Design of Mechanically Robust High-T_g Polymers: Synthesis and Dynamic Mechanical Relaxation Behavior of Glassy Poly(ester carbonate)s with Cyclohexylene Rings in the Backbone

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ABSTRACT: High-T_g yet mechanically robust polymers are desirable but difficult to realize. To explore whether the insertion of a motionally active molecular entity in the backbone could produce polymers with both high T_g and yet are not brittle, three series of high-T_g glassy polycarbonates/polyesters/poly(ester carbonate)s were designed and synthesized. The secondary relaxation behavior of these polymers was studied by dynamical mechanical analysis (DMA). Incorporation of cyclohexylene groups (C-rings) in the main chain of polymers made from two rigid and bulky monomers, spirobiindane bisphenol (SBI) and trimethylcyclohexylbisphenol (Tmc), respectively, changes the γ relaxation process dramatically in peak shape and position in these polymers. No such change is observed in polycarbonate polymers made from cyclohexylbisphenol (BPAZ), or ZPC for short. Through monitoring the γ relaxation with gradual structural change, C-rings in the main chain backbone are proposed to undergo active ring inversion. The γ relaxation of ZPC is proposed to be mainly due to side-chain C-ring inversion. The narrowing on the high-temperature side of the γ relaxation peak of the polycarbonate of Tmc is proposed to be due to the restricted motion of its axial phenyl rings. A linear correlation between relaxation strength and total C-ring concentration was found for all the polymers.

1. Introduction

1.1. High-T_g Glassy Polymers and Molecular Motion. The polycarbonate of bisphenol A combines the properties of high toughness, optical clarity, and the relatively high T_g of 150 °C. Recently, Prime and Feger[1] pointed out that high-temperature polymers with glass transition temperatures greater than 150 °C will be key materials in the computer and electronics industries. Unfortunately, high-T_g polymers are often brittle.

To increase T_g, bulky and rigid chemical units can be incorporated into polymer chains. In a survey, Heijboer[2] pointed out that the introduction of stiff rings in the main chain is the most promising way for obtaining thermoplastics which possess useful moduli above 100 °C, whereas the stiffening of polymers by bulky side groups (as in poly(vinylcarbazole), T_g = 210 °C) is less promising because the latter type of polymers is mostly brittle. But in general, both methods will result in very brittle polymers. For example, by introducing two methyl groups ortho to the carbonate group of BPA-PC, tetramethylbisphenol A polycarbonate (TMBPA-PC) with a T_g of 200 °C is obtained[3]; by replacing BPA with SBI (2,2′,3,3′-tetrahydro-3,3,3′,3′-tetramethyl-1,1′-spirobi-[1*H*-indene]-6,6′-diol), a polycarbonate (SBI-PC) with a T_g 230 °C is produced.[4] But both polymers are extremely brittle at room temperature. Efforts have been taken to improve their ductility by copolymerizing with bisphenol A, but this results in a lowering of T_g. A common feature of these two polymers is that they are both restricted in their local molecular motions. In SBI-PC, SBI is locked into a twisted bulky banana shape wherein the phenyl rings cannot move. SBI-PC chains should therefore have a very limited, confined local motion.[5] In TMBPA-PC, the local motion is restricted by the steric interaction between the carbonate groups and their methyl groups, though this may not be the only consequence of the methyl substitution. By contrast, the polycarbonate of Tmc (4,4′-(3,3,5-trimethylcyclohexylidene)diphenol) has a high T_g of 240 °C, while its mechanical properties are said to be comparable to those of BPA-PC.[6] The motions are also restricted in Tmc-PC: in solution the axial phenyl ring has a much restricted motion with an activation energy of about 10 kcal/mol, while the equatorial phenyl ring has a much freer rotation with an activation energy less than 3 kcal/mol,[7] but the motions of the carbonate group are apparently not restricted. These examples suggest a very important influence of molecular motions on mechanical properties. Molecular motions in solid polymers reveal themselves in relaxations probed by, for example, dynamic mechanical analysis (DMA). Typically, multiple peaks are observed in a DMA spectrum, which are labeled from higher to lower temperatures with the successive letters of the Greek alphabet α, β, γ, and so on. The α relaxation is associated with the glass transition process. In general, the β relaxation in polymer glasses forms a shoulder on the lower temperature side of the T_g and is actually due to structural relaxation rather than a specific motion because its appearance and shape depend on the thermal and mechanical histories of the specimen. On the other hand, the γ relaxation is only slightly affected by such histories and is usually due to motions of polymer segments or side groups. Molecular motion as demonstrated by main-chain secondary γ relaxation has long

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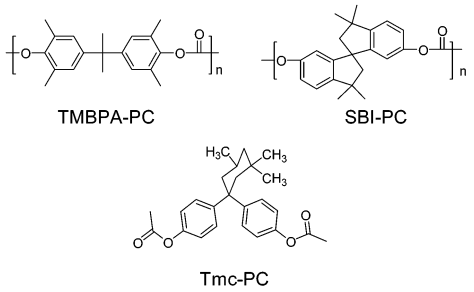

Figure 1. Chemical structures of TMBPA-PC, SBI-PC, and Tmc-PC.

been correlated with desirable mechanical properties, such as impact strength.[8,9] BPA-PC is well-known for its toughness and has also a pronounced γ relaxation at −100 °C (1 Hz). The correlation between this relaxation and its ability to yield and high toughness is well documented.[8−11] Jho and Yee[12] and Xiao and Yee[13] have proposed that a cooperative segmental motions involving several repeating units is the origin of the γ relaxation of BPA-PC; however, it is not the objective of this paper to further explore this relaxation.

The scale of segmental cooperativity in certain polymers can be curtailed or enhanced, as we attempt to show in this series of papers. In previous work, the terephthalate group was found to be a decoupler in multiblock copoly(ester carbonate)s.[14] The ether linkage group was believed to decouple the motions of the bisphenol unit from that of the sulfone unit in polysulfone.[15] These authors used results from DMA, yield stress, and toughness to support their conclusions. Chen, Yee, and Moskala[16] and Liu and Yee[17] discovered that by periodically inserting cyclohexylene rings (C-rings) into the backbones of polyesters or polycarbonates shear yielding became easier, while crazing strength was increased. The C-ring was shown by NMR[31] to undergo chair−boat−chair (CBC) conformational transition despite being part of the backbone. This inversion results in the excursion of adjoining groups, which must enhance the molecular motion. The C-ring inversion was also correlated by these authors to a characteristic γ relaxation peak in DMA.

In this paper, research designed to see whether the incorporation of these C-rings into the backbone of polymers with very bulky and rigid structures, such as SBI-PC, can still induce or enhance segmental molecular motion and thereby improve mechanical properties is described. Indeed, increases in the glass transition temperatures and also enhancement in their ability to yield were found. The physics behind these observations has been investigated. In this paper, the synthesis and characterization of these polymers are reported. Results on mechanical and relevant physical properties will be reported in companion papers. Before proceeding to describe the results, it is necessary to briefly summarize molecular motions known as γ relaxations associated with main-chain C-rings.

