Effect of Linkage Groups on Motional Cooperativity in the Secondary Relaxations of Some Glassy Polymers

Lei Li and Albert F. Yee*

Macromolecular Science and Engineering Center, University of Michigan, Ann Arbor, Michigan 48109

Received May 31, 2001

ABSTRACT: The secondary relaxation of bisphenol A polycarbonate (BPA-PC) is due to a cooperative motion that includes several repeat units. We believe that the linkage between neighboring BPA segments plays an important role in requiring this long-range cooperativity. It is expected that a more flexible linkage would require less motional cooperativity. To demonstrate this idea, polyformals based on the comonomer BPA, tetramethylbisphenol A (TMBPA), and methylene chloride with controlled sequence structure were synthesized, and DMA studies were conducted. The results show that the secondary relaxation behavior of copolyformals is not dependent on the block length of BPA segments, which suggests that the molecular motion does not require in-chain cooperation. The lower in-chain motional cooperativity of BPA-PF is attributed to the lower rigidity of the formal linkage.

Introduction

The secondary relaxations of glassy polymers have been widely studied in the past several decades since these relaxations have been generally correlated to the mechanical behavior of the glassy polymers. In a broad review, Boyer[1] compared the temperature dependence of impact strength of several polymers to their secondary relaxation peaks and found that transitions occur near loss peak temperatures. However, other researchers have disputed the existence of any general correlation.[2−4] In addition to the differences in frequencies and experiment variables between the varying types of tests, as noted by Heijboer,[5] the key reason for the failure of the general correlation may be the different nature of the molecular motions that contribute to the secondary relaxation. Heijboer asserted that if a secondary relaxation is caused by main-chain motions, it is generally connected with an appreciable increase in impact strength; however, if a secondary relaxation is caused by side-chain motions, it has little influence on the impact strength. Heijboer's results suggest that the molecular origin of the secondary relaxation of glassy polymers is key to understanding the correlation between secondary relaxations and mechanical behavior of glassy polymers.

Secondary relaxations of glassy polymers have been characterized by dynamic mechanical analysis (DMA), dielectric spectroscopy (DS), NMR, and neutron scattering. DS and NMR are more powerful for probing the motions of special chemical groups. However, these local motions may not necessarily be related to mechanical secondary relaxation, because the probes are not mechanical in nature. Although DMA cannot be used to determine the molecular origin of the secondary relaxation directly, it is possible to obtain definitive information when a homologous series of polymers is investigated.[6] The molecular origin of the secondary relaxation of bisphenol A polycarbonate (BPA-PC) has been extensively investigated. Several chemical groups along the backbone are capable of motion: rotation of the methyl groups in the isopropylidene group, a rocking motion of the isopropylidene group and of the carbonate group, and flips of the phenylene groups. NMR studies provided the temperatures at which these chemical groups move. Davenport[7] found that the low-temperature relaxation process (−193 to −123 °C at 24.5 MHz) was correlated to the onset of the methyl rotation. Smith[8] asserted that the methyl rotation is activated between −150 and −100 °C at about 100 kHz, while the flip of phenylene groups is activated between −30 and 10 °C. However, it was uncertain whether the molecular origin of the secondary relaxation is due to one of the independent motions mentioned above or a cooperative segmental motion. Cooperative segmental motions are collections of local motions from various chemical groups, which interrelate to each other in certain ways. The scale of cooperative segmental motion, i.e., motional cooperativity, is the number of chemical groups involved in this cooperative segmental motion. Some researchers[9−11] believed that the molecular origin of the secondary relaxation of BPA-PC is the cooperative motion of the carbonate group and the neighboring phenylene group. Davenport[7] indicated that two methyl groups and two neighboring phenylene groups have to move as one unit. A comprehensive review of the previous studies of the secondary relaxation of BPA-PC was conducted by Yee and Smith.[12] They concluded that the independent motions of small molecular moieties by themselves could not induce the mechanical loss of the secondary relaxation since each provides only small volume fluctuations, if any. They further concluded that the molecular origin of the secondary relaxation of BPA-PC must be a cooperative segmental motion and the motion extends to at least one entire repeat unit. Jones[13] proposed that the secondary relaxation of BPA-PC involves a conformational interchange between neighboring carbonate groups from cis−trans to trans−trans conformational states accompanied by flips of the adjacent phenylene rings. In Jones' model, clearly the cooperative motion extends to more than one repeat unit. More recently, Shih and Chen[14] observed long-range cooperative motions composed of two repeat units

10.1021/ma010943w CCC: $22.00
Published on Web 12/14/2001

in BPA-PC based on molecular dynamics simulation. In addition to in-chain cooperation, interchain cooperation was also studied. Yaris[15] performed a generalized Langevin dynamics simulation on BPA-PC and concluded that interchain cooperation plays an important role in the secondary relaxation. There is a general consensus among recent researchers that the secondary relaxation of BPA-PC is a cooperative motion although the exact nature of the motion remains unclear.[16] Jho and Yee[6] and later Xiao and Yee[17] were able to estimate the extent of the in-chain cooperation. They investigated the secondary relaxation behavior of a series of copolycarbonates based on BPA-PC and tetramethylbisphenol A (TMBPA) PC and found that only when the block length of BPA segments is larger than seven can the relaxation peak of BPA-PC reemerge. On the basis of this result, they concluded that the secondary relaxation of BPA-PC is a cooperative motion and the molecular motion extends to seven repeat units. Later, Marks[18] investigated the secondary relaxation behavior of the copolycarbonates based on BPA-PC and tetrabromobisphenol A PC. He also found that the secondary relaxation behavior of the copolymers is strongly dependent on the block length and arrived at a similar conclusion. These results demonstrate unambiguously that large-scale in-chain cooperative segmental motion exists in the secondary relaxation of BPA-PC. Xiao and Yee[19] further concluded that this large-scale cooperative motion in BPA-PC is key to its ductile behavior and impact strength. This research, along with earlier results by Heijboer,[5] suggests that the scale of the molecular motion in the secondary relaxation is closely related to the mechanical behavior of glassy polymers. This idea was further supported by Liu and Yee.[20] On the basis of the study of two series of polyestercarbonates containing 1,4-cyclohexylene group, they proposed that chair−boat−chair conformational transitions of cyclohexylene group could couple with the motions of neighboring segments and give rise to large-scale cooperative motion. This motion increases the dynamic volume fluctuations and thus facilitates ductile shear yielding.

