Scale of Cooperative γ-Relaxation of Bisphenol A Polycarbonate

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ABSTRACT: A series of copolymers was designed and synthesized to elucidate the nature of bisphenol A polycarbonate (BPA-PC) γ-relaxation. Specifically, the investigation was focused on the extent of cooperativity and the origin of this cooperative motion. The structure of bisphenol A polycarbonate was modified to different extents by inserting units of bulkier monomer analogue, tetramethylbisphenol A, into the polymer main chain at regular intervals. The dynamic mechanical relaxation technique was used to follow the change of relaxation behavior of the copolymers. The dynamic mechanical spectra of the synthesized homologues suggest that the intrachain interactions are the dominant factor of this cooperative relaxation and the extent of the cooperation is about seven repeat units. These results may explain why BPA-PC has such outstanding ductility.

I. Introduction

The γ-relaxation of bisphenol A polycarbonate has been subjected to extensive investigations. Interpretation of the motion of each constituent group as characterized by NMR and dielectric relaxation techniques was critically reviewed by Jho and Yee.[1] They concluded that the motion responsible for the relaxation is cooperative based on the following observations: (1) independent motions of the constituent groups (methyl, carbonate, and phenylene) of bisphenol A polycarbonate are unable to induce the mechanical relaxation, (2) the motions are considered to be correlated to each other (possibly except for the methyl group), (3) a large-scale motion must be sought as the motion responsible for the mechanical relaxation, and (4) the distance of this motional correlation extends over at least one repeat unit of bisphenol A polycarbonate.

The conclusion was further justified by the observed dynamic mechanical behaviors of alternating multiblock copolymers of bisphenol A and tetramethylbisphenol A.[1] Only one secondary relaxation peak was found in the dynamic mechanical spectrum of poly(bisphenol A carbonate)-*alt*-(tetramethylbisphenol A carbonate). The peak is located at a temperature intermediate between the relaxation peaks of the respective homopolymers, which indicated that more than one repeat unit was needed for the motion. By systematically increasing the block lengths from one repeat unit, multiple peaks reemerged when the block length became long enough. At a block length of nine units for each type of comonomer, one secondary relaxation peak for each of the components was restored at their corresponding peak temperatures. In addition, a third peak at an intermediate temperature thought to be due to the motion of the interlinking part of the two blocks was observed. These results suggest that the γ-relaxation of bisphenol A polycarbonate is due to the cooperative motion of a surprisingly large number of repeat units along the chain.

Some researchers using NMR and dielectric techniques[2-7] have also speculated that the molecular motion must be cooperative in order to be fully consistent with their experimental data. For example, Schaefer,[4] based on his dipolar rotational spin-echo ^{13}C NMR experiment, had proposed that the motion must involve at least two rings down the chain and four or five other rings on other chains. However, these speculations, though reasonable in light of Jho's work, were not supported directly by their own experimental results. The scale of the motion was postulated to be between six and nine repeat units in Jho's work, and the origin of such a large-scale cooperative motion was not given. Jho's results are also not anticipated by theoretical models such as Tonelli's,[8] Bicerano's,[9] and Suter's.[10] Therefore, it is of theoretical significance to understand the scale and the origin of the cooperative motion.

The correlation distance, however, was not unambiguously determined by Jho.[1] Furthermore, such extensive intrachain cooperative motion in the glass is apparently contradictory to most conventional theories and beliefs. It is necessary to determine this correlation distance in a more precise manner. In this paper, our attention will be focused on the determination of the extent of cooperative motion in the γ-relaxation of bisphenol A polycarbonate. The rationale behind this phase of the research is 2-fold: First, from a notional viewpoint, secondary relaxation can involve large-scale cooperative motion. The motional correlation distance may in turn be used, as we will show in the following discussion, to help us elucidate whether this cooperative γ-relaxation is dominated by intermolecular or intramolecular interactions. Second, from a practical viewpoint, since this cooperative motion is thought to be closely related to bisphenol A polycarbonate's superior ductility, it might be desirable when designing new molecular architectures, to preserve such types of cooperative motions as we tailor-make new materials with optimum properties. The suggestion that intramolecular interactions dominate the relaxation is supported by the fact that there is a long correlation distance, which is unlikely in the case of strong intermolecular couplings.

Selection of Polymer Homologues. The scale of cooperative motion referred to above is the number of repeat units involved statistically in the relaxation processes. To determine this, the structure of bisphenol A polycarbonate must be perturbed to different extents and the changes of its relaxation behavior studied. The correlation distance can be determined as the point where the perturbation begins to vanish. A bulkier monomer analogue of bisphenol A, tetramethylbisphenol A, was used to perturb the structure. Thus units of tetramethylbisphenol A were inserted into the bisphenol A polycarbonate main chain at regular intervals, starting from the alternating copolycarbonate of bisphenol A and the tetramethylbisphenol A. The changes in the relaxation behaviors due to the presence of the tetramethylbisphenol A units were followed by means of the dynamic mechanical spectrum. Once the number of repeat units in the bisphenol A block exceeds its cooperative distance, the

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characteristic relaxation peak observed for the bisphenol A homopolymer is deemed fully restored.

There are several reasons for choosing tetramethylbisphenol A as the second component: (1) the homopolymers of bisphenol A and tetramethylbisphenol A polycarbonates are thermodynamically miscible;[21] there is no possible phase separation in their block copolymers; (2) these homopolymers all exhibit a cooperative type of molecular relaxation; therefore, the incorporation of the bulkier tetramethylbisphenol A unit does not fundamentally change the character of polycarbonate's in-chain cooperative motion but merely perturbs the spectral pattern; (3) at 1.0 Hz the intermediate type linkages will generate a relaxation peak in the vicinity of 0 °C, whereas the relaxation peak of bisphenol A polycarbonate is located at −100 °C. It is therefore relatively easy to detect the separation of the two relaxation peaks.

II. Results and Discussion

A. Synthesis. 1. Synthesis of Oligomers. The purpose of the present study is to determine the in-chain correlation distance of the cooperative relaxation. Thus, the control of block length is crucial, especially for those copolymers with short block lengths. One can usually control the molecular weight through an unbalanced feeding of monomers, which is well described by Caruther's equation.[11] This method also ensures that the oligomers produced possess hydroxyl functionalities through feeding a calculated excess of bisphenols over bischloroformates. The polydispersity of the oligomers, however, cannot be controlled by this method.[12] For example, in using this method oligomers with an apparent number-average length equivalent to three repeat units will have significant amounts of oligomers with greater lengths than the mean value, e.g., pentamers and heptamers. These longer oligomers will then form correspondingly longer blocks in the block copolymers. The relaxation peaks arising from those longer blocks may overshadow the relaxation behavior of the short blocks. Such artifacts may lead to erroneous conclusions. Therefore, a narrow molecular weight distribution is essential for the synthesis of low molecular weight oligomers. As has been pointed out by Case,[12] there are two major approaches to the synthesis of narrow molecular weight distribution oligomers through the condensation method. One is to protect one of the hydroxyl groups on the bisphenol monomer and leave the other one accessible to the reaction. After the reaction, the protecting group will be cleaved and further condensation allowed to proceed. This method can, in principle, give monodispersed oligomers, but it involves very many steps and is nearly impossible in practice. The second approach is to differentiate the reactivity of the two functional groups of a monomer. This is the approach used in the present study.

Bisphenol A monosodium salt is used in the synthesis since the phenyl oxide has a much higher reactivity with chloroformate than the phenyl hydroxyl group does. However, partial equilibrium between the phenyl oxide and the phenyl hydroxyl groups may exist, which can lead to a higher polydispersity. To counter such a tendency, care has been exercised to minimize exchange reactions by choosing suitable solvents and by lowering the reaction temperature. Trimers with different structures have been synthesized with the combination of bischloroformate and 2 equiv of bisphenol monosodium salt (Scheme I).