1.2. γ Relaxation Associated with Main-Chain C-Rings. Cyclohexane undergoes ring inversion in either the gaseous or the liquid state. The various kinetic parameters for the chair−chair interconversion, such as activation energy (ΔE^*), enthalpy of activation (ΔH^*), entropy of activation (ΔS^*), and preexponential factor f_0, have been established by various techniques, such as NMR,[18,19] IR,[20] and molecular simulation.[21,22] Generally, the equation expressing the rate of inversion is $f = f_0 e^{-\Delta E^*/RT}$, where the activation energy is 11 kcal/mol and the preexponential factor f_0 is 2×10^{13} Hz. So at room temperature, in both the solution and the gaseous states, cyclohexane rings undergo inversion at a rate of close to megahertz. Intuitively, in a polymer molecule, the motion of a backbone cyclohexyl ring should be much more restricted than in a liquid if indeed it is possible. However, chair−chair cyclohexyl ring interconversion was shown by Heijboer[23] in his study on dynamic mechanical properties of polymers containing saturated rings as side groups. Thus, a very strong case has been built to support the notion that this ring inversion is the origin of the γ relaxation in poly(cyclohexyl methacrylate) (PCHMA) and other polymers containing a C-ring as side groups or as plasticizers.[24] Heijboer's thesis was substantiated by the works of later researchers.[25−27]

The relaxation study of polymers with C-rings in the main chain is seldom reported. The earliest assignment of main-chain C-ring inversion as the molecular origin of γ relaxation in polymers appears to be by Baccaredda, Magagnini, and Giusti.[28] In a study of the secondary relaxation of poly(1,4-cyclohexylene ether) (PCHE) and poly(cyclohexylethylene oxide) (PCHEO), a prominent relaxation peak below T_g at 305 K (5260 Hz) was observed. The peak temperature was found at around 30 °C higher than that of PCHMA at the same frequency, and the peak itself was also wider. Main-chain C-ring inversion was considered by them as the basis for this γ relaxation. The broadening and upshift of the relaxation peak were tentatively attributed to the stronger hindrance (due to the bilateral enchainment of the cyclohexylene rings) which opposed the movement of the rings individually. Similar assignments came from some researchers even for polymer networks. In a study of dynamic mechanical properties of cycloaliphatic epoxy networks, a secondary relaxation peak at around −80 °C at 1 Hz was found by Udagawa et al.[29]

By comparison with the works of Heijboer[24] and Baccaredda et al.,[28] this relaxation was concluded to be due to molecular motions of the cyclohexyl rings. Later, a solid-state ^{13}C NMR study was performed on these polymer networks by the same authors;[30] from $T_{1\rho}^{C}$ measurements, the C-ring motions were found to be restricted and much slower than those in PCHMA. A series of copolyesters of poly(ethylene terephthalate) (PET) and poly(1,4-cyclohexylenedimethylene terephthalate) (PCT) with different amounts of main-chain C-rings were studied by Chen et al.[31] On the basis of DMA and solid-state ^{13}C NMR results, it was proposed that the secondary relaxation is caused by the C-ring inversion. Dipolar rotational spin echo ^{13}C NMR was used to detect large-amplitude molecular motions of the cyclohexylene rings of the copolyesters and PCT at 300 K. On the basis of these results, the hypothesis that there is active C-ring inversion in these main-chain polymers found strong support.[31] This hypothesis found further support in the work by Liu and Yee,[17] which incorporated cyclohexylene rings periodically into BPA-PC. It was found that the γ relaxation peaks of these copolymers were very different from those of BPA-PC; however, they were very similar to those of PCT in peak position and shape. The conclusion that the γ relaxation in these copolymers is caused by the chair−boat−chair transition of cyclohexylene rings was reported by these authors.[17] Furthermore, a very significant proof was provided by the DMA study of a poly(ester carbonate)

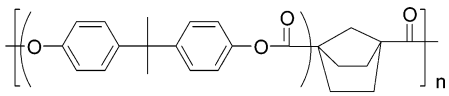

Figure 2. Polymer structure of B_3H.

B_3H (Figure 2).[32] In B_3H, the cyclohexylene ring is locked by a carbon bridge; hence, the conformational transition of C-rings from one chair conformation to another would not be possible. The relaxation peak typical of that involving C-rings was found to have disappeared, and a relaxation peak the same as that of BPA-PC was found to reemerge. By contrast, in dielectric and mechanical relaxations studies of polyformal networks containing C-rings in the backbone by Calleja et al.,[33] it was concluded that the γ relaxation (which are referred to as the β relaxation in their work) is due to the conformational changes in the skeletal bonds of the acyclic part of the polymer chain and not the main-chain C-ring inversion. This conclusion was based on the observation that the activation energy for the γ relaxation was around 18 kcal/mol, which was significantly larger than 11.5 kcal/mol, the energy involved in the chair−chair inversion.

1.3. Design of Polymers in This Study. As stated previously, the objective of this study is to explore whether the insertion of motionally active units into the backbone of an otherwise high-T_g but brittle polymer could induce ductile behavior. To this end three families of glassy polycarbonates/polyesters/poly(ester carbonate)s were examined. T_g was increased by using spirobiindane bisphenol (SBI), trimethylcyclohexylbisphenol (Tmc), and cyclohexylbisphenol (BPAZ) as the main backbone units. Some of these high-T_g polymers are brittle. The possibility of inducing segmental motion was provided by the insertion of cyclohexyl rings into the backbone via ester linkages.

2. Experimental Section

2.1. Synthesis. In this work, the molecular design called for the periodic insertion of C-rings into the backbone of polycarbonates via ester linkages. It might be ideal for testing properties of the copolymers if the block lengths are precisely controlled. However, it would take too much time and effort to synthesize large quantities of copolymers with precisely controlled block lengths. Moreover, the macroscopic behavior is probably not very sensitive to the regularity of the block length.[13] Consequently, the block copolymers were prepared using a relatively simple procedure, which included two steps. The first step was the synthesis of oligomers, and the second was the polymerization of the oligomers to form polymers with desired structures.

2.1.1. Starting Materials. Bisphenol A (BPA) (99+%), 4,4′-cyclohexylidenebisphenol, phenol, dihydroisophorone (3,3,5-trimethylcyclohexane-1-one), cumylphenol, *N*,*N*-dimethyl-4-aminopyridine (DMAP), *N*,*N*-dimethylaniline, triethylamine (Et3N), thionyl chloride, 1,4-cyclohexane dicarboxylic acid, anhydrous tetrahydrofuran (THF), silica gel (230−400 mesh), and Davison 12 silica gel were purchased from Aldrich Chemical Co. and used as received. 1.9 M (20 wt %) phosgene toluene solution was supplied by either Fluka Chemical Corp. or Matheson. These chemicals were also used as received without further purification. Solvents such as methylene chloride, 2-propanol, toluene, and hexanes were purchased from Aldrich Chemical Co. or Fisher Scientific, and were used as received.

2.1.2. Synthesis of Monomers. SBI (2,2′,3,3′-tetrahydro-3,3,3′,3′-tetramethyl-1,1′-spirobi[1*H*-indene]-6,6′-diol) was synthesized according to a patented method.[34] ^{1}H NMR (300 MHz, $CDCl_3$, ppm): 1.29 (s, 6H, CH_3), 1.35 (s, 6H, CH_3), 2.25 (q, 4H, CH_2), 2.9 (m, 1H, OH), 6.20 (m, 2H, arom H), 6.7 (m, 2H, arom H), 7.0 (m, 2H, arom H), 7.90 (m, 1H, OH).

Tmc (4,4′-(3,3,5-trimethylcyclohexylidene)diphenol) was made according to a reported method.[35] ^{1}H NMR (300 MHz, $CDCl_3$, ppm): 0.401 (s, 3H, CH_3), 0.972 (s, 6H, CH_3), 0.857−3.06 (m, 7H, CH, CH_2), 6.637−6.745 (2d, 4H, Ar H), 7.031−7.206 (2d, 4H, Ar H), 8.018−8.086 (2s, 2H, OH).

