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Molecular Level Model for Motion and Relaxation in Glassy Polycarbonate

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ABSTRACT: A local chain motion is proposed for the low-temperature loss peak in glassy polycarbonate: namely, a correlated conformational interchange between two neighboring carbonate units. One carbonate unit starts with a trans–trans conformation and the other with a cis–trans conformation. The interchange is produced by a rotation about one of the CO bonds in each of the carbonate units. The cis–trans conformation diffuses down the chain composed of largely trans–trans units by the repeated action of this process. The phenylene group attached to the other side of the carbonate unit from the rotating CO bond undergoes a π flip as rotation about the CO bond occurs though intermolecular couplings in the bulk polymer may also link the π flips to the interchange. This motion is consistent with existing solid-state proton, carbon, and deuterium line shape data on the phenylene group. It also agrees with the presence of a substantial dielectric and dynamical mechanical loss peak linked in time to the occurrence of π flips. This motion produces a volume fluctuation by translation of the bisphenol A unit between the rearranging carbonate units; and this volume fluctuation can diffuse down the polymer chain as the cis–trans conformation diffuses. Diffusion of a change in backbone shape and a volume fluctuation down the polymer chain is a process which could initiate the rapid reduction of a macroscopic strain.

The local chain dynamics of glassy polycarbonate has intrigued many investigators over the past 25 years. Traditional experiments probing dielectric relaxation[1–8] and dynamic mechanical relaxation[6–13] below the glass transition indicated large-scale motion with very broad loss peaks at low temperatures (the γ relaxation). These experiments were not suitable for defining the specific geometry of the motions in polycarbonate (Figure 1) though certain implications from studies of a variety of structural analogues[7,8,13] did provide useful information in developing proposals for motions. Wide-line NMR studies[14,15] also observe relaxation effects below the glass transition; but the lack of structural specificity produced only general conclusions comparable to the dielectric and dynamic mechanical work.

Recently, more sophisticated solid-state NMR line shape studies have provided some very detailed geometric information. The first definitive line shape result[16] was obtained on a structural analogue of BPA polycarbonate which contained only phenylene protons (Figure 2). The proton spectrum showed the undiminished persistence of a dipolar splitting between adjacent phenylene protons up to the glass transition. This implied that the virtual bond corresponding to the phenylene group could not be reorientating in space. It did allow for either translation of the phenylene group or reorientation of the phenylene group about the C_1C_4 axis. This conclusion was later confirmed for the polycarbonate in Figure 1 through observations on a partially deuterated form.[17]

Subsequent attention centered on the phenylene group

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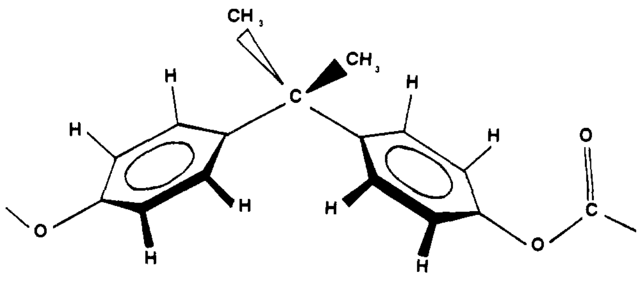

Figure 1. BPA polycarbonate repeat unit.

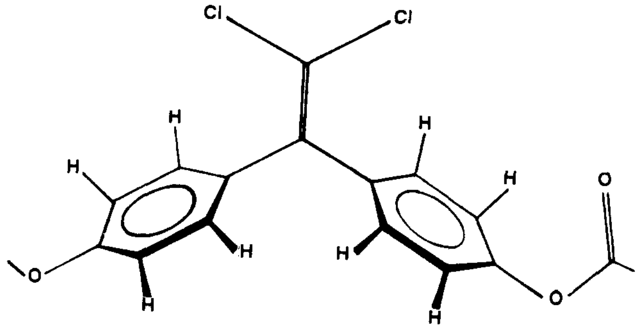

Figure 2. Chloral polycarbonate repeat unit: an analogue of BPA polycarbonate.

