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Correlation between Conformational Features and the Glass Transition Temperatures for a Homologous Series of Polycarbonates

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Introduction

Attempts to predict functional properties of molecules and establish structure–property relationships via computer modeling and simulation are currently intense activities in the materials-oriented industries and the scientific community. Methodologies for computer modeling of polymer conformations and calculation of properties such as the crystalline state structure, solution configuration, etc. are well established.[1,2] Recently, from the conformational analysis of poly(methylphenylsilane) it was possible to interpret the localized hole transport behavior, as well as the molecular weight dependence of absorption maxima in the UV spectra, from a stereochemical point of view.[3]

In a recent paper,[4] a comparison of the conformational features of polycarbonates with different types of substituents at the C_α atom was presented, in terms of the rotations Φ and Ψ (see Figure 1) of contiguous phenyl groups. The small value of the characteristic ratio $\langle r^2\rangle_0/nl^2$ and its temperature coefficient were rationalized as due to the equal energy of the conformers which lead to flat-helical and extended-helical shapes. Cyclic polycarbonates were also found to be stereochemically possible. In addition, the conformational map showed features that could account for the phenyl motion that has been detected by NMR studies.

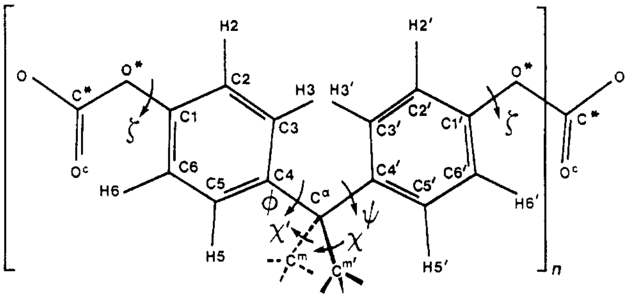

Figure 1. Schematic representation of the bisphenol A polycarbonate chain, with relevant torsional angles marked.

One of the properties of polymers that is of importance is the glass transition temperature. It has long been recognized[5] that the local conformational flexibility of the chain would influence the T_g although it would not be the only determining factor. Others such as intermolecular interactions and their resultant effect on the cooperative motion of the chain segments would also contribute to the glass transition. Of course, the conformational flexibility would have an influence on the segment mobility at the local level. Tonelli[6] examined the effect of sequence distribution on the T_g for a variety of copolymers, by calculating the conformational entropy of the diad sequence and using the rotational isomeric state scheme. There have been a few recent attempts in the literature to correlate the local conformational characteristics of polymers with their glass transition temperatures.[7-9] Since in a previous paper[4] we compared the relative flexibilities of a homologous series of polycarbonates, an effort has been made here to relate the conformational flexibility of this series of polycarbonates, with different types of substituents at the C_α atom, to their glass transition temperatures. Calculations were performed for polycarbonates with the following substituents: (i) CH_3, CH_3 (2,2-diphenylpropane); (ii) H,H (diphenylmethane); (iii) H, CH_3 (1,1-diphenylethane); (iv) H, C_6H_5 (triphenylmethane); (v) CH_3, C_6H_5 (1,1,1-triphenylethane); (vi) C_6H_5, C_6H_5 (tetraphenylmethane); (vii) cyclohexyl (1,1-diphenylcyclohexane); (viii) CCl_2 (1,1-dichloro-2,2-diphenylethylene).

Calculation of Conformational Entropy

The relationship between T_g and the conformational features of the chain is explored on the basis that the T_g is related to the conformational entropy, S. Within this framework, the calculation of the conformational entropy includes only the interactions that depend on the torsional variables such as Φ, Ψ, and χ shown in Figure 1. The value of the torsion angle ζ was kept constant[4] since the substituent at the C_α atom is not expected to have an influence on this angle due to the large distance of separation. Deformation of bond angles at the C_α atom is a distinct possibility but this is ignored here. The defor-

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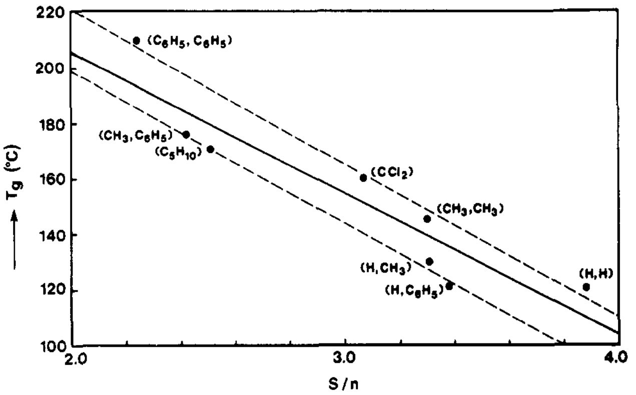

Figure 2. Plot of the calculated conformational entropy S/n (cal·mol^{-1}·deg^{-1}) versus the experimental T_g values for the polycarbonates with different substituents at the C_α atom.

mation of bond lengths can be neglected without affecting the results due to the large energy involved in such a process.

