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Correlation between the Shear Yielding Behavior and Secondary Relaxations of Bisphenol A Polycarbonate and Related Copolymers

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ABSTRACT: Two series of polycarbonate block copolymers were synthesized, and their mechanical properties were evaluated by uniaxial tension experiments. One series which consists of the block copolymers of Bisphenol A and tetramethyl-bisphenol A polycarbonates was used to find correlations between their ability to shear yield and their secondary relaxations. The other series of such copolymers in which the intrachain motional correlation distance was limited by inserting flexible linkages between the block units was used to test the effect of the extent of the scale of in-chain secondary relaxation on ductility. We found that the activation of cooperative secondary relaxation at the temperature and time scale of the stress-strain experiment is necessary for the copolymers to be able to yield. Our results also show that the availability of large-scale main-chain cooperative motion is beneficial for shear yielding. When the scale of in-chain cooperative motion is small, a higher temperature is needed in order to have the copolymer yield at moderate strain rates. When the scale of in-chain cooperative motion is large, the brittle to ductile transition temperature shifted to a much lower temperature.

I. Introduction

The macroscopic fracture behavior of solid polymeric materials is often described in terms of being ductile or brittle. Although highly desirable, such behavior is difficult, if not impossible, to correlate with molecular structures or relaxation processes because the macroscopic ductility or brittleness of any material is affected by complex interactions between external factors such as the state of the stress applied, the rate of deformation, the temperature, etc., and material and specimen factors such as the specimen geometry, the amount and severity of flaws, the crystalline morphology, the thermal history, presence of corrosive agents, etc. Specifically in the case of polymers, the molecular weight and the cross-link density are also important factors. Not withstanding these complex factors, meaningful correlation can still be made under carefully controlled (e.g., specimens with similar thermal histories and flaw distribution) and relatively simple conditions. The condition we have chosen to make the correlation—a dumbbell-shaped specimen subjected to simple tension—satisfies this requirement. In favorable situations, the understanding we gain in simple tension may be used to explain deformation behavior under more complex conditions. To further simplify the situation, we shall consider only the case of high molecular weight ($M_n \gg 2M_c$ where M_c is the critical molecular weight for entanglement effects to occur) glassy thermoplastics. Yet, even under such restrictive conditions, a number of complications can still occur and we must carefully define what we mean by "ductile" and "brittle". The following consideration is therefore necessary.

In simple tension, the specimen can either undergo shear yielding or crazing. Shear yielding may in turn be followed by necking and neck propagation or by immediate rupture of the specimen without forming a stable neck. In the latter scenario, the specimen may appear macroscopically to be brittle even though microscopically there is shear plasticity on the fracture surface. We shall consider all rupture preceded by shear yielding to be ductile because stable neck formation and neck propagation are highly sensitive to the condition of the test specimen, e.g., the presence of surface flaws, sharp radii, etc. At a given combination of strain rate or temperature, shear yielding may not be possible, and the specimen would then form crazes (in the case of thermoplastics) which eventually transform into cracks. Such fractures are macroscopically and microscopically brittle in the sense that little or no shear plasticity is detectable on the fracture surface. But as the crazes grow, the stress state in the specimen may change in such a way as to give rise to tearing, which can involve very localized shear plasticity. We shall still consider this type of fracture to be brittle because the initial stress state caused crazing first.

The tensile deformation behavior of many glassy polymers can thus be considered as the competition between crazing and shear yieldings.[1,2] Wellinghoff and Baer[1] have made a correlation between the chemical structure of polymers which show preference for either crazing or shear yielding. They found that vinyl polymers which have flexible main-chain linkages such as polystyrene (PS) and poly(methyl methacrylate) (PMMA) (which they termed type I polymers) are generally brittle and undergo crazing, whereas polymers which have main-chain motions, e.g., polycarbonate (PC) (which they termed type II polymers), are relatively ductile and generally undergo extensive shear yielding at ambient temperatures.[3] A similar observation was also made earlier by Vincent.[4]

The link between molecular structure and macroscopic fracture behavior is thought to be the sub-T_g relaxation.[5,16] If the relaxation is unrelated to a side-group motion, as in type II polymers, then the polymer would undergo bulk shear yielding,[1] while if the sub-T_g relaxation is associated with side-group motions, as in type I polymers, the material would be brittle. Such correlations have not always been found valid. Wyzgoski and Yeh[6] have shown, for example, that when the γ relaxation in PC is suppressed by the addition of certain low molecular mass diluents, the polymer actually exhibits increased ductility. In addition, annealing a polymer has little effect upon the γ relaxation but makes the polymer more brittle. Still, many researchers have attempted to correlate the secondary

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relaxation with the large strain properties of polymers. Even though direct correlation has been established for only a few polymers,[7,8] usually in terms of similarities in activation energies, the relationships are more suggestive than substantial. There are perhaps several reasons for such an absence of good correlation. First, dynamic mechanical measurements are typically made in the linear viscoelastic regime, while plastic deformation and failure occur at much larger strains. Second, although most of the thermoplastics exhibits sub-T_g relaxation, the types of molecular motions responsible for the relaxations vary from one material to another. Even for type II polymers, for which the relaxations are all due to main-chain motions, the scale of molecular motion may not be the same.[9] Furthermore, dynamic mechanical measurements give little hint as to the nature and extent of intermolecular interactions beyond allowing one to compare the apparent activation energies of the relaxation in a series of homologues. In large-scale deformation, there is no doubt that long-range intermolecular interactions would come into play.

