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Secondary Relaxation Motion in Bisphenol A Polycarbonate

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ABSTRACT: The nature of the molecular motion responsible for the mechanical secondary relaxation process of bisphenol A polycarbonate (BPA-PC) was studied. To characterize the secondary relaxation motion, dynamic mechanical behaviors of an alternating copolymer and alternating multiblock copolymers of BPA-PC and tetramethylbisphenol A polycarbonate (TMBPA-PC) were investigated. The dynamic mechanical spectrum of the alternating copolymer showed only one secondary relaxation peak at an intermediate temperature, indicating that more than one repeating unit is needed for the motion of BPA-PC. With systematically increasing block lengths from one repeating unit, multiple peaks reemerged. At a block length of nine units for each type of comonomer, two secondary relaxation peaks for each component were restored at their corresponding temperatures. In addition, a third peak at an intermediate temperature was observed, which is thought to be due to the motion of the interlinking part of the two blocks. These results suggest that the secondary relaxation of BPA-PC is due to the cooperative motion of several repeating units along the chain. The results of dynamic mechanical analyses of the blends of BPA-PC and TMBPA-PC indicate that the molecular motion has contributions from intermolecular interactions.

Introduction

The secondary relaxation behavior of bisphenol A polycarbonate (BPA-PC) has been extensively studied since the relaxation is believed to be closely related to the mechanical properties of BPA-PC. However, the molecular origin of the mechanically detected secondary relaxation of BPA-PC has not been unambiguously characterized. The main reason is that dynamic mechanical spectroscopy (DMS), which directly probes the mechanical relaxation, is not able to identify the motion with specific molecular species. Other dynamic techniques including dielectric relaxation and NMR have also been used to characterize the molecular origin of relaxations in solid polymers. In fact, these techniques have been more successful for characterizing the motion in terms of specific groups. Some of these results have found considerable agreement among themselves. The motions characterized by these techniques, however, are not necessarily related to the mechanical secondary relaxation, simply because the probes used are not mechanical in nature.

Although the molecular origin of the secondary relaxation cannot be determined directly by DMS, it is possible to characterize it when a homologous series of polymers is investigated. For example, the secondary relaxations of acrylate polymers were successfully characterized with DMS using a homologous series.[1] Another DMS work[2] revealed some important aspects of the secondary relaxation of BPA-PC on the basis of the resuls on a series of polycarbonates with systematic structural variations. In the present study, the origin and the scale of the mechanical secondary relaxation motion are characterized with a series of copolymers containing BPA-PC.

Background

Previous investigations on the molecular origin of the secondary relaxation motion in BPA-PC are reviewed, and our approach to this subject will be proposed. The suggested motions will be examined in two aspects; first, whether or not the motions are correlated to the other groups in the chain, and, second, whether the motions can induce the mechanical relaxation by themselves. The relaxation we are interested in is the one associated with the DMS peak of BPA-PC located at around −100 °C at 1 Hz. In this discussion, this relaxation will be referred to as the γ relaxation or just the secondary relaxation. BPA-PC is a heteroatom backbone polymer whose repeating unit consists of an isopropylidene group, two phenylene rings, and a carbonate group. It is useful to understand the physical structure and conformations of BPA-PC. Structural information is obtained through various molecular dynamics calculations and crystallographic studies using model compounds.[3-8] It is believed that the carbonate group forms a planar structure due to the partial double-bond character of the two bonds between the carbonyl carbon and the ether oxygens. The partial double-bond character is clearly demonstrated by the fact that the lengths of these two bonds (1.32 Å) are shorter than the usual C(paraffinic)–O(ether) bond length of 1.43 Å, although they are longer than the regular carbonyl double bonds (1.23 Å).[7-9] The trans–trans conformation along the C(phenyl)–O(ether)–C(carbonyl)–O(ether) bonds should be energetically the most favored conformation.[3] A recent crystallographic study[7] shows the angle between the two ether oxygen–carbonyl carbon bonds to be 108°, which is much smaller than the usual sp^2 bond angle of 120°. As a result, the angle between the virtual phenylene bonds (the angle between the two phenylene 1,4-axes) must be 134°. The difference between this angle and the bond angle between the two phenylene axes around the quaternary carbon (109.5° or 108° by some) makes the contour of the chain nonlinear or "bananalike".[5] In a depolarized light scattering study,[6] the angle between the phenylene plane and the carbonate plane in BPA-PC was estimated to be 46°. The orientation of the two phenylene planes separated by the carbonate group can be either asymmetrically skewed to different directions or distorted to the same direction, as the energy difference between these two orientations is calculated to be very small.[3] By inspecting the resultant conformation of BPA-PC (see Figure 1), one would realize that the chain is neither flat nor linear. Another point one would realize is that motion of an individual group independent of other groups in the chain might not be facile, possibly except for the methyl group.

By ^2H NMR studies of BPA-PC with deuterated methyl groups,[10,11] the methyl group motion was characterized as a rotation about its C_3 axis. While a couple of NMR[12,13] and molecular dynamics studies[3,4] suggest that the me-

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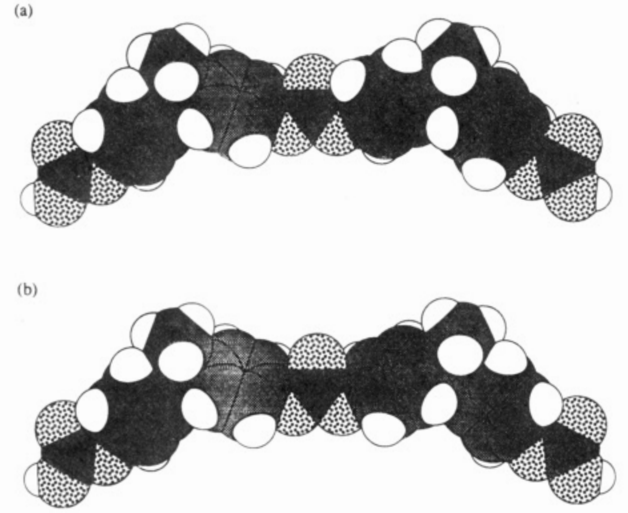

Figure 1. Three-dimensional structure of BPA-PC with two repeating units showing "bananalike" conformation. The two phenylene rings around the carbonate group are (a) skewed to different directions and (b) distorted to the same direction.

thyl group motion is correlated to either the adjacent phenylene group motions or the chain motion, another NMR study[14] concludes that this type of correlation is unlikely. While the presence of intrachain correlation of the methyl group motion is not clear at this point, the absence of interchain correlation of this motion is obvious from various experimental results.[11,15,16] The methyl group rotation is not expected to induce the mechanical relaxation, since the group is small and its rotation does not require any additional volume. In addition, the methyl group rotation has been detected by ^{2}H NMR and broadline NMR from far below the mechanical secondary relaxation temperature (T_γ).[10-12] The inability of the methyl group motion in inducing the mechanical secondary relaxation was also inferred by a DMS work by Yee and Smith.[2] It was shown that changing the isopropylidene group to somewhat bulkier groups does not result in higher T_γ's. Recognizing also the absence of interchain coupling, it is concluded that the methyl group rotation alone is not directly connected to the mechanical secondary relaxation process of BPA-PC.