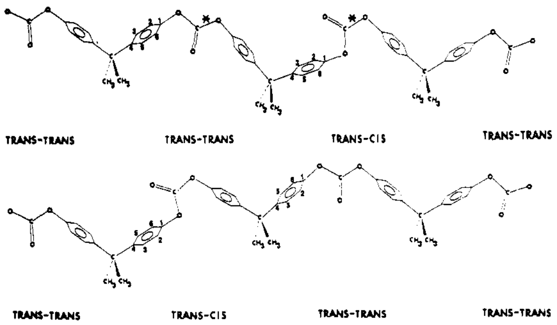

Figure 3. BPA polycarbonate chains. The carbonate CO bonds with asterisks indicate points of bond rotation. The phenylene rings undergoing flips in association with the CO bond rotations are numbered. The correlated conformational change from the top chain to the lower chain involves two neighboring carbonate groups and is produced by the CO rotations which interchange the trans–trans and trans–cis conformations. Note that the choice of a trans–cis unit in the figure is arbitrary. If a cis–trans unit were used, the other phenylene rings would be flipped so over a period of time all rings could be flipped as the cis–trans and trans–cis conformations diffuse along the chain. Conventional bond angles of 109° are used for all backbone bonds except the carbonate bonds, which are set at 120°. These choices lead to an 11° change in the C_1C_4 axis of the phenylene groups in the BPA unit between the carbonate units undergoing conformational change. If the bond angles suggested by Flory and Williams[33] are employed, the C_1C_4 reorientation of the phenylene group is less than 11°.

and three solid-state NMR experiments were performed to further determine the geometry of motion. The first report came from deuterium NMR[18] which concluded that the phenylene group was undergoing π flips. Because the deuterium quadrupolar interaction is axially symmetric, some room for doubt remained. However, a carbon-13 carbon shift anisotropy study confirmed the π flip conclusion while eliminating other possibilities;[17] and a carbon-13 rotational dipolar study also came to the π flip conclusion.[19]

A carbon-13 chemical shift anisotropy line shape study has also been made on the carbonate carbon.[20] However, the line shape changed little with temperature and the spatial orientation of the principal axes of the shielding tensor are not well-known for this group. The large dielectric loss can only be associated with motion of the carbonate group so it is quite unusual that the anisotropy study does not reflect the motion.

Both deuterium and carbon-13 dipolar line shape data are also available for the methyl groups.[18,19] The spectra indicate methyl group rotation and possibly some small amount of backbone oscillation but no other major reorientation.

Relaxation maps have been prepared showing that proton spin relaxation, NMR line shape collapse, dielectric loss, and dynamic mechanical loss are all at least phenomenologically related in time.[21,22] Since the only clearly defined motion is π flips, legitimate questions have been raised as to how exchange of a symmetric group between two equivalent minima could produce a large mechanical loss. Also motion of the phenylene group will not account for dielectric relaxation.

It is the purpose of this report to propose a model which can draw the various relaxation studies to a common picture. The picture or model is qualitative though quantitatively consistent with geometric data from NMR line shape studies and leads to a mechanism for both a sizable dielectric and mechanical loss.

Model

The model is relatively simple and is displayed in Figure 3. The polycarbonate chain in the glass is composed of largely trans–trans units with respect to the carbonate group with an occasional cis–trans or trans–cis unit. The fundamental motion is the exchange of a cis–trans (*or trans–cis*) conformation of the carbonate with a trans–trans conformation of a neighboring carbonate. This exchange is produced by rotation about one of the CO bonds in each of two carbonate groups. As rotation about the CO carbonate group occurs, the phenylene group attached to the other side of the same carbonate group flips about its C_1C_4 axis. The C_1C_4 axis and the CO carbonate bond direction on the other side of the carbonate group are nearly though not exactly parallel. Intermolecular coupling in the bulk polymer as well as intramolecular coupling could link the π flips to the conformational interchange.