The block length and the structure of the trimers were characterized by ^{1}H-NMR spectra. Figure 1 is the ^{1}H-NMR spectrum of a bisphenol A carbonate trimer. The two doublets at 6.73 and 7.08 ppm are the resonance peaks of the protons on the terminal phenylene ring. The multiple peaks between 7.16 and 7.25 ppm were due to the resonance of the inner phenylene protons. The integral ratio of these two groups of peaks is 1:2, indicating that the length of the oligomer is three repeat units. To further confirm the structure of the BPA trimer, derivatization techniques were applied. Trichloroethylchloroformate, a common protecting group for a phenolic hydroxyl group,[13] was used to convert the hydroxyl groups in BPA trimers to trichloroethylcarbonate groups. An excess amount of trichloroethylchloroformate was employed to ensure quantitative yield of the reaction. By converting the hydroxyl end groups in the oligomers to trichloroethylcarbonate groups, the peaks at 6.73 and 7.08 ppm disappeared. Instead the ethyl protons in the terminal group introduced a peak at 4.85 ppm, far from the methyl proton peak. This separation made the calculation of relative peak areas quite easy and unambiguous. The average degree of polymerization calculated from this peak ratio was in good agreement with the expected value.

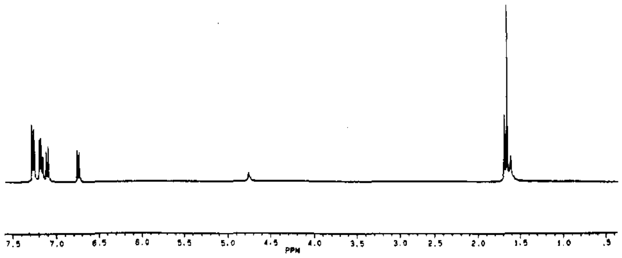
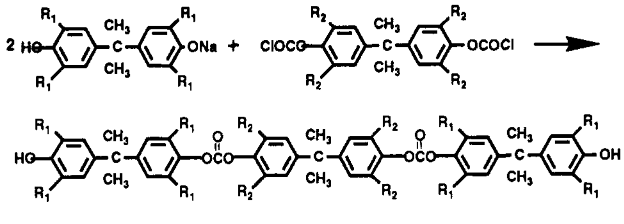


Figure 1. ^{1}H-NMR spectrum of a bisphenol A carbonate trimer.

Scheme I
Synthesis of Trimers



B3, When R_1=H, R_2=H; T3, When R_1=CH$_3$, R_2=CH$_3$;
BTB, When R_1=H, R_2=CH$_3$; TBT, When R_1=CH$_3$, R_2=H.

TMBPA carbonate trimer, BPA–TMBPA–BPA carbonate, and TMBPA–BPA–TMBPA carbonate were also synthesized by similar procedures. Their structures were also confirmed by the proton NMR.

We note that the oligomers with a number average degree of polymerization equal to seven and nine were synthesized in a different manner. It is difficult to synthesize such long oligomers with the above method and a slightly higher polydispersity is thought to be tolerable for large block copolymers. The unbalanced monomer feeding method was employed in synthesizing these oligomers. They were then polymerized in situ without separation. It has been reported[14] that bisphenol carbonate oligomers can be synthesized by an unbalanced monomer feeding method at low temperatures. The molecular weight distribution of oligomers obtained using such a method was reported to be about 1.40.

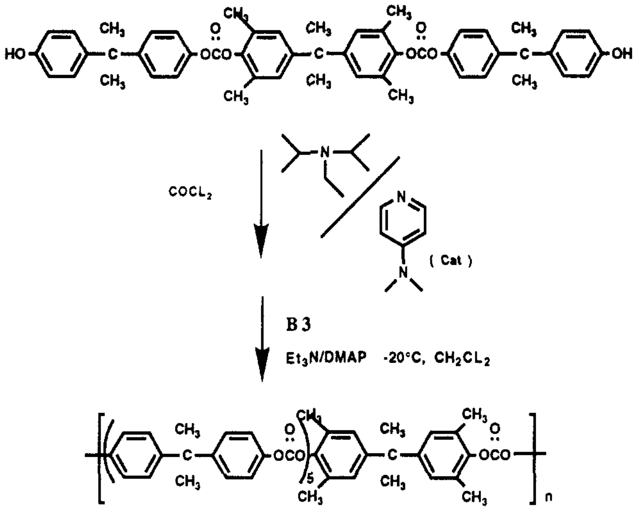
In summary, four types of bisphenol trimers with well-defined structures were synthesized by reacting 1 equiv of bischloroformates with 2 equiv of bisphenol monosodium salts. These oligomers form the structural basis of the copolymers with well-defined architectures.

2. Synthesis of Polymers. The blocks were formed and incorporated in situ for most of the polycarbonate

Table I
Physical Properties of Synthesized Copolymers

sample ID	T_g (°C)	M_n	M_n/M_w
BT5	178	17 500	2.6
BT3	177	18 654	2.7
B3T	155	14 330	2.4
B5T	152	13 299	2.8
B7T	148	14 790	2.5
B9T	147	15 105	2.8

Scheme II
Synthesis of the Copolymer



block copolymers. In a typical procedure, the preformed oligomer of the other component reacted, in many cases interfacially, with bisphenol A in the presence of phosgene. The advantage of interfacial polymerization is that high molecular weight products are readily obtained through a balanced monomer feed to the interfacial reaction site.[15] For a polymer with a designed architecture, however, the incorporation of blocks with controlled molecular weights is as important as obtaining high molecular weights for the copolymer. Since, in a typical interfacial polymerization, an alternating copolymer of the two reactive monomers is obtained, some of the desired polymers can be obtained through interfacial polymerization of preformed oligomers with other kinds of monomers or oligomers. The conventional interfacial method must be modified in order to preserve the desired block composition of the copolymers. In an interfacial polymerization, an aromatic bischloroformate will be hydrolyzed in the presence of a base.[16] These hydrolyzed oligomers will subsequently react with other bischloroformate oligomers, resulting in a change in the molecular weights of the oligomers. We found that the hydrolysis reaction could be eliminated by controlling the pH value of the solution between 7.0 and 8.0 and by lowering the polymerization temperature to 0 °C (sodium chloride was added to prevent the freezing of the aqueous phase). A complex catalyst pair, DMAP/triethylamine, was used, allowing the polymerization reaction to proceed as fast as necessary at such a low temperature. An example of such a synthesis is given in the Experimental Section on the preparation of bisphenol A–tetramethylbisphenol A alternating copolymer with a high molecular weight (Table I). Some other block copolymers, such as B3T and BT3, can also be synthesized by this method. Here B and T denote BPA and TMBPA units, respectively, and the numeral denotes the number of monomers in each block. However, this procedure could not be used as a general one in the present study since not all of the oligomers are soluble in water.

An alternative solution polymerization was also investigated in our research as a general procedure to serve our purpose. The advantage of this method is that the molecular weights of the oligomers remain intact during the solution polycondensation. One might argue that the carbonate exchange reaction might also alter the block composition. It has been shown[16] that such an exchange reaction does not happen even at 80 °C. Therefore, there is no need to be concerned about its occurrence as long as the low-temperature polymerization method is used. One disadvantage of this method is the low molecular weight of the resulting copolymers. It is to be expected, since a strict equimolar balance of the reactants is required for the formation of high polymers, and that is not always true in the experiment. The bischloroformate-terminated oligomers are taken directly from the previous step, and the amount of oligomers participating in the polycondensation may not be exactly the same as that calculated at the start of the previous step. This slight imbalance in the coreactants results in chain termination and significantly degrades the molecular weight of the resulting copolymer. Another reason for the lower molecular weights is that side reactions, such as the decomposition of chloroformate groups, cause termination of the main reactions. For dynamic mechanical studies, copolymers with sufficient mechanical strength are essential. Therefore, obtaining a relatively high molecular weight for the copolymers is as crucial an issue for them as having a well-defined structure.

