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Effect of the Local Motions of Chemical Linkages on Segmental Mobility in Poly(ester carbonate) Block Copolymers

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ABSTRACT: A series of glassy bisphenol poly(ester carbonate) copolymers containing various linkage groups were synthesized, and the segmental motions were investigated by dynamic mechanical analysis (DMA). DMA results indicate that strong coupling exists between the motion of the cyclohexylene ring and those of neighboring segments, and the segmental mobility of the resulting polymers is thus enhanced. In contrast to the cyclohexylene ring conformational transition, the motions of terephthalate, bicyclo[2.2.1]heptane-1,4-dicarboxylate, and bicyclo[2.2.2]octane-1,4-dicarboxylate linkages are relatively independent of their environments, and therefore their incorporation does not cause much variation in polymer mobility. These results are consistent with those of a dipolar rotational spin-echo ^{13}C NMR study,[1] which show that the cyclohexylene dicarboxylate linkage is most likely to undergo the chair−boat−chair conformational transition, while the terephthalate, bicyclo[2.2.1]heptane-1,4-dicarboxylate, and bicyclo[2.2.2]octane-1,4-dicarboxylate linkages are mainly capable of rotational motions in these copolymers.

Introduction

It is generally accepted that mechanical properties of glassy polymers, such as yield and crazing, are closely related to molecular mobility.[2−4] Principally, molecular motions are the source of stress relaxations for glassy polymers. However, not all modes of molecular motions that polymers possess contribute equally to such relaxations. As suggested by previous work,[5,6] molecular motions involving large-scale cooperativity are most effective in relaxing the applied stress.

The effect of cooperative motions was clearly illustrated by Heijboer's impact study on polymers with side chain motions or main chain motions.[3] In this work, he found that main chain motions play a key role in impact strength, while side chain motions, which are very local, have little effect. It seems clear that the movement of an individual functional group is insufficient for relaxing the applied stress. Only when local motions from various chemical moieties correlate to each other in certain ways, e.g., through in-chain or interchain interactions, can the scale of this collective motion become extended and the influence magnified.

Although the importance of cooperative motions is now recognized,[5,6] our understanding of the relationship between chemical structures and cooperative motions is still limited. The reason for this lies essentially in the complexity of interactions between local motions in solid glasses. These interactions may involve chemical groups either in the same chain or in different chains. For instance, in bisphenol A polycarbonate (BPA-PC), where the interactions between chemical groups have been intensively investigated due to the polymer's well-known toughness, both in-chain and interchain cooperativity have been observed.[7−20] Different models,[21−23] emphasizing either in-chain or interchain interactions, have been postulated to explain the large-scale cooperativity in BPA-PC. On the basis of their calculation on energy barrier of phenylene ring π-flip motion in glassy BPA-PC, Whitney and Yaris[24] determined that BPA-PC chains must move apart in order to accommodate the π-flip motion. Goetz et al.[25] then provided an explicit molecular picture for the phenylene ring π-flip; that is, the flipping can be turned on and off, i.e., gated, by the chain dynamic motions. Although this picture needs further examination, it explicitly requires that the interchain and in-chain interactions be coupled in BPA-PC. This scenario gives a more complete description of motional cooperativity. On the other hand, it also indicates that the cooperative motions are very complicated, since both in-chain and interchain interactions must be considered.

To shed further light on the situation, we developed a system that can be used to examine cooperative motions at a relatively local scale.[5,7] It is known that some chemical groups have simple and well-defined motions; examples are phenylene π-flip and the conformational transition of cyclohexane rings. These motions can exist even in solid polymers. For example, the existence of the so-called chair−boat−chair conformational transition of 1,4-cyclohexylene ring (Figure 1) has been confirmed in a series of poly(ethylene terephthalate) (PET)/poly(1,4-cyclohexylenedimethylene terephthalate) (PCT) copolymers (Figure 2), based on a systemic study by Chen et al.[26] If these chemical groups are introduced into polymer chains as linkages between segments, the local motions of these chemical groups could cause subsequent changes in segmental motions, depending on how the chemical groups interact with their neighboring segments. By comparing the changes in segmental mobility with respect to the chemical structures of the different functional groups, we should be able to deduce the conditions for strong cooperativity.

In this study our primary effort is to examine the influence of local motions of several chemical groups on segmental motions in a series of bisphenol poly(ester carbonate)s. These chemical groups, including 1,4-cyclohexylene dicarboxylate, terephthalate, bicyclo[2.2.1]heptane-1,4-dicarboxylate, and bicyclo[2.2.2]octane-1,4-dicarboxylate (Figure 3) possess fast movements, as

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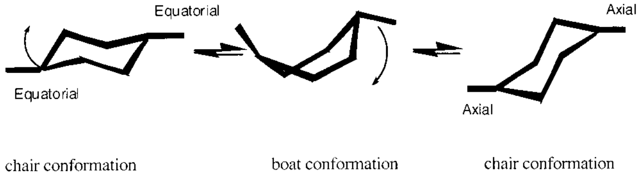


Figure 1. Chair−boat−chair conformational transition of 1,4-cyclohexylene ring.

determined by DRSE ^{13}C NMR.[1] According to a study by Chen et al.,[26] the 1,4-cyclohexylene ring is most likely to undergo the chair−boat−chair conformational transition. For the remaining linkages, the chemical structures suggest that rotational motions around the 1,4-axes seem reasonable. These rotations are certainly subjected to different degrees of restrictions. Therefore, by comparing chain dynamics of the resulting copolymers, we can examine how these local motions contribute to segmental mobility in polymers.

Experimental Section

A. Synthesis. The block copolymers used in this paper were prepared according to the two-step synthesis procedure reported in our previous paper[27] (Scheme 1). Bisphenol A (BPA) or tetramethylbisphenol A (TMBPA) oligomers were first synthesized by unbalanced feeding of BPA or TMBPA with its corresponding bis(chloroformate)s. Then, the oligomers were reacted with dicarboxylic chlorides of different linkages, i.e., 1,4-cyclohexylene dicarboxylic chloride, terephthaloyl chloride, bicyclo[2.2.1]heptane-1,4-dicarboxylic chloride, and bicyclo[2.2.2]octane-1,4-dicarboxylic chloride, to form polymers with the desired structures. The block copolymers containing 1,4-cyclohexylene linkage have the structures $(-B_xC-)_n$ and $(-T_xC-)_n$, but are denoted B_xC and T_xC for simplicity, where B represents bisphenol A, T represents tetramethylbisphenol A, C represents 1,4-cyclohexylene dicarboxylate, and x indicates the average number of bisphenol A units separated by adjacent cyclohexylene linkages. The nomenclature for copolymers with other linkages is basically similar to that for B_xC, except that t represents terephthalate, H represents bicyclo[2.2.1]heptane dicarboxylate, and O represents bicyclo[2.2.2]octane dicarboxylate. The chemical structures of these linkages are shown in Figure 3.

To demonstrate the effect of the cyclohexylene conformational transition on neighboring segments, a copolymer, D_2TC (Figure 4), was synthesized, where D represents 2,6-dimethylbisphenol A (DMBPA) and *T* represents tetramethylbisphenol A as before. It has been observed that the π-flip motion of the unsubstituted DMBPA phenylene rings in DMBPA-PC (Figure 4) is partially hindered.[25] By measuring the π-flip motion of the same phenylene rings in D_2TC, we should be able to determine how the cyclohexylene linkage influences motions of its neighboring units.