The conformational entropy was calculated by evaluating the energy of the conformations generated by varying the torsional angles Φ, Ψ, and χ (and χ') over the entire range of 0 to 340° at intervals of 20°. Although the rotation of the methyl group is 3-fold symmetric and that of the phenyl substituents is 2-fold symmetric, the χ's in all the cases were varied from 0 to 340°, in order to allow the same number of states for the substituents in this comparative study. For the (CH_3, CH_3) substitution, for example, this requires 104 976 conformations. If an interval of 10° is chosen, the total number of states would be 1 679 616. Previous studies of this type used an interval of 30° for the rotations and found it to be satisfactory.[6] The details of the geometrical and potential energy parameters have been given before.[4,10]

The conformational entropy is given by

$$S = -R\sum_i P_i \ln P_i \tag{1}$$

where

$$P_i = \exp(-E_i/RT)/Z \tag{2}$$

The subscript i refers to each of the states, E_i is the corresponding energy, and the partition function Z is given by

$$Z = \sum_i \exp(-E_i/RT) \tag{3}$$

Since the series of polycarbonates compared here have one, two, or no side-group rotations, the relationship between T_g and the normalized conformational entropy S/n is examined in this paper. Here n is the total number of backbone and side-group rotations. For the (CH_3, CH_3) substitution, $n = 4$. In the case of the cyclohexyl substitution, since the two chair forms of the side group were taken into account, $n = 3$ was used. A value of 300 K was assigned for T. Since we are concerned here with the effect of the relative flexibilities of a homologous series of polymers on the T_g, the same temperature was used for all cases to calculate the entropy. Other authors have followed the same approach.[7,8,11] Tonelli's calculations[6] employed the actual T_g of the homopolymer chains since his work was aimed at examining the change in the T_g with copolymer sequence distribution of a given pair of monomers.

Conformational Entropy and Glass Transition Temperature

Figure 2 shows a plot of the calculated conformational entropy S/n versus the T_g values taken from the literature[12-15] for these polycarbonates. It is seen that the T_g depends inversely on S/n. A linear regression analysis showed that the relationship between S/n and T_g for the homologous series of polycarbonates can be expressed as

$$T_g = -51.1(S/n) + 308.4 \tag{4}$$

where T_g is expressed in degree Celsius. The correlation coefficient is 0.93. The solid line in Figure 2 corresponds in eq 4.

Although the partition function for the (CH_3, CH_3) substitution was significantly larger than that for the (H, H) substitution,[4] the conformational entropy per bond rotation is higher for the latter. Similarly, the values of Z for (H, C_6H_5) and (C_6H_5, C_6H_5) substitutions are similar, but the S/n and T_g differ substantially for these two cases. Thus, the partition function itself does not provide a relative measure to rationalize the differences in the T_g's of two polymers. Figure 2 also shows that monosubstitution with a methyl or phenyl group does not affect the T_g significantly. However, disubstitution with a phenyl group reduces the value of S/n and increases the T_g substantially, as a comparison of the (CH_3, C_6H_5) and (C_6H_5, C_6H_5) substitutions would show: the T_g of the latter is 34 deg higher. Between the (H, CH_3) and (CH_3, CH_3) substitutions, the difference in the T_g is about 15 deg. On the other hand, between (H, C_6H_5) and (CH_3, C_6H_5) substitutions, the difference is 55 deg; the (H, CH_3) and (CH_3, C_6H_5) substitutions differ in T_g by 46 deg.

It is seen from Figure 2 that the set of points corresponding to the polycarbonates with symmetric substitution (e.g., CH_3, CH_3) fall above the solid line and those with asymmetric substitution below. Although the number of polymers included is limited, a regression analysis using only the symmetrically substituted polycarbonates yields a correlation coefficient of 0.996, with

$$T_g = -55.6(S/n) + 332.5 \tag{5}$$

The upper dashed line in Figure 2 corresponds to eq 5. Likewise, the correlation coefficient with only the polycarbonates with asymmetric substitution is 0.997, with

$$T_g = -54.8(S/n) + 308.6 \tag{6}$$

The lower dashed line in Figure 2 corresponds to eq 6. Although the cyclohexyl substituent is chemically symmetric, when appended to the C_α atom, it is geometrically asymmetric with respect to the contiguous phenyl groups, as discussed previously.[4] This leads to the tentative conclusion that symmetric substitution affects the T_g differently than asymmetric substitution.