The synthesis of bischloroformates of SBI, Tmc, and cyclohexyl-BPA (BPAZ) was according to a reported method.[17]

Bischloroformate of SBI was recrystallized with hexanes, and the final yield was 48%. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): 1.35−1.398 (2s, 4H, CH_2); 2.237−2.418 (2dd, 4H, CH_2); 6.62 (m, 2H, Ar H), 7.08 (m, 2H, Ar H), 7.21 (m, 2H, Ar H).

Bischloroformate of Tmc was purified by column chromatography, using hexane:acetone = 10:1 as eluent; the product was obtained as a colorless viscous liquid, and the final yield was 67%. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): 0.323 (s, 3H, CH_3); 0.956 (s, 6H, CH_3); 0.819−2.615 (m, 7H, CH_1, CH_2), 7.034−7.375 (m, 8H, Ar H).

Bischloroformate of BPAZ was purified by column chromatography, using hexane:acetone = 10:1 as eluent; the product was obtained as a colorless viscous liquid, and the final yield was 83%. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): 1.53−2.34 (m, 10H, CH_1, CH_2); 7.06−7.34 (m, 8H, Ar H).

2.1.3. Synthesis of Polymers. *Synthesis of Polycarbonates*. Poly(oxycarbonyloxy-1,4-phenylene-3,3,5-trimethyl-1-cyclohexylidene-1,4-phenylene), TmcPC: In a 500 mL three-necked round-bottom flask, equipped with a magnetic stirring bar, a dropping funnel, and an air condenser, 10 g (32.21 mmol) of Tmc, 6.6 g (64.412 mmol) of triethylamine, and 0.8 g of *N*,*N*-dimethyl-4-aminopyridine (DMAP) were dissolved in 160 mL of anhydrous methylene chloride. The solution was then cooled to 0 °C using an ice water bath. Addition of 14.46 g (32.21 mmol) of bischloroformate of Tmc in 40 mL of methylene chloride was initially at a very high rate and was gradually slowed down toward the end of the reaction. The whole process took about 30 min. The reaction mixture was then allowed to warm to room temperature and kept for 1 h. Then 1 g of cumylphenol in 30 mL of methylene chloride was added to the viscous solution to end-cap the polymer chains. The solution was stirred for another 30 min 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 repeatedly (three times) redissolved in methylene chloride, precipitated from 2-propanol, filtered, and dried. 20 g (92%, yield) of TmcPC was obtained. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): 0.332 (s, 3H, CH_3), 0.97 (s, 6H, CH_3), 0.828−2.678 (m, 7H, CH_1, CH_2), 7.066−7.36 (m, 8H, Ar H).

Poly(oxycarbonyloxy-1,4-phenylene-1-cyclohexylidene-1,4-phenylene) or ZPC. The polymerization of ZPC was the same as that of TmcPC. A yield of 95% was obtained. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): 1.531 (m, 6H, side-chain C-ring), 2.252 (bs, 4H, side-chain C-ring), 7.144−7.166 (d, 4H, Ar H), 7.265−7.287 (d, 4H, Ar H).

Synthesis of Polyesters and Poly(ester carbonate)s with C-Rings in the Polymer Backbone. The copolymers were synthesized using the solution condensation polymerization method. For poly(ester carbonate)s, oligomers were synthesized first by unbalanced feeding of bisphenols and their corresponding chloroformates. 1,4-Cyclohexanedicarboxylic acid chloride was then introduced to form the block copolymers. Cumylphenol was the end-capping agent. The copolymers are denoted as Tmc_xC, TmcCBC, Z_xC, ZCBC, SCBC, and SC. Their structures are shown in Figure 3, and *x* represents the average number of repeat units within each bisphenol polycarbonate block. Typical procedures for making polyesters and poly(ester carbonate)s are shown for Tmc_1C and Tmc_3, respectively.

Tmc_1C: In a 500 mL three-necked round-bottom flask, equipped with a magnetic stirring bar, an air condenser, and an additional funnel, 10 g (32.21 mmol) of Tmc, 6.6 g (64.42 mmol) of triethylamine (TEA), and 0.8 g of *N*,*N*-dimethyl-4-aminopyridine (DMAP) were suspended in 160 mL of methylene chloride at 0 °C. 6.74 g (32.21 mmol) of 1,4-cyclohexanedicarboxylic acid chloride in 100 mL of methylene chloride

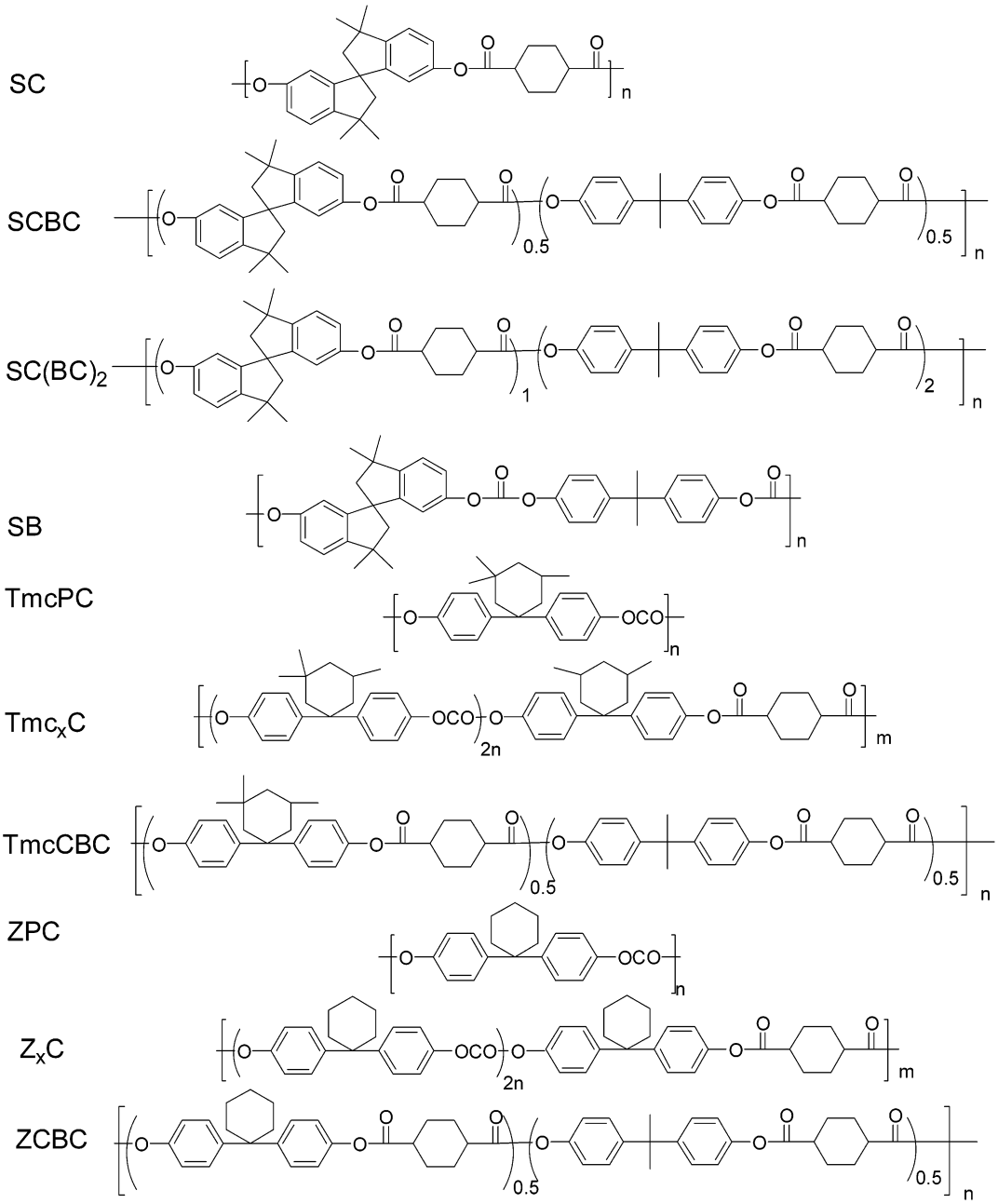

Figure 3. Chemical structures and short names for all the polycarbonates, polyesters, and poly(ester carbonate)s.

