and CH_2–CH_3 bonds. The torsional barrier for the C–C_6H_5 bond was considered small and hence was neglected. As in the previous calculations, the Coulombic interactions were not included. In comparing the flexibility of the various polycarbonates, the partition functions were calculated in two ways: the main-chain partition function Z was calculated by Boltzmann averaging the energies corresponding to the (ϕ,ψ) states, with the side groups in their minimum-energy position corresponding to each of these states. The main-chain and side-chain partition function Z' (flexibility of the whole segment) was calculated by Boltzmann averaging all the energies corresponding to (ϕ,ψ) and all the side-group rotation angles. While for BPAPC this entails summation over four interdependent rotation angles each at 10° intervals, for the (ethyl,ethyl) substitution, the summation is over six interdependent rotation angles, as described above.

Table I
Calculated Steric Characteristics of Polycarbonates with Articulated Side Groups

substitution	energy at minimum (kcal/mol)	main-chain partition function Z	steric factor σ_s	main- and side-chain partition function Z'
$(CH_3,CH_3)^a$	1.87	179.3	0.138	410.6
(CH_3,CH_2CH_3)	1.51	75.8	0.058	349.4
(CH_2CH_3,CH_2CH_3)	1.17	45.0	0.035	389.0
$(CH_3,C_6H_5)^a$	5.61	41.7	0.032	133.9
$(CH_3,CH_2C_6H_5)$	−2.22	61.9	0.048	257
$(CH_2C_6H_5,CH_2C_6H_5)$	−0.04	15.2	0.012	47.9
$(H,H)^a$	−3.05	84.5	0.065	84.5
$(H,CH_3)^a$	−1.16	41.1	0.032	75.2
(H,CH_2CH_3)	−3.19	38.9	0.03	334.8
$(H,C_6H_5)^a$	3.68	70.6	0.054	118.8
$(H,CH_2C_6H_5)$	−4.69	39.3	0.03	256

[a] The results for nonarticulated cases were taken from ref 13.

In classical polymer science, the relative steric restrictions of various polymers are expressed in terms of the steric factor defined by

$$\sigma = (\langle r^2\rangle_0/M)/(\langle r^2\rangle_0/M)_f \qquad (1)$$

where the numerator corresponds to the characteristic ratio of the experimental end-to-end distance and the subscript f refers to theoretical free rotation. In the case of poly(p-phenylenes) as well as polycarbonates, both σ and the characteristic ratio are close to unity, and hence these polymers are usually described as freely rotating chains. This was rationalized in the early papers[20-23] as due to the equal energy of the two or more symmetrically situated preferred conformations enabled by the rotational symmetry of the backbone phenyl moiety. Although the concept of the freely rotating chain as applied to poly(p-phenylenes) and polycarbonates is a mathematical convenience in treating the average properties of the chain, the steric factor $\sigma \approx 1$ in all these cases does not distinguish them in terms of the realistic steric restrictions imposed by the side groups and the linkage atom (C, O, S, etc). Thus neither the conventional steric factor nor the characteristic ratio (e.g., $C_\infty = (\langle r^2\rangle_0/nl^2)_\infty$) is a useful parameter for comparing the relative flexibilities of the polycarbonates discussed here. To compare these polymers more realistically based on the steric energy considerations, we define a steric factor[24]

$$\sigma_s = Z/Z_f \qquad (2)$$

where Z is the calculated main-chain partition function described above and Z_f corresponds to the partition function for free rotation. With the intervals of 10° in ϕ and ψ used here, Z_f is simply 1296. Although eq 2 applies here to main-chain flexibility, it can be extended to the flexibility of the whole segment including the side groups by calculating the appropriate partition function. It is realized that the values of Z would differ from the results of one investigator to another depending upon the force fields used, the geometrical allowances, etc. However, it is still a better representation of the steric restrictions in polymers.