Although the role of interchain interaction has not been clearly understood in the secondary relaxation in BPA-PC,[6] we have already seen clearly that the large-scale in-chain cooperative segmental motion is strongly correlated to ductile and tough behavior. To further improve the mechanical behavior of polymers and provide valuable information on new polymer design, it is important to understand which factors influence the motional cooperativity. Linkage groups, such as ether and ester, are chemical moieties that connect two neighboring segments by covalent bonds. It is believed that the rigidity of linkage groups influences the motional cooperativity between two neighboring segments on both sides of the linkage. Paul and co-workers[16] conducted DMA studies on a series of poly(ether sulfone)s and found that long-range in-chain cooperative motion is not required in the secondary relaxation of these polymers. By comparing the secondary relaxation behaviors of poly(ether sulfone)s to that of polycarbonates, they further concluded that more flexible linkage groups might provide weaker coupling. However, when they compared two polymers, they changed not only the linkage groups but also the neighboring segments, which renders their conclusion ambiguous. To validate their idea, further research is required. The carbonate linkage in BPA-PC is similar to the ester linkage.

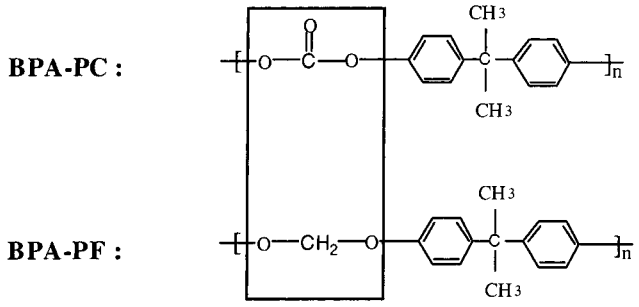

Figure 1. Chemical structure of BPA-PC and BPA-PF.

Because of the resonance effect, the two bonds between the carbonyl carbon and the ether oxygens are partial double bonds. This character renders the carbonate linkage more rigid than a single bond, and we believe this may be the cause for the cooperative nature of the secondary relaxation of BPA-PC. To verify this idea, in this research, we replaced the carbonate linkage with a more flexible linkage, formal (−O−CH_2−O−) linkage in which the resonance effect does not exist. The chemical structures of BPA-PC and BPA-polyformal (PF), as shown in Figure 1, are exactly the same except for the linkage groups. Following Xiao and Marks' approach,[17,18] we synthesized a series of copolyformals with controlled sequence structure and investigated the linkage effect by comparing DMA results of polyformals to that of polycarbonates.

Experimental Section

A. Synthesis. A series of copolyformals based on the comonomer BPA, TMBPA, and methylene chloride with controlled sequence structure were synthesized. Because the reactivity of BPA is higher than TMBPA due to the steric effect, we changed the feed sequence to control the sequence structure. A series of homopolymers, namely, BPA-PF, dimethylbisphenol A (DMBPA)-PF, and TMBPA-PF were also synthesized to further clarify the motional cooperativity in the secondary relaxations of polyformals. These homopolymers were synthesized by Hay[21−23] previously. In this research, we followed Hay's synthesis procedure. The chemical structures of these polyformals and copolyformals are shown in Figure 2.

Starting Materials. Methylene chloride, 4-methoxyphenol, 1-methylpyrrole (NMP), potassium hydroxide, chloroform, acetone, methanol, HCl solution, BPA (99+%), and DMBPA (98+%) were supplied by the Aldrich Co. and used without further purification. TMBPA was kindly donated by the Bayer Co.

Synthesis of BPA-PF. Into a 250 mL flask equipped with a magnetic stirrer and a reflux condenser were charged BPA (13.68 g), 4-methoxyphenol (0.111 g), methylene chloride (49.32 g), and 90 mL of NMP. The mixture was stirred under nitrogen until a homogeneous solution was obtained. At this point KOH (11.16 g) was added. The mixture was at 75 °C under nitrogen for 4 h. Then the reaction mixture was precipitated in methanol (500 mL). The precipitate was filtered and washed twice with water and once with 5% HCl solution. The polymer was further purified by precipitation from chloroform in methanol and then from chloroform in a 1/1 (v/v) mixture of acetone/methanol.

Synthesis of DMBPA-PF. The synthesis procedure of DMBPA-PF is the same as BPA-PF except that 4-methoxyphenol was not used. In the case of BPA-PF, the reactivity of BPA is so high that 4-methoxyphenol is added to control the molecular weight. The reactivity of DMBPA is lower than that of BPA, and addition of 4-methoxyphenol, which will result in low molecular weight, is not necessary.

Synthesis of TMBPA-PF. The synthesis procedure of TMBPA-PF is the same as that of DMBPA-PF.