1. Synthesis of Monomers. (1) 1,4-Cyclohexylene dicarboxylic chloride was converted from 1,4-cyclohexylene dicarboxylic acid according to Scheme 2.[27] Its NMR spectrum verifies that all the 1,4-cyclohexylene rings are in the trans configuration.

^{1}H NMR (300 MHz, $CDCl_3$, ppm): 2.74 (m, 2H, $\mathrm{C}H$); 2.31 (m, 4H, $\mathrm{C}H_2$); 1.58 (m, 4H, $\mathrm{C}H_2$).

(2) Bicyclo[2.2.1]heptane-1,4-dicarboxylic acid was synthesized according to the procedure reported in ref 28 (Scheme 3). The dicarboxylic acid was converted to bicyclo[2.2.1]heptane-1,4-dicarboxylic chloride using the similar reaction procedure in Scheme 3. The final product is a platelike, white crystal with a melting point of 38−39 °C.

^{1}H NMR (300 MHz, $CDCl_3$, ppm): 1.83 (m, 4H, $\mathrm{C}H_2$); 2.06 (s, 2H, $\mathrm{C}H_2$); 2.18 (m, 2H, $\mathrm{C}H_2$).

(3) Bicyclo[2.2.2]octane-1,4-dicarboxylic acid was synthesized according to the procedure reported in ref 29 (Scheme 4). The dicarboxylic acid was converted to bicyclo[2.2.2]octane-1,4-dicarboxylic chloride using the similar reaction procedure in Scheme 3. The final product is a platelike, white crystal with a melting point of 48−51 °C.

^{1}H NMR (300 MHz, $CDCl_3$, ppm): 1.95 (s, $\mathrm{C}H_2$). ^{13}C NMR (300 MHz, $CDCl_3$, ppm): 28; 51; 178.

(4) Synthesis of 2-(3,5-dimethyl-4-hydroxyphenyl)-2-(4-hydroxyphenyl)propane (dimethylbisphenol A or DMBPA) (Scheme 5) 2-(4-hydroxyphenyl)-2-propanol: A 250 mL flame-dried flask, equipped with a magnetic stirrer, a gas inlet, which led to a dry nitrogen tank, and a vacuum line outlet, was first evacuated with a mechanical pump. Dry nitrogen gas was then purged into the flask. This process was repeated several times to remove oxygen and residual moisture in the flask. Through a serum seal, 50 mL (80 mmol) of 1.6 M *n*-butyllithium in hexane was added into the flask by a syringe. The solution was then cooled to −78 °C by a dry ice acetone bath. A solution of 6.92 g (40 mmol) of 4-bromophenol in 15 mL of anhydrous THF was added into butyllithium solution slowly, and the mixture was allowed to be warmed gradually. A thick gel was formed at about 20 °C, which indicated the completion of the reaction. A 20 mL aliquot of anhydrous THF was then added to reduce the viscosity of the mixture, followed by the addition of 2.32 g (40 mmol) of anhydrous acetone in 5 mL of THF after the mixture was cooled to −78 °C again. The reaction mixture was then warmed to room temperature. Finally, the reaction system was quenched by 50 mL of saturated aqueous ammonium hydrochloride solution.

In the reaction mixture was added 50 mL of ethyl acetate. The solution was washed with 50 mL (2 × 25 mL) of saturated aqueous ammonium hydrochloride solution, followed by 150 mL (3 × 50 mL) of distilled water. After most of the solvent was evaporated under reduced pressure, a white precipitate of 2-(4-hydroxyphenyl)-2-propanol (3.12 g) was formed gradually at room temperature. The yield was 52%.

^{1}H NMR (300 MHz, d_6-acetone, ppm): 1.46 (s, 6H, i-pro$\mathrm{C}H_3$); 3.88 (s, 1H, i-pro$\mathrm{O}H$, D_2O exchangeable); 7.33 (m, 2H, $\mathrm{Ph}H$); 6.75 (m, 2H, $\mathrm{Ph}H$); 8.10 (s, 1H, $\mathrm{PhO}H$, D_2O exchangeable)

Dimethylbisphenol A. In a 50 mL flask, equipped with a magnetic stirrer, were added a mixture of 2.5 g (16.5 mmol) of 2-(4-hydroxyphenyl)-2-propanol and 6.0 g (49.2 mmol) of dimethylphenol. The mixture was molten and held at 50 °C. HCl gas generated in situ by adding concentrated sulfuric acid into 35% HCl solution was introduced. The reaction was allowed to proceed for 4 h. The mixture was separated by a column loaded with 300 mL of silica gel. The column was first eluted with toluene to remove excess amounts of dimethylphenol and then with hexanes/acetate (5/2 ratio) solution to obtain DMBPA. After the solvent was evaporated, a white powder was formed. The crude product was recrystallized from toluene, and the final yield was 38%. The melting point of DMBPA was 126 °C.

^{1}H NMR (300 MHz, d_6-acetone, ppm): 1.55 (s, 6H, i-pro$\mathrm{C}H_3$); 2.17 (s, 6H, $\mathrm{PhC}H_3$); 6.70 (m, 2H, $\mathrm{Ph}H$); 6.80 (s, 2H, $\mathrm{Ph}H$); 6.99 (s, 1H, $\mathrm{PhO}H$, D_2O exchangeable); 7.03 (m, 2H, $\mathrm{Ph}H$); 8.03 (s, 1H, $\mathrm{PhO}H$, D_2O exchangeable).

2. Synthesis of Polymers. Polymers except D_2TC were synthesized according to the procedures in Scheme 1. Besides 1,4-cyclohexylene dicarboxylic chloride, different linkages, such as terephthaloyl chloride, bicyclo[2.2.1]heptane-1,4-dicarboxylic chloride, and bicyclo[2.2.2]octane-1,4-dicarboxylic chloride, were used to react with bisphenol oligomers to form polymers (Figure 5). The glass transition temperature T_g and molecular weight of these polymers are presented in Tables 1 and 2.

Synthesis of D_2TC. 1.057 g (4.12 mmol) of DMBPA, 0.020 g (0.09 mmol) of cumylphenol, 1.04 g (10.30 mmol) of triethylamine (TEA), and 0.025 g of *N*,*N*-dimethyl-4-aminopyridine (DMAP) were suspended in 40 mL of dichloromethane at room temperature in a 100 mL three-neck reaction flask equipped with a mechanical stirrer. The solution was held at 0 °C in an ice water bath when 0.431 g (2.06 mmol) of 1,4-cyclohexylene dicarboxylic chloride in 10 mL of dichloromethane was slowly added over a period of 10 min. The solution was then warmed to 40 °C, before adding 0.843 g (2.06 mmol) of TMBPA bis(chloroformate) in 10 mL of dichloromethane slowly to produce a viscous solution. The solution was allowed to react for another 10 min. The reaction mixture was then allowed to be