These problems can be solved if the side reactions can be eliminated and if the reaction can be speeded up so that the polymerization begins as soon as the oligomers combine. If the reaction proceeds rapidly enough, a balanced molar ratio of the two oligomers can be achieved by adding one oligomer into the other at a suitable rate. Since the reaction finishes as soon as the oligomer is added, a high molecular weight copolymer should be obtained at the point where the balanced molar ratio criterion is fulfilled. The side reactions can be eliminated by lowering the reaction temperature. The only difficulty with this technique is how to increase the reaction rate.

Different catalysts, such as pyridine, triethylamine, pyridine/triethylamine, pyridine/DMAP, and triethylamine/DMAP, were tried in order to lower the reaction temperature and increase the reaction rate. It was found that triethylamine/DMAP formed the most suitable catalyst/acid acceptor pair. It allowed the reaction to proceed very quickly, even at −30 °C, which was ideal for our study. Model polymerization reactions were performed in a temperature range of −30 to +80 °C in order to determine the optimum reaction temperature. This temperature was found to be between −20 and −10 °C.

A typical polymerization process is described below: BPA carbonate trimer was phosgenated to form the corresponding bischloroformate at −30 to −25 °C. After purification, the bischloroformate was immediately coupled with a little less than the stoichiometric amount of bisphenol A–tetramethylbisphenol A–bisphenol A carbonate by slow addition through a dropping funnel while the solution was rapidly stirred and cooled at −25 °C. The resulting viscous solution was first precipitated from methanol. It was then further purified by reprecipitating from acetone. The synthesis scheme of the copolymer is shown in Scheme II. A more detailed description of the synthetic procedure is given in the appendix.

The structure of the copolymer was characterized by its NMR spectrum. The ^{1}H-NMR spectrum of B5T (Figure 2) shows that the resonance peaks at 6.73 and 7.08 ppm,

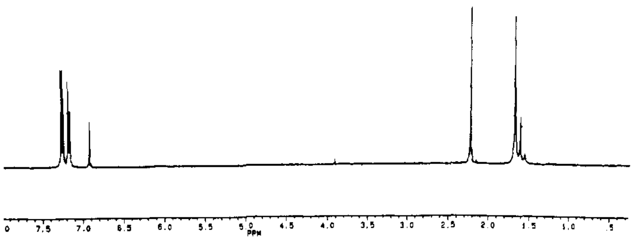


Figure 2. ^{1}H-NMR spectrum of poly(pentabisphenol A carbonate)-*alt*-(tetramethylbisphenol A carbonate) (B5T).

which are due to the resonance of the terminal phenylene protons of the oligomers, disappeared and merged to 7.16 and 7.23 ppm, indicating the formation of carbonate linkages. The characteristic resonance peaks at 6.90 and 2.20 ppm signified that the tetramethylbisphenol A unit was also incorporated in the copolymers. A 1:5 area ratio of the peaks at 6.90 and 7.16 ppm demonstrates that every five BPA carbonates is linked with one tetramethylbisphenol A carbonate unit. The above NMR data confirmed that the synthesized polymer had the expected structure.

The polymer has a T_g of 152 °C, which was determined by DSC, and a specific viscosity of 0.52 (0.5 g/dL, $CHCl_3$ at 20 °C). The molecular weight of this polymer was also characterized by GPC. Its number-average molecular weight was 13 299, and the polydispersity was 2.8 using a monodispersed polystyrene standard as reference (THF was used as the solvent). These results further confirm that the desired copolymer with a sufficiently high molecular weight was indeed obtained. All other copolymers were also carefully characterized by the above techniques which indicated they had the desired structures and appropriate molecular weight. Some of their physical properties are listed in Table I.

In summary, the structure of bisphenol A polycarbonate was modified to different extents by inserting a bulkier monomer analogue, tetramethylbisphenol A, into the polymer main chain at every several bisphenol A repeat units. Thus, a series of bisphenol A polycarbonate homologues with different extents of structural perturbation were synthesized.

B. Dynamic Mechanical Studies. The two main objectives of this paper, i.e., the determination of the origin and the scale of the bisphenol A polycarbonate cooperative γ-relaxation, will be accomplished by measuring the dynamic mechanical relaxation spectra of the synthesized copolymers. The dynamic mechanical spectra were obtained from a spectrometer built in out laboratory which is based on a linear motor driver unit and a Hewlett-Packard data acquisition unit controlled by an HP computer.

1. Origin of Cooperative Relaxation. Before interpreting the dynamic mechanical spectra of the synthesized copolymers, let us revisit their structures and give a qualitative prediction of their dynamic mechanical spectra, assuming that either intermolecular interaction or small-scale localized main-chain motion is responsible for the γ-relaxation. The polymers used in the present study are BPA-PC, B9T, B7T, B5T, B3T, BT, BT3, BT5, and TMBPA-PC where B denotes a bisphenol A carbonate unit, T denotes a tetramethylbisphenol A carbonate unit, and the numbers denote the number of repeat units in each block. The glass transition temperatures of the BPA-PC and TMBPA-PC homopolymers and their copolymers versus the molar fraction of TMBPA monomer in the copolymers are plotted in Figure 3. As the contents of bulky tetramethylbisphenol A are systematically increased, the T_g's of the copolymers are also gradually increased.

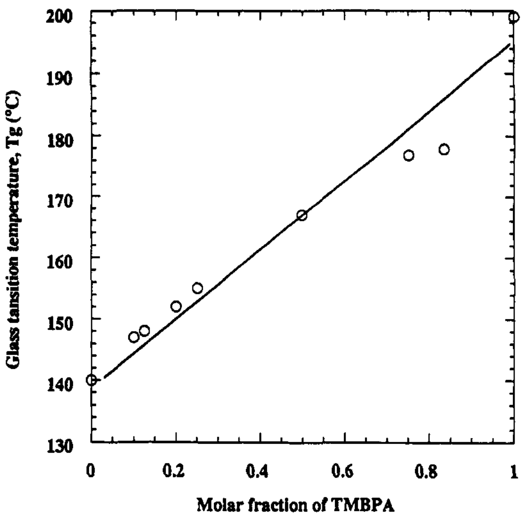


Figure 3. Glass transition temperatures of the block copolymers as a function of the TMBPA molar fraction.

One can explain this by arguing that (1) the bulkier tetramethylbisphenol A unit has to overcome a higher torsional energy barrier in order to proceed with the micro-Brownian type of motion and (2) the energy barrier is also increased when several bulkier units are moving cooperatively.

If one believes that the γ-relaxation is solely caused by intermolecular interaction and localized main-chain motion, one may be able to predict the relaxation behaviors of the synthesized homologous copolymers based on the bundle model proposed by Schaefer.[18] The bundle model is a two-dimensional lattice model. The molecular chains are assumed to form bundles or regions over which the main chains are locally parallel. No long-range periodicity is assumed. The important interchain correlation is considered to be transverse to the main-chain axis, and the cross-section of the molecule is assumed to be elliptical in shape. In his model, Schaefer proposed that the motions responsible for the γ-relaxation of bisphenol A polycarbonate are the ring flips of several nearest molecular chains. The flips of the rings are equivalent to the flips of the elliptical bundles. When a bundle undergoes a flip with respect to its surroundings, it has to interact with the nearest bundles. Thus cooperative flips of several nearest bundles are needed to allow the individual the phenylene ring flips. This model is consistent with Schaefer's experiment, in which, as external hydrostatic pressure was increased, the flipping of the rings was suppressed.

In the context of Schaefer's model, the dimethylphenylene rings of the tetramethylbisphenol A unit can be considered as forming bigger bundles compared to phenylene rings. Hence, the higher the content of tetramethylbisphenol A, the more bundles in the lattice which become bigger bundles. Since the energy barrier for the cooperative flips of bigger bundles is higher than that for small ones, the relaxation transition temperature should increase as the tetramethylbisphenol A content of the copolymer is increased.