Rationalizing the above difference between symmetric and asymmetric substitutions is difficult at this time, given the limited number of examples treated here. Asymmetric substitution leads to lowering of the T_g when one compares the (CH_3, C_6H_5) and (C_6H_5, C_6H_5) cases or the (H, CH_3) and (CH_3, CH_3) side groups. Asymmetric chains are also subject to tacticity considerations, as discussed previously[16] with respect to poly(α-methylbenzyl). To our knowledge, there is no record of investigations of the effect of tacticity in the case of asymmetrically substituted polycarbonates. The intermolecular (chain packing) interactions at the local segmental level can be expected to be different for the symmetrically and asymmetrically substituted chains, and this can influence the T_g. Whether the pattern seen in Figure 2 is real or fortuitious needs further investigation.

Hopfinger et al.[7,8] recently published relationships between the T_g and the conformational entropy. Rather than dealing with the actual polymer segment as in the present calculations, these authors calculated the conformational entropy of fragments of molecules and used the group additivity concept to predict the T_g. In addition, they used the mass moments of the side group atoms in a multiple regression analysis, although the contribution from this factor was found to be small. This is neglected in the present calculations.

Conclusions

The correlation derived here is based on the calculations for a homologous series of polycarbonates, with different substituents at the C_α atom. While the group additivity method of Hopfinger et al.[7,8] can be used generally for any polymer for which the appropriate contribution factors are known, the method of calculating the conformational entropy for the actual polymer segment, as adopted here, is useful for comparing a homologous series. Since all that is required is the energies of all the possible states of the segment, this method can be conveniently coupled with the usual conformational analysis of a related series of polymers. The different set of relationships between S/n and T_g for the symmetric and asymmetric substituents indicated in the present calculations is also worthy of further investigation.

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Study of the Relative Molecular Mobilities of Bisphenol A and Cyclohexyl Polycarbonates by CP/MAS NMR Spectroscopy

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Introduction

A comparison of the conformational features of polycarbonates with different types of substituents at the C_α atom was published recently.[1] In terms of the molecular motion of the phenyl group, the conformational analysis showed that the nature of the substituent dictates whether the phenyl groups execute π-flips or large scale local oscillations. In addition, the steric map of the Bisphenol A polycarbonate (BPAPC) could account for the model derived from NMR studies[2] that involves both π-flip and small-amplitude motions of the phenyl groups and supported the concept of synchronous rotation of contiguous phenyl groups. The calculations[1] for cyclohexyl polycarbonate showed that the steric freedom in this case is less than that of BPAPC.

Polycarbonate is perhaps the most extensively studied polymer with regard to molecular motion,[3] using NMR and dynamical mechanical spectroscopy (DMS). In addition to BPAPC, Jones et al.[4] analyzed the molecular motion in chloral polycarbonate and concluded that the molecular motion in this case is restricted compared to that in BPAPC. Yee and Smith[5] compared polycarbonates with different types of substituents, using DMS.

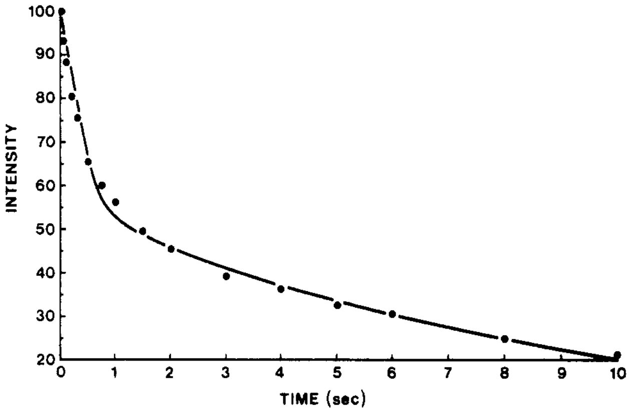

Figure 1. Intensity of the ortho carbon resonance as a function of time during ^{13}C relaxation of BPAPC at 0 °C.

In this paper, a comparison of the results of the ^{13}C spin–lattice relaxation measurements performed on BPAPC and the cyclohexyl polycarbonate is presented. The use of ^{13}C spin–lattice relaxation measurements to probe molecular dynamics is attractive since the NMR measurements can be carried out without specific isotopic enrichment, allowing application to any polycarbonate.

Experimental Section

A sample of BPAPC with M_w = 100 000 and two samples of cyclohexyl polycarbonate with M_w = 16 000 and 77 000 were

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