The exchange of the cis–trans (*or trans–cis*) and trans–trans conformations is similar to the correlated conformational changes seen by Helfand[23–26] in computer simulations of polyethylene chains. In the glassy solid the exchange of the conformations is likely to be more nearly correlated relative to dilute solution reflecting stronger intermolecular interactions. This would lead to barrier heights from 1 to 2 times the CO bond rotation energy depending on the degree of correlation, though in the computer simulations of polyethylene, the barrier heights were found to be near one bond rotation energy. This CO bond is found to have a low barrier,[21,27,28] about 10 kJ, according to several theoretical calculations.[21,28] The whole potential surface for polycarbonates for bond rotation consists of similarly low barriers[27] so compensating small distortions could aid the proposed conformational change; and, in addition, the high degree of motion in polycarbonate glass provides a more liquidlike environment for a conformational change relative to most glassy polymers.

The virtue of the proposed correlated conformational change is that the chain ends do not have to translate. In this particular example in the polycarbonates, the bisphenol A (BPA) unit of the polymer is not significantly reoriented except for a flip of a phenylene group about the C_1C_4 axis. The one BPA unit between the two carbonates which interchange conformation is translated and slightly reoriented. This translation of a BPA unit can diffuse along the chain as the cis–trans or trans–cis unit migrates down the backbone; and this migration is typical of a diffusional motion along the backbone of the chain.

Note that there is only one type of motion in the sense that a cis–trans interchange with a trans–trans must be energetically equivalent with a trans–cis interchange with a trans–trans. However, the intramolecular coupling of one of these symmetry-related motions is proposed to affect only one of the phenylene groups in a BPA unit. The other phenylene ring in a BPA unit is coupled to the other interchange. Referring to Figure 3, a trans–cis to trans–trans interchange flips rings on the right side of BPA units while a cis–trans to trans–trans the left side of BPA units.

The motion proposed is a segmental motion but is limited in nature. The BPA units are not significantly though slightly reoriented in space and would not be reoriented in the model until the glass transition is reached. The carbonate unit is reorienting but not isotropically and again isotropic rotational reorientation does not take place until the glass transition is reached. Single, uncorrelated backbone rotations producing conformational changes are the type of motion which would produce isotropic averaging and would be anticipated at the glass transition temperature, T_g.

In time, the proposed motion is complex. If bond directions of an individual carbonate unit are followed in an isolated chain, they would have a correlation function similar to that proposed by Helfand for correlated motion, the Bessel function of order zero. However, a compensating reorientation of a nearby carbonate unit occurs soon after the first reorientation. Thus, the correlation function for dielectric loss under these circumstances would be more complex than the bond direction correlation function. An assumption of the model proposed here is that the lifetimes of the states before and after the correlated motion composed of two rotations about CO bonds are long compared to the times between the two rotations. All of these motions are discussed in terms of isolated chains but the nature of the glass also strongly influences the correlation function.

Relationships of the Model to Relaxation Data

The model can be compared to NMR data first since these results place the greatest restrictions on proposed motions. To begin with, the model is consistent with the preservation of the proton dipolar Pake doublet.[16] The phenylene group undergoes flips about the C_1C_4 axis and translation but only about a 10° or less reorientation of the C_1C_4 axis corresponding to the virtual backbone bond. It is important that the CO rotation axis is nearly parallel to the C_1C_4 axis for there to be little C_1C_4 axis reorientation.[21]

The model includes π flips as a motion coupled to the isomerization of the carbonate unit. This coupling could be both intramolecular and intermolecular in origin. The π flips would appear to be geometrically simple but in frequency the motion would appear complex since it is coupled to a segmental type of motion which diffuses along the chain. Thus, the geometric restrictions determined by proton, deuterium, carbon-13 CSA, and carbon-13 dipolar line shapes and the broad T_1 and $T_{1\rho}$ relaxation minima[21] are consistent with the proposed motion.