was added to the solution. The addition of 1,4-cyclohexanedicarboxylic acid chloride was initially at a very high rate and was gradually slowed down toward the end of the reaction. The whole process took about 30 min. 1 g of cumylphenol in 59 mL of CH_2Cl_2 was added to end-cap the polymer chain. After stirring the viscous polymer solution for another 30 min, the reaction mixture was then 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 redissolved thrice in methylene chloride, precipitated from 2-propanol, filtered, and dried. 14 g of Tmc_1C was obtained. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): 0.345 (s, 3H, CH_3); 0.976 (broad s, 6H, CH_3); 0.868−2.677(m, 17H, CH, CH_2); 6.88−7.36 (m, 8H, Ar H).

Tmc_3C: In a 500 mL three-necked round-bottom flask, equipped with a magnetic stirring bar, an air condenser, and an additional funnel, 10 g (32.21 mmol) of Tmc, 6.6 g (64.42 mmol) of triethylamine (TEA), and 0.8 g of *N*,*N*-dimethyl-4-aminopyridine (DMAP) were suspended in 160 mL of methylene chloride at 0 °C. 7.27 g (16.11 mmol) of bischloroformate of Tmc in 50 mL of methylene chloride was slowly added over a period of 50 min. The solution was then held at room temperature for another 30 min. 3.37 g (16.11 mmol) of 1,4-cyclohexanedicarboxylic acid chloride in 50 mL of methylene chloride was added to produce a very viscous solution. The addition of 1,4-cyclohexanedicarboxylic acid chloride was initially at a very high rate and was gradually slowed down toward the end of the reaction. The whole process took about 30 min. 1 g of cumylphenol in 59 mL of CH_2Cl_2 was added to end-cap the polymer chain. After stirring the viscous polymer solution for another 30 min, the reaction mixture was then 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 redissolved thrice in methylene chloride, precipitated from 2-propanol, filtered, and dried. 17 g of Tmc_3C was obtained. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): 0.345 (broad s, 9H, CH_3); 0.976 (broad s, 18H, CH_3); 0.835−2.68 (m, 31H, CH, CH_2); 6.88−7.36 (m, 24H, Ar H).

Table 1. Molecular Weight and Glass Transition Temperature of the Polymers

polymer	M_n	M_w	T_g/°C
SC	51K	778K	275
SCBC	39K	77K	246
SB	126K	262K	198
TmcPc	106K	204K	240
Tmc_5C	80K	137K	245
Tmc_3C	75K	119K	252
Tmc_1C	40K	84K	283
TmcCBC	66K	131K	257
ZPC	32K	79K	182
Z_5C	92K	164K	190
Z_3C	63K	109K	195
Z_1C	52K	111K	228
ZCBC	87K	171K	220

The molecular weights and glass transition temperatures are shown in Table 1.

2.2. Characterization. ^{1}H NMR and ^{13}C spectra (δ ppm) were recorded on either a Bruker AC-200 (200 MHz) or a Bruker AM-300 (300 MHz) spectrometer. Unless noted otherwise, all spectra were recorded in $CDCl_3$ or CD_3COCD_3 with TMS as an internal standard. D_2O was used to exchange phenolic hydroxyl proton whenever applicable. Relative molecular weights (M_w, M_n) and molecular weight distributions were determined using a Waters GPC at 35 °C with THF as solvent (1.0 mL/min). Waters 2487 UV detector at wavelength 254 nm was used to observe the retention times of the polycarbonates and their copolymers. The molecular weight obtained was relative to polystyrene standards, which were used to establish a calibration curve. The glass transition temperature T_g of the polymers was measured using a Perkin-Elmer DSC-7 at a heating rate of 10 °C/min. T_g was read as the midpoint of the transition in heat flow. All measurements were made under a nitrogen atmosphere, while cooling of the DSC cell was accomplished by using an ice/water bath.

2.3. Sample Preparation and Testing Conditions for DMA. Dry polymer powders were dissolved in CH_2Cl_2 to make 5% solutions. Each solution was filtered through a microfilter and spread on clean glass slides. The solvent was evaporated at room temperature overnight. The films were then floated off the glass slides with distilled water. They were placed under vacuum at 65 °C for 48 h to remove any residual solvent. All the films were visually clear and were confirmed to be amorphous by DSC scan. The dynamic mechanical analysis was performed using a TA Instruments 2980 DMA on amorphous films with typical dimensions of 8 mm × 5 mm × 0.1 mm (length × width × thickness) without further thermal treatment. A tensile displacement amplitude of 7 μm which resulted in a nominal strain of ~0.1% was applied. An autostrain of 150% was used to compensate for thermal expansion. The samples were run in the iso-step mode from −150 °C to close to T_g in 7.5 °C intervals with cooling achieved by a liquid nitrogen cooling accessory. The samples were held for 10 min at each testing temperature to allow thermal equilibration to occur. A sinusoidal displacement was applied at frequencies of 0.3, 1, 3, 10, and 30 Hz at each testing temperature.

3. Results and Discussion

3.1. Side-Chain C-Ring Characterization in ZPC and TmcPC. The aromatic parts of the ^{13}C NMR spectra of TmcPC and ZPC are shown in Figure 4. The assignment of the spectrum for ZPC has been reported by Zhao et al.[36] Because the cyclohexyl group undergoes rapid ring inversion, the two phenyl groups interchange