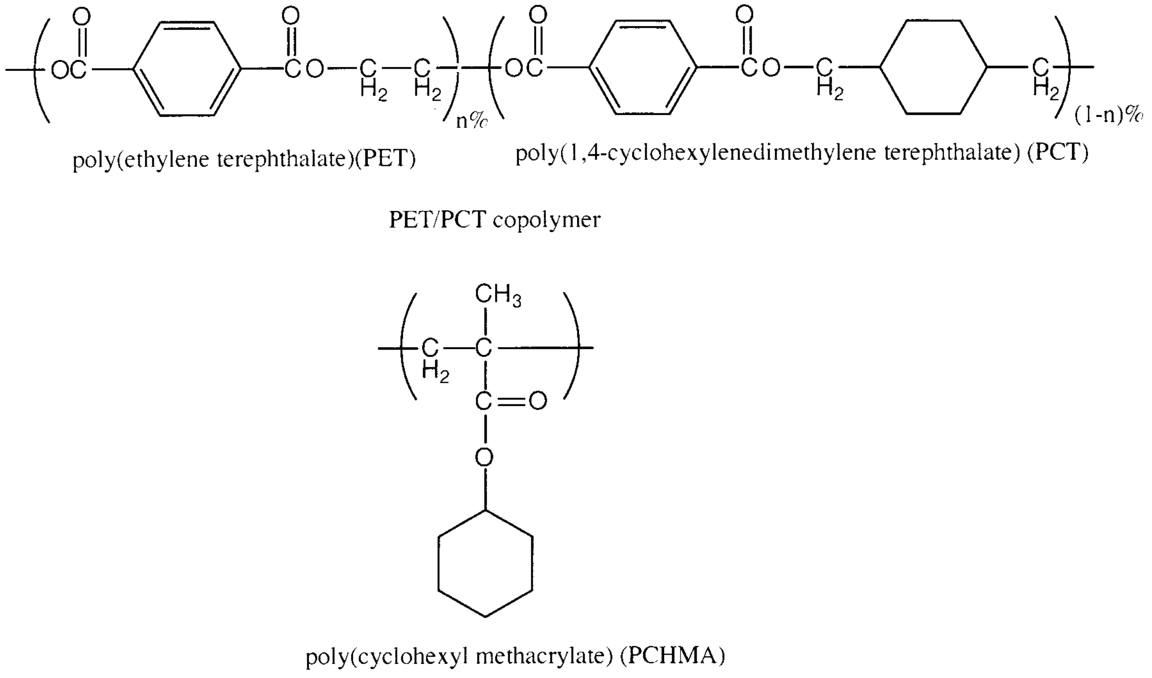


Figure 2. Chemical structures of PET/PCT copolymers and PCHMA.

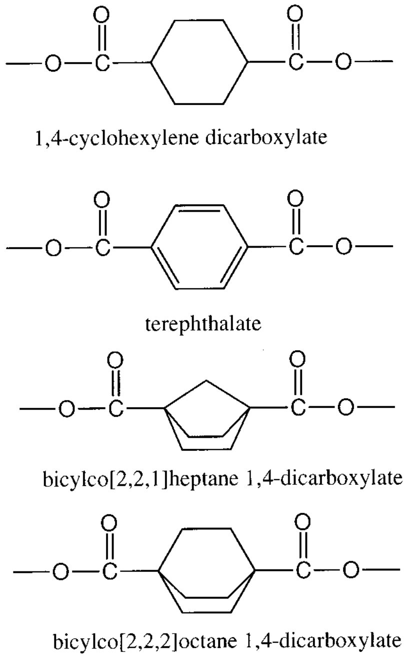


Figure 3. Chemical structures of linkages.

cooled to room temperature, before being poured into a blender filled with a large quantity of 2-propanol. The white polymer was precipitated, filtered, and dried. To remove impurities thoroughly, the polymer was thrice dissolved in dichloromethane, precipitated from 2-propanol, filtered, and dried. 1.96 g (97%, yield) of D$_2$TC was obtained. The molecular weight of the polymer is 23 000 g/mol, and the glass transition temperatures (T_g) is 182 °C.

^{1}H NMR (300 MHz, CDCl$_3$, ppm): 1.53 (s, 6H, i-proCH_3); 1.62 (s, 12H, i-proCH_3); 1.74 (m, 4H, CH_2); 2.08 (s, 12H, PhCH_3); 2.24 (s, 12H, PhCH_3); 2.32 (m, 4H, CH_2); 2.66 (m, 2H, C*H*); 6.92 (m, 8H, Ph*H*); 7.28 (m, 4H, Ph*H*)

B. Dynamic Mechanical Analysis (DMA). DMA was performed on thin amorphous films with typical dimensions of 50 mm × 5 mm × 0.06 mm (length × width × thickness). To prepare these films, the polymer powders were first dried in a vacuum at 10 °C below their glass transition temperatures for 24 h. Then 10% polymer solutions in either dichloromethane or 1,2-dichloroethane were spread on clean glass slides and dried at room temperature overnight to form thin films. Using a razor blade, the films were cut into strips with dimensions mentioned above and floated off the glass slides in distilled water. The specimens were further held under vacuum at 90−100 °C for at least 24 h to remove remaining solvent and moisture. Prior to the DMA measurement, each sample was heated to 15 °C above T_g for 15 min, followed by quenching to room temperature. All the film specimens were optically transparent, suggesting the absence of crystallinity.

DMA was performed on a custom-made spectrometer comprised of a linear driver motor unit, a load cell, a displacement gauge, and a Hewlett-Packard control and data acquisition system. The sample chamber contained a liquid nitrogen bath and a pair of heating rods. The temperature of the chamber was controlled by a LakeShore model 340 temperature controller with a silicon diode temperature sensor with sensitivity of 0.001 °C. The actual temperature of the chamber was maintained to within ±0.10 °C. The measurement temperatures ranged from −140 °C to the glass transition temperature in 5 or 10 °C intervals, and at each temperature, the samples were held for 10 min prior to the measurement to allow for thermal equilibration.

C. Uniaxial Tensile Test. Dog-bone-shaped tensile bars for the polymers were compression molded at temperatures 70 °C above their respective T_g's and quenched down to room temperature. The specimens were then polished using fine grit sand paper. Prior to the measurements, the specimens were placed back into the mold and heated to 15 °C above their respective T_g's for 15 min before being quenched back down to room temperature. The dimensions of the specimens were 50 mm × 3 mm × 3 mm (length × width × thickness). The gauge length was 12.7 mm.

Uniaxial tensile tests of poly(ester carbonate)s at room temperature were conducted with a screw-driven testing machine (Instron 4502). The yield stresses were based on the original cross-sectional areas of the specimens and are therefore nominal stresses.