As a consequence of the planarity and rigidity of the carbonate group, the motion of the carbonate group alone would not be expected to be facile. In a recent molecular mechanics calculation,[3] the rocking motion of the carbonate group over a range of ~70° was suggested. A 40° rocking motion about the chain axis plus a 15° rocking along the carbonyl axis was also proposed by Henrichs and co-workers[17] in a variable-temperature ^{13}C NMR study with carbonyl-carbon-tagged BPA-PC. The carbonate motion is expected to be correlated to other groups. Since the phenylene group is the adjacent group, it is tempting to conclude that the carbonate group motion and the phenylene group motion are correlated. Indeed, almost all recent dielectric studies and some NMR studies have proposed the cooperative motion of the carbonate and phenylene groups as the motion responsible for the secondary relaxation of BPA-PC,[12,18-20] although some earlier investigators[21,22] incorrectly suggested the carbonate motion alone as the source of the secondary relaxation due apparently to lack of other experimental information. Since the carbonate group is the only group with an appreciable dipole moment, the motions of the carbonate group proposed above (the rocking motion) may account for the observed dielectric loss peak of BPA-PC. However, it is not conceivable that this small-scale motion alone can induce the mechanical secondary relaxation. This was clearly shown in a DMS study.[2] On comparison of the DMS of BPA-PC and the polyformal of BPA (where the carbonyl group is replaced with a methylene group), the same T_γ was observed, despite the fact that the glass transition temperature of poly(BPA-formal) is lower than that of BPA-PC by 60 °C. We conclude that the motion of the carbonate group in BPA-PC is coupled to the motion of the adjacent phenylene groups but is not considered to be able to induce the mechanical relaxation by itself.

The motion of the phenylene groups has been most extensively studied among other groups. Advances in various high-resolution NMR techniques have enabled many researchers to study virtually every aspect of the phenylene motion. Proton spin-lattice relaxation study,[23] deuterium line-shape analysis,[24] ^{13}C line-width and spin-lattice relaxation study,[25] ^{13}C dipolar rotational spin-echo study,[13] and ^{13}C chemical shift anisotropy analysis[26] have been used successfully and complementarily to detect and characterize the phenylene group motion. Although their points of view of the overall picture of the secondary relaxation motion are different, it appears that they agree with each other on the nature of the phenylene group motion, which is a π (180°) flip about its 1,4-axis augmented by smaller amplitude oscillations about the same axis. There are still some controversies regarding the features of the phenylene motion other than π flip. It should be noted that the motion suggested by NMR results is not a unique motion that can be easily determined by a single type of experiment. Rather it is based on a simulated motion that gives the best fit to experimentally observed NMR line shapes and relaxation times, and quite a few experiments using various techniques and theoretical considerations have been sought to define the nature of the motion. Since π-flip motion alone could not give a perfect fit to the experimental data, an additional or complementary motion had to be developed, in which some controversies arose. Nevertheless, there is a consensus that the NMR-sensitive phenylene group motion is primarily π flips plus some small-scale oscillation.

In the discussion above, the carbonate motion is considered to be correlated to the phenylene motion. It is therefore obvious that the one side of the phenylene group is motionally correlated to the adjacent carbonate group. On the other side, where it is connected to the quaternary carbon, a higher degree of correlation between the two phenylene rings separated by the isopropylidene group is expected. The interaction between two ortho hydrogens in the two phenylene rings should be stronger than that between the phenylene hydrogen and the carbonyl oxygen due to the difference in dihedral angle (see Figure 1), as shown also by a recent ab initio calculation.[8] This high degree of correlation between the two phenylene rings was also experimentally proved in a DMS study with structural variations on the rings.[2] In that study, DMSs of polycarbonates with one phenyl ring (asymmetrically) substituted with a chlorine and both rings(symmetrically) substituted with one chlorine each were examined. Symmetrically substituted Cl_2BPA-PC has a mechanical loss maximum at 45 °C, and asymmetrically substituted ClBPA-PC has its maximum at 5 °C. If the two phenyl rings in ClBPA-PC flip independently, there should be two loss maxima at −100 °C for the unsubstituted ring and at +45 °C for the substituted ring. The presence of a single peak strongly suggests that the two rings in BPA-PC flip synchronously. Having proved the correlated motion of two phenylene rings in a repeating unit of BPA-PC, the motion of one phenylene ring is considered to be correlated on both sides, for the correlation with the carbonate group has already been postulated. Therefore, the correlation distance extends at least to one repeating unit. In fact, one can further imagine that the correlation would extend over even more than one repeating unit without any significant difficulty. These possibilities will be investigated in this paper. For the time being, we argue that the phenylene motion is correlated to adjacent groups at both ends of the 1,4-axis.

