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Notes

An Experimental Determination of the Local Chain Conformation of Bisphenol A Polycarbonate

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Calculations by various groups[1-8] have indicated that the internal barrier for synchronous rotation of the aromatic rings with the methyl groups of Bisphenol A polycarbonate is only a few kilocalories per mole. Likewise the inherent barrier to ring rotation imposed by the carbonate group appears to be small.[9-11] Nevertheless, the experimental barrier to rotation of the aromatic rings is almost 10 kcal/mol.[12] Intermolecular interactions clearly raise the barrier to ring rotation from that expected from intramolecular forces alone.

How important are intermolecular forces in determining the local ground-state conformation of the polycarbonate chain? In a completely randomly packed amorphous polymer with dominance of the ground-state conformation by intermolecular forces we would expect a wide distribution of conformations. The presence of a single conformation would indicate either that intramolecular forces control the ground-state conformation or that local packing is nonrandom. We present here evidence that there is indeed a single preferred conformation for the polycarbonate chain.

Figure 1 shows ^{13}C NMR spectra of Lexan 145 polymer taken with magic angle spinning. At room temperature there is a single signal for the proton-bearing 4 and 4′ aromatic carbons, but at 105 K there are two partially resolved signals.[13] The 3 and 3′ carbons give a single NMR resonance, as do the methyl groups.

The low-temperature spectrum of Bisphenol A polycarbonate is comparable to the room-temperature spectrum of largely amorphous poly(phenylene oxide), for which there also are two signals for the proton-bearing aromatic carbons.[14] Adjacent aromatic rings in poly(phenylene oxide) are oriented roughly perpendicular to each other. This feature, when combined with slow rotation of the aromatic rings, leads to nonequivalent environments for the proton-bearing aromatic carbons. A similar explanation accounts for the low-temperature spectrum of Bisphenol A polycarbonate. The 4 and 4′ carbons have nonequivalent local environments, and at low temperature, where the aromatic rings in the polycarbonate are static on the NMR time scale, there are two resolved NMR signals. At room temperature rapid ring flipping[15-17] averages the two signals of the 4 and 4′ carbons into a single resonance.

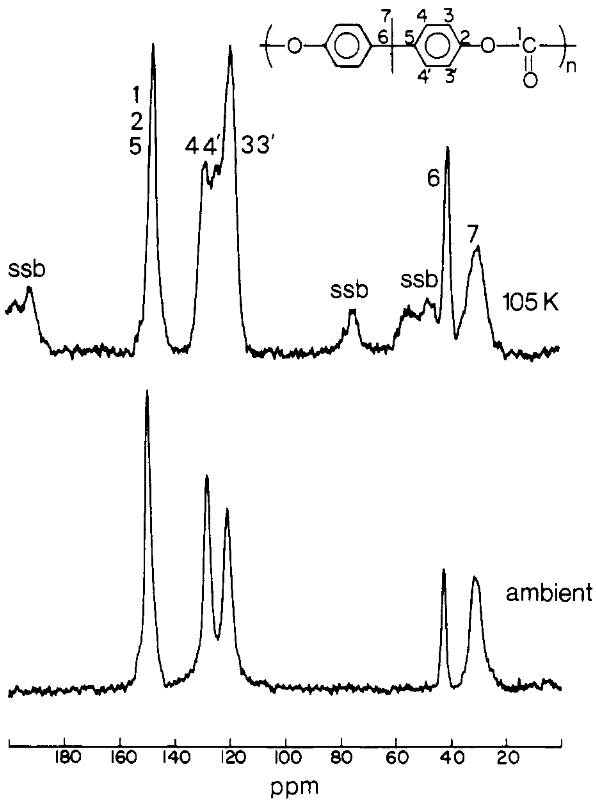

Figure 1. ^{13}C NMR spectra taken with magic angle spinning and the cross-polarization technique of Lexan 145 polymer in a probe from Doty Scientific, Inc., operating at a ^{13}C observation frequency of 25.1 MHz in a Bruker CXP-100 spectrometer. The 90° proton pulse duration was 3.8 μs. The spinning speed at room temperatures was 3116 Hz. At low temperature the spinning rate varied between 1780 and 1832 Hz. The ambient probe temperature was uncontrolled. The low temperature is the nominal value at the controller. Checks of the temperature of a thermocouple inserted in a dummy spinner at various temperatures below 200 K showed that the actual probe temperature was 5–10 K higher than the nominal temperature. The polymer showed no signs of crystallinity when observed by differential scanning calorimetry.