Results

Glass Transition Temperature. The glass transition temperatures of polymers studied are presented in Tables 1 and 2. As shown in Table 1, T_g of B_xC increases

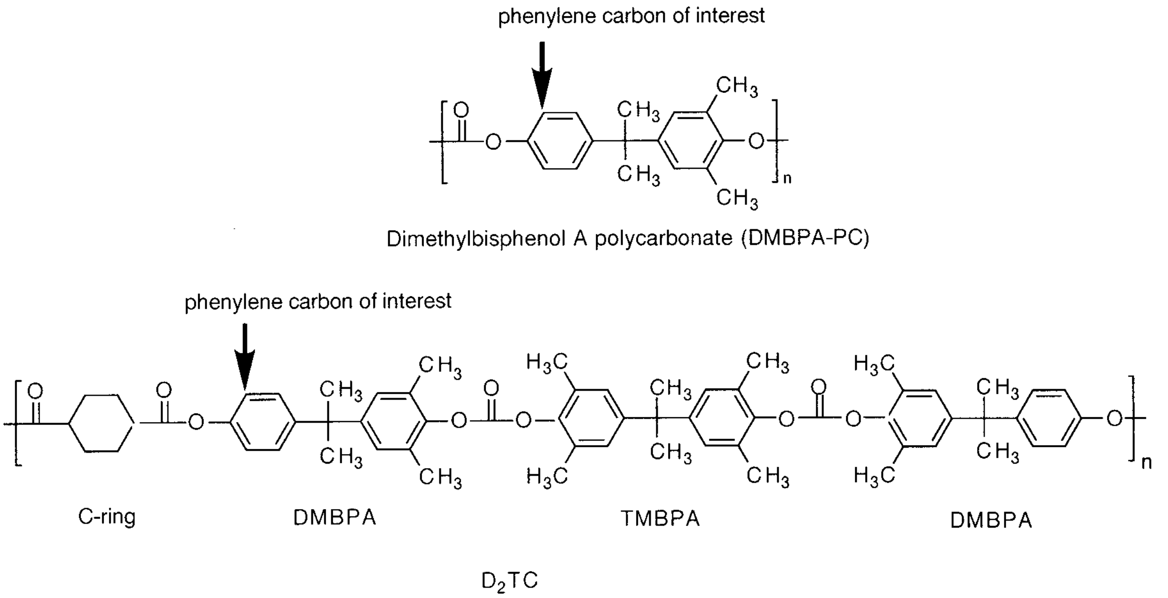
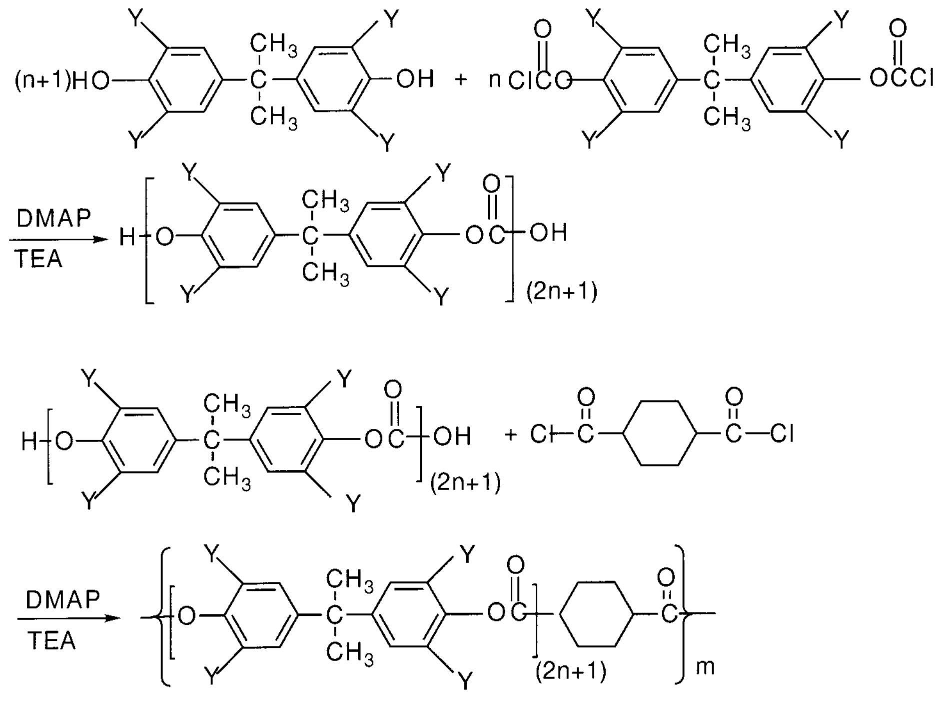


Figure 4. Chemical structures of DMBPA-PC and D$_2$TC.

Scheme 1. Synthesis of Poly(ester carbonate) Block Copolymers

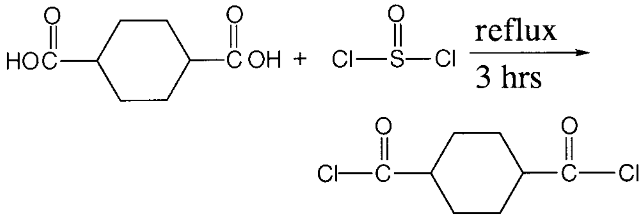


Y=-H n=1, polymer is B$_3$C;
n=2, polymer is B$_5$C;
n=3, polymer is B$_7$C;
n=4, polymer is B$_9$C.

Y=-CH$_3$ n=1, polymer is T$_3$C;
n=2, polymer is T$_5$C;
n=3, polymer is T$_7$C;
n=4, polymer is T$_9$C.

with increasing cyclohexylene content, while those of T$_x$C remain close to 200 °C. A similar trend is observed in BPA and TMBPA copolymers containing other dicarboxylate linkages, terephthalate, bicyclo[2.2.1]heptane dicarboxylate, and bicyclo[2.2.2]octane dicarboxylate (Table 2). It should be noted that B$_x$t and B$_x$C have very similar T_g's. This observation suggests that the cyclohexylene linkage contributes as much dipolar interactions as the terephthalate linkage as far as the T_g is concerned. If we consider the fact that all of the cyclohexylene linkages in B$_x$C are in the trans configuration, and a dominant percentage of the cyclohexylene rings, at least 92%, stays in the lowest energy, well-extended "chair" state, it is not surprising to find that the cyclohexylene linkage is not as flexible as it might seem. Conversely, with an extremely flexible tetramethylene dicarboxylate linkage (A), B$_3$A copolymer (M_n = 26 000) has a much lower T_g (124 °C).[30] Although the incorporation of the cyclohexylene linkage does not facilitate the glassy transition, it does not necessarily

Scheme 2. Synthesis of 1,4-Cyclohexylenedicarboxylic Chloride



curtail the segmental mobility of these copolymers at temperatures below T_g.[6,27] We will focus on the segmental mobility of these copolymers in the rest of this paper.

Local Motions of Linkages. As mentioned above, it is most likely that the 1,4-cyclohexylene linkage undergoes the chair–boat–chair conformational transition, whereas the terephthalate and the bicyclo linkages are capable of restricted rotational motions around their 1,4-axes at room temperature. However, regardless of the great difference in motions of linkages next to the biphenols in these copolymers, the phenylene rings in BPA flip and the dimethylphenylene rings in TMBPA do not. This is easy to understand, because the BPA phenylene rings flip too fast for DRSE technique to tell the difference. In contrast, the rotation of the dimethyl-substituted phenylene rings in TMBPA are so hindered by neighboring chains that they are stalled even with very mobile chemical groups adjacent to them.

To demonstrate the effect of the cyclohexylene conformational transition on neighboring segments, the π-flip motion in the unsubstituted phenylene rings in DMBPA-PC and D_2TC (Figure 4) was compared. It is very clear that this π-flip motion is partially hindered in DMBPA-PC as the carbons of interest have a sideband ratio (sb_2/sb_1) of 0.74.[25] With the cyclohexylene linkage inserted next to the DMBPA, the π-flip is facilitated ($sb_2/sb_1 = 0.66$)[30] despite the increased content of the immobile group, dimethylphenylene rings, in the polymer backbone.