It is believed by many that there is a relationship between the phenylene motion and the mechanical relaxation process, based on the similarities in time scale and activation energy of the two processes and the fact that both are affected by physical aging and antiplasticization.[11,13,26-28] The argument that both processes occur on comparable time scales[13] seems to be reasonable, although selections of particular data of activation energy and mechanical T_γ can significantly affect this conclusion (by as much as 2 decades). However, the argument that the activation energy determined by NMR studies is comparable to that determined in dynamic mechanical studies needs some explanation, since the estimation of activation energy from NMR results is neither straightforward nor unambiguous. The activation energy determined in an NMR experiment is not a real activation energy of the motion but a method-dependent estimation that gives the best fit to the data.[13,24,29] As a result, the values determined in different techniques show discrepancies, which makes the comparison of the value to that by DMS less reliable, as one of the NMR groups pointed out.[30]

There are some good reasons why a direct relationship between the phenylene motion and the mechanical relaxation motion should be questioned. First of all, the π-flip motion itself cannot induce mechanical relaxation, since the flipping motion is a jump between two symmetrical potential wells and is not expected to cause any volume fluctuation or mechanical loss. For the phenylene motion to be mechanically significant, it has to be correlated to other molecular units. The second argument against the relationship between the phenylene motion and the mechanical relaxation is that π-flip motions have been observed in other polymers such as aromatic polyesters[16] and even in brittle cross-linked epoxides and epoxide prepolymers.[31] If π-flip motion alone can account for the mechanical loss in BPA-PC and in these other polymers, some factors other than secondary relaxation has to be assigned to the superior mechanical properties of BPA-PC. On the other hand, if we admit the notion of the relationship between the mechanical properties and the secondary relaxation process in BPA-PC, then the mechanical relaxation should contain other motions than just π-flip. For an additional piece of evidence that questions the relationship, it was shown, in NMR studies, that the phenylene motion is greatly slowed by antiplasticization,[16,24] which also suppresses the mechanical loss.[28] It was argued that, if the phenylene motion is responsible for the mechanical loss, then the corresponding dynamic mechanical relaxation peak should shift to a higher temperature.[24] This argument seems conceivable, since the distribution of correlation times of the phenylene motion has been shown to be broadened to longer times. To be exact, the corresponding mechanical peak should also be broadened to higher temperatures if the phenylene motion alone is responsible for the mechanical relaxation. The mechanical relaxation spectrum of antiplasticized BPA-PC observed by several groups of investigators shows little change in peak temperature, while the intensity of the peak is much suppressed.[28,30] Another striking experimental evidence is the fact that the polycarbonate of *m,m′*-dihydroxybiphenyl, in which phenylene flip is impossible, nevertheless still has a mechanical secondary relaxation peak.[32]

Considering all the arguments for the presence and absence of a relationship, one might conclude that the uncorrelated phenylene π-flip motion does not induce the mechanical seconary relaxation process, although the motion may participate in the mechanical relaxation through extensive correlation with other molecular units. It should be noted that most NMR groups recognized this problem and have suggested some explanations either by proposing a larger scale process or by just denying the notion of a direct relationship. Jones[33] proposed an isomerization process, and Schaefer and co-workers[27] proposed an interchain cooperation of π flips, which will be discussed later. On the other hand, Wehrle, Hellmann, and Spiess[24] concluded their ^{2}H NMR study by stating that π flip does not participate in the mechanical relaxation process but merely acts as an indicator for it.

As the independent motions of the constituent groups (methyl, carbonate, and phenylene) of BPA-PC have been shown to be unable to induce the mechanical relaxation, and the motions are considered to be correlated to each other (possibly except for the methyl group), a larger scale motion has to be sought as the motion responsible for the mechanical relaxation. In fact, the correlations between the two phenylene motions and between the phenylene and the carbonate motion appear so intense that independent motions of these groups seem unrealistic. Even with ignoring the possibly correlated methyl motion, the correlations between phenylenes and carbonate comprise a "correlation distance" exceeding one repeating unit. The argument that the correlation distance may exceed one repeating unit was made earlier in a DMS study of polycarbonates with structural variations.[2] It was suggested in that study that the motion of at least one repeating unit is the origin of the mechanical secondary relaxation. To test this thesis, Yee[34] examined the DMS of the copolymer of BPA-PC and another polycarbonate, tetramethylbisphenol A polycarbonate (TMBPA-PC), whose mechanical secondary relaxation temperature is 70 °C at 10 Hz. The dynamic mechanical spectrum of a random copolymer of BPA- and TMBPA-carbonate with a 3/1 mole ratio showed a single secondary relaxation peak. If the mechanical relaxation is induced by the motion of one repeating unit or a specific group therein, then two peaks should have been observed for this copolymer. The presence of a single peak clearly showed that the correlation distance extends over more than one repeating unit. A correlated motion of chain segments including both monomer units must be involved. Since the sequence structure of that copolymer was not well characterized, the length of the correlation distance or how many repeating units are involved in the motion could not be determined. Throughout that study, however, the participation of cooperative motions larger than one repeating unit in the mechanical secondary relaxation process was unambiguously proved.

Through the review of previous investigations, we appreciate that some details of the physical structure and the motion of individual groups in BPA-PC have been better defined by virtue of recent advances in molecular dynamics calculations and NMR techniques. The major conclusion from the review is that the motions of the groups are closely correlated to each other. The distance of this motional correlation was shown to extend over at least one repeating unit of BPA-PC,[34] although the quantitative determination of the distance was not possible. In the present study, to determine the correlation distance, the DMS of the copolymers containing BPA-PC with well-defined sequence structures will be investigated. The length of BPA-PC blocks will be systematically increased from one repeating unit. It is expected that copolymers with block lengths shorter than the intrachain correlation distance will give a single relaxation peak. At the point where the block length is equivalent to the correlation distance, multiple peaks would emerge. For this series of experiments, it is necessary to find a suitable second component polymer whose T_γ is well separated from that of BPA-PC so that the peaks are located unambiguously. TMBPA-PC was selected as the second component due to its high T_γ and miscibility with BPA-PC. After the intrachain cooperativity is investigated, the possibility of the contribution of interchain interaction will also be examined.

Experimental Section

Specimens. BPA-PC used was Lexan resin from the General Electric Co. TMBPA-PC and the copolycarbonates were prepared in our laboratory. The copolymers examined were a perfectly alternating copolymer (B1T1) and alternating multiblock copolymers with block lengths of six and nine for each component (B6T6 and B9T9). The syntheses of the polymers are discussed elsewhere.[35] Film specimens were cast from 5 w/v % solutions of chloroform and dried. Immediately before the measurements, the films were heated to 15 °C above their respective glass transition temperatures, held for 30 min, and rapidly cooled to room temperature to erase the previous thermal histories. A typical size of the film was 50 mm long, 5 mm wide, and 0.075 mm thick. All copolymers were optically clear and showed no signs of crystal formation. We also note that BPA-PC and TMBPA-PC are completely miscible. We therefore do not expect domain formation in the copolymers.