Results and Discussion

Table I shows the energy at the minima, the main-chain partition function Z, the steric factor σ_s, and the main- and side-chain partition function Z' for the polycarbonate segments with different types of substituents at the central carbon atom. It is seen that for the (methyl,ethyl) substitution, the energy at the minimum is lower than that of BPAPC. However, the partition function Z is

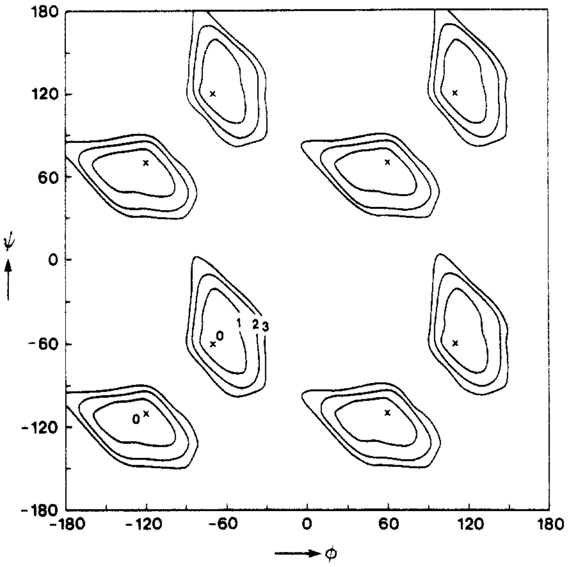

Figure 2. Isoenergy contour map for the polycarbonate segment with (CH_3,CH_2CH_3) substitution. Contours are drawn relative to the minimum marked by ×.

significantly smaller for the (CH_3,CH_2CH_3) substitution. One of the three hydrogens of the methyl group being replaced by a carbon atom of the ethyl group substantially reduces the main-chain flexibility. Such a substitution eliminates the threefold symmetry of the rotation about the C_α–C_β bond, and an entire range of conformations which would place this bond and the terminal methyl group in proximity to the $C_{\beta'}$ methyl group are rendered inaccessible. This reflects on the partition function Z' for the whole segment, which is smaller for the (CH_3,CH_2CH_3) side group as compared with BPAPC.

Figure 2 shows the energy map as a function of ϕ and ψ for the case of (CH_3,CH_2CH_3) substitution. The minima occur at (ϕ,ψ) = (60°,70°) and symmetrically related positions. This is similar to the minimum-energy positions calculated for BPAPC. A significant feature of the conformational map is that the minima are localized and the continuous range of conformations which facilitate synchronous rotation of the contiguous phenyls within a low energy barrier (as with BPAPC) is lost by the ethyl substitution. The calculated barrier between the minima at (60°,70°) and (110°,120°) is ~6 kcal·mol^{-1}. With the calculations performed at 10° intervals, out of the 1296 skeletal conformations, only 136 are within 1 kcal·mol^{-1} above the minimum. The steric factor σ_s = 0.058 is significantly less than that of BPAPC.

For the (CH_2CH_3,CH_2CH_3) substitution, the energy at the minimum is lower than that for both (CH_3,CH_3) and (CH_3,CH_2CH_3) substitutions. However, the main-chain partition function Z is significantly smaller, due to the substitution of one hydrogen from both methyl groups. The segment partition function Z' is comparable to that of BPAPC mainly due to the contributions from the rotational states of the two terminal methyl groups. The extent of the main-chain rigidity can be discerned from a comparison of the steric factors given in Table I. Out of the 1296 skeletal conformational states, only 72 are within 1 kcal·mol^{-1} above the minimum. Figure 3 shows the energy map for this case. The minima occur at (60°, 60°) and symmetrically related positions. This again is similar to the case of BPAPC. The minima are localized and the synchronous rotation of the contiguous phenyls is inhibited. The localized minima and the restricted rotations indicate that the π flip of the phenyl groups would be of low incidence. Thus, placing a CH_2 spacer reduces the energy at the minima but increases the rigidity of the main chain.

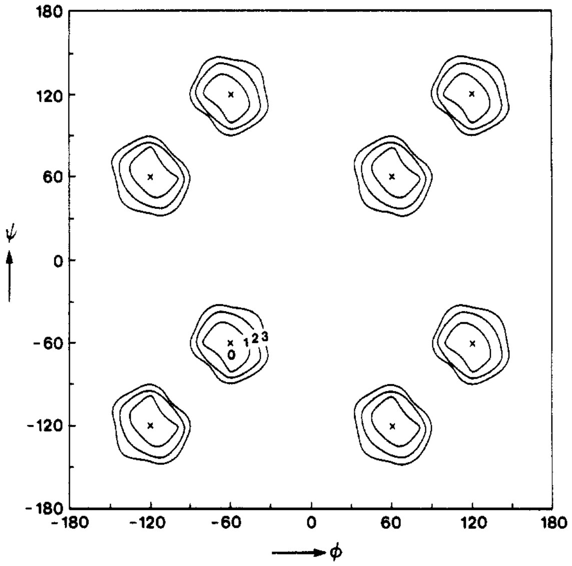

Figure 3. Isoenergy contour map for the polycarbonate segment with (CH_2CH_3,CH_2CH_3) substitution. Contours are drawn relative to the minimum marked by ×.