Dynamic Mechanical Analysis (DMA). The γ-relaxation behavior of the synthesized polymers was studied to determine the effect of motions of linkage groups on segmental motion. As we show in previous work,[27] the γ-peaks of B_xC copolymers are dominated by the conformational transition of the cyclohexylene ring (Figure 6). On the other hand, in T_xC, the full relaxation occurs only when TMBPA polycarbonate block motions are activated at 50 °C (Figure 7). The activation energies of γ-relaxation processes in B_xC and T_xC were calculated from the peak temperatures in DMA spectra measured at 30, 10, 3, and 1 Hz. The γ-peak activation energies in B_xC are closer to that of PCT (15.6 kcal/mol) than to BPA-PC (13.0 kcal/mol), while those in T_xC are close to that of TMBPA-PC (24.6 kcal/mol) (Table 1). This supports our analysis of DMA spectra of B_xC copolymers in the previous paper:[27] The high-energy process is dominant in the secondary relaxation in these copolymers. Therefore, the conformational transition of the cyclohexylene ring must couple to motions of its neighboring groups along the chain; otherwise, the characteristic peak of the C-ring would be observed. By necessity, there must also be cooperative motion of neighboring chains due to the excursion in each chain caused by the conformational transitions.

The secondary relaxations of BPA-PC, B_3t, B_3H, and B_3C are compared in Figure 8. The shapes of these peaks, except for that of B_3C, are quite similar, although there may be small shifts in the peak positions. It suggests that the insertion of terephthalate and bicyclo[2.2.1]heptane-1,4-dicarboxylate groups does not distinctively alter the inherent segmental motions in the polymers. In contrast, the γ-relaxation of B_3C differs drastically from that of BPA-PC in terms of both shape and peak position. Likewise, great similarity can be observed in the secondary relaxations in TMBPA-PC and T_3t, while T_3C has a prominent shoulder at the lower temperature side of its peak (Figure 9). Hence, different types of linkage motions, namely the rotational motion and chair–boat–chair conformational transition, result in different polymer segmental motions.

Yield Stress. As shown in our previous papers,[6,27] yield is facilitated by the incorporation of cyclohexylene linkages into B_xC and T_xC copolymers. We propose that the cyclohexylene ring conformational transition enhances segmental mobility and in return helps to relax the applied stress more efficiently. In contrast, terephthalate and bicyclo[2.2.1]heptane-1,4-dicarboxylate groups have the opposite effect (Figure 10): yield stresses instead increase in copolymers containing these linkages. It indicates that the segmental mobility does not benefit much form the insertion of these linkages.

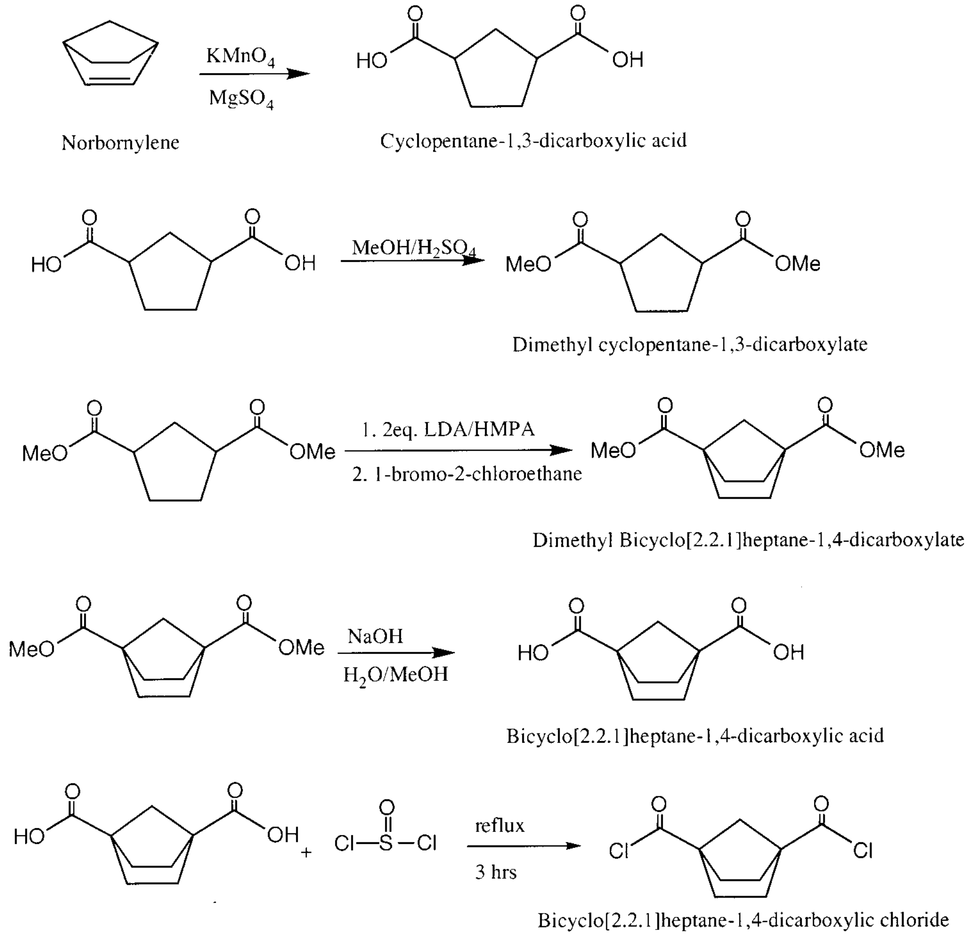
Discussion

The cyclohexylene ring conformational transition in solid polymers has been described in detail by Chen et al.[26] During the transition, the two energy minima, i.e., the chair conformations, can be transformed to each other via an energetically less favorable twisted boat conformation (Figure 1). In this process, as shown by simulation using the software program Cerius2, chemical groups linked to the ring are forced to move excursively.[27] Consequently, a large-amplitude perturbation is introduced into polymer chains by this conformational transition.

The consequent effect of cyclohexylene conformational transition on segmental motions can be directly observed in the dynamic mechanical spectra of the polymers containing these rings in the main chain. For instance, in a series of PET/PCT copolymers, the characteristic relaxation peaks at about −65 to −70 °C (1 Hz) have been attributed to the conformational transition of the cyclohexylene ring by Chen.[26] Similar secondary relaxation peaks (Figure 6) are also observed at −65 °C (1 Hz) in B_xC copolymers.[27] In both B_xC and PET/PCT copolymers, the amplitude of the secondary relaxation peak increases with cyclohexylene content. Clearly, the cyclohexylene ring conformational transition strongly couples with the kinematics of its neighboring segments,[27] and segmental mobility is enhanced in these polymers as a result. Consequently, it is reasonable to surmise that this is the molecular basis for the observed correlation; viz., yielding is facilitated and crazing is retarded with increasing cyclohexylene content in these polymers.[6,31]

Not all local chemical motions that include the conformational transition of the cyclohexylene ring will necessarily grant polymers greater segmental mobility. Weakly correlated motions are found less likely to benefit segmental mobility. One example is poly(cyclohexyl methacrylate) (PCHMA) (Figure 2), which exhibits a sharp relaxation peak at −70 °C (DMA at 1 Hz). Heijboer[3] attributed this relaxation to the conformational transition of the cyclohexyl side group. The