Instrumentation. The instrument used for the dynamic mechanical measurements consists of a linear motor, a load transducer, and a displacement transducer. The sine waves were produced by a Wavetek waveform generator and transmitted to the driver unit via a power amplifier. The displacement signal and the resultant load signal were amplified and recorded with a digital storage oscilloscope. These digitized signals were processed in a microcomputer by a cross-correlation technique. The load and displacement transducers were calibrated to convert the electronic signals to engineering quantities. The load transducer was calibrated with standard weights. The displacement transducer was calibrated by known displacements as measured with a dial guage. For the dynamic measurements, the first 10 cycles were discarded for the transient effect to settle and the next 10 cycles were recorded for the computation of a data set. The stress-strain signals were recorded digitally in an X-Y plotter, on which the achievement of a perfect ellipse was checked. With a typical strain amplitude of 0.2%, the resolution of the tan δ value was better than 1×10^{-3} at 11 Hz, the frequency used for all measurements. The temperature was scanned. The temperature range was achieved by initially cooling with liquid nitrogen and heating with heating coils at the bottom of the sample chamber. The temperatures were measured by a digital temperature indicator equipped with an RTD element. The heating rate was about 1.5 °C/min for the temperature range between −150 and −80 °C and was less than 0.8 °C/min for the temperatures above −80 °C to the glass transition temperature of the polymers. A commercial instrument (Du Pont dynamic mechanical analyzer Model 983, DMA) was also used with frequency variations, but due to its poor resolution, especially at lower temperatures, the data were taken only for the calculation of activation energies.

Results and Discussion

Scale of Intrachain Cooperative Motion. To elucidate the scale of intrachain cooperativity of the γ motion of BPA-PC, the DMS of the multiblock copolymers of BPA-PC and TMBPA-PC is examined. In a previous study,[34] the DMS of a 3/1 random copolymer of BPA-PC and TMBPA-PC exhibited a single secondary relaxation peak at an intermediate temperature, which suggests that the cooperativity extends over one repeating unit. In the present study, the block length is increased systematically from one, where a single peak is expected as in the above study, to several repeating units until separate peaks reemerge at the temperatures corresponding to the T_γ's of the homopolymers. Since the thin film specimens were used and the thicknesses of the specimens were not accurately determined, the storage and loss moduli could not be accurately measured. As a result, the moduli were calibrated with the moduli values measured in the tensile tests at room temperature using larger specimens.[36]

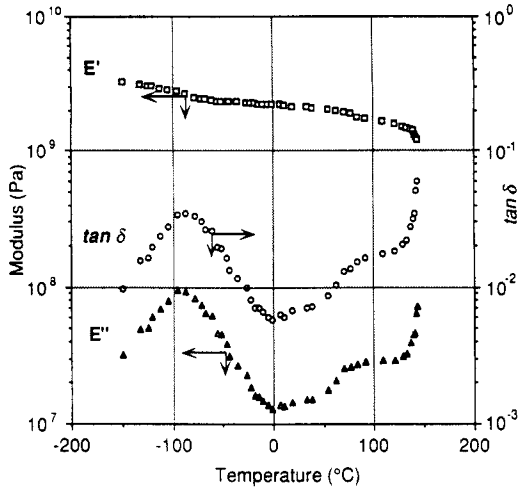

Figure 2. Dynamic mechanical spectrum of BPA-PC recorded at 11 Hz.

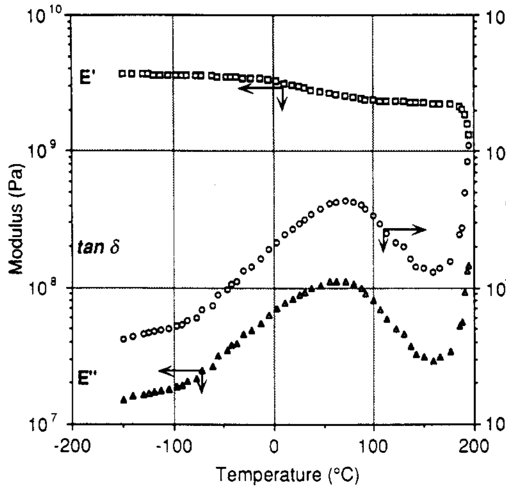

Figure 3. Dynamic mechanical spectrum of TMBPA-PC recorded at 11 Hz.

DMS of BPA-PC and TMBPA-PC homopolymers obtained at 11 Hz are shown in Figures 2 and 3. The higher secondary relaxation temperature (70 °C) of TMBPA-PC can be attributed to the relative stiffness of the chain compared to that of BPA-PC, since this relaxation is also thought to be due to a cooperative motion of repeating units, as will be proven later. DMS of the alternating copolymer of BPA- and TMBPA-PC (B1T1) is shown in Figure 4. As expected, the spectrum shows only one relaxation peak at an intermediate temperature of 0 °C, between the relaxation temperatures of BPA-PC and TMBPA-PC homopolymers. One important fact is demonstrated by this result: the independent motion of

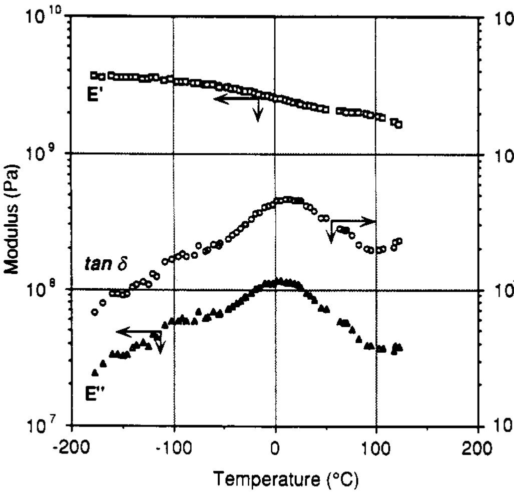

Figure 4. Dynamic mechanical spectrum of the alternating copolymer, B1T1, recorded at 11 Hz.

a specific group inside one repeating unit cannot induce the mechanical relaxation of BPA-PC. This conclusion was tentatively reached by investigating individual motions, which were considered unable to induce the mechanical relaxation, but it is experimentally verified here. The same argument is also applicable to the motion of TMBPA-PC, since if the motion of a specific group can induce the mechanical relaxation of this polymer, a separate peak should have been observed at 70 °C. The motion involved in the mechanical peak observed in B1T1 is undoubtedly the cooperative motion of the two types of monomer units. The correlation distance in this particular copolymer, however, cannot be determined. The smallest unit of this motion should be a unit consisting of one BPA and one TMBPA units, but the actual correlation distance may well be much larger than this unit.