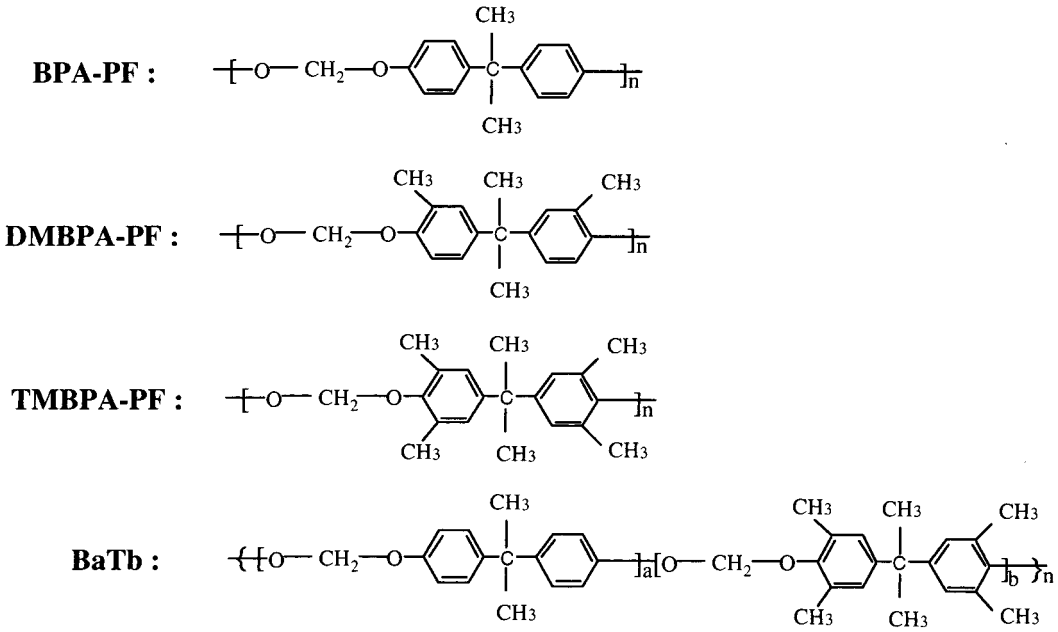

Figure 2. Chemical structure of polyformals.

Synthesis of B1T9-PF. Into a 250 mL flask equipped with a magnetic stirrer and reflux condenser were charged BPA (0.91 g), TMBPA (10.22 g), methylene chloride (32.88 g), and 60 mL of NMP. The mixture was stirred under nitrogen until a homogeneous solution was obtained. At this point KOH (7.44 g) was added. The mixture was at 75 °C under nitrogen for 4 h. Then the reaction mixture was precipitated in methanol (500 mL). The precipitate was filtered and washed twice with water and once with 5% HCl solution. The polymer was further purified by precipitation from chloroform in methanol and then from chloroform in a 1/1 (v/v) mixture of acetone/methanol.

Synthesis of B4T4-PF. Into a 250 mL flask equipped with a magnetic stirrer, an addition funnel, and a reflux condenser were charged TMBPA (5.68 g), methylene chloride (16.44 g), and 30 mL of NMP. The mixture was stirred under nitrogen until a homogeneous solution was obtained. At this point KOH (7.44 g) was added. The mixture was heated. In about 10 min, a solution of BPA (4.56 g), methylene chloride (16.44 g), and 30 mL of NMP was added drop by drop. It took about 1 h to finish adding the solution. During the process, the temperature was controlled at 75 °C. The mixture was at 75 °C under nitrogen for another 2 h. Then the reaction mixture was precipitated in methanol (500 mL). The precipitate was filtered and washed twice with water and once with 5% HCl solution. The polymer was further purified by precipitation from chloroform in methanol and then from chloroform in a 1/1 (v/v) mixture of acetone/methanol. The ^{1}H NMR analysis showed that the number-average block length of the copolymer is around 4. Therefore, the copolymer is named B4T4-PF.

Synthesis of B2T2-PF. Into a 250 mL flask equipped with a magnetic stirrer, an addition funnel, and reflux condenser were charged BPA (0.34 g), TMBPA (2.84 g), methylene chloride (9.45 g), and 18 mL of NMP. The mixture was stirred under nitrogen until a homogeneous solution was obtained. At this point KOH (3.72 g) was added. The mixture was heated, and at the same time, a solution of BPA (1.94 g), methylene chloride (6.99 g), and 12 mL of NMP was added drop by drop. It took about 35 min to finish adding the solution. During the process, the temperature was controlled at 75 °C. The mixture was at 75 °C under nitrogen for another 1 h. Then the reaction mixture was precipitated in methanol (500 mL). The precipitate was filtered and washed twice with water and once with 5% HCl solution. The polymer was further purified by precipitation from chloroform in methanol and then from chloroform in a 1/1 (v/v) mixture of acetone/methanol. The ^{1}H NMR analysis showed that the number-average block length of the copolymer is around 2. Therefore, the copolymer is named B2T2-PF.

Table 1. Physical Properties of Polyformals

polymer	T_g (°C)	M_n (10^3 g/mol)	M_w (10^3 g/mol)
BPA-PF	90	20	80
DMBPA-PF	87	152	313
TMBPA-PF	123	18	100
B1T9-PF	118	61	118
B2T2-PF	110	188	380
B4T4-PF	110	240	612

B. DSC. Glass transition temperatures were determined via DSC (Perkin-Elmer DSC 7) at a heating rate of 10 °C/min. Glass transition temperatures (T_g) were taken as the midpoint of the jump in the heat flux curves. The data, which are shown in Table 1, were from precipitated polymer powders.