If this model is completely valid for the case of polycarbonate relaxation, we should expect the γ-relaxation transition temperatures of our synthesized materials to follow the trend of the α-relaxation temperatures. Therefore, a gradual increase of γ-transition temperature versus volume or molar fraction of tetramethylbisphenol A should be obtained. This expectation is qualitatively shown as a solid line in Figure 4. Our experimental results are then compared with this prediction.

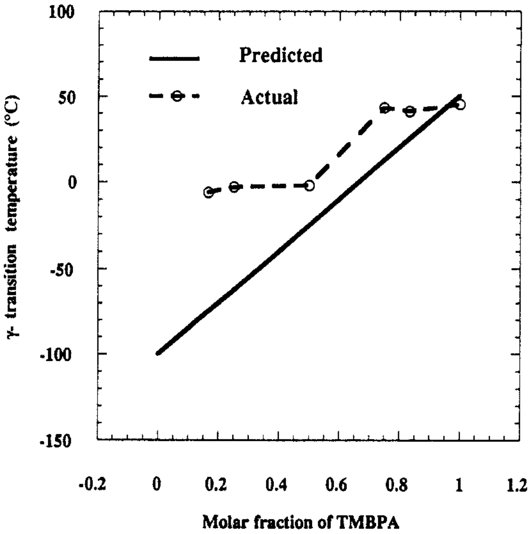


Figure 4. Predicted and experimental γ-transition temperatures as a function of TMBPA molar fraction of the block copolymers.

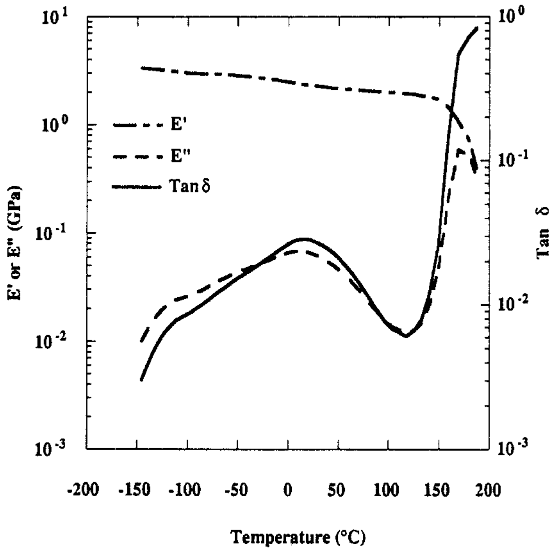


Figure 5. Dynamic mechanical relaxation spectrum of BT5.

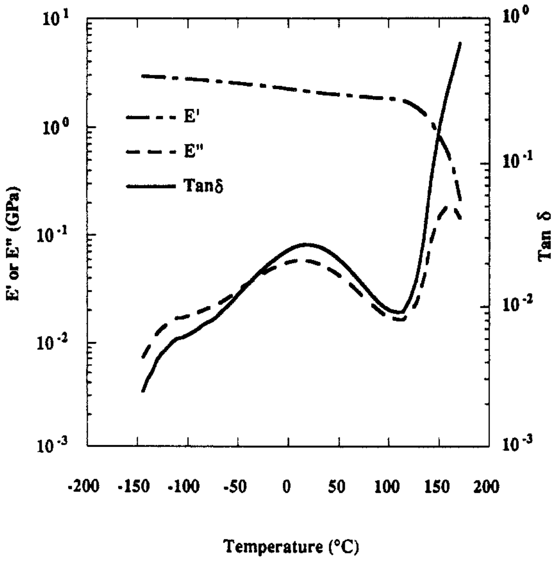


Figure 6. Dynamic mechanical relaxation spectrum of BT3.

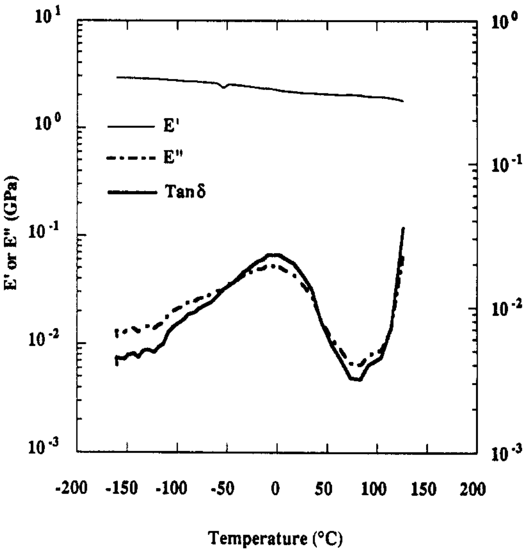


Figure 7. Dynamic mechanical relaxation spectrum of BT.

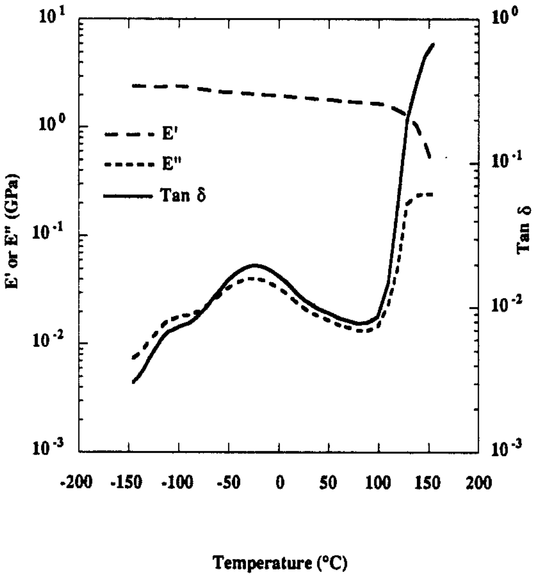


Figure 8. Dynamic mechanical relaxation spectrum of B3T.

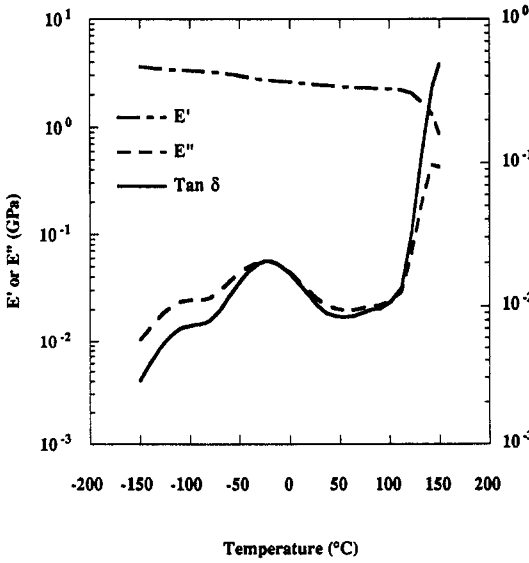


Figure 9. Dynamic mechanical relaxation spectrum of B5T.

The dynamic mechanical spectra of the copolymers are shown on Figures 5–11. Except for B7T and B9T, which clearly showed two relaxation peaks, all other copolymers have only a single γ-relaxation peak. This conclusion becomes even clearer when the spectra are shown together (Figures 12 and 13). One might argue that B5T has two low-temperature relaxation peaks, a matter addressed in the Discussion section.