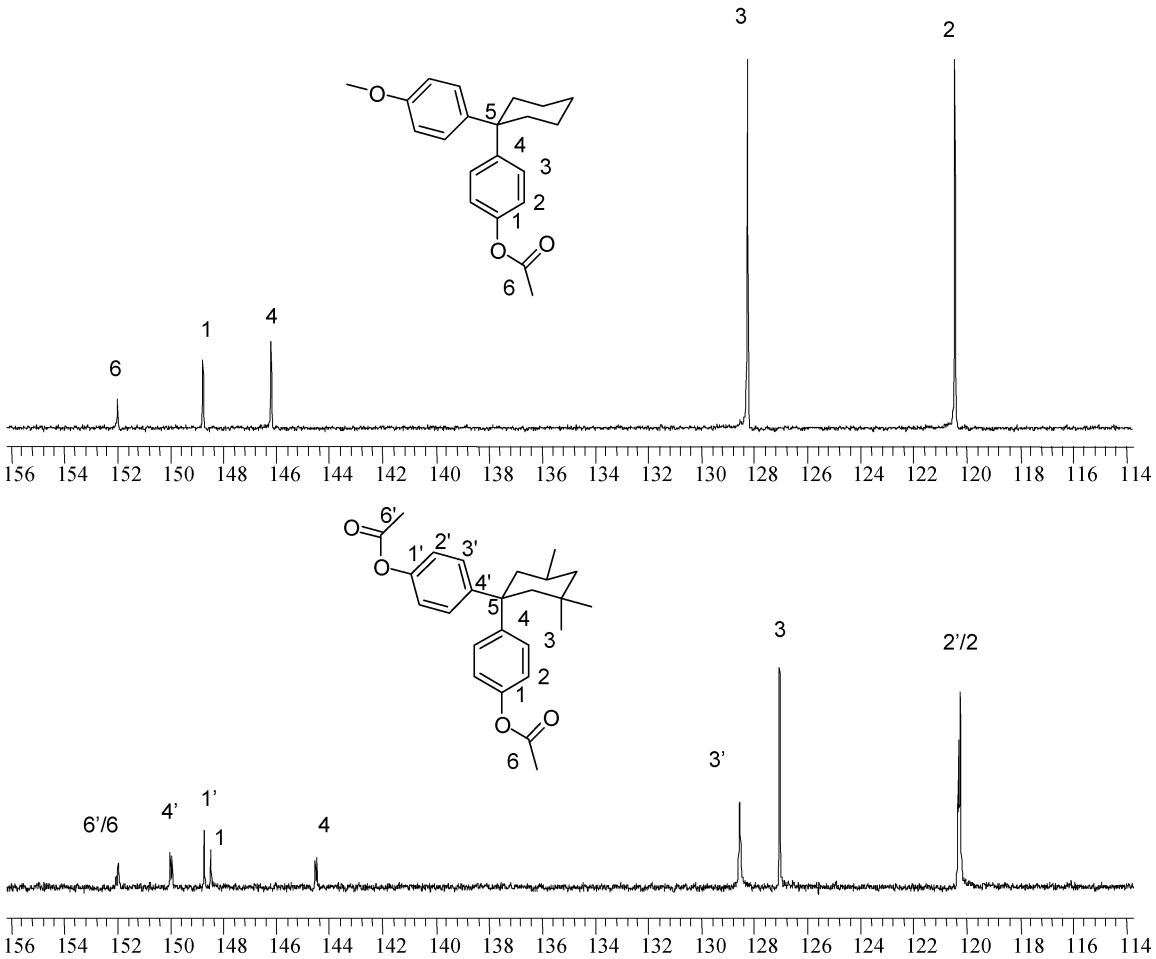

Figure 4. ^{13}C NMR of the polycarbonates of Tmc and BPAZ: aromatic region.

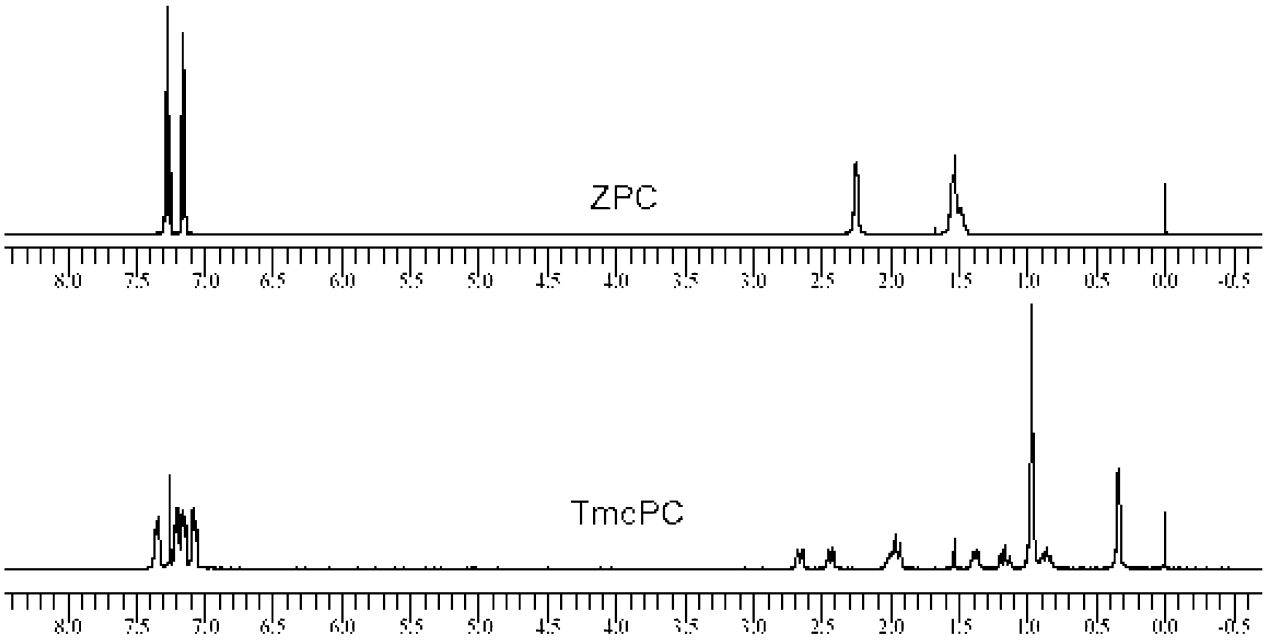

Figure 5. ^{1}H NMR of TmcPC and ZPC.

their positions from equatorial to axial rapidly in the time scale of chemical shift, so the two phenyl rings are equivalent, and have the same chemical shift. By contrast, in TmcPC, every carbon signal corresponding to ZPC is split into two peaks. This indicates that the two phenyl rings are no longer chemically equivalent: one is equatorial and the other axial. The chemical shifts around 144.5 and 150 ppm are assigned to carbon 4 and 4′, respectively. The chemical shift difference of ca. 6 ppm is within the range of an axial−equatorial ^{13}C shift for carbons directly bonded to a cyclohexyl ring. The assignment of the high field line at 144.5 ppm to the equatorial carbon is according to Zhao et al.[36] The chemical inequivalence of the two phenyl rings shows that the C-ring does not undergo rapid ring inversion in the time scale of chemical shift. This conclusion is further verified by ^{1}H NMR results as shown in Figure 5. For ZPC, in the aromatic region, the lower field set of signals is due to the hydrogen ortho to the oxygen group, while the upper field set is due to the hydrogen meta to the oxygen group; within each set, the peaks are from H−H couplings. In TmcPC, each set corresponding to ZPC is split into two. The signals from the two geminal methyl groups also confirm that the C-ring does not undergo ring inversion. The equatorial methyl group has chemical shift at 0.97 ppm, but the axial one exhibits a peak at 0.332 ppm, which is unexpectedly shifted to the upper field. This is because the C-ring is locked into a chair form; thus, the axial methyl group is held parallel to the axial phenyl ring. Consequently, the shielding effect from the phenyl ring current shifts the chemical shift of the axial CH_3 hydrogens to the upper field.

C-ring inversion is active in ZPC in solution but not observed in the solid state in the chemical shift time scale,[36] thus indicating that conversion on the millisecond time scale in the temperature range of −100 to 100 °C does not occur. If it occurs, it should be on a much longer time scale. This point will be discussed further along with the DMA results.