C. GPC. Molecular weights were determined by gel permeation chromatography (GPC-Waters). The measurements were made by using an UV detector, THF solvent (1 mL/min, room temperature), and a calibration plot constructed with polystyrene standards. The results are shown in Table 1.

D. ^{1}H NMR Analysis. The sequence structure of copolyformals was characterized by ^{1}H NMR. Proton NMR spectra were obtained at 200 MHz on a Bruker WM-200 FT-NMR. Deuterated chloroform was used as the solvent, with tetramethylsilane as the internal reference. All chemical shifts were reported in δ units downshift from tetramethylsilane.

E. DMA. The secondary relaxation behavior of the polyformals was studied with a TA-DMA 2980 instrument in the tensile mode on film specimens. The specimens were run in the iso-step mode in 7.5 °C intervals and were held for 6 min at each temperature interval to allow for thermal equilibration. The thin film specimens had typical dimensions of 10 mm × 4 mm × 0.1 mm (length × width × thickness), and they were made by compression molding at 80−100 °C above their respective T_g's. Prior to the DMA measurements, the samples were heated to 15 °C above their respective T_g's for 15 min and then quenched down to room temperature in order to erase their previous thermal histories.

Results

A. ^{1}H NMR Analysis of the Sequence Structure of the Copolyformals. The sequence structure of the copolyformals was characterized by ^{1}H NMR. The number-average sequence length was estimated by analyzing the diads in the copolymers.[18,24] In the copolyformal chain, there are three types of diads: BB, TT, and BT (shown in Figure 3). We chose the hydrogens

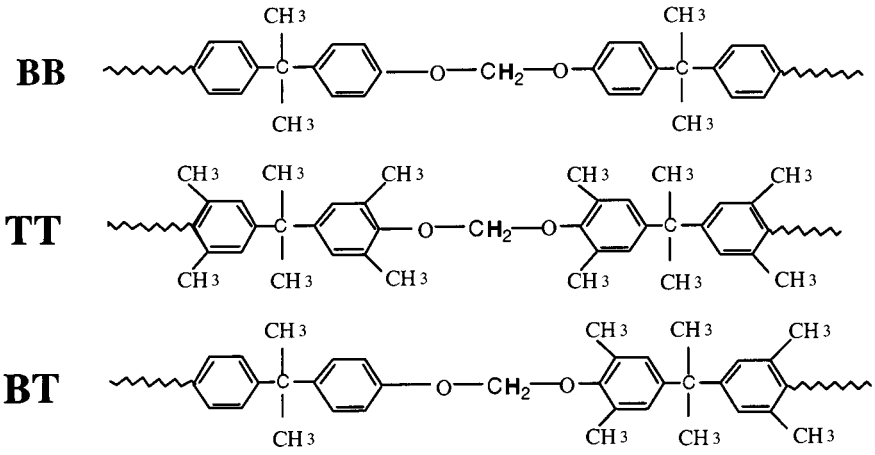

Figure 3. Structure of diads in copolyformals.

in formal linkage (−O−C**H**$_2$−O−) as "information hydrogens". The hydrogens of the formal linkage in different diads have different chemical shifts. By calculating the integrals of these NMR peaks corresponding to different diads, we were able to estimate the relative amount of different diads. On the basis of the following equations[18,24]

$$L_{nB} = (N_{BB} + 0.5N_{BT})/0.5N_{BT}$$

$$L_{nT} = (N_{TT} + 0.5N_{BT})/0.5N_{BT}$$

where L_{nB} is the number-average sequence length of BPA segments, L_{nT} the number-average sequence length of TMBPA segments, N_{BB} the relative amount of BB diad, N_{BT} the relative amount of BT diad, and N_{TT} the relative amount of TT diad.

The number-average sequence length of BPA segments and TMBPA segments in the copolyformal was characterized. The NMR spectra are shown in Figure 4. By comparing the NMR spectra of homopolymers and copolymers, the peak assignment was made, and the results are listed in Table 2. The integrals of different diads and the number-average sequence length of BPA segments and TMBPA segments in different copolymers are shown in Table 3.

B. Secondary Relaxation Behavior of Polyformals. In terms of commonly used nomenclature, the sub-T_g secondary relaxation peaks are identified as β, γ, δ, etc., in the order of the decreasing temperature below T_g, which is designated α. Generally, the β-peak in glassy polymers forms a shoulder on the lower temperature side of the T_g and is probably related to structural relaxation rather than a specific molecular motion. The β-peak is often attributed to either nonequilibrium packing defects created by quenching the sample from above T_g or orientational stresses introduced during processing and can be reduced or eliminated by annealing.[25−27] On the other hand, the γ-peak is only slightly affected by thermal history and is due to intrinsic molecular motions. In this paper, the secondary relaxation refers to the γ-relaxation.