Recently reported crystal structures of the bis(phenyl carbonate) of Bisphenol A[7,18] suggest a favored local conformation for Bisphenol A polycarbonate that is consistent with the NMR results. In both of the known crystal modifications of the model compound the aromatic rings are twisted with respect to the isopropylidene group so that the 4 and 4′ carbons interact differently with the methyls and the adjacent aromatic ring.[19] In the absence of rapid 180° flipping of the aromatic rings, the 4 and 4′ carbons should give rise to chemically shifted NMR signals.

Although a particular methyl group is closer to the 4′ aromatic carbon than to the 4 carbon in one of the adjacent aromatic rings, it is closer to the 4 carbon than to the 4′ carbon in the other ring. Thus each methyl group is in a similar chemical environment, and there should be a single NMR signal for both carbons. In one of the crystal structures of the model compound there is an actual

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2-fold axis of symmetry between the methyl groups that makes them rigorously equivalent.[18]

In principle, if the 4 and 4′ carbons are nonequivalent, the 3 and 3′ carbons should also be nonequivalent. In practice the distance of the 3 and 3′ carbons from the methyl groups and the adjacent aromatic rings means that they are relatively insensitive to the effect of these groups. In the model compound the planar carbonate group is oriented close to the perpendicular with respect to the aromatic rings. Thus it affects the environment of the 3 and 3′ carbons equally. The absence of splitting for the 3 and 3′ carbons in the spectrum of the polymer is an indication that the carbonate group in the polymer is oriented well out of the plane of the adjacent ring in the polymer, as it is in the model compound.

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(19) Ideally, one would like to observe that the 4 and 4′ carbons of the model compound give NMR signals separated to about the same degree as the signals in the polymer. Unfortunately, the presence of the aromatic rings on the ends of the model compound leads to a very complicated NMR spectrum in the aromatic region. The signals from the 4 and 4′ carbons have not yet been identified.

Communications to the Editor

Slowing Down of Polymer Diffusion near a Wall

The theory of polymers confined to narrow slits and pores has been considered by several authors, and it appears that both the static and the dynamic aspects of the phenomena are well understood.[1–3] Attempts have been made to apply the predictions of the scaling theory to experiments on polymer diffusion through porous media.[4]

The situation is very different when one considers the behavior of polymers in solution near a single repulsive (i.e., impenetrable, nonadsorbing) wall. While the static aspects of the theory have been worked out (for semidilute solutions) and self-similar polymer density profiles have been predicted,[5,6] to the best of our knowledge, the problem of polymer diffusion near an interface has not been previously considered, presumably because there were no experimental techniques that could be used for studying wall depletion layers in dilute polymer solutions. The situation has changed now with the introduction of evanescent wave methods[7,8] that can detect variations of polymer density profiles on scales smaller than polymer dimensions. These techniques have been recently applied to the study of flow effects on wall depletion,[9] a question that has been also studied theoretically by the present author.[10] Slowing down of polymer diffusion near a wall was observed by forced Rayleigh scattering in the evanescent wave mode.[11] In this paper, we study the problem of polymer diffusion in solution, near a repulsive wall.

Consider a polymer of N monomers of size a such that away from the interface its bulk radius of gyration is $R_B \simeq aN^{\nu}$ where ν is the Flory exponent.[3] The bulk diffusion coefficient is given by

$$D_B \simeq k_B T / \eta_s R_B \tag{1}$$

where k_B is the Boltzmann constant, T is the temperature, and η_s the solvent viscosity (numerical factors are suppressed in our notation). This expression takes into account hydrodynamic interactions between the monomers, due to which the polymer diffuses as a nondraining sphere of radius R_B. Now, let us assume that the polymer is placed in solution at a distance z from a wall. As long as this distance is much larger than polymer dimensions, the polymer diffusion coefficient remains unaffected by the presence of a wall. When R_B/z becomes of the order of, but larger than, unity, the polymer mobility is affected by the presence of the wall, an effect that has been studied in the context of hydrodynamics of rigid bodies.[12] In the latter case, the friction coefficient diverges when the distance from the wall approaches the dimensions of the rigid object, and thus the mobility in the plane parallel to the wall vanishes. No such singular behavior is expected for the flexible polymer.

The z-dependence of the polymer diffusion coefficient describing its two-dimensional mobility in the plane $z =$ constant can be obtained by the following scaling argu-

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