The most severe test of the model could have come from the carbon-13 anisotropy line shapes of the carbonate itself.[20] Unfortunately the spectra are not decisive in either supporting or rejecting the model. As mentioned, the line shape is not strongly temperature dependent and the principal shielding axes are not well located. A further complication arises from the fact that the model proposes an interchange from a *cis*–trans (*or trans–cis*) to a trans–trans conformation which would imply that the observed line shape would actually be composed of two superimposed though probably similar shielding tensor line shapes. Since the trans–trans conformation is assumed to predominate, the carbonate CSA tensor would largely reflect this fact and may not change drastically with temperature. Further examination of the carbonate CSA line shape might be fruitful but would involve locating the principal axes for both the trans–trans and cis–trans conformations.

Dilute-solution NMR relaxation data also show an apparent coupling or cooperativity between phenylene group rotation and segmental motion.[29] The solution data also indicate a preference for correlated segmental motions over a rotation about a single backbone bond[29] though both processes occur.

Dielectric loss would be substantial according to the model and linked to NMR data as is observed. The magnitude of the loss should be large since it involves both a partial reorientation of the carbonate group and a change from trans–trans to cis–trans (*or trans–cis*) conformation which could well have different dipole moments. On the other hand, the overall motion is an interchange of dipole moments associated with the carbonate units. If the interchange were simultaneous, only a small loss would appear likely since the carbonates and the BPA units are only slightly reoriented. Many repeat units could be reoriented a small amount as the cis–trans conformation diffuses along the chain which could lead to a larger loss. However, the computer simulations in polyethylene originally leading to the proposal of correlated segmental motions show such processes to be close in time but not simultaneous. The correlation function for dielectric loss and the magnitude of the dielectric loss under these circumstances is not known by the author, though further consideration of this aspect might be fruitful.

The dynamic mechanical loss would also be significant since a segmental motion involving two different conformations with different populations is involved. The carbonate unit changes shape, which should lead to a shear loss, and the BPA unit is translated, which should lead to a volume fluctuation and bulk loss. The arguments for a complex correlation function and an indeterminate loss amplitude made for dielectric relaxation on the basis of the nature of correlated motion would also appear to apply to the mechanical problem as well. However, both a shear and bulk loss are reported[31] and they occur at approximately the same frequency. The amplitude of the bulk loss is larger than the shear loss, which is physically reasonable since the small carbonate unit changes shape and the large BPA unit is moved so as to occupy a new volume. Volume fluctuations or relative motions of neighboring chains have been proposed before[16,32] but no repeat unit level mechanism was suggested.

The amplitude of the bulk loss is reduced by cross-linking.[30] Volume fluctuations can be diffused along the chain by the cis–trans (*or trans–cis*), trans–trans interchange in the un-cross-linked polymer but such volume fluctuation diffusion would be impeded by cross-links leading to the diminished bulk loss in these systems.

In quenched polycarbonate samples, a low-temperature shoulder (β relaxation) to the glass transition peak can be observed in the dynamic mechanical spectrum.[13] Larger volume defects may exist at some places in a quenched sample; and, with the proposed model, a localized strain could be diffused down the chain to the large volume defect. At this defect, segmental motions comparable to those of the glass transition could take place to relieve the

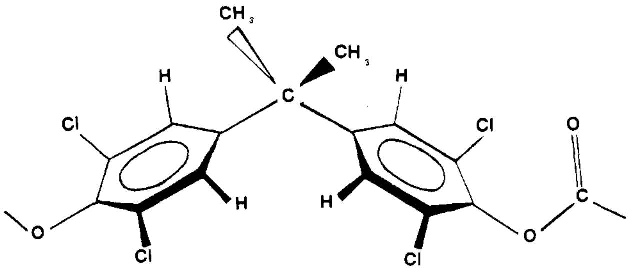

Figure 4. Substituted polycarbonate repeat unit.