TMBPA-PF is a highly crystalline polymer. It is so brittle that it is impossible to run a DMA test. Therefore, we synthesized B1T9-PF, which is amorphous and not that brittle, to investigate the secondary relaxation behavior of TMBPA-PF. In B1T9-PF, there are only 10% BPA segments, and the motion of TMBPA segments should not change too much. DMA results of the BPA-PF, DMBPA-PF, and B1T9-PF at 1 Hz are shown in Figure 5. BPA-PF has a secondary relaxation peak at around −95 °C, which is consistent with previous results.[12] B1T9-PF has only one small relaxation peak at around −110 °C. This result is surprising because, in polycarbonates, the temperature of the secondary relaxation peak of TMBPA-PC is much higher than that of BPA-PC.[6,12,17] In B1T9-PF, BPA segments average only 10%. Therefore, the motion of TMBPA segments should dominate in this secondary relaxation. Because there are four methyl substitutes in TMBPA, the mobility of the TMBPA segments should be lower than BPA segments, and the secondary relaxation peak of B1T9-PF should shift to higher temperatures compared to BPA-PF. One possible explanation is that the small relaxation peak at −110 °C is due to the motion of B segments and other mobile segments, such as formal linkage. The motion of T segments can only be activated at the temperature higher than T_g. The DMA result of DMBPA-PF strongly supports this idea. At 1 Hz, DMBPA-PF has two relaxation peaks at −100 and 20 °C, respectively. To verify that the relaxation peak at 20 °C is not due to structural relaxation, a DMA test was conducted after the specimen was annealed at 70 °C for 1 week. The DMA results of quenched and annealed DMBPA-PF at 1 Hz are shown in Figure 6. Clearly, there is only very small change of the relaxation peak at 20 °C, which suggests this is peak is due to a specific molecular motion instead of structural relaxation. The existence of the higher temperature relaxation at 20 °C strongly supports our speculation on B1T9-PF. It is very possible that, in DMBPA-PF, low-temperature motion is due to the formal linkage and high-temperature motion is due to the phenylene ring and neighboring isopropylidene group, and those two motions are separable. The molecular origin of the secondary relaxation in this series of polyformals will be discussed later in the Discussion section.

The DMA results of BPA-PF, B1T9-PF, and two copolyformals are shown in Figure 7. Both B2T2-PF and B4T4-PF have only one relaxation peak at the same temperature, and the secondary relaxation behaviors of these two polymers are almost exactly the same. This result suggests that the secondary relaxation behavior of the copolyformals is independent of block length of the BPA segments. Based on Xiao's result,[17] the secondary relaxation peak of BPA-PC reemerges when the block length of BPA segments is larger than seven. However, as shown here, the secondary relaxation peak of BPA-PF can be recovered even when the block length

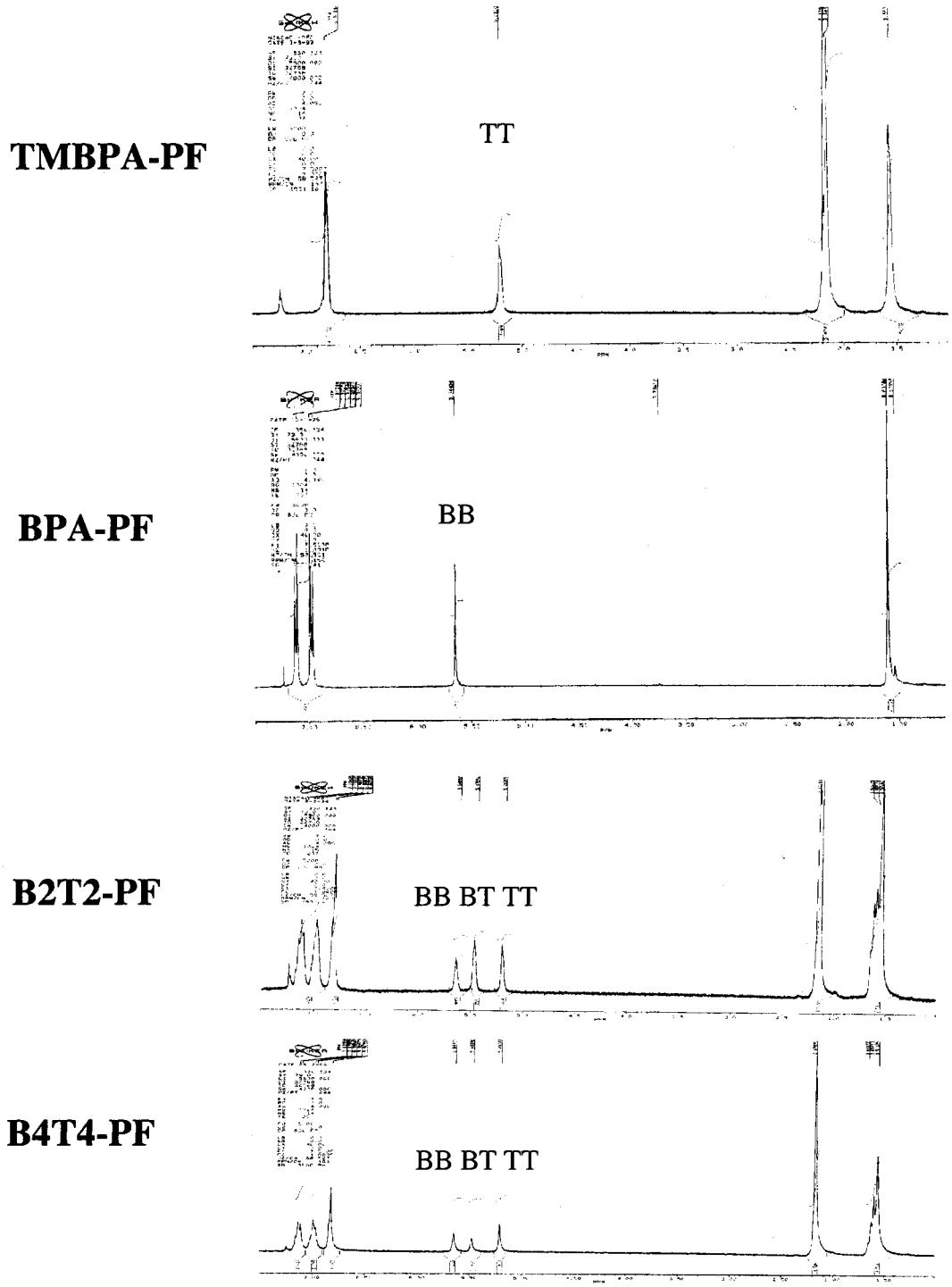

Figure 4. ^{1}H NMR spectra of polyformals and copolyformals.