The activation energies for the peaks of BPA-PC, TMBPA-PC, and B1T1 were calculated with the loss moduli data obtained by using DMA at three frequencies and the Arrhenius-type relationship. Although the activation energies are not directly relevant to the current question, the values are reported here. The obtained activation energies for BPA-PC, TMBPA-PC, and B1T1 are 13.4, 24.5, and 20.5 kcal/mol, respectively. The previously reported activation energies in the literature for BPA-PC[2] and TMBPA-PC[37] are 13 and 19 kcal/mol, respectively.

The DMS of a multiblock copolymer, in which block lengths are six for each component (B6T6), is shown in Figure 5. The first feature observed is that there is a peak at a low temperature. The peak is small in intensity with a maximum tan δ value of 0.008 ($E'' \sim 2.7 \times 10^7$ Pa); though small, it was reproducible in repeated experiments. The peak temperature was also reproducible and is located at −125 °C. The other peak at a higher temperature in the spectrum is broad and intense. This spectrum may be better analyzed in comparison with the spectrum of the other multiblock copolymers whose block lengths are nine for each component (B9T9) in Figure 6 (see Figure 7 for comparison). In B9T9, the lower temperature peak is bigger (with a maximum tan δ value of 0.02 and E'' of 6.5×10^7 Pa) than that of B6T6 and the peak temperature is now at −100 °C. The higher temperature peak in B9T9 is again extremely broad.

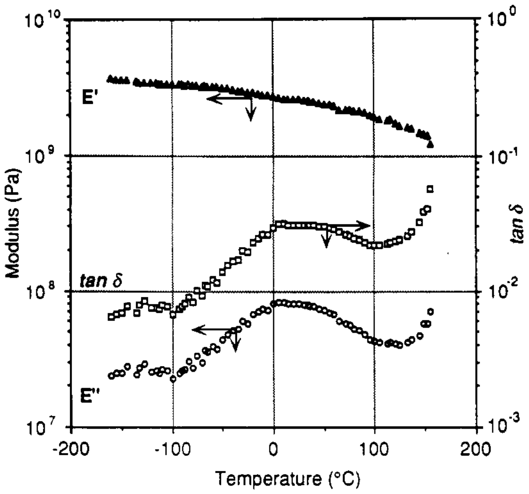

Figure 5. Dynamic mechanical spectrum of the multiblock copolymer whose block lengths are six for each component, B6T6, recorded at 11 Hz.

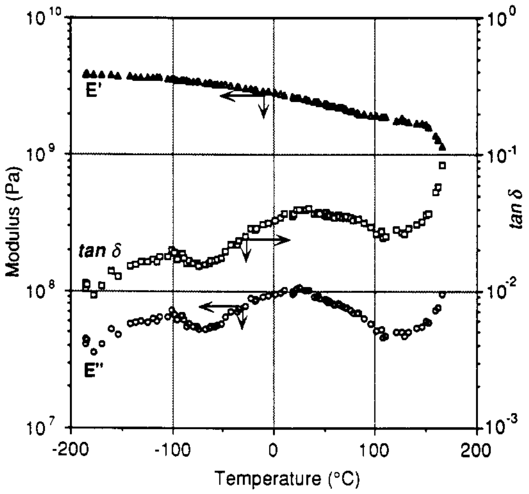

Figure 6. Dynamic mechanical spectrum of the multiblock copolymer whose block lengths are nine for each component, B9T9, recorded at 11 Hz.

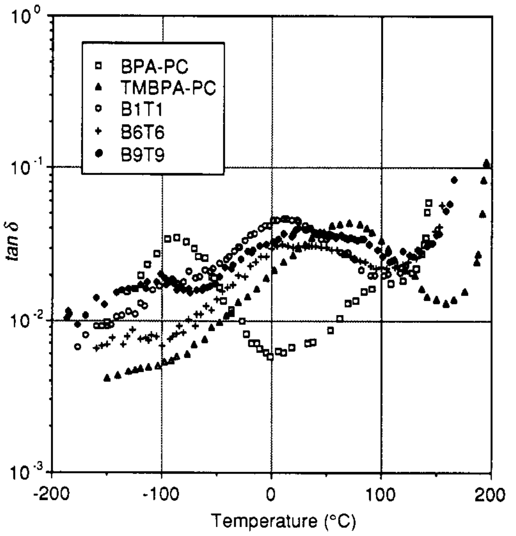

Figure 7. Dynamic mechanical spectra of BPA-PC, TMBPA-PC, and the copolymers recorded at 11 Hz.

The breadth of the higher temperature peaks in the spectra of B6T6 and B9T9 can be considered to be due to a superposition of the two peaks. To examine this possibility, the widths of the peaks are compared to those of the peaks in the spectra of the homopolymers and B1T1. The full-widths at half-height (ΔT) of the peaks in B6T6 and B9T9 are 160° and 180°, respectively, while the ΔT's of the peaks in TMBPA-PC and B1T1 are 110° and that of BPA-PC is 90°. Judging from the relative widths of the peaks, it seems not unreasonable to consider the higher temperature peaks in the block copolymers as the superposition of two peaks. These composite peaks should show separation at a very low frequency test, although the peak separation was not successful at 0.01 Hz with a DMA. An even lower frequency, which would not be practical, appears to be necessary for the separation of these peaks. The three peaks in the spectra are designated as the lower, intermediate, and higher temperature peaks, in order of increasing temperature.