strain. In this context, the glass transition motion could be thought of as a rotation about a single backbone bond with no subsequent compensating correlated motion. In this manner, new directions of backbone bonds are produced, yielding the nearly isotropic spatial averaging observed at the glass transition. In an annealed sample, the diffusion process still takes place but the larger volume defects do not exist and the glass transition type segmental motions will not occur. The shoulder thus disappears in agreement with observation.[13]

The effect of structural modification on the dynamic mechanical spectrum also points to the key role of the CO bond in the carbonate unit. Substitution of the bridge group of the BPA unit has little effect on the low-temperature loss peak.[13] Substitution on the phenylene group at positions ortho to the carbonate shift the loss peak to higher temperature. For instance, the loss peak of the polycarbonate shown in Figure 4 occurs 200 °C above the loss in BPA polycarbonate.[13] These ortho substitutions greatly increase steric interactions in the vicinity of the carbonate group and would tend to block rotation both about the CO carbonate bond and about the C_1C_4 axis of the phenylene group. Thus, the proposed motion is consistent with a large effect produced by phenylene group substitution ortho to the polycarbonate and lesser effect from substitution of the quaternary carbon at the BPA bridgehead. Another structural modification, replacement of the carbonate by a formal group, leads to a similar dynamic mechanical spectrum[13] because the crucial CO bonds are present in both the carbonate and formal group though the geometry changes from about 120° to about 109° bond angles.

Lastly, the subject of impact resistance is considered. The polycarbonate of BPA shows good impact resistance over a wide range of temperatures.[31] The diffusion of a conformation involving chain translation and an associated volume defect along the chain provides a mechanism at a molecular level which could lead to the rapid dissipation of a macroscopic strain. The diffusion along the chain to a large volume defect to relieve strain is also a promising proposal to reduce larger strains and would lead to the loss of good impact resistance in annealed samples again in agreement with observation.

Conclusion

Polycarbonate is a special system with generally low conformational barriers to rotation. The geometry of the carbonate unit allows for a process in which the large component of the repeat unit, BPA, is not appreciably reoriented while the small carbonate unit is reoriented. This is a partial segmental reorientation short of the isotropic segmental motion associated with glass transition. The model proposed here is quantitatively consistent with the geometric requirements of the NMR data. It is qualitatively consistent with the presence of significant dielectric and dynamic mechanical loss. It is also qualitatively consistent with broad loss peaks or relaxation minima since it is associated with a relatively complex motion: diffusion of a conformation along the chain backbone in a glassy solid. It couples the π flips to this more complex conformational change in agreement with relaxation maps[21] though the flips are not the key motion contributing to the mechanical and dielectric properties. The model involves a process which could lead to long-range dissipation of strain though it starts with a specific local chain motion.

The data in hand do not absolutely lead to the motional model proposed here though they are consistent with it. The leading alternative motional model would be oscillation of the BPA unit and the carbonate unit. Certainly such oscillation exists. The *phenylene* group data display this motion in addition to flips and Henrichs[20] favors oscillation as the best explanation of the carbonate CSA data. However, it is hard for this author to see how an oscillation of the order of ±20° at room temperature can lead to the large mechanical and dielectric losses observed in BPA polycarbonate. A jump between two different states with unequal populations separated by a barrier seems a more plausible mechanism for large losses.

The role of intermolecular couplings vs. intramolecular coupling in the proposed motion is not entirely clear. Certain motions can be argued to be unlikely on the basis of intermolecular interactions. For instance, rotation of the two rings and bridgehead as a unit about the oxygen–oxygen axis is unlikely because it would sweep out a large volume, thus involving significant intermolecular interactions in the bulk. The motion proposed here reorients only the small carbonate group as opposed to the whole BPA unit. The phenylene group motion of π *flips involves no net reorientation and requires a much smaller fluctuation in the surroundings. The BPA unit is translated as a whole in the proposed motion which corresponds to a very specific motion which may lead to experimentally testable consequences. The separation of the relative role of intramolecular and intermolecular interactions in the coupling of* π *flips to the cis–trans (or trans–cis) to trans–trans interchange is unresolved. The* π *flips are proposed to be coupled by both factors but the relative importance is not easily assessed.* In any case, it is hoped that the act of proposing this model will lead to new quantitative tests which can discriminate more decisively among possible models.