Table 2. ^{1}H NMR Spectrum Assignments for Copolyformals

diad	chemical shift (ppm)
BB	5.649
BT	5.478
TT	5.213

Table 3. Diad Content and Number-Average Sequence Length in Copolyformals

polymer	BB	BT	TT	L_{nB}	L_{nT}
B2T2	0.8520	1.6328	1.2336	2.00	2.50
B4T4	0.2802	0.3627	0.1712	4.27	5.24

of BPA segments is as short as 2. The above-mentioned DMA results of homopolymers even suggest that the molecular motions of different chemical groups in one repeat unit are separable. Clearly, in BPA-PF, long-range in-chain cooperation is not required in the secondary relaxation process.

Discussions

A. Effect of Linkage Rigidity on Motional Cooperativity. The difference of motional cooperativity in the secondary relaxation between BPA-PC and BPA-PF is attributed to the different rigidity of formal and carbonate linkages.

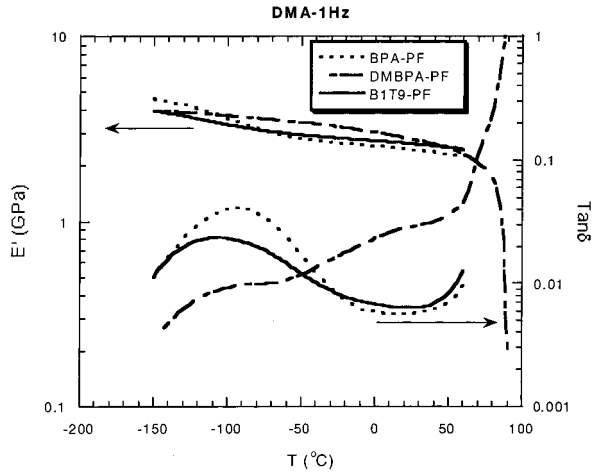

Figure 5. DMA Results of polyformals at 1 Hz.

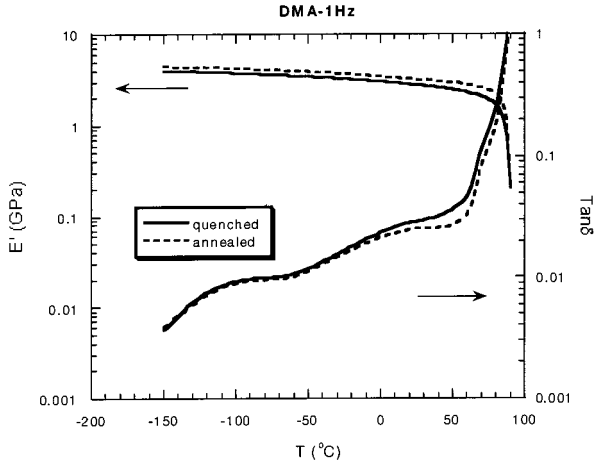

Figure 6. DMA Results of DMBPA-PF at 1 Hz.

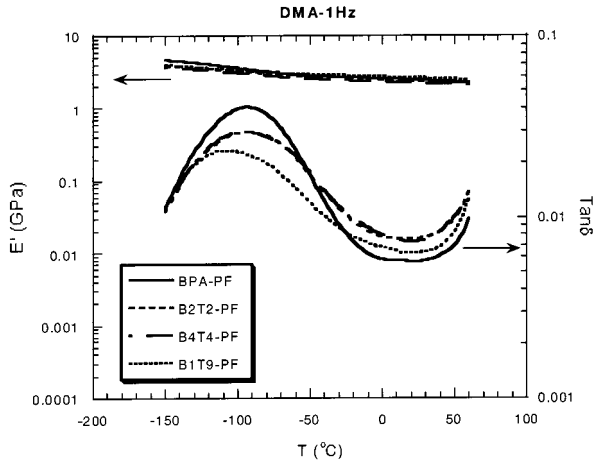

Figure 7. DMA Results of polyformals and copolyformals at 1 Hz.

In a linkage group, such as ether or ester, the most important motion is the rotation of the chemical bonds in the linkage.[28] The rigidity of a linkage group is determined by the rotational energy barriers of the chemical bonds in the linkage.[28] Rotational energy barriers of different chemical bonds in ether, ester, and amide linkage are shown in Figure 8. These values were obtained by computer simulation based on aromatic model compounds.[28−31] Different authors obtained different values based on different assumptions. The values listed in Figure 8 are the average values. In each

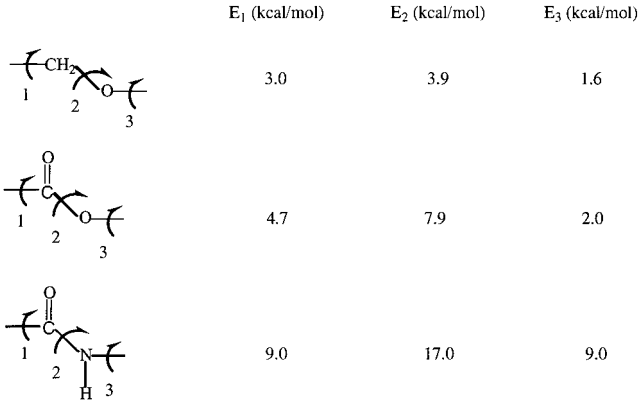

Figure 8. Rotational energy barriers of the chemical bonds in different linkages.