The lower temperature peaks in the block copolymers are undoubtedly the restoration of the BPA-PC γ peak due to the cooperative motion in the BPA blocks. In B6T6, however, the motion appears only partially restored, while it seems to be fully restored in B9T9, judging by the peak intensity and temperature. Despite the same overall composition (50% BPA units and 50% TMBPA units), the peak intensity in B6T6 is smaller than that in B9T9. That means the relaxation strength and thus the scale of the motion in B6T6 are smaller than those in B9T9. The reason for the smaller motion is attributed to a constraint, by which otherwise extendable motion is restricted. The restriction imposed on the BPA block in this copolymer should be the adjacent TBMPA blocks, if the effect of different chain environments is ignored for now. Since the scale of the intrachain cooperativity reached in B6T6 is smaller than that in BPA-PC, this cooperativity cannot represent the correlation distance of the BPA-PC γ motion. The intensity of the lower temperature peak in B9T9 is higher than that in B6T6 and is actually higher than half of the γ peak intensity of BPA-PC ($E'' \sim 1.0 \times 10^8$ Pa). At first sight, it appears that the cooperativity achieved in BPA-PC is fully restored in this copolymer and the nine units are sufficient for the cooperative motion of BPA-PC. However, there are difficulties that would not make the interpretation of the present results straightforward. Generally speaking, a direct comparison of peak intensities in two different polymers cannot be justified. First of all we do not know what determines the intensity of a peak. There is no theory that describes the magnitude of mechanical relaxation peaks quantitatively, though there is a theory that defines the area under the dielectrical relaxation peak in the frequency domain.[38] Partly adapting that theory, we can assume that the peak intensity is proportional to the number and the relaxation strength of the relaxing species. Since the relaxing species in BPA-PC and the B9T9 copolymer are the same (BPA units), we can further assume that the peak intensity is proportional to the number of BPA units in motion, although the relaxation strength can also be different. Another factor is the background loss, which is dependent on instrument, material, and temperature.[39] By ignoring the temperature and material dependence, the background loss was determined for the current instrument with a piece of steel specimen. It has a tan δ value of 0.003, which is equivalent of a E'' value of 1.0×10^7 Pa for BPA-PC and of 1.2×10^7 for B9T9. In addition, the effect of the molecular environment should affect the intensity comparison, since the interchain structures of BPA-PC and the copolymers are different. Taken all together, it seems practically impossible to determine the correlation distance by comparing the peak intensities, unless one assumes that the intensity is directly dependent on the number of the relaxing species and that the temperature dependence of the background loss and the effect of environment are small. In fact, these assumptions are not totally unreasonable, or the error involved might be small compared to the possible experimental error. As we compare the peak intensities with these assumptions, the intensity of the lower temperature peak in B9T9 is roughly half of the peak intensity in BPA-PC. This result indicates that the cooperativity of the BPA-PC γ motion is fully restored.

Since it appears that the cooperativity of the motion in B9T9 can represent that in BPA-PC, we should be able to determine the correlation distance of the secondary relaxation motion in BPA-PC. It appears to be between six and nine repeating units. In determining the correlation distance, however, there is one more problem, that is, the fact that both ends of the BPA blocks are flanked by TMBPA blocks, which can restrict the motion of the adjacent BPA units, since at this lower relaxation temperature TMBPA blocks are not in motion. Therefore, it is possible that not all nine BPA units in the BPA block are in motion in B9T9. This situation should be the same in B6T6. Of course we do not know how many units are restricted from motion by the TMBPA blocks, and the number of BPA units in motion in B9T9 as well as in B6T6 cannot be precisely determined. As a result, the correlation distance remains somewhat ambiguous. It seems that determining the exact correlation distance with a resolution of one or two repeating units is not possible in the present study, considering also the molecular weight distributions in the blocks.[35] One may suggest that the distance can be found by extending the length of the BPA block or both blocks until the intensities of the corresponding peaks no longer change. Such experiments may be valuable, but, due to the same problems listed above, the results will still suffer from interpretational difficulties. Further extension of the block lengths was not carried out partly due to recognition of these problems and partly due to difficulties in preparing the block copolymers with larger block lengths.[35] According to the discussions up to this point, the intrachain correlation distance of the mechanical secondary relaxation motion of BPA-PC may be best described as "several repeating units".

The two peaks at higher temperatures in the block copolymers are considered now. The higher temperature component is undoubtedly due to the motion of the TMBPA blocks. In the spectra, the composite peak covers the temperature range where the secondary relaxation peak of TMBPA-PC homopolymer is observed. This is more obvious in the spectrum of B9T9, where the composite peak broadens to the high-temperature side, compared to that of B6T6. Since the broadening of the composite peak to the higher temperature can be considered to be due to the increased intensity of the higher temperature peak, the correlation distance of TMBPA-PC is larger than at least six repeating units. Again this argument does not take into account the effect of environment. The upper bound of the correlation distance could not be determined, since there is no facile way to determine if the intensity is saturated in B9T9. It may well be larger than nine units. We only conclude that the secondary relaxation motion of TMBPA-PC needs the cooperation of a multiple number of repeating units larger than six.

The intermediate temperature peak is assigned to the motion of the interlinking parts of the copolymer chain between BPA and TMBPA blocks. This designation appears to be reasonable, because the peak temperature is comparable to that of the alternating copolymer and because this is the only part of the block copolymer chain whose motion was not assigned to a relaxation peak. The relative intensity of the intermediate peak in comparison with the higher temperature peak is higher in B6T6 than in B9T9, which justifies its assignment, for the relative population of the interlinking part is larger in B6T6 than in B9T9. We can presume the intermediate peak would have its maximum at a temperature close to 0 °C, by referencing the peak temperature of B1T1. But, of course, there is no guarantee that the two motions can be activated at the same temperature because the number of units participating in the motion is not known.

As a summary, the motion responsible for the mechanical secondary relaxation of BPA-PC requires intrachain cooperation of several repeating units, with the scale probably less than nine units. The secondary relaxation motion of TMBPA-PC also requires intrachain cooperation of several repeating units, probably more than six. It was hoped that the correlation distances would be determined through the study with copolymers, but various complexities in interpretation made the results less quantitative. Nevertheless, the cooperative nature of the secondary relaxation motion in BPA-PC as well as in TMBPA-PC is unambiguously demonstrated.

Nature of the Intrachain Cooperativity. A hypothesis on the nature of the observed cooperativity is offered. The motional cooperativity in BPA-PC was more or less expected when we concluded the review of the previous studies and now is experimentally verified. The motional correlation between groups along the chain was considered to be so extensive that the independent motion of a molecular moiety appeared impossible. Therefore it is expected that the correlated motion would persist until the motion encounters a constraint. In other words, the correlation distance would be determined by the restriction imposed on the chain. A constraint that exists in glassy polymers would be the entanglements. As an entanglement may be defined as a topological constraint on a chain given by its neighbors, the entanglement points may well serve as the constraints for the chain motion. The average molecular weight between entanglements in BPA-PC was determined as 2400,[40,41] which is equivalent to 9.5 repeating units. Then the correlation distance of BPA-PC, in view of persistent correlation, would be 9 or 10 repeating units, if we assume that all the units between entanglements are in motion.