3.2. γ Relaxation. 3.2.1. Sub-T_g γ Relaxation of Polymers Based on SBI. The fact that SBI-PC has a γ relaxation similar to that of BPA-PC was reported by Stueben[4] three decades ago. Even though the peak position and intensity are essentially identical to that of BPA-PC, this polycarbonate was found to be extremely brittle. The brittleness of this polymer would not be surprising if the chemical structure of SBI is considered. The SBI moiety is bulky and locked in a twisted conformation. The phenyl rings cannot rotate unless the entire moiety moves as a unit, which is highly unlikely in the glassy state. The freezing-in process near T_g suggests that it should also be dominated by the bulkiness of the SBI unit. Presumably the lack of segmental motion makes the polymer very brittle. The γ relaxation of this polymer was also reported by Pessan et al.[44] and studied by Wimberger-Friedl and Schoo[5] in more detail. Wimberger-Friedl and Schoo concluded that the phenyl motion was not required for the typical γ relaxation of polycarbonate at low temperature, and the relaxation was from the motion of carbonate groups, though this possibility is disputed by recent NMR results from Schaefer's group.[45]

The DMA spectra are changed drastically by the incorporation of C-rings into the polymer backbones. Shown in Figure 6 are the DMA 1 Hz spectra for SBI-PC, SB, BPA-PC, SC, and SCBC. At around −70 °C, a prominent peak appears in SC and SCBC; the γ peak typical of polycarbonate for SBI, SB, and BPA at around −100 °C is not exhibited by these two polymers. The new peak at −70 °C either could be due to a shift to higher temperatures by the γ peak typical of PC's or is related to that in PCT[31] due to similarities in both shape and peak position. In SC, the motions are much simpler than those of PCT; motions of the C-ring, its neighboring ester groups, and their cooperative motion are the only possibilities. Since the introduction of ester groups into BPA-PC does not generate a new relaxation peak at all,[37] the new peak at −70 °C cannot be due to the ester group alone. So the most probable motion is that of C-ring inversion. This inversion probably involves the cooperative motion with its neighbor ester groups. By having the BPA moiety on the backbone of SCBC, one could reasonably expect the secondary relaxation peaks

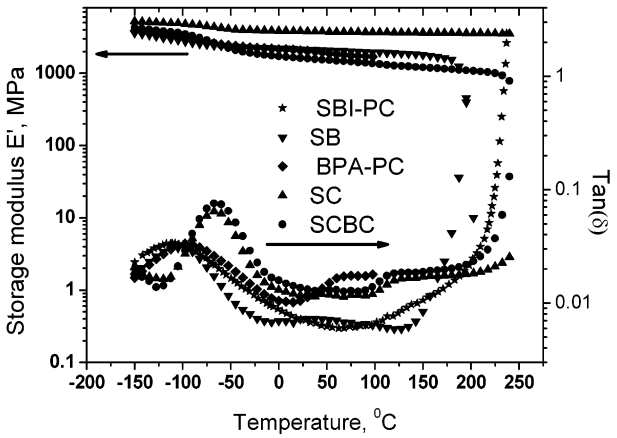

Figure 6. DMA spectra of SBI-PC, SB, SC, BPA-PC, and SCBC at 1 Hz. The spectrum of SBI-PC is reproduced from the work of Pessan et al.[44]

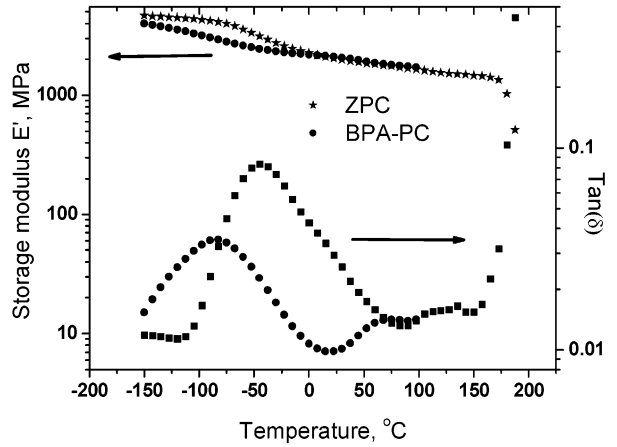

Figure 7. DMA spectra of ZPC and BPA-PC at 10 Hz.

to be different, yet its DMA spectrum is basically the same as that of SC. The similarity in the DMA spectra among these polymers and their similarity to that of PCT suggest strongly that all of them involve C-ring motion, and most probably the ring inversion, if the NMR results for PCT are taken into account. This conclusion will be further corroborated in the following sections.

3.2.2. γ Relaxation of Polymers Based on BPAZ. The DMA spectrum of ZPC does not follow the general observation that the γ relaxation of BPA-based polycarbonates is not changed by the replacement of the isopropylidene groups.[11] In fact, replacement of the isopropylidene group by a cyclohexyl group shifts the γ relaxation peak up by nearly 40 °C at 10 Hz (see Figure 7). This upshift was reported by McHattieet al.[38] and by Hörth et al.[39] An explanation for the origin of this relaxation was not offered, but the assertion that the flexible cyclohexyl ring improved the chain packing was made by McHattie et al.[38] This assertion provided the basis for explaining the occurrence of the relaxation at a higher temperature because of a smaller free volume. This free volume explanation has two shortcomings. First, the upshift of nearly 150 °C at 1 Hz of the γ relaxation of tetramethylbisphenol A polycarbonate compared with that of BPA-PC[11] cannot be explained by free volume effects because the free volume of the former is larger than that of the latter;[40] second, the amount of free volume depends on the method used to obtain it. The occupied volume at 0 K needs to be

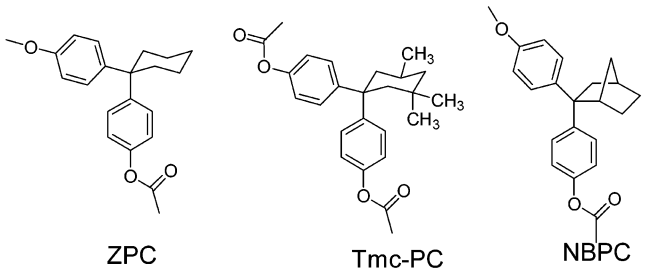

Figure 8. Chemical structures of ZPC, Tmc-PC, and NBPC.

estimated in order to calculate the free volume, but different estimation methods such as those of Sugden and of Bondi give quite different results.[38] The free volume explanation is therefore rendered ambiguous. Finally, the notion that free volume allows motion is given by McHattie et al. The opposite causal relationship, i.e., excited motion gives rise to free volume, was not offered by these authors. Although this notion is controversial, it is beyond the scope of this work to discuss it. Solution- and solid-state NMR studies on the dynamics of ZPC were conducted by Zhao et al.[36] In solution, the C-rings were observed to undergo rapid ring inversion with an activation energy of 6.7 kcal/mol and correlation time prefactor of 6.5×10^{-11} s. But in the corresponding solid ring inversion in the chemical shift time scale over the temperature range of −100 to 100 °C was not found, which meant that if ring inversion did occur, its rate must have been slower than kilohertz. In the solution state at low temperature as well as in the solid state, the two phenyl rings are not equivalent, as observed by these authors. The axial phenyl ring was found to be much more restricted in motion than the equatorial ring, and from the line shape analysis of the bridging carbon linking the two phenyl rings, an activation energy of 12.9 kcal/mol for the relaxation was calculated. On the basis of these results, shifting of the γ relaxation peak due to the more restricted motion of the axial phenyl ring was proposed. This explanation appears plausible but may not be the main reason if other molecular structures are considered.

As discussed in the above, in TmcPC, there exists severe steric interactions between the axial phenyl ring and the axial methyl group as evidenced by NMR results. This is also true in bisphenol norbornane polycarbonate (NBPC) (see Figure 8). But TmcPC has a γ relaxation peak much like that of BPA-PC. This will be shown later in the discussion of the relaxation of Tmc polymers. NBPC was also shown to have a similar relaxation peak to that of BPA-PC.[38] So obviously, the large upshift in the temperature of the γ relaxation of ZPC cannot be explained by the restricted rotation of phenyl rings alone. In solution, the C-rings in both TmcPC and NBPC have not been observed to undergo ring inversion, but in ZPC fast chair−chair conformational transitions are observed. In the solid state a relaxation peak at around −50 °C at 10 Hz, which is typical of relaxations involving C-ring inversion, is not observed in TmcPC or NBPC, while in ZPC it is observed. Thus, the dominance of C-ring inversions in causing the upshift and broadening of the γ relaxation peak is suggested.