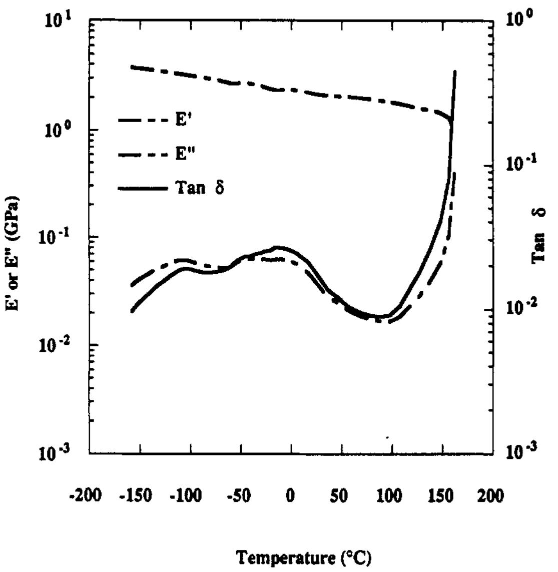


Figure 10. Dynamic mechanical relaxation spectrum of B7T.

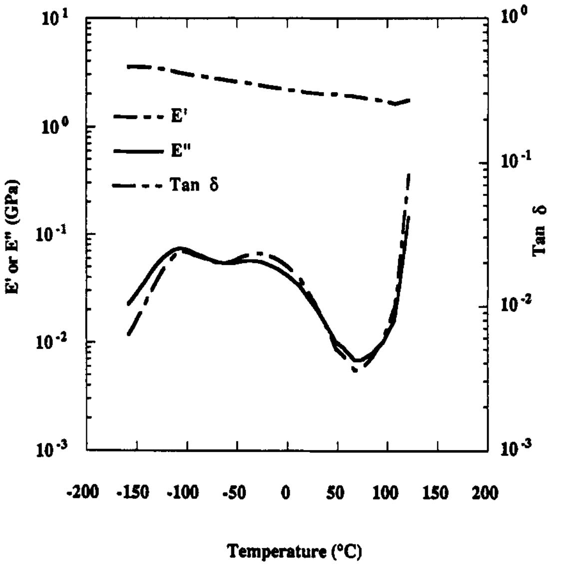


Figure 11. Dynamic mechanical relaxation spectrum of B9T.

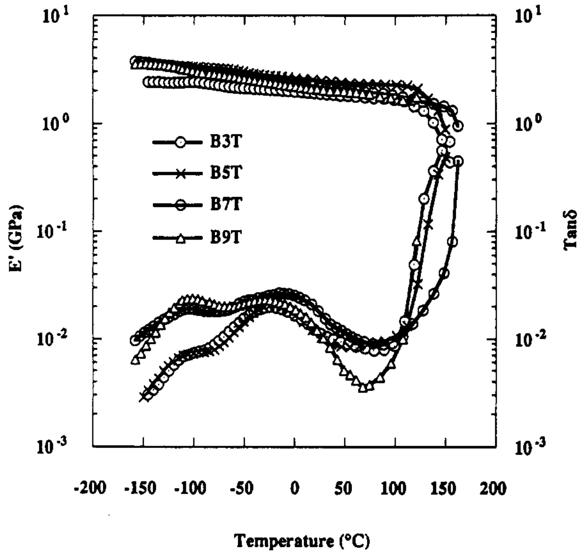


Figure 12. Dynamic mechanical relaxation spectra of Group I copolymers.

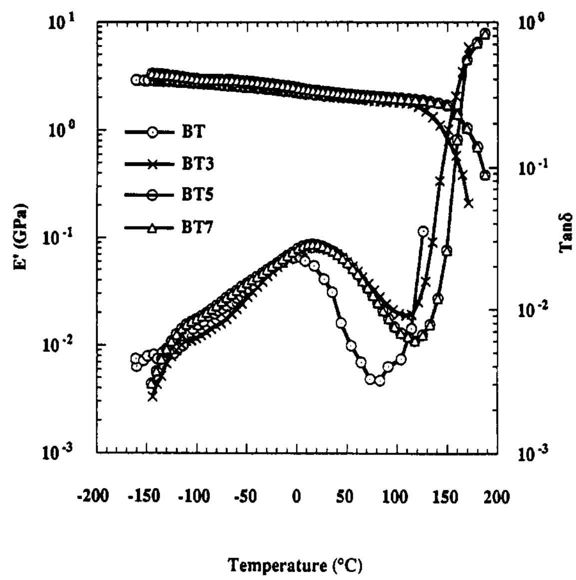


Figure 13. Dynamic mechanical relaxation spectra of Group II copolymers.

It is probably easier to first compare experimental results against the prediction based on the simple bundle model. Then the nature of the relaxation can be drawn based on this comparison. When the block length is shorter than five repeating units, a single γ-relaxation peak is obtained. This is consistent with the idea of cooperative relaxation. As shown by the dashed line in Figure 5, when the γ-relaxation peak temperatures are plotted against the molar fraction of the tetramethyl bisphenol A monomer unit, a significant deviation from the prediction based on the model is observed. Instead of a gradual increase in the transition temperature as the molar fraction of the bulky tetramethylbisphenol A units increases, it was found that there is a discontinuity in the transition temperature. The model cited above is not able to explain this phenomenon. The copolymers can be classified into two groups, according to their γ-transition temperatures. Group I includes B5T, B3T, and BT which all have about the same γ-relaxation temperatures in the vicinity of −2 °C at 1.0 Hz. Group II includes BT3 and BT5 which have γ-transition temperatures very close to that of the tetramethylbisphenol A homopolymer. Both Group I and II polymers show cooperative γ-relaxation behavior. The similar transition temperatures of Group I polymers indicate that the interlinking part of the block copolymer has a strong influence on the relaxation behaivor of the polymers. Even when the block length of bisphenol A carbonate increases to five repeating units, the relaxation temperature was still about the same as that for the alternating copolymer. This implies that there must be some kind of interaction causing the moieties, which are far apart along the molecular chain, to move cooperatively. Consequently, the origin of this cooperative motion is considered to be strong intrachain coupling.

At this point, it is still not known exactly how the subgroups along the chain interact with each other. This could probably be better understood by supplemental NMR studies, which are currently beyond our research capability. The dynamic mechanical spectra of the copolymers indicate that the rate-limiting step of this cooperative relaxation is the thermal activation process of the larger repeat units. For example, the rate-limiting steps of Group I copolymers is the thermal activation process of the intermediate type linkage, which is located at −2 °C, at 1.0 Hz, whereas for Group II copolymers, the rate-limiting steps are the thermal activation of tetramethylbisphenol A blocks. The increase of the transition temperature of a bulky unit is mainly due to the coupling of relaxing species with their surroundings. This phenomenon can be explained by the coupling model[19,20] and has been confirmed by NMR line-shape studies.[7] In dilute solutions bisphenol A polycarbonate and tetrachlorobisphenol A polycarbonate have very similar phenylene flip relaxation times although the tetrachlorobisphenol A moiety is much bulkier than bisphenol A. That is because there is little intermolecular interaction in the dilute solution. However, as the concentration increases, intermolecular interaction appears and the phenylene ring relaxation time of tetrachlorobisphenol A polycarbonate increases more rapidly than that of bisphenol A polycarbonate. In the solid state, the phenylene rings of tetrachloropolycarbonate are nearly immobile. This is consistent with the idea that intermolecular interaction does participate in this relaxation.[7] Although the strength of intermolecular coupling has a strong influence on the relaxation time function and activation energy, the primitive motion of the relaxing species is still dominated by the intramolecular interactions. This may be the reason why intramolecular interactions dominate the secondary relaxation. This conclusion is further supported by the dynamic mechanical studies by Fischer et al.[21] of polymer blends made from a pair of miscible polymers, bisphenol A polycarbonate and tetramethylbisphenol A polycarbonate. Their data show that the relaxation peak temperature of each homopolymer does not change with the blend composition, but the intensity of each peak is proportional to the volume fraction of the homopolymers. This conclusion was questioned by Jho.[1] He carefully repeated Fischer's experiments and found that the relaxation peak temperature of bisphenol A polycarbonate is shifted to lower temperatures and its magnitude is depressed as the content of tetramethylbisphenol A polycarbonate in the blend is increased. Although these results suggest that intermolecular interaction is stronger than was proposed by Fischer's study, it does not alter our conclusions.