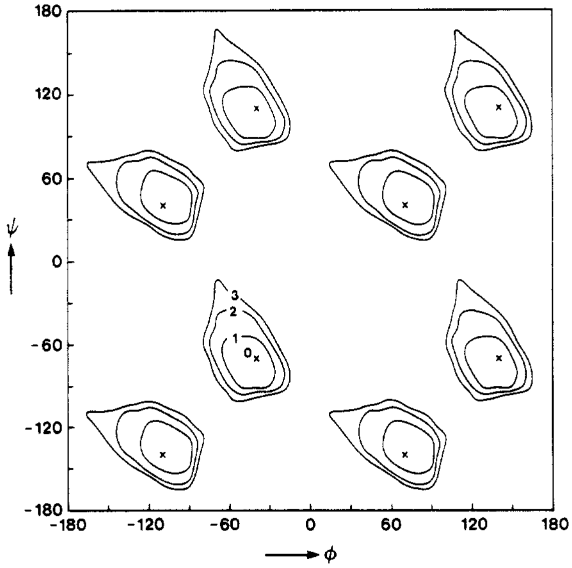

Figure 4. Isoenergy contour map for the polycarbonate segment with (CH_3,$CH_2C_6H_5$) substitution. Contours are drawn relative to the minimum marked by ×.

The energy contours for the (CH_3,$CH_2C_6H_5$) substitution, shown in Figure 4, are very similar to those for the (CH_3,CH_2CH_3) substitution. The minima are localized and synchronous rotation of the phenyls is impeded. Only 96 states out of 1296 are within 1 kcal·mol^{-1}, as compared with 136 in the case of (CH_3,CH_2CH_3) substitution. This is reflected in the lower values of the partition functions Z and Z' and the steric factor. The energy at the minimum, however, is lower than any of the cases discussed above. Comparison of the (CH_3,C_6H_5) and (CH_3,$CH_2C_6H_5$) cases (Table I) shows that the energy at the minimum is significantly reduced by the CH_2 spacer and the partition functions Z and Z' are both higher. However, both Z and Z' are lower than those of BPAPC.

The energy map for (H,CH_2CH_3) substitution is shown in Figure 5 and the map for (H,$CH_2C_6H_5$) substitution is similar, including the locations of the minima. However, the energy at the minimum for the latter is lower by about 1.5 kcal·mol^{-1}. In both cases, the energy at the minimum is significantly lower than for the case of the (H,CH_3)

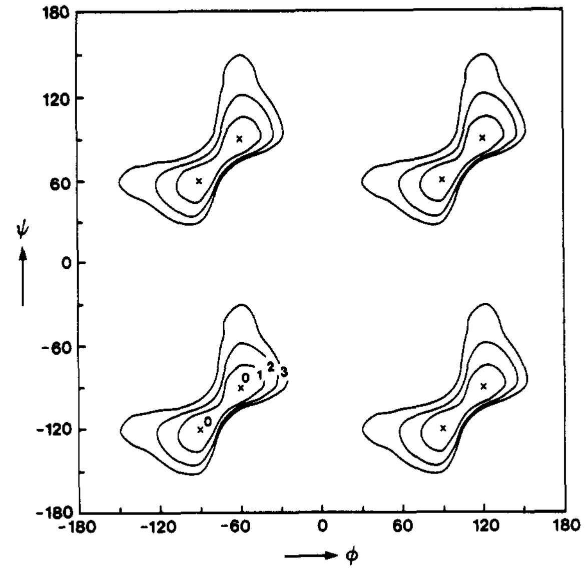

Figure 5. Isoenergy contour map for the polycarbonate segment with (H,CH_2CH_3) substitution. Contours are drawn relative to the minimum marked by ×.

substitution. Whereas the main-chain partition function Z is about the same for both cases, the value of Z' is significantly higher for the (H,CH_2CH_3) substitution than for the ($H,CH_2C_6H_5$) case. Comparing the (H,CH_3) and (H,CH_2CH_3) cases, the main-chain partition function is not affected significantly by the CH_2 spacer but the overall partition function Z' increases substantially. But with (H,C_6H_5) and ($H,CH_2C_6H_5$) substitutions, the CH_2 spacer decreases the energy at the minimum as well as the main-chain partition function but increases Z'.