The shape and position of the γ relaxation peak in ZPC, compared to SBI-PC (see Figure 9), are not changed dramatically by the incorporation of C-rings into the polymer backbone. The peak shapes and peak positions remain the same. When main chain C-ring

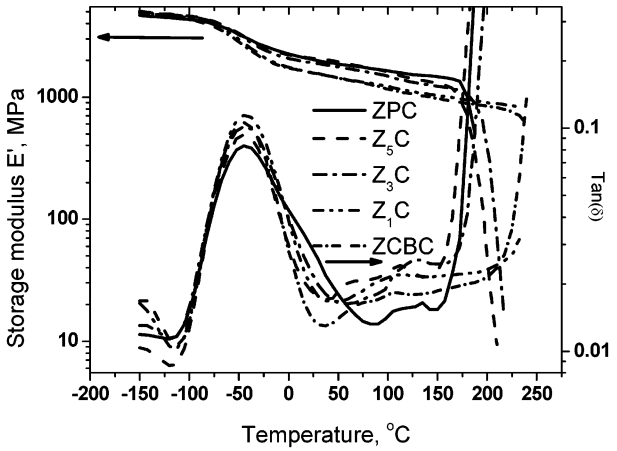

Figure 9. DMA spectra of ZPC, Z_xC, and ZCBC at 10 Hz.

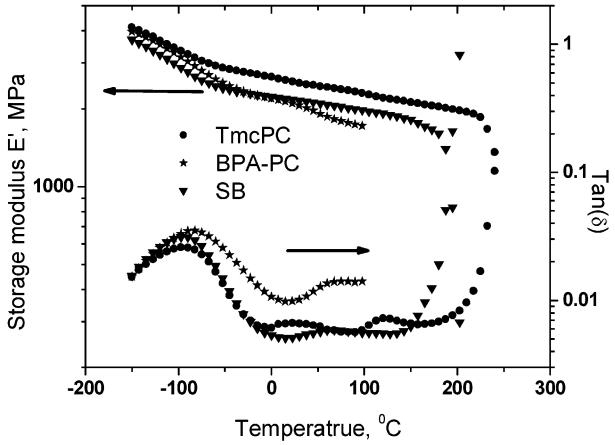

Figure 10. γ relaxation of TmcPC, SB, and BPAPC at 10 Hz.

content is increased from ZPC to Z_1C, the damping peak intensity and the relaxation strength (change in the storage modulus) are both increased. The change in the damping peak intensity with the change in main-chain C-ring content suggests strongly the conclusion that main-chain C-rings are involved in the γ relaxation in the BPAZ polymers. The similarity in peak position and peak shape indicates that ZPC, ZCBC, and Z_xC have similar relaxation mechanisms, which all involve C-rings. The peak in ZPC involves side-chain C-rings, while that in Z_xC involves both side-chain and main-chain C-ring inversion. The similarity between the motions of side-chain and main-chain C-rings is not surprising since they are identical in mechanism; the only difference is the degree of their coupling with their neighbors. The degree of this coupling is difficult to determine but may be inferred from the change in other properties with the change in C-ring content. In describing DMA damping peak intensity for ZPC, ZCBC, and Z_xC, not only the change in main-chain and side-chain C-ring concentration but also the total C-ring concentration need to be considered. This may explain why ZCBC has a lower peak intensity than Z_1C, for even though it has the largest main-chain C-ring content, its total C-ring concentration is smaller. This will be elaborated on later in a quantitative discussion of the correlation between relaxation strength and total C-ring concentration. An activation energy of 13.4 kcal/mol and prefactor of 6.0×10^{13} s^{-1} are calculated for the γ relaxation of ZPC according to the peak position and its corresponding frequency. At room temperature and 100 °C, the ring flipping frequency should be around 10 and 85 kHz, respectively. Now, if the γ relaxation in ZPC is due to the C-ring inversion, then why do the solid-state NMR results by Zhao et al.[36] show that the C-ring inversion does not occur on the millisecond scale? There are two possible ways to explain the apparent discrepancy. First, the frequencies calculated according to the activation energy and prefactor are only for the peak position. Since the relaxation peak is very broad (at 1 Hz it covers the range from around −110 to 50 °C), at a fixed frequency and temperature, some relaxations may be activated, while others are not; second, the solid-state NMR spectrum by Zhao et al.[36] has very broad peaks: the resonance at 143 ppm is the 4e carbon (the labeling is the same as that in Figure 4), and the 4a carbon is obscured by the C1 resonance at 150 ppm. The collapsed signal for C4 due to rapid ring inversion should be around 147 ppm according to their solution NMR results, but this is also obscured by the C1 resonance. So it is very possible that some C-rings do undergo rapid ring inversion, but its signal is obscured by the broad line width. By taking all the results discussed so far into account, the conclusion that the γ relaxation in ZPC involves the C-ring inversion can be drawn.

3.2.3. γ Relaxation of Polymers Based on Tmc. The TmcPC peak (tan δ) is much narrower and has a smaller peak intensity than that of BPA-PC. The peak position is around 10 °C lower than that of BPA-PC peak at 10 Hz (see Figure 10). As discussed in the polymer structure section, the bulky side chain C-ring on TmcPC is locked in a chair form in the time scale of NMR chemical shift due to the severe steric interaction between the axial phenyl ring and the axial methyl group. It was shown in solution ^{13}C NMR study by Hägg et al.[7] that the axial phenyl ring has a much restricted motion with an activation energy of about 10 kcal/mol, while the equatorial phenyl ring has a much freer rotation with an activation energy less than 3 kcal/mol. The 10 kcal/mol rotational activation energy is much larger than that in BPA-PC in solution, which is around 3 kcal/mol as reported by O'Gara et al.[41] The narrowing of the peak on the high-temperature side may be accounted for by this restricted motion of axial phenyl ring. This conjecture can be corroborated by the result in the SB polymer. The SBI moiety does not have the ability to rotate its phenyl rings. The relaxation peak, as shown in Figure 10, is also much narrower than that of BPA-PC. Furthermore, the γ relaxation peaks of SB and TmcPC are strikingly similar. This phenomenon was also observed by Wimberger-Friedl and Schoo[5] in their DMA study of copolycarbonates of SBI and BPA. With the increase in BPA content in the copolymer, the higher temperature side of the DMA curve is broadened systematically. This broadening was attributed to the contribution of BPA's motion, specifically, the phenyl ring motions. Figure 11 shows the γ relaxation peak of TmcPC, the copolymers Tmc_xC, and TmcCBC. As with main-chain C-ring incorporation in SBI polymers, the γ relaxation behavior of these polymers changes dramatically. The peak of TmcPC disappears, and a new peak typical of the relaxation with C-ring inversion emerges at a higher temperature in Tmc_xC and TmcCBC. In Tmc_5C and Tmc_3C, the peaks are more asymmetric with a trace of TmcPC's relaxation on the lower temperature side. With increase in C-ring content, the damping peak intensity also increases and the peak

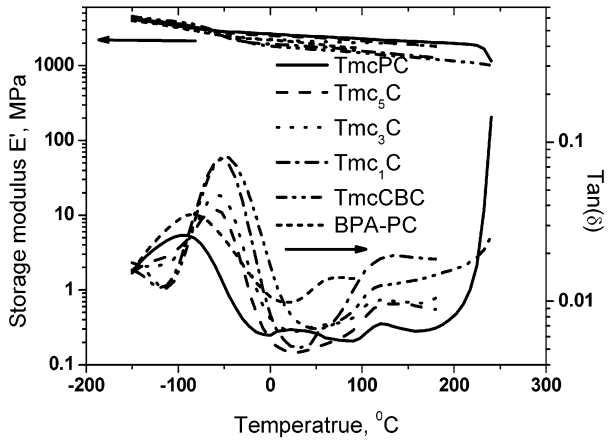

Figure 11. γ relaxation of polymers based on Tmc at 10 Hz.