The conclusion from the above discussion is that the cooperative γ-relaxation originates from intramolecular interactions and the scale of such a cooperative motion is larger than five repeat units. In the next section, the correlation distance of this extensive cooperative in-chain motion will be more precisely determined.

2. Scale of the Cooperative Motion. The correlation distance referred to here is the statistical number of repeat units involved in this cooperative relaxation. In this and previous studies the perturbation method is used. In the previous approach,[14] a series of alternating block copolymers of bisphenol A and tetramethylbisphenol A polycarbonates was synthesized. The block length of each component was the same. Based on the original idea, as the block length of each component was gradually increased, a point would be reached where the bisphenol A block would be so long as to become insensitive to the existence of the bulkier tetramethylbisphenol A blocks. Dynamic mechanical measurements were used to monitor the relaxation behaviors of the synthesized copolymers. However, an immediate difficulty was encountered concerning the interpretation of dynamic mechanical spectra. Theoretically, once the characteristic γ-relaxation peak of a bisphenol A homopolymer is revealed from the spectrum of the copolymer, one can then determine the correlation distance. In order to interpret the spectra, however, a standard basis is needed from which one can determine when the characteristic relaxation is revealed. Obviously, the relaxation peak temperature is the first criterion. Yet, there is no theory that can be followed on the definition of the relaxation strength. Therefore an assumption is made that the relaxation strength is proportional to the volume fraction of the relaxing species.[22] The γ-relaxations of bisphenol A polycarbonate and tetramethylbisphenol A polycarbonate are both cooperative relaxations. To define the relaxation strength, we have to first know the extent of cooperativity, which is the value we are trying to determine in the present study. For the block copolymers synthesized by Jho, three relaxation peaks emerged in the dynamic mechanical spectra. The first peak was due to the relaxation of the tetramethylbisphenol A block, the second peak at the intermediate temperature was due to relaxation of interlinking parts, and the peak at the lowest temperature was due to the relaxation of the bisphenol A blocks. Because the three peaks overlap, it is difficult to resolve the spectra. Therefore, the cooperative distance of the bisphenol A polycarbonate γ-relaxation could not be more precisely determined than somewhere between six to nine repeat units.

To avoid the difficulties mentioned above, only a "small" perturbation is applied to the system. In other words, only one tetramethylbisphenol A monomer is inserted between the bisphenol A polycarbonate blocks. The block length of bisphenol A was systematically increased from one repeat unit to nine repeat units. Of course, the determination of the relaxation strength is again the major issue. This problem could be solved rather easily because of the unique structure of the copolymers. When the block length is shorter than the correlation distance, the relaxation would be dominated by the interlinking part of the molecules. Therefore, the relaxation peak in the vicinity of −2 °C would be the dominant relaxation. This is what has been found for Group I copolymers. When the block length of bisphenol A carbonate is equal to the correlation distance, the characteristic relaxation peak of bisphenol A polycarbonate homopolymer should be revealed. Because only one tetramethylbisphenol A unit is put in between the bisphenol A blocks, the cooperative relaxation character should not change except for the relaxation peak shifting to a higher temperature. Furthermore, the cooperative relaxation of the interlinking part should involve nearly the same number of the bisphenol A units as the bisphenol A blocks which are undergoing independent relaxation. When the block length of bisphenol A is equal to its correlation distance, the number of bisphenol A cooperative relaxation species should be the same as that of the interlinking part. Since only a small fraction of tetramethylbisphenol A is incorporated in the copolymer, it would be valid to assume that the volumes of the two types of relaxation species are approximately the same. Thus, one should expect that when the block length is equal to the cooperative relaxation correlation distance the characteristic relaxation peak of bisphenol A polycarbonate would have approximately the same intensity as the relaxation peak of the interlinking part. When the block length exceeded the critical correlation distance, the characteristic relaxation peak of bisphenol A carbonate should gradually become more intense than the peak of interlinking relaxation.

To determine the scale of the relaxation, we direct our attention to Group I copolymers plus B7T and B9T. The dynamic mechanical relaxation spectra of BT and B3T both have a single γ-relaxation peak which is due to the cooperative relaxation of the interlinking parts. For B5T, there is a new minor peak at −110 °C which could be due to the relaxation of the bisphenol A blocks. The intensity of this peak is so low that there is difficulty in establishing if the characteristic relaxation of bisphenol A polycarbonate has been fully restored. The loss maximum of this new peak is about 0.008 in tan δ. Compared to the loss maxima of bisphenol A with a tan δ value of 0.05, this new peak is not statistically significant even if we take the dilution effect into consideration. There are two possible reasons for the appearance of this new peak. One is the absorption of solvent vapor in the sample.[23] The other, more likely possibility is the polydispersity of the oligomers. The trimers we synthesized have a polydispersity of 1.30. Those oligomers with longer length than average could also be the source of this new peak. Thus, we conclude that the correlation distance should be longer than five repeat units. As shown in Figure 11 the dynamic mechanical spectra of B7T show two dominant peaks with equal intensities, one centered at −100 °C and the other at −5 °C. The peak at −100 °C had a tan δ value of 0.06 which is comparable to that of pure bisphenol A polycarbonate. Based on previous arguments, it is concluded that the characteristic relaxation of bisphenol A is fully restored at this point. Because the relaxation peak of intermediate linkage has the same high as that for bisphenol A carbonate, it was further concluded that the cooperative relaxation correlation distance is seven repeat units. The dynamic mechanical relaxation spectrum of B9T is very similar to that of B7T except that the intensity of the relaxation peak of bisphenol A carbonate blocks is a little higher than that of the relaxation peak of the intermediate linkage. This spectrum suggests that the correlation distance of the cooperative γ-relaxation is less than nine repeat units but greater than five repeat units. Therefore, we conclude that the scale of this cooperative motion is seven repeat units long.

III. Summary

In this paper, a series of block copolymers are designed and their syntheses described. These copolymers were designed to elucidate the nature of bisphenol A polycarbonate's γ-relaxation. Specifically, the investigation was focused on determining the extent of cooperativity and the origin of this cooperative motion. The dynamic mechanical spectra of the synthesized homologues suggest that the intrachain interactions are the dominant factor of this cooperative relaxation and the extent of the relaxation is about seven repeat units. These results are consistent with previous investigations and intuitive speculations but are more precise and less ambiguous.

IV. Experimental Section

Detail experimental procedures are given in the appendix.

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Appendix. Experimental Section

I. Synthesis. A. Overview. All block copolymers were synthesized in two steps. The first step was the synthesis of oligomers. The second was the polymerization of the oligomers to form polymers with the desired structures. A modified low-temperature solution polymerization was found to be the best general preparation procedure and was employed to synthesize all of the copolymers, although some of the copolymers can be synthesized through other methods, such as interfacial polymerization.

B. Starting Materials. Phosgene was supplied by a 20 wt % (1.9 M) solution in toluene from Fluka. *N,N*-Dimethyl-4-aminopyridine, trichloroethylchloroformate (TCECF), and bisphenol A (99+%) were supplied from the Aldrich Co. and were used without further purification. Tetramethylbisphenol A was kindly donated by E. I. du Pont de Nemours & Co. and Dow Chemical Co. All the solvents were purchased from the Aldrich Co. and used without further purification.

C. Characterization. Proton NMR spectra were obtained at 300 MHz on a Bruker WM-300 FT-NMR spectrometer. Deuterated chloroform was used as the solvent, with tetramethylsilane as the internal reference. All chemical shifts were reported in δ units down shift from tetramethylsilane. Gel permeation chromatography was performed using a Waters GPC interfaced with a HP microcomputer. THF was used as a carrier/solvent, and the results were calibrated using narrow molecular weight distribution polystyrene standards. Differential scanning calorimetry (DSC) was conducted using a Perkin-Elmer TA-7 system. Scans were run at 20 K/min, and glass transition temperatures were determined from the second scan of the powder samples.