It was shown that the full relaxation strenth BPA-PC is restored in B9T9. The problem in designating the correlation distance as nine repeating units was the possibility that the motions of the terminal BPA units are restricted by adjacent TMBPA blocks. This problem may be resolved, since the restriction imposed by TMBPA blocks in B9T9 and that by entanglements in BPA-PC can be compared. Then the correlation distance in BPA-PC may be designated as the length between the entanglements. Although this hypothesis is based on several assumptions, it seems that those assumptions as well as the hypothesis itself are not totally unreasonable.

Interchain Interaction. Having proved an intrachain cooperation that spans several repeating unit, we naturally expect that this cooperation is intermolecularly correlated also. Also, for a secondary relaxation motion to affect the mechanical properties of the polymer, the motion must get some contributions from interchain interactions. There are some evidences that support the existence of interchain interaction in BPA-PC. The fact that the mechanical secondary relaxation peak is suppressed by physical aging supports the existence of interchain interaction, since physical aging is considered to affect the interchain structure only. Although some researchers believe that secondary relaxation processes are not affected by physical aging,[42,43] many others do not agree:[44,45] It appears that secondary relaxation motions involving larger scale main-chain motions are affected by physical aging, while the effect is not noticeable for the small-scale motions involving only side chains or groups. The fact that the phenylene motion is suppressed by external hydrostatic pressure[46] is an indirect evidence for the notion of interchain interaction. The most direct evidence for the existence of interchain interactions was given by the results of dynamic bulk relaxation (DBR) measurements, which measure the volumetric components of relaxation.[47] A DBR spectrum of BPA-PC[34] shows a pronounced peak of K'' (loss bulk modulus) at the same temperature as that of E''. This result indicates that the secondary relaxation of BPA-PC has a strong bulk component, which, in turn, supports the notion that the molecular motion responsible for the mechanical relaxation does interact with neighboring chains.

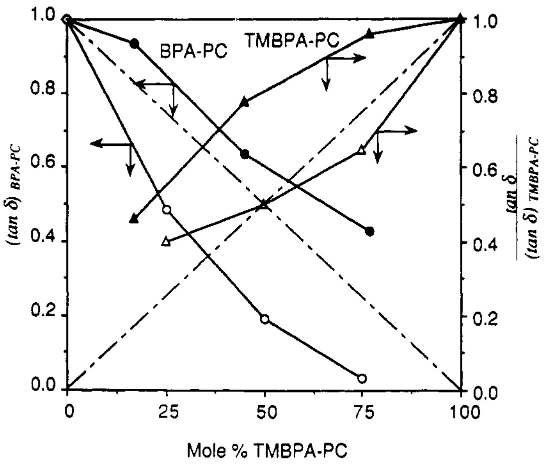

Figure 8. Relative peak intensities of BPA-PC and TMBPA-PC in the blends of the two polymers. Filled circles and triangles are from the result by Fischer and co-workers.[30] Open circles and triangles are from the result of the present study. Diagonal straight lines indicate the pure dilution effects.

While the existence of the interaction appears to be evident by various experimental support, one blend study apparently contradicts this notion. In a dynamic mechanical study of the miscible blends of BPA-PC and TMBPA-PC with several compositions, Fischer and co-workers[30] found that the intensities of both secondary relaxation peaks vary in proportion to the respective volume fractions. Since they also found no significant shift in the peak temperatures, they concluded that the two polymers relax completely independently of another, despite the proximity of the chain segments of both polymers in the blend. This experimental observation and the conclusion therefrom would seem to contradict the notion of the existence of interchain interaction in BPA-PC. To examine their result more closely, the peak intensities from their data are plotted against the mole ratio as shown in Figure 8. Since the intensities of peaks of BPA-PC ($\tan\delta = 0.035$) and TMBPA-PC (0.054) are different, to normalize the data, the ratio of the intensities to the peak intensities of the corresponding homopolymers are plotted. The background losses are also taken into account according to the discussion above. It is seen that the rates of change are neither linear nor the same for the two components: the TMBPA-PC peak decreases more slowly than the BPA-PC peak. Since, however, the difference does not appear to be significant enough to refute their conclusion and since their data points were not close enough (10 °C/point) to each other, we decided to repeat the experiment.

The blends of BPA-PC and TMBPA-PC with three compositions (25, 50, and 75 mol % of TMBPA-PC) were tested. The blends appeared to be miscible and judged by their transparency and the single glass transitions found

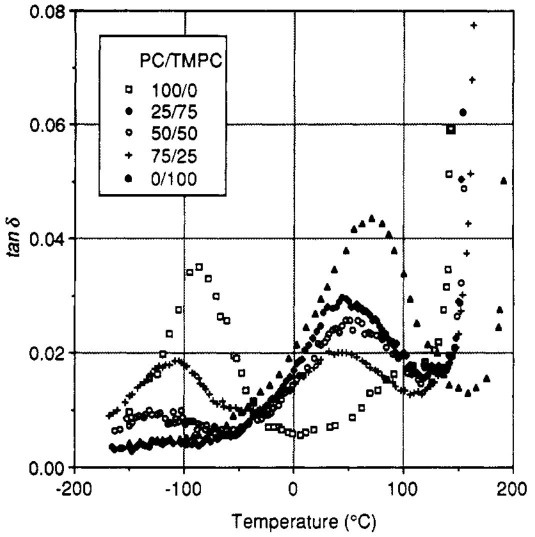

Figure 9. Dynamic mechanical spectra of the blends of BPA-PC and TMBPA-PC recorded at 11 Hz. Compositions are in mole percent.