Scheme 3. Synthesis of Bicyclo[2.2.1]heptane-1,4-dicarboxylic Chloride

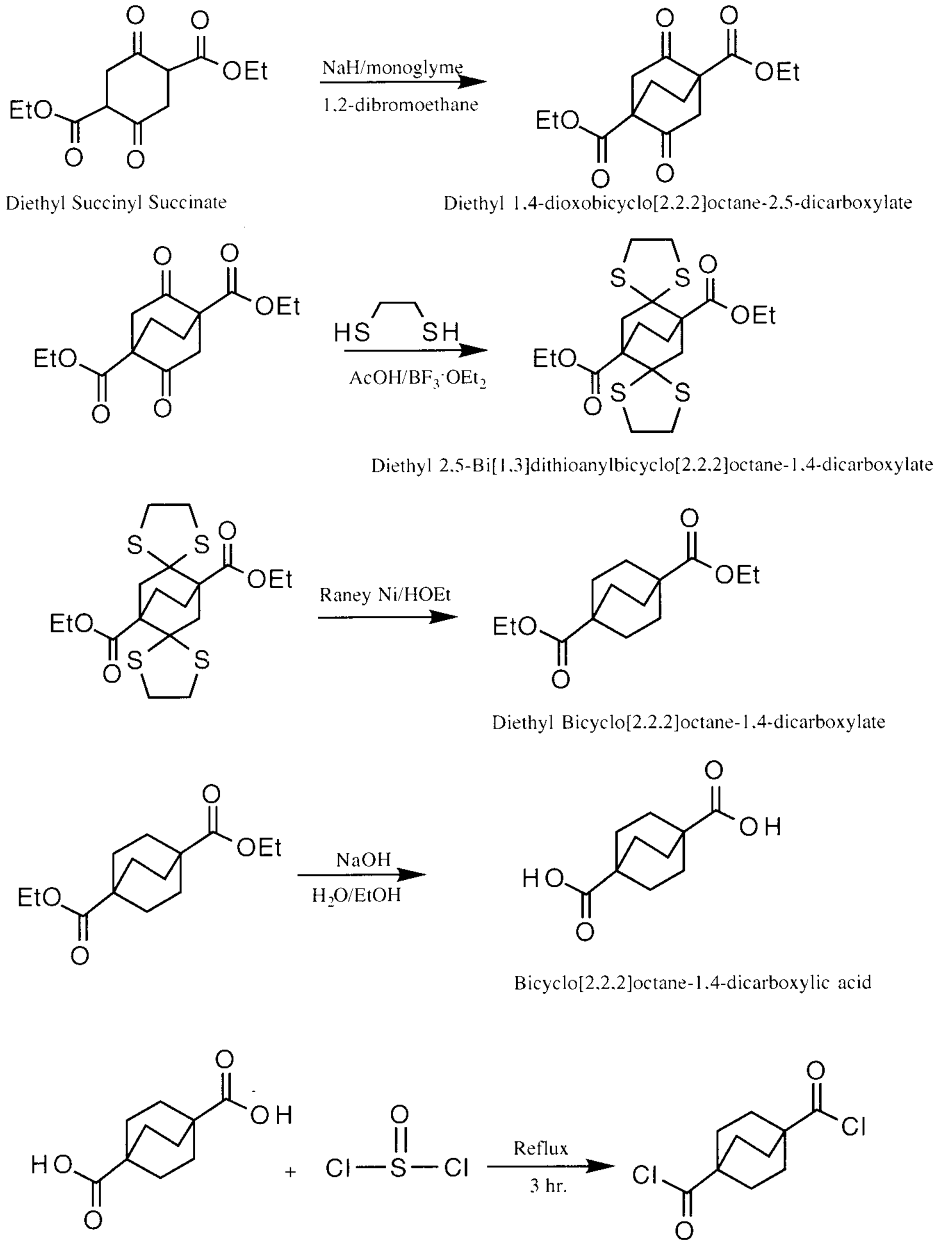


activation energy of this motion (11.5 kcal/mol)[32] is similar to that of the isolated cyclohexane molecules (10.8 kcal/mol),[33] which suggests that the side groups are only weakly correlated with their surroundings. He further found that even though the incorporation of the cyclohexyl group increases the strength of the secondary relaxation, there is not a corresponding increase in impact strength. Although terephthalate, bicyclo[2.2.1]heptane-1,4-dicarboxylate, and bicyclo[2.2.2]octane-1,4-dicarboxylate are linked in main chains of polymers instead of side chains, these groups exhibit a similar behavior to the cyclohexyl group in PCHMA. Little change in the secondary relaxations (Figure 8) and decreased tendency to yield (Figure 10) immediately suggest that motions of these linkages contribute little to the segmental motions.

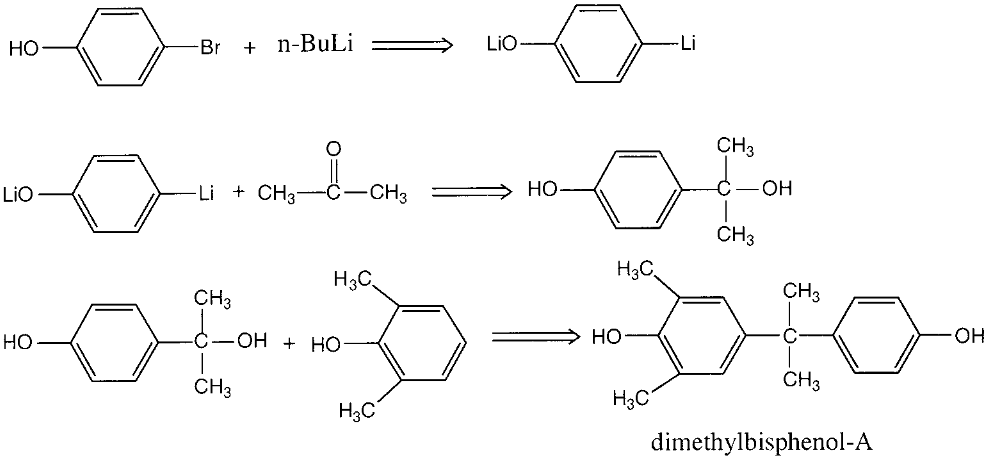
The different effects on segmental mobility by inserting terephthalate, bicyclo linkages, and cyclohexylene linkage lie in the differences in chemical structures of these linkages. Terephthalate has a planar structure and is therefore capable of only a π-flip motion about its 1,4-axis instead of the conformational transition available to the cyclohexylene ring. Here the π-flip motion can be considered as a special case for restricted rotational motion. Bicyclo[2.2.1]heptane and bicyclo[2.2.2]octane linkages can be approximately viewed as cyclohexylene rings locked in the boat conformation by the bridging methylene or ethylene. The bicyclo[2.2.2]octane ring is able to rotate rapidly around its 1,4-axis because of the 3-fold symmetric structure, while the rotational motion is hampered in bicyclo[2.2.1]heptane ring due to the less symmetric ring structure. The restricted rotational motions of terephthalate and bicyclo linkages are presumably able to occur without any strong cooperation from their in-chain neighbors owing to modest or absence of need for additional space. Therefore, the resulting segmental mobility does not benefit much from motions of these linkages. In other words, such local motions should create minimal disturbance on their neighbors if they are indeed the driving motions. Unlike the restricted rotational motions, the conformational transition of the cyclohexylene linkage can drive neighboring segments to move correspondingly. Inevitably, the energy landscape for interchain interactions is considerably changed by this large-amplitude movement. As a result, the segmental mobility is altered compared to original BPA polycarbonate segments.