D. Synthesis of Monomers. 1. Synthesis of 2,2-Bis(4-hydroxyphenyl)propane Monosodium Salt [BPA Monosodium Salt]. A total of 2 g of NaOH was dissolved in 150 mL of anhydrous methanol and was cooled to 0–5 °C by an ice-water bath. Then 11.4 g (0.05 mol) of bisphenol A was added to the methanol solution and stirred for 0.5 h. After the methanol was evaporated under vacuum, the forming white powder was washed with 200 mL of acetone, filtered under a nitrogen atmosphere, and dried under vacuum. The amount of monosodium salt thus obtained was 12.2 g. The final yield was 99%. The melting point was 280 °C (decomposition).

2. Synthesis of 2,2-Bis(3,5-dimethyl-4-hydroxyphenyl)propane Monosodium Salt [TMBPA Monosodium Salt]. The synthesis procedure of TMBPA monosodium salt was very similar to the one for BPA monosodium salt except that tetramethylbisphenol A was used as the starting material. The final yield was 90%. The melting point of TMBPA monosodium salt was 257–260 °C.

E. Syntheses of Oligomers. 1. Tribisphenol A Carbonate (BPA Trimer). For this synthesis 1.88 g (0.0075 mol) of BPA monosodium salt was suspended in 10 mL of *N,N*-dimethylacetylamide (DMAc) under rapid magnetic stirring and was cooled to 0 °C. A solution of 1.2 g (0.0034 mol) of BPA bischloroformate in 10 mL of DMAc was added to the monosodium salt solution. As soon as the bischloroformate was added, a clear solution was formed, followed by a white precipitation. The reaction was allowed to proceed for an additional 10 h at room temperature. Then the reaction mixture was poured into 200 mL of distilled water. The white precipitate was collected by filtration and washed with methanol. The final product was dried under vacuum at 60 °C. The final yield was 65%.

^{1}H-NMR (300 MHz, $CDCl_3$, ppm): 1.60 (2 s, 18 H, i-PrCH_3); 6.73 (d, 4 H, Ph*H*); 7.08 (d, 4 H, Ph*H*); 7.16–7.25 (m, 16 H, Ph*H*).

2. Tritetramethylbisphenol A Carbonate (TMBPA Trimer). The synthesis procedure of TMBPA trimer was very similar to the one for BPA trimer except for using tetramethylbisphenol A bischloroformate and tetramethylbisphenol A monosodium salt as the starting materials and with a relatively longer reaction time. The final yield was 80%.

^{1}H-NMR (300 MHz, $CDCl_3$, ppm): 1.60 (2s, 18 H, 6i-PrCH_3); 2.18–2.25 (2s, 36 H, PhCH_3); 6.70–6.90 (m, 12 H, Ph*H*).

3. (Bisphenol A)-(Tetramethylbisphenol A)-(Bisphenol A) Carbonate. The synthesis procedure of (bisphenol A)-(tetramethylbisphenol A)-(bisphenol A) carbonate oligomer was very similar to the synthesis of BPA trimer except for using tetramethylbisphenol A bischloroformate reacting with 2 equiv of BPA monosodium salt at room temperature. The final yield was 79%.

^{1}H-NMR (300 MHz, $CDCl_3$, ppm): 1.60-1.70 (2s, 18 H, 6i-$PrCH_3$); 2.22 (s, 12 H, $PhCH_3$); 6.60-7.29 (m, 20 H, PhH).

4. (Tetramethylbisphenol A)-(Bisphenol A)-(Tetramethylbisphenol A) Carbonate. The synthesis procedure of (bisphenol A)-(tetramethylbisphenol A)-(bisphenol A) carbonate oligomer was almost the same as the synthesis of BPA trimer except for using bisphenol A bischloroformate reacting with 2 equiv of tetramethylbisphenol A monosodium salt at room temperature. The final yield was 73%.

^{1}H-NMR (300 MHz, $CDCl_3$, ppm): 1.57-1.70 (2s, 18 H, 6i-$PrCH_3$); 2.25 (s, 24 H, $PhCH_3$); 6.60-7.29 (m, 16 H, PhH).

F. Synthesis of Polymers. 1. Synthesis of Poly[(bisphenol A carbonate)-*alt*-(tetramethylbisphenol A)] (Alternating Copolymer). The polymer can be synthesized both by the interfacial polymerization method and by the solution polymerization method.

For the interfacial polymerization, a four-neck round-bottomed flask with four indentations was used in order to achieve better mixing. For this synthesis, 8.8 g (0.038 mol) of bisphenol A was suspended in 100 mL of a 20% NaCl aqueous solution and 16.4 g (0.040 mol) of tetramethylbisphenol A bischloroformate was dissolved into 100 mL of dichloromethane. Both solutions were added to the reaction flask. After the whole system was cooled to -5 to 0 °C by an ice-NaCl bath, 0.5 g of *N,N*-dimethylaniline and 0.5 mL of triethylamine were added as catalysts. The reaction was carried out with intensive mechanical mixing, and the pH value of the reaction mixture was monitored by a pH meter and was controlled by adding 1.0 M NaOH dropwise to the system. The pH value of the reaction mixture was kept between 7.0 and 8.0 at the early stage of the reaction and was raised to 12.5 at the end of the reaction. After the completion of the reaction, the mixture was transferred to a separation funnel. The organic layer was washed with distilled water, followed by a dilute HCl solution (~0.01 M), and finally with distilled water. The organic phase was then poured into 500 mL of methanol to precipitate the copolymer. The polymer was collected by filtration and was further purified by reprecipitation from chloroform to methanol.

The polymer was also prepared by the "ultral" low-temperature solution polymerization method which was very similar to the following description.

2. Synthesis of Poly[(pentatetramethylbisphenol A carbonate)-*alt*-(bisphenol A carbonate)] [BT5]. Low-temperature solution polymerization was employed in this synthesis. The polymerization reaction was completed in two steps. The first step was the formation of bischloroformate-terminated oligomers. The second step was the polymerization of bischloroformate-terminated oligomers with phenylhydroxy-terminated oligomers at low temperature. In the first step, 4.525 g (0.005 mol) of TMBPA trimer and 0.122 g (0.001 mol) of *N,N*-dimethyl-4-aminopyridine were dissolved in 15 mL of anhydrous toluene and combined with 15 mL of a phosgene-toluene solution (1.9 M). The reaction mixture was cooled to -60 °C by a dry ice-acetone bath, and 1.50 g (0.010 mol) of diisopropylethylamine was added as an acid acceptor. The reaction temperature was allowed to slowly increase to room temperature and was kept at room temperature for an additional 3 h. The forming diisopropylethylamine hydrochloride was then removed by centrifugation. Toluene and trace amounts of the unreacted phosgene were removed under vacuum. The remaining chloroformate-terminated oligomer was redissolved in 25 mL of dichloromethane and transferred into a dropping funnel. In another round-bottomed flask with a mechanical stirrer, 3.766 g (0.0048 mol) of (tetramethylbisphenol A)-(bisphenol A)-(tetramethylbisphenol A) carbonate and 0.3 g of *N,N*-dimethyl-4-aminopyridine were dissolved in 50 mL of CH_2Cl_2 and then cooled to -30 °C. The CH_2Cl_2 solution of chloroformate-terminated oligomer formed in the first step was added dropwise into this hydroxy-terminated oligomer, which was kept under intensive mechanical agitation. At the same time, 1.08 g (0.010 mol) of triethylamine was added by a syringe. The viscosity of the reaction mixture increased sharply at the end of this step, indicating the formation of a high polymer. The reaction temperature was then increased to room temperature to order to complete the reaction. Finally, the reaction mixture was washed with distilled water until free of chloride ions in the aqueous phase. The organic phase was then poured into 600 mL of methanol to precipitate the polymer. The forming polymer was purified by reprecipitating from dichloromethane and methanol and dried at 60 °C under vacuum. The final yield of this reaction was 92%, based on the hydroxy-terminated oligomer.