in DSC scans as well as in the DMS. T_g's determined by DSC change approximately in proportion to the concentration of TMBPA-PC. The DMS's of the blends are shown in Figure 9. The temperatures of both relaxation peaks shift to lower temperatures. An explanation for the temperature shifts cannot be given at this point. Only the intensities of the peaks are discussed. The peaks are much more severely suppressed compared to Fischer and co-workers' results. More importantly, the rate of suppression is different for the two polymers. The peaks of BPA-PC are more severely suppressed, and, in fact, the loss peak disappears in the 25/75 (BPA-PC/TMBPA-PC) blend. The extent of suppression is less severe in the TMBPA-PC peaks; in the 75/25 blend the loss peak is still quite pronounced. To compare the rates of suppression in the two components, the peak intensities were plotted against the blend composition and shown in Figure 8. The rates of decrease in intensity are neither linear not proportional for the composition for both components. These results suggest that the molecular motions in both polymers are affected by the neighboring chains and more generally by the environment. The difference in the rates of suppression for the two polymers is remarkable. The peak intensity of BPA-PC is much more rapidly decreased compared to that of TMBPA-PC. In other words, the molecular motion of BPA-PC is affected by neighboring TMBPA-PC chains to larger extents than the converse. This may be explained by the relative stiffness of the two chains and the temperatures of the relaxations. BPA-PC motion is more severely restricted by stiffer and not yet relaxed TMBPA-PC chains, while TMBPA-PC chain motion is less affected by relatively soft and already relaxed BPA-PC chains. Of course, the fact that the motion is affected by changes in the environment means the motion includes a contribution from interchain interactions. If the motion is a purely intrachain motion, the intensity must be decreased linearly with concentration, probably according to dilution effect (as shown by the diagonal straight lines in Figure 8). It is therefore concluded that the mechanical secondary relaxation motion in BPA-PC as well as that in TMBPA-PC are intermolecularly cooperative.

While the interpretation differs from that by Fischer and co-workers, some support to the current interpretation can be found. Mutual antiplasticization effects in miscible polymer blends are well known,[37] which makes pure dilution effects less probable. For a more direct evidence, in a DMS study of miscible BPA-PC/PMMA blends, Landry and Henrichs[48] found that the γ pak of BPA-PC is greatly suppressed in the 80/20 (wt % BPA-PC/PMMA) blend and the peak disappears in the 50/50 blend, while the room-temperature secondary relaxation peak of PMMA is not suppressed (decreases in proportion to the concentration). Taking into account relative density and molecular weights, their result is reasonable and consistent with the result of the present experiment. Since the secondary relaxation motion of PMMA is essentially a side-group motion accompanied by a small-scale backbone motion, its interchain cooperativity should be smaller than that in BPA-PC. As a result the motion in PMMA is less affected by the neighboring BPA-PC chains, while the interchain cooperativity of BPA-PC is greatly suppressed by neighboring PMMA chains. Their ^2H NMR spectra of the blends indicate that the phenylene motion in BPA-PC is also greatly hindered by blending with PMMA. This result also supports the notion of interchain interaction. In summary, it is concluded that the cooperative motion of BPA-PC includes interchain interaction.

Secondary Relaxation Motion of BPA-PC. On the basis of the observations in this experiment, some speculations on the nature of the cooperative motion are given. As the cooperativity of the motion in BPA-PC is characterized to extend to several repeating units along the chain and to neighboring chains, the mode of the motion by this large motion unit should attract attention. Several models that imply the cooperativity of the motion were proposed. Jones[33] proposed the cis–trans isomerization as the major contributor to the secondary relaxation of BPA-PC observed in mechanical and dielectric relaxation experiments. The fundamental motion is the exchange of a trans–cis (or cis–trans) conformation of the carbonate with a trans–trans conformation of the neighboring carbonate. As the rotation about the C(carbonyl)–O(ether) bond of a carbonate group occurs, a counterrotation of the neighboring carbonate has to follow to prevent the movement of the entire chain. This small reorientation causes the translation of the BPA unit between two carbonates, and this translation is proposed to diffuse down the chain as a segmental motion. This attractive model is at the stage of hypothesis and has yet to be proven experimentally, although the isomerization process was deemed possible with relatively small energy barriers by some molecular dynamics studies.[3,8] There is a point that is far more important than the numerical values of energy barriers, that is, the fact that the C(carbonyl)–O(ether) bond has a partial double-bond character, which was not considered in calculation results cited above. The rotation about a partially double bond would not be as easy as suggested in this model.

Schaefer and co-workers[27] proposed a model that contains the intermolecularly cooperative phenylene flippings. They recognized that the flipping of the phenylene groups alone cannot account for the observed mechanical relaxation and proposed a model based on small-scale main-chain wiggling.[13] According to this model, it is possible for BPA-PC chains to form a "bundle" by very local parallelization of the chains. Inside the bundles the phenylene rings are flipping cooperatively with the rings of the neighboring chains and result in main-chain movements (wiggles). This model still needs direct experimental evidence to circumvent the questions arising from structural considerations. Even if the parallelization or ordering of the chains of that size (3 × 3 matrix[46]) is possible, the bananalike structure of BPA-PC makes this type of cooperation unlikely. The two phenylene rings in two neighboring chains may not be in close contact with each other when the two chains are parallelized (see Figure 1): By parallelization, a phenylene ring in one chain is adjacent to the carbonate group of the other chain instead of the phenylene group. It should be noted that Mitchell[49] proposed the preferred structure in the BPA-PC to be a random conformation and the parallel packing of the chains to be less probable, based on his X-ray study. He also suggested that proximity of the phenylene rings to each other is more favored in unaligned chains.

It appears that the earlier models including restricted rotational oscillation motion of the chain proposed by Davenport and Manuel[50] and the chain wiggling by Schaefer[51] are worthy of closer inspection when they are taken with some modifications. Both models consider the BPA unit between the carbonate groups as a rigid body. This notion is not correct, since the flipping of the phenylene motion has been observed and more importantly the motional correlation cannot propagate effectively through the completely rigid body. But if we understand the notion as the relative flexibility of the carbonate group compared to other groups, these models, i.e., the rotational oscillation or wiggling of the chain, may be able to represent the motion of the BPA-PC chain. More generally, the motion may be described as the reorientation of the chains, as proposed by Boyd and co-workers,[52] who suggested a large volume of material as the relaxing species. Of course, in BPA-PC, the reorientating volume should contain several repeating units along the chain and the neighboring chins. If one realizes the essentially random conformation of the chains,[49] the number of neighboring chains and thus the volume of material cooperatively moving must be large. As a consequence, the mechanical secondary relaxation motion of BPA-PC may be thought of as a reorientational motion of the segments in a volume of material that includes several repeating units and a multiple number of chains.

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Registry No. TMBPA-PC (copolymer), 52684-16-9; TMBPA-PC (SRU), 38797-88-5; BPA-PC (copolymer), 25037-45-0; BPA-PC (SRU), 24936-68-3; BPA-PC-TMBPA (copolymer), 55067-63-5; BPA-PC-TMBPA (block copolymer), 132410-03-8.