Let us now examine how the motion of neighboring groups, i.e., the π-flip of phenylene rings in bisphenol blocks, may be affected by the cyclohexylene conformational transition. According to Geotz et al.,[25] the phenylene ring π-flip is gated by interchain interactions. If segmental mobility could cause volume fluctuations around polymer chains, phenylene rings should flip faster. For copolymers containing weakly coupled linkages, such as terephthalate and bicyclo linkages, no change is expected in the phenylene ring π-flip motion.[1] In contrast, we would expect to see changes in phenylene ring motion in B_xC and T_xC, since a significant change in the interchain and in-chain environments is introduced into polymer segments by the cyclohexylene ring. However, little change can be observed in the dipolar sideband ratios for phenylene ring carbons in

Scheme 4. Synthesis of Bicyclo[2.2.2]octane-1,4-dicarboxylic Chloride



Scheme 5. Synthesis of Dimethylbisphenol A (DMBPA)



B$_x$C relative to those in BPA and for dimethylphenylene carbons in T$_x$C relative to those in TMBPA, respectively. For T$_x$C, the interchain hindrance is so strong that even the enhanced segmental fluctuations do not allow the dimethylphenylene ring to flip. As for B$_x$C, limitations of the DRSE experimental technique used may prevent

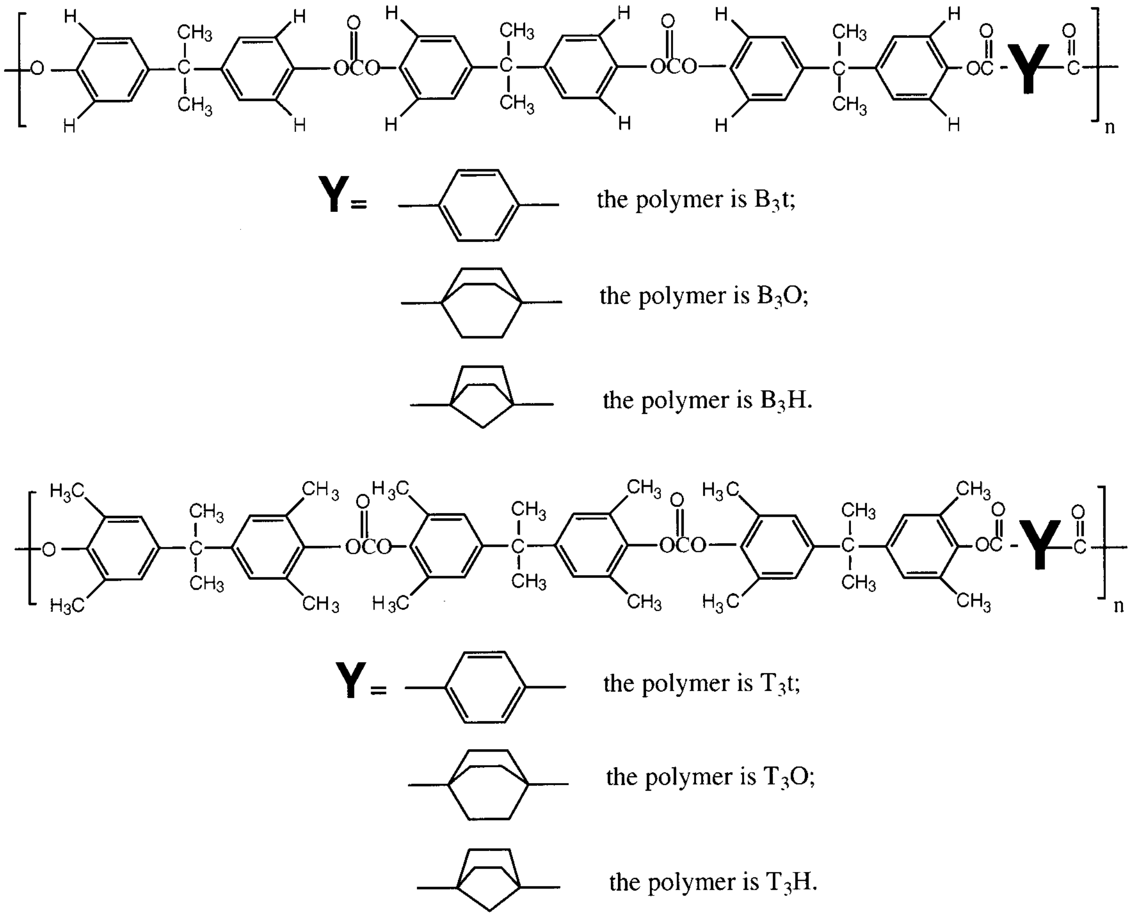


Figure 5. Chemical structures of BPA and TMBPA poly(ester carbonate)s with different linkages.

Table 1. Number-Average Molecular Weights (M_n), Polydispersity Index (PDI) Measured by GPC with THF as Solvent, Glass Transition Temperatures Measured by DSC at a Rate of 10 °C/min, and Activation Energies (ΔE_{act}) of the γ-Relaxation of B_xC and T_xC Copolymers

polymers	M_n ($\times10^4$)	PDI	T_g (°C)	ΔE_{act} (kcal/mol)
BPA-PC	3.6	2.5	150	13.0 ± 0.5
B_9C-PEC	3.6	2.3	158	
B_7C-PEC	3.6	2.3	159	15.3 ± 0.5
B_5C-PEC	2.8	2.6	161	15.6 ± 0.5
B_3C-PEC	3.5	2.6	172	15.7 ± 0.5
TMBPA-PC	3.1	1.6	200	24.6 ± 0.5
T_9C-PEC	3.0	1.6	198	22.9 ± 0.5
T_7C-PEC	3.6	1.5	197	23.3 ± 0.5
T_5C-PEC	3.3	1.7	202	23.3 ± 0.5
T_3C-PEC	3.2	1.8	206	24.0 ± 0.5

Table 2. Number-Average Molecular Weights (M_n), Polydispersity Index (PDI) Measured by GPC with THF as Solvent, and Glass Transition Temperatures of Copolymers Measured by DSC at a Rate of 10 °C/min

polymers	M_n ($\times10^4$)	PDI	T_g (°C)
B_3t-PEC	3.5	2.5	169
B_5t-PEC	3.6	2.3	161
B_7t-PEC	3.6	2.3	158
B_9t-PEC	2.8	2.6	156
B_3H-PEC	2.7	2.6	156
B_3O-PEC	2.9	2.6	152
T_3t-PEC	3.4	2.4	210
T_3H-PEC	3.1	2.5	209
T_3O-PEC	3.3	2.3	210