^{1}H-NMR (300 MHz, $CDCl_3$, ppm): 1.60 (s, TMBPA i-$PrCH_3$); 1.65 (s, BPA i-$PrCH_3$); 2.21-2.28 (2 s, TMBPA $PhCH_3$); 6.9 (s, TMBPA PhH); 7.15-7.25 (2d, BPA PhH).

3. Synthesis of Poly[(tritetramethylbisphenol A carbonate)-*alt*-(bisphenol A carbonate)] [BT3]. The synthesis procedure of poly[(tritetramethylbisphenol A carbonate)-*alt*(bisphenol A carbonate)] was identical to the synthesis of poly[(pentatetramethylbisphenol A carbonate)-*alt*-(bisphenol A carbonate)] except for the use of bisphenol A bischloroformate reacting with 1 equiv of tritetramethylbisphenol A carbonate at -15 °C. The final yield was 87%.

^{1}H-NMR (300 MHz, $CDCl_3$, ppm): 1.60 (s, TMBPA i-$PrCH_3$); 1.65 (s, BPA i-$PrCH_3$); 2.21-2.28 (2s, TMBPA $PhCH_3$); 6.90 (s, TMBPA PhH); 7.15-7.25 (2d, BPA PhH).

4. Synthesis of Poly[(tetramethylbisphenol A carbonate)-*alt*-(tribisphenol A carbonate)] [B3T]. The synthesis procedure of poly[(tetramethylbisphenol A carbonate)-*alt*-(tribisphenol A carbonate)] was identical to the synthesis of poly[(pentatetramethylbisphenol A carbonate)-*alt*-(bisphenol A carbonate)] except for the use of bisphenol A bischloroformate reacting with 1 equiv of tritetramethyl bisphenol A carbonate at -15 °C. The final yield was 89%.

^{1}H-NMR (300 MHz, $CDCl_3$, ppm): 1.60 (s, TMBPA i-$PrCH_3$); 1.69 (s, BPA i-$PrCH_3$); 2.20 (s, TMBPA $PhCH_3$); 6.90 (s, TMBPA PhH); 7.15-7.25 (2d, BPA PhH).

5. Synthesis of Poly[(tetramethylbisphenol A carbonate)-*alt*-(pentabisphenol A carbonate)] [B5T]. The synthesis procedure of poly[(tetramethylbisphenol A carbonate)-*alt*-(pentabisphenol A carbonate)] was very similar to the one for poly[(pentatetramethylbisphenol A carbonate)-*alt*-(bisphenol A carbonate)]. First, BPA trimer was phosgenated to form the corresponding bischloroformate at -30 to -25 °C, as described in the formation of bischloroformate-terminated TMBPA trimer. After being purified, the bischloroformate was immediately coupled with a stoichiometric amount of bisphenol A-tetramethylbisphenol A-bisphenol A carbonate at a temperature range of -25 to -10 °C. DMAP and triethylamine served as catalyst and acid acceptor. The purification procedure was the same as that used for the other copolymers. The final yield was 93%.

^{1}H-NMR (300 MHz, $CDCl_3$, ppm): 1.60 (s, TMBPA i-$PrCH_3$); 1.69 (s, BPA i-$PrCH_3$); 2.22 (s, TMBPA $PhCH_3$); 6.90 (s, TMBPA PhH); 7.16–7.26 (2d, BPA PhH).

6. Synthesis of Poly[(tetramethylbisphenol A carbonate)-*alt*-(heptabisphenol A carbonate)] [B7T]. Instead of using the combination of various trimers, a different approach was used in the preparation of this oligomer. The hydroxy-terminated bisphenol A oligomer was synthesized with an unbalanced monomer feed. The oligomer was prepared in situ. In a 1000–mL four-neck round-bottomed flask with a mechanical stirrer and a dropping funnel, 18.3 g (0.08 mol) of BPA and 0.36 g of DMAP were dissolved in 200 mL of CH_2CL_2 containing 16.7 mL of triethylamine (0.12 mol) and the whole system was cooled to −20 °C. A solution of bisphenol A bischloroformate (21.2 g, 0.06 mol) in 150 mL of CH_2Cl_2 was added to the reaction flask within 1 min under vigorous agitation. The reaction mixture was allowed to warm up to room temperature for 1 h and was then cooled down to −25 °C for the polymerization reaction. An additional 5.85 mL of triethylamine was added to the solution as an acid acceptor for the polymerization reaction. Finally, a solution of 8.59 g (0.020 mol) of tetramethylbisphenol A bischloroformate in 60 mL of CH_2Cl_2 was added dropwise to the reaction mixture at −10 °C, which was under vigorous agitation. After polymerization, the resulting viscous solution was washed with distilled water until free of chlorine ions in the aqueous phase. The viscous organic phase was then poured into excess amounts of methanol to precipitate the copolymer. The copolymer was collected by filtration and was further purified by reprecipitation from acetone. The final yield was 95%.

^{1}H-NMR (300 MHz, $CDCl_3$, ppm); 1.60 (s, TMBPA i-$proCH_3$); 1.69 (s, BPA i-$proCH_3$); 2.22 (s, TMBPA Ph-CH_3); 6.90 (s, TMBPA Ph-H); 7.16–7.26 (2d, BPA Ph-H).

7. Synthesis of Poly[(tetramethylbisphenol A carbonate)-*alt*-(nonabisphenol A carbonate)] [B9T]. The synthesis procedure of poly(tetramethylbisphenol A carbonate)-*alt*-(nonabisphenol A carbonate)] was very similar to the synthesis of poly[(tetramethylbisphenol A carbonate)-*alt*-(heptabisphenol A carbonate)]. Instead of using a 4/3 molar ratio of bisphenol A vs bisphenol A bischloroformate, a 5/4 molar ratio was employed to form oligomers with an average length equal to nine repeating units. These oligomers were then polymerized with a stoichiometric amount of tetramethylbisphenol A bischloroformate in situ to form the desired copolymer. The purification procedure was identical to that of B7T.

^{1}H-NMR (300 MHz, $CDCl_3$, ppm): 1.60 (s, TMBPA i-$PrCH_3$); 1.69 (s, BPA i-$PrCH_3$); 2.22 (s, TMBPA $PhCH_3$); 6.90 (s, TMBPA PhH); 7.16–7.26 (2d, BPA PhH).

II. Dynamic Mechanical Measurements. A. Fabrication of Specimens. Films of the copolymers for dynamic mechanical analysis were cast on glass plates using a 10 w/v % solution of chloroform. They were allowed to dry in a desiccator for 48 h and then were peeled off the glass plate and dried for 24 h at 60 °C in a vacuum oven. Just before the measurements, the films were heated to 15 °C above their respective glass transition temperatures, held for 15 min, and rapidly cooled to room temperature to erase their previous thermal histories. The typical specimen had dimensions of length × width × thickness of 30 mm × 2.5 mm × 0.15 mm, respectively. All copolymers were optically clear and showed no signs of crystal formation.

B. Dynamic Mechanical Measurements. All the dynamic mechanical spectra of corresponding block copolymers were obtained from a spectrometer built in our laboratory which is based on a linear motor driver unit and a Hewlett-Packard data acquisition unit controlled by an HP computer. The measurements were performed at a temperature range of −150 °C to the T_g of the copolymers with a scan rate ∼1.5 °C/min. Two frequencies, 1.0 and 10.0 Hz, were used for the measurements at each temperature.

Because the films cast from the chloroform solution usually are nonuniform in thickness, the geometric dimension of the films cannot be measured accurately. The specimen grips also introduce end effects which lead to systematic errors in the measured Young's moduli. To overcome this problem, the moduli were calibrated against Young's moduli obtained from the tensile experiments.

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