linkage group listed here, altogether there are three chemical bonds involved in the motion of the linkage group, the most important rotation is about bond 2, since it determine the cis or trans conformations. Ether linkage is a flexible linkage, and the rotational energy barriers of the three bonds are relatively low. Because of the resonance effect, bond 2 in the ester linkage is a partial double bond, and the rotational energy barrier of this bond is much higher than that of the ether linkage. Therefore, the ester linkage is more rigid than the ether linkage. In amide linkage, the resonance effect is even stronger, so the rotational energy barriers are even higher.

The function of a linkage group in the molecular motion is twofold: First, it obviously serves as a linkage that connects two neighboring segments. When the linkage is flexible, the two neighboring segments tend to move independently. When the linkage is rigid, the two neighboring segments may move cooperatively.[16] Second, a linkage group also serves as a mobile unit, and its own motion definitely influences the chain mobility. Since carbonate linkage, which is similar to ester linkage, is more rigid than formal linkage, which is similar to ether linkage, it provides more in-chain cooperation in BPA-PC. Recently, Marks[32] reported that there is only one secondary relaxation peak in 2,2′-dibromobisphenol A. The chemical structure of this polymer is similar to our DMBPA-PF. But we observed two secondary relaxation peaks in DMBPA-PF. Clearly, the difference in motional cooperativity in these two polymers can be attributed to the difference in linkage rigidity.

Hay[21] investigated some mechanical properties of BPA-PF and compared them to BPA-PC. He found that the impact strength of BPA-PF is much lower than that of BPA-PC. We believe this difference can be attributed to the different motional cooperativity between BPA-PF and BPA-PC. In BPA-PC, large-scale in-chain cooperative motion gives rise to larger volume fluctuation, which renders energy dissipation process under stress more effective.[19,20] In BPA-PF, the absence of this large-scale cooperative motion may be the reason for its low impact strength. Comparison of BPA-PF and BPA-PC provides us another example to show that it is misleading to directly correlate secondary relaxation behavior and mechanical properties of the glassy polymers without considering for the nature of the molecular motion. The secondary relaxation peaks of BPA-PC and BPA-PF are very similar. However, different motional cooperativity results in totally different impact resistances.

B. The Molecular Origin of the Secondary Relaxation in BPA-PF. Jones[33] investigated molecular motions of different chemical groups in BPA-PF, based on ^{13}C and ^{1}H spin−lattice relaxation study on BPA-PF solution. Although molecular motions of some chemical groups in solution may not be necessarily the same as in glassy state, this result can still provide useful information on possible motion modes in BPA-PF. Jones found that, similar to BPA-PC, phenylene group rotation, methyl group rotation, and formal group rotation are possible in BPA-PF. However, to what extent those motions contribute to the secondary relaxation of BPA-PF remains unclear.

In the present paper, we discuss how these motions of different chemical groups contribute to the secondary relaxation peaks. The exact motion mode will not be discussed, simply because DMA cannot provide such precise information. BPA-PF only has one relaxation peak at −95 °C. Two methyl substitutes on the phenylene rings in DMBPA-PF result in two relaxation peaks; one remains −95 °C while the other shifts to 20 °C. This result suggests that there are two types of molecular motions that correspond to two relaxation peaks in DMBPA-PF, and the higher temperature peak is related to the motion of phenylene groups. A previous study[12] on BPA-PC suggests that methyl group rotation itself cannot induce the mechanical loss of the secondary relaxation since it provides only small volume fluctuations, if any. Moreover, it is believed that two methyl groups and two phenyl groups have to move cooperatively.[7] This cooperative motion should not be affected by the replacement of carbonate with formal linkage, since the formal linkage is not directly connected to the methyl groups. Therefore, we propose that, in DMBPA-PF, the higher temperature relaxation is due to motions of phenylene groups and methyl groups and the lower temperature relaxation is due to motion of the formal linkages alone. In BPA-PF, these two types of motions may occur at almost the same temperature although they are separable; therefore, only one relaxation peak is observed. In DMBPA-PF, two methyl substitutes on the phenylene rings reduce the mobility of the phenylene rings, and this relaxation peak shifts to higher temperature. In B1T9-PF, four methyl substitutes further reduce the mobility of the phenylene rings, and this relaxation peak shifts to even higher temperature, which may be above T_g. Certainly, this proposed molecular mechanism requires further confirmation.

We conclude that the rigidity of linkage groups influences both the in-chain motional cooperativity and the segmental mobility of the polymers in the secondary relaxation process. Chain mobility of BPA-PF should be higher than BPA-PC because the formal linkage is more flexible than the carbonate linkage. One remaining question is why the secondary relaxation peak of BPA-PF is located at roughly the same temperature as that of BPA-PC. To explain this, we have to consider both in-chain and interchain interactions. The DMA test is a macroscopic mechanical test. Both in-chain and interchain interaction contribute to the overall result. When we discuss the rigidity of the linkage groups, only the in-chain interaction is taken into consideration. To obtain a complete picture requires that we also consider interchain interactions. Polyformals are easier to crystallize than polycarbonates,[34] which suggests that the polyformal chain can pack more easily than the polycarbonate chain. We speculate that there is more interchain constraint in BPA-PF than in BPA-PC. If that is the case, then on one hand the more flexible formal linkage will increase the chain mobility of BPA-PF compared to BPA-PC, while on the other hand this stronger interchain constraint will decrease the chain mobility of BPA-PF. Eventually, BPA-PF and BPA-PC still have the secondary relaxation peaks located at roughly the same temperature. This speculation certainly requires further validation.