The ($CH_2C_6H_5,CH_2C_6H_5$) substitution restricts the main-chain flexibility severely, and the main-chain partition function (Table I) is lower than for any of the cases discussed above. Only 24 states out of 1296 are within 1 kcal·mol^{-1} above the minimum. Yet, the energy at the minimum is lower than that of the (CH_2CH_3,CH_2CH_3) case.

The cases discussed above show that with a CH_2 spacer, the planarity of the phenyl substituent reduces the energy of the segment (at the minima) as compared to the sphericity of the methyl substituent.

The locations of the minima for the polycarbonates, with H as at least one of the substituents, deserve comment. It is known that with BPAPC, the conformation of the contiguous phenyls with $(\phi,\psi) = (90°,90°)$ is of high energy. However, with (H,H) substitution, the minimum occurs at $(\phi,\psi) = (90°,90°)$ (see Figure 4 of ref 13). The same finding has been reported by other authors.[25] With (H,CH_3), (H,CH_2CH_3), or ($H,CH_2C_6H_5$) substitution, the minimum occurs with the value of 90° for one of the torsions, although both torsions being 90° is of high energy. In all these cases, minima occur at (90°,60°) and (120°, 90°) and other symmetrically related positions.

Conformational Entropy and the Glass Transition Temperature

The group contribution method has been suggested as one of the approaches for calculating the glass transition temperatures of polymers.[26-28] Hopfinger et al.[27] published equations to predict the T_g, based on a regression analysis of the observed T_g and conformational entropy. The conformational entropy of the repeat unit of the polymer was calculated by adding those of the fragments of the repeating unit. A modification to the Koehler–Hopfinger model has been discussed recently by Vaz.[28] A number of years ago, Tonelli[29] used the calculated conformational entropy of the repeat units to rationalize the variation of T_g with copolymer composition.

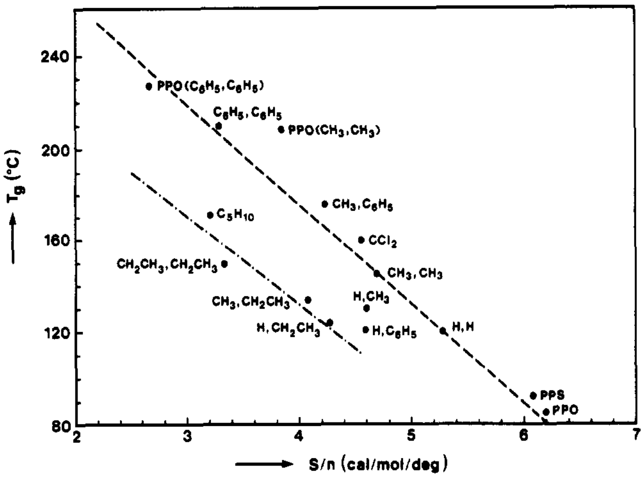

Figure 6. Plot of the calculated conformational entropy S/n versus the experimental T_g values for the polycarbonates with different types of substituents at the C_α atom. Also included are the results corresponding to poly (p-phenylenes).

In a previous publication,[19] we reported the calculation of conformational entropies for a homologous series of polycarbonates with different types of substituents at the C_α atom. This was based on the calculation of conformational entropy for the repeat unit, rather than as a group contribution. The conformational entropy per bond rotation (S/n) was shown to correlate linearly with the T_g of these polycarbonates.

To verify if the relationship between S/n and T_g calculated for these polycarbonates holds for chains with articulated side groups also, the conformational entropies were calculated for polycarbonate segments with (CH_3,CH_2CH_3), (CH_2CH_3,CH_2CH_3), and (H,CH_2CH_3) substitutions at the C_α atom. These calculations require, for every skeletal state, summation over the entire conformational space of the substituents i.e., from 0 to 360 ° since some of them possess threefold symmetry and others do not. The calculations were performed at intervals of 10°. A temperature of 300 K was used, as before. The results are plotted in Figure 6. Also shown in this figure are the results for the polycarbonates which were treated in the previous paper. These are the results of the present calculations performed at intervals of 10° for the rotations, instead of at 20° intervals as was done before.[19] The experimental T_g values were taken from refs 26, 30, and 31. The value of T_g for (H,CH_2CH_3) substitution is not available in the literature and hence a value of 123 °C, corresponding to the ($H,CH_2CH_2CH_3$) substitution was used here as an approximation. The T_g corresponding to the former is probably higher by about 5–10 K.