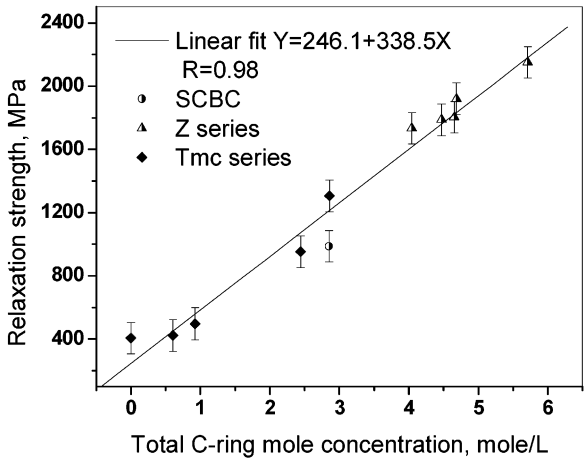

Figure 12. Correlation between the relaxation strength and the total C-rings mole concentration for polymers based on SBI, Tmc, and BPAZ.

broadens. This change in intensity with C-ring content can be due to two reasons. First, molecular motion can be enhanced by the C-ring incorporation; second, a pure concentration effect is at work here. To understand this and also explain the similar question in polymers based on BPAZ, the γ relaxation is discussed quantitatively in terms of relaxation strength.

3.2.4. Relaxation Strength. A suitable quantitative parameter to describe a relaxation, besides the peak position, the activation energy and the breadth of the relaxation, is the relaxation strength. In DMA the effect of activating a molecular motion on the modulus is indicated by relaxation strength. It can be obtained from the change in storage modulus or loss modulus with temperature. Heijboer's method in obtaining the relaxation strength[23] is followed here.

As shown in Figure 12, there is a nice linear correlation between the relaxation strength and the C-ring mole concentration. Only main-chain C-rings for polymers based on SBI and Tmc are included in the molar C-ring concentration since they do not have side-chain C-rings; however, for polymers based on BPAZ, both main-chain and side-chain C-rings are included in the total concentration. This linear correlation indicates that there is no difference in effect, at least in terms of relaxation strength, between the side-chain C-rings and main-chain C-rings. A strong coupling between the side-chain C-ring on the BPAZ moiety and backbone phenyl rings was reported by Zhao et al.[36] On this basis, the

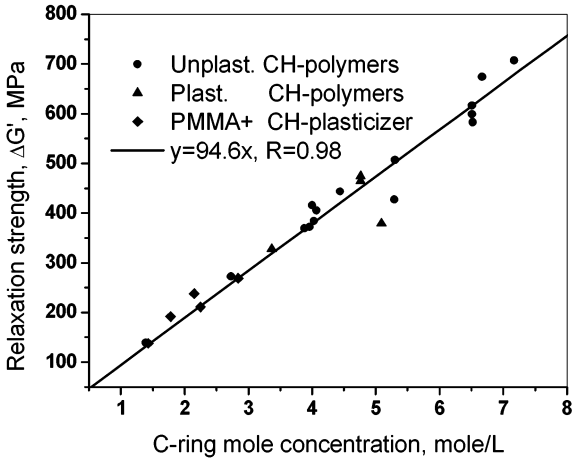

Figure 13. Relaxation strength of cyclohexyl motion vs C-ring concentration for polymers containing the cyclohexyloxycarbonyl group in the polymer or in the plasticizer.

main-chain C-ring could be expected to have the same or stronger coupling with their neighbors, but the degree of coupling cannot be determined by the DMA results obtained thus far. A linear dependency of relaxation strength $\Delta G'$ on the number of C-ring groups per unit volume (see Figure 13) has been demonstrated by Heijboer,[23] who also found that the local environment of the group had no effect on $\Delta G'$. It does not matter whether the C-ring is part of a plasticizer molecule or part of the side chain in a plasticized or nonplasticized polymer. Even though, there is a linear correlation between the relaxation strength and the C-ring concentration in both Heijboer's system and ours; the value of relaxation strength per mol/L of C-rings is different. Since $\Delta G'$ was used by Heijboer and $\Delta E'$ was used in the current work, the results cannot be compared directly. However, using $\Delta E' = 2\Delta G'(1 + \mu)$ by assuming that $\mu = \mu'$ and by assuming Poisson's ratio μ to be 0.38, Heijboer's results can be compared with the current results. Thus, $\Delta E'$ is around 261 MPa per mol/L for Heijboer's polymers, which is much smaller than the 338 MPa per mol/L of polymers studied in this work. This difference is too large to be caused by any error in converting from G' to E', which should introduce an uncertainty of around 20 MPa per mol/L at most. However, the relaxation strength is related to ΔU_0, the conformational energy difference between one chair form and the other one after ring inversion.[23,42] The smaller ΔU_0 is, the larger the relaxation strength should be. The C-rings in Figure 13 have $\Delta U_0 = 0.7$ kcal/mol. For C-rings with $\Delta U_0 = 0$, $\Delta G'$ was 113 MPa per mol/L,[42] which after conversion into $\Delta E'$ is around 312 MPa per mol/L, which can be compared favorably with 338 MPa per mol/L of our polymers. Since ΔU_0 of C-rings in BPAZ is 0 kcal/mol, and those in main-chain C-rings are around 2.2−2.4 kcal/mol (estimated by assuming an equatorial ester group is favored by 1.1−1.2 kcal/mol over an axial one[43]) they may have different relaxation strengths, but the difference is within experimental error.

4. Conclusions

From solution NMR, it has been shown that the side-chain C-rings on the Tmc moiety are locked in a chair form because ring inversion in the time scale of chemical shift did not take place. On the other hand, the C-rings on ZPC invert rapidly in solution, and by analysis of

solid-state NMR results in the literature and our DMA results, it can be concluded that the ring inversion is still active in the solid state. Similar peak positions and shapes to those of BPA-PC were exhibited in the DMA spectra of polycarbonate of SBI and Tmc, but they are much narrower on the high-temperature side. This narrowing is from the lack of phenyl ring motion in SBI and the restricted axial phenyl ring rotation in Tmc. The γ relaxation peak in ZPC is upshifted nearly 40 °C at 10 Hz compared to that of BPA-PC. From the peak position, shape, and activation energy, it is proposed that this relaxation peak is due to the inversion of the side-chain C-rings with coupling to the backbone motion. The incorporation of main-chain C-rings changes the DMA spectra dramatically in Tmc and SBI polymers but causes no significant change in ZPC polymers except the damping intensity and relaxation strength. The peak typical of BPA-PC disappears in Tmc_xC, TmcCBC, SC, and SCBC, but a new peak, which is typical of the relaxation involving C-ring inversion, is revealed. This is in line with the DMA behavior of polymers based on ZPC. As the relaxation peak in ZPC is in part due to the side-chain C-ring inversion, the incorporation of main-chain C-ring inversion does not generate a new peak but merely changes the peak intensity. All the DMA spectra are analyzed in terms of relaxation strengths. There is a linear correlation between the relaxation strength and the total C-ring concentration in our polymers. The relaxation strength is similar to that in Heijboer's system, namely, polyacrylic polymers.

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