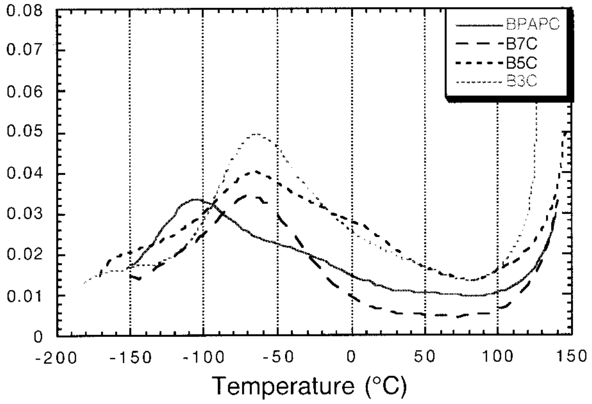


Figure 6. DMA spectra of BPA-PC and B_xC at 1 Hz.

us from detecting changes in the flipping rate. Normally, phenylene rings in BPA segments flip extremely rapidly (300 kHz).[34] At such a fast rate, it is very difficult to detect the influence of the neighboring chains on the increasing flipping rate by the sideband ratios from the DRSE experiment if the rate already exceeds 10 kHz at 300 K. However, if the phenylene flipping motion was already less than 10 kHz from interchain steric hindrance, then the effect of segmental mobility on the increasing neighboring phenylene π-flip motion could be demonstrated using the DRSE technique. By comparing the sideband ratios of the unsubstituted phenylene rings in DMBPA-PC and D_2TC (Figure 4), it becomes obvious that the incorporation of the cyclohexylene linkage increases the neighboring phenylene π-flip motion. Such an effect has also been observed[26] in PET/PCT copolymers (Figure 2). In amorphous PET, the terephthalate phenylene rings cannot flip. As the cyclohexylene content increases in the copolymers, the phenylene rings become more and more free to flip.

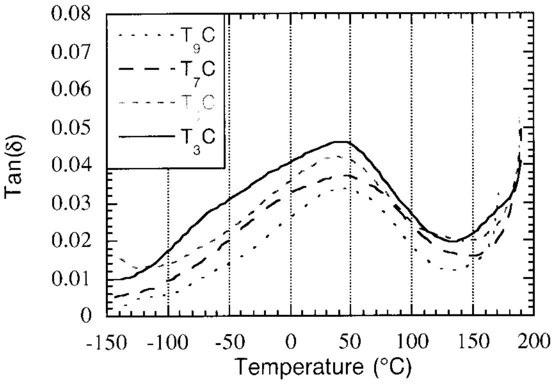


Figure 7. DMA spectra of TMBPA-PC and T_xC at 1 Hz.

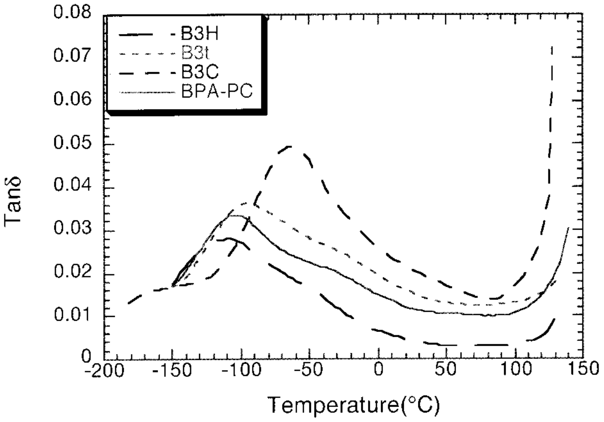


Figure 8. DMA spectra of BPA-PC, B_3t, B_3H, and B_3C at 1 Hz.

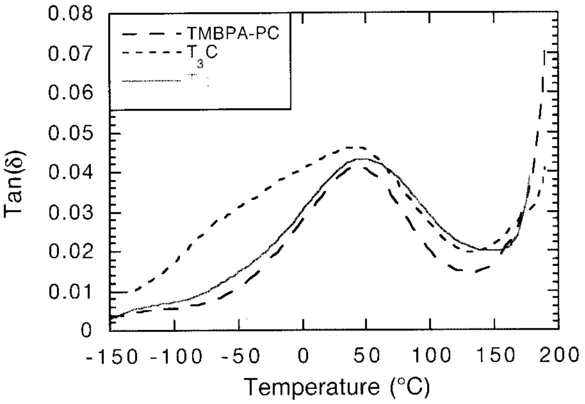


Figure 9. DMA spectra of TMBPA-PC, T_3t, and T_3C.

Similar to the situation in B_xC copolymers, the chain dynamics is significantly increased in the PET/PCT copolymer as the cyclohexylene linkage content is increased. While it is clear that the phenylene π-flip is predominantly determined by the intermolecular gating, the conformational transition of cyclohexylene rings may not be directly correlated to the phenylene π-flip. However, as the segmental mobility is enhanced by the cyclohexylene conformational transition, and the instantaneous distances between polymer chains are enlarged, the intermolecular gating may be influenced, and the phenylene rings along the chains may become more ready to flip.

The discussions above makes it quite clear that extensive cooperativity requires a necessary condition, i.e., strong couplings between individual functional groups and neighboring segments, including both in-chain and interchain units. In our case, the cyclohexylene conformational transition apparently couples much more strongly to the neighboring segments than the restricted rotational motions and therefore contributes more significantly to segmental mobility. We expect that some other intrinsic characteristics of motions of chemical groups, such as amplitude and rate, are also critical to cooperativity. For example, to contribute strongly to the segmental mobility, a chemical group must generate a large-amplitude fluctuation. In addition, rates of resulting cooperative motions must be closely related to those of individual functional group motions. However, a detailed study of these factors in the light of cooperativity is outside the scope of this paper.

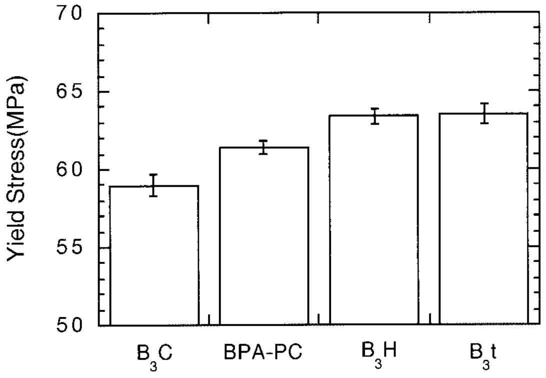


Figure 10. Yield stresses of B_3C, BPA-PC, B_3H, and B_3t at a strain rate of 2.62 × 10^{-3}/s at room temperature.

Conclusion

In this paper, effects of local motions of specific chemical groups on segmental mobility are investigated in a series of glassy poly(ester carbonate) copolymers which contain various linkages. We find that the chair–boat–chair conformational transition of 1,4-cyclohexylene dicarboxylate linkage couples strongly to motions of its neighboring segments and results in enhanced segmental mobility. On the other hand, a weak interaction is observed between linkages capable of only restricted rotational motions, including terephthalate, bicyclo[2.2.1]heptane-1,4-dicarboxylate, and bicyclo-[2.2.2]octane-1,4-dicarboxylate linkages and neighboring segments. As a result, incorporation of these linkages does not benefit polymer segmental mobility much. Hence, we propose that in order to achieve large-scale cooperative motions, perturbations generated by local motions, such as chair–boat–chair conformational transition, must be strongly coupled to its neighboring segments.

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