Conclusions

A series of polyformals based on BPA, DMBPA, TMBPA, and methylene chloride were synthesized. Copolyformals based on the comonomer BPA, TMBPA, and methylene chloride with controlled sequence structure were also synthesized, and DMA studies were conducted on both polyformals and copolyformals. The results show that the secondary relaxation behavior of copolyformals is not dependent on the block length of BPA segments, and the molecular motions of different chemical groups are separable in polyformals. By comparing motional cooperativity of the secondary relaxation in BPA-PF to BPA-PC, in which an in-chain cooperative motion extends to several repeat units, we conclude that the linkage between neighboring BPA segments must play an important role in motional cooperativity. A more flexible linkage would require less motional cooperativity. The lower in-chain motional cooperativity of BPA-PF is attributed to the lower rigidity of the formal linkage.

Acknowledgment. We acknowledge the Eastman Chemical Company and the National Science Foundation (Grant DMR-9422049) for financial support. We thank Dr. Jianwei Liu and Dr. Xiangyang Li for helpful discussions.

References and Notes

(1) Boyer, R. F. *Polym. Eng. Sci.* **1968**, *8*, 161−185.
(2) Vincent, P. I. *Polymer* **1974**, *15*, 111−116.
(3) Glover, A. P.; Johnson, F. A.; Radon, J. C. *Polym. Eng. Sci.* **1974**, *14*, 420−428.
(4) Kastelic, J. R.; Baer, E. J. *Macromol. Sci. Phys.* **1973**, *137*, 679−703.
(5) Heijboer, J. *J. Polym. Sci., Part C* **1968**, *16*, 3755−3763.
(6) Jho, J. Y.; Yee, A. F. *Macromolecules* **1991**, *24*, 1905−1913.
(7) Davenport, R. A.; Manuel, A. J. *Polymer* **1977**, *18*, 557−563.
(8) Smith, P. B.; Bubeck, R. A.; Bales, S. E. *Macromolecules* **1988**, *21*, 2058−2063.
(9) Garfield, L. J. *J. Polym. Sci., Part C* **1970**, *30*, 551−559.
(10) Stefan, D.; Williams, H. L. *J. Appl. Polym. Sci.* **1974**, *18*, 1279−1293.
(11) Watts, D. C.; Perry, E. P. *Polymer* **1978**, *19*, 248−254.
(12) Yee, A. F.; Smith, S. A. *Macromolecules* **1981**, *14*, 54−64.
(13) Jones, A. *Macromolecules* **1985**, *18*, 902−906.
(14) Shih, J. H.; Chen, C. L. *Macromolecules* **1995**, *28*, 4509−4515.
(15) Whitney, D. R.; Yaris, R. *Macromolecules* **1997**, *30*, 1741−1751.
(16) Aitken, C. L.; Mchattie, J. S.; Paul, D. R. *Macromolecules* **1992**, *25*, 2910−2922.
(17) Xiao, C.; Yee, A. F. *Macromolecules* **1992**, *25*, 6800−6809.
(18) Marks, M. J. *J. Appl. Polym. Sci.* **1994**, *52*, 467−481.
(19) Xiao, C.; Jho, J. Y.; Yee, A. F. *Macromolecules* **1994**, *27*, 2761−2768.
(20) Liu, J.; Yee, A. F. *Macromolecules* **1998**, *31*, 7865−7870.
(21) Hay, A. S.; Williams, F. J.; et al. *J. Polym. Sci., Lett.* **1983**, *21*, 449−457.
(22) Hay, A. S.; Williams, F. J.; Relles, H. M.; Boulette, B. M. *J. Macromol. Sci., Chem.* **1984**, *A21*, 1065−1079.
(23) Hay, A. S.; Williams, F. J.; et al. *Polym. Prepr. (Am. Chem. Soc., Polym. Div.)* **1982**, *23*, 117−118.

(24) Yamadera, R.; Murano, M. *J. Polym. Sci.* **1967**, A-1, 5, 2259−2268.
(25) Illers, K. H.; Breuer, H. *J. Colloid Sci.* **1963**, *18*, 1−31.
(26) LeGrand, D. G.; *J. Appl. Polym. Sci.* **1969**, *13*, 2129−2147.
(27) LeGrand, D. G.; Emhardt, P. F. *J. Appl. Polym. Sci.* **1969**, *13*, 1707−1719.
(28) Percec, V.; Zuber, M. *Polym. Bull. (Berlin)* **1991**, *25*, 695−700.
(29) Hurdue, N.; Grigoras, M.; Stoleru, A.; Ionescru, D. *J. Serb. Chem. Soc.* **1997**, *62* (6), 473−480.
(30) Coulter, P.; Windle, A. H. *Macromolecules* **1989**, *22*, 1129−1136.
(31) Tashiro, K.; Masamichi, K.; Tadokoro, H. *Macromolecules* **1997**, *10*, 4413−420.
(32) Marks, M. J.; Sekinger, J. K. *Polymer* **1995**, *36*, 209−215.
(33) Hung, C.; Shibata, J. H.; Jones, A. *Polymer* **1987**, *28*, 1062−1070.
(34) Li, L.; Yee, A. F., unpublished results.

MA010943W