Figure 6 shows that a linear correlation exists between the calculated values of S/n and the measured T_g for polycarbonates with (H,H), (H,CH_3), (H,C_6H_5), (CH_3,CH_3), CCl_2, (C_6H_5,CH_3), and (C_6H_5,C_6H_5) substituents. As discussed previously, the partition function itself does not always provide a relative measure to rationalize the difference in the T_g's of two polymers, the example being the case of (H,H) and (CH_3,CH_3) substitutions. In the previous paper, it was concluded that polycarbonates with symmetric substituents follow a different relationship between S/n and T_g than those with asymmetric substitution. However, the results shown in Figure 6 indicate otherwise. The fortuitous distinction between the symmetric and asymmetric substitutions which emerged in the previous calculation is due to the coarse interval of

20° chosen for the rotation angles for the calculation of the entropy. A number of conformational states which would have otherwise contributed to the calculated entropy were thus missed by the choice of the large interval. Apart from this, the effect of the substituents on the T_g (e.g., methyl vs phenyl) which was discussed before is borne out by the present results as well. The dashed line in Figure 6 corresponds to the relationship

$$T_g = -43.2(S/n) + 348.7 \qquad (3)$$

with a correlation coefficient of 0.95, for 11 polymers and standard deviations of 4.7 and 21.9, respectively, for the slope and the intercept.

The case of the articulated substituents, however, departs significantly from the rest in Figure 6. Although the (CH_3,CH_3) and (CH_2CH_3,CH_2CH_3) substituents lead to the same T_g, the calculated conformational entropy is significantly lower for the latter. The values of S/n for (CH_2CH_3,CH_2CH_3) and (C_6H_5,C_6H_5) substitutions differ very little. However, the T_g of the latter is higher by 60 K. Similar is the trend with (H,CH_2CH_3) and (C_6H_5,CH_3) substitutions. The T_g of the latter is higher by 50 K, although the values of S/n are similar. This shows that in addition to the conformational entropy, other factors such as the size or "volume" of the side group and its mass influence the T_g. The "volume" of the side group is expected to affect the intermolecular cohesion. While this volume contribution is perhaps similar in the case of nonarticulated substitutions, it becomes significant with the articulated side chains. Figure 6 also shows that there is a linear trend between S/n and T_g among the articulated side groups. The lower line in Figure 6 corresponds to the relationship

$$T_g = -37.7(S/n) + 284.4 \qquad (4)$$

with a correlation coefficient of 0.94 for 4 polymers and standard deviations of 10.0 and 37.4, respectively, for the slope and the intercept. These results show that even among the polycarbonates in a homologous series, the articulated side chains follow a different correlation with T_g than the others. Apart from pointing out this difference, no attempt is made here to reconcile the differences due to the volume contributions.

As an aside, a few other cases shown in Figure 6 correspond to poly(*p*-phenylenes): poly(phenylene oxide), poly(2,6-dimethylphenylene oxide), poly(2,6-diphenylphenylene oxide), and poly(phenylene sulfide). A study of the relative conformational restrictions and the steric factors ($\sigma_s = Z/Z_f$) of these polymers has been published.[24,32] The relationship between S/n and the T_g for these polymers follows the same trend as for the polycarbonates.

Conclusions

The calculations discussed here show that the articulated side groups decrease the energy of the segment as compared to that of BPAPC. However, in all these cases, the main-chain flexibility is significantly reduced. This implies that it is possible to conceive of polycarbonates with high main-chain rigidity but with low energy of the segment. In addition, a polycarbonate with the same T_g as that of BPAPC but with more skeletal rigidity can be achieved by choosing a substituent such as (CH_2CH_3,CH_2CH_3), the T_g of which is the same as that of BPAPC. Although only a limited number of cases of articulated side chains have been discussed here, the effect of the CH_2 spacer can be expected to be valid for the longer side chains as well. It is also likely that increasing the number of methylene spacers would lower the steric restriction in the case of side chains terminated with a phenyl group. Polycarbonates with longer side chains can thus be expected to exhibit side-chain liquid crystalline behavior, due to the skeletal rigidity imposed by these side groups.

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