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Multiple Field Spin–Lattice Relaxation Study of Dissolved Poly[4,4′-bicyclo[2.2.1]heptan-2-ylidenebis(phenyl carbonate)]

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ABSTRACT: A dilute-solution spin–lattice relaxation time study was performed on a bisphenol polycarbonate similar to the polycarbonate of bisphenol A except the methyl groups of the bisphenol unit are replaced by a norbornyl ring. Carbon-13 relaxation times are measured at three Larmor frequencies: 22.6, 62.9, and 126 MHz. Motion of the norbornyl group is seen to be isotropic, which implies segmental motion is isotropic since the group is rigidly incorporated into the backbone. Relaxation caused by this segmental motion is interpreted in terms of the Hall–Helfand correlation function. The apparent activation energies for cooperative and individual bond transitions are 24 and 30 kJ/mol, respectively, while the corresponding Arrhenius prefactors are 6×10^{-14} and 17×10^{-14} s, respectively. The phenyl groups undergo this same segmental motion plus restricted rotation about the C_1C_4 axis but not full anisotropic rotation. Since full anisotropic rotation is observed in bisphenol A polycarbonate, the larger norbornyl group would appear to sterically hinder phenylene group rotation. In the bulk polymer a low-temperature dynamic mechanical loss peak comparable to that of bisphenol A polycarbonate has been observed for the norbornyl-substituted polymer. This implies phenylene group rotation is not the primary element contributing to dynamic mechanical loss. An alternative motion based on correlated conformational interchange between carbonate groups is an explanation for the low-temperature loss peak, which is in better agreement with the findings of this study.

Introduction

A series of dilute-solution spin–lattice relaxation studies have been made on the polycarbonate of bisphenol A (BPA) and related structural analogues.[1-4] These studies have shown the presence of several rapid local motions in BPA including cooperative segmental transitions, phenylene group rotations, and methyl group rotations. The addition of substituents to the phenylene ring of BPA significantly slows phenylene group rotation and, to a lesser extent, slows segmental motion. The BPA analogue of interest in this report is abbreviated NBPC and is shown in Figure 1 relative to BPA.

This repeat unit is selected because the large norbornyl ring should alter the local motions and yet the low-temperature dynamic mechanical loss peak remains similar to that of BPA.[5] An association between phenylene group motion in solution and the γ or low-temperature loss peak has been noted before.[2] Solution spin–lattice relaxation measurements are capable of determining the motion of the phenylene group and the associated apparent activation energies in a situation where these parameters are dominated by intramolecular interactions.

The NBPC has an added bonus as a subject of a dilute-solution study. The norbornyl ring is most likely rigid and rigidly attached to the backbone. If this is true, all carbons in the ring should only be undergoing segmental motion. However, nearly every carbon has a different direction for the carbon–proton dipolar vectors. This situation can provide a test for the isotropic character of segmental motion, in the sense that all carbon-13 T_1's should be equal despite the differences in orientation if the number of directly bonded protons and differences in bond length are considered.

Also a correlation function recently developed by Hall and Helfand[6] has been used to characterize segmental motion in dissolved polymers.[3,4,7] The NBPC data reported here provide an additional test of this function since three different carbon-13 Larmor frequencies were employed.

Experimental Section

High molecular weight NBPC was dissolved to 10 wt % in perdeuterio-1,1,2,2-tetrachloroethane, subjected to five freeze–pump–thaw cycles, and flame sealed. Three spectrometers were used: a Bruker WM250 and a Bruker SXP (20-90), both at Clark University, and a Bruker WM500 at Yale University. The pulse sequence was the standard $(\pi-\tau-\pi/2)$. A temperature calibration was carried out for each probe. For the SXP, a thermocouple was inserted in the probe, while for the WM500 and WM250 the chemical shift vs. temperature method was employed. The standard calibration samples were, for high-temperature, ethylene