Our recent study showed that the γ relaxation of Bisphenol A polycarbonate (BPA-PC) is a cooperative relaxation involving as many as seven repeating units.[11,12] This cooperative motion can be decoupled by inserting a more flexible linkage, such as an ester.[9] These results make it possible for us to better correlate the γ relaxation with large mechanical deformation by putting long-range correlated motion into consideration.

Poly[(tetramethyl-Bisphenol A carbonate)-*b*-(Bisphenol A carbonate)] block copolymers were synthesized in order to correlate the mode of failure under uniaxial tensile stress with the spectral position of the γ relaxation. Copolymers with various degrees of cooperativity were also prepared by linking polycarbonate oligomers with terephthaloyl linkages. In those block copolymer homologues, the longer the block lengths are, the larger is the scale of cooperative motion. This series of the block copolymers was used to correlate the scale of cooperativity with ductility. The reason for choosing these particular units is that the homopolymers from each of these units, which are completely miscible, have relaxation peaks that are characteristic of cooperative motions and their transition temperatures are far apart at frequencies accessible to typical low-frequency dynamic mechanical measurement techniques. Because of such properties, one should expect to see two relaxation peaks in their dynamic mechanical spectra when the motion is decoupled. The two relaxation peaks also show the activation sequence of two different types of blocks. A secondary purpose of this study is to test the practical merit of the synthesized polymers with respect to their mechanical and damping behaviors. Tetramethyl-Bisphenol A polycarbonate (TMBPA-PC) homopolymer, which has a T_g that is much higher than that of BPA-PC (~200 vs ~150 °C), is brittle at room temperature. It was our hope to improve its ductility by inserting the ductile and mobile Bisphenol A blocks between the bulky tetramethyl-Bisphenol A units which we speculate are principally responsible for the brittleness of the homopolymer.

II. Experimental Section

1. Synthesis of Copolymers with Various Degrees of Cooperativity (Group A). The synthesis of copolymers with good control of the block lengths is detailed elsewhere.[11] However, it is practically impossible to scale-up the synthesis of copolymers with strictly controlled structures and block lengths when large quantities of the materials are needed for testing the macroscopic mechanical properties. Since macroscopic behavior is probably less sensitive to the regularity of the blocks, the control of block length distribution is relaxed in the synthesis described here. The block copolymers were prepared following some conventional procedures: the oligomers were synthesized by unbalanced feeding of monomers and coupled with terephthaloyl chloride *in situ* to form the block copolymers. Sufficient amounts of copolymers were obtained with relative ease by using this approach. The notation of the synthesized copolymers in this paper is generalized in the form of B*n*t*T*n, where B represents represents Bisphenol A polycarbonate blocks, *t* in the center represents terephthaloyl linkages, T represents tetramethyl-Bisphenol A polycarbonate blocks, and *n* represents the number of repeat units within each block.

Table 1. Physical Properties of Group A Copolymers

sample id	T_g (°C)	M_n	M_w/M_n
B3*t*T3	204	28 242	2.04
B5*t*T5	198	34 239	1.97
B7*t*T7	191	34 294	1.64

The synthesis of B3*t*T3 is given here to represent a typical method of preparation of these series of block copolymers. Hydroxyl-terminated oligomers with number-average degrees of polymerization equal to 3 were prepared in the following way. In a 1000-mL four-neck round-bottomed flask with a mechanical stirrer and a dropping funnel, 22.829 g (0.10 mol) of Bisphenol A and 0.36 g of DMAP were dissolved in 100 mL of CH_2Cl_2 containing 13.92 mL (0.10 mol) of triethylamine, and the whole system was cooled to −30 °C. A solution of 17.56 g (0.05 mol) of Bisphenol A bis(chloroformate) in 100 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 over 1 h and was again cooled down to −25 °C for the polymerization reaction. Hydroxyl-terminated tetramethyl-Bisphenol A carbonate trimer was prepared in another flask. A total of 28.40 g (0.10 mol) of tetramethyl-Bisphenol A and 0.36 g of DMAP were mixed in with 100 mL of CH_2Cl_2 containing 13.92 mL (0.10 mol) of triethylamine, and the whole mixture was cooled to −20 °C. A solution of tetramethyl-Bisphenol A bis(chloroformate) (20.45 g, 0.05 mol) in 100 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 2 h and then cooled back down to −20 °C.

To polymerize the oligomers, the above solutions were combined at −20 °C and an additional 28 mL of triethylamine was added to the solution as an acid acceptor for the polymerization reaction. Finally, a solution of 20.6 g (0.10 mol) of terephthaloyl chloride in 100 mL of CH_2Cl_2 was added dropwise to the reaction mixture which was under vigorous agitation between −10 and 0 °C. After polymerization, the forming viscous solution was washed with distilled water until the aqueous phase became free of chlorine ions. The viscous organic phase was then poured into an excess amount of isopropyl alcohol to precipitate the copolymer. The copolymer was collected by filtration and was further purified by reprecipitation from 40/60 ispropyl alcohol/dichloromethane. The final yield was 95%. The ^{1}H-NMR spectrum showed that the resulting copolymer had the expected structure.

Other copolymers, such as B5*t*T5 and B7*t*T7, were synthesized in a similar manner. Their structures were also confirmed by ^{1}H-NMR spectroscopy. The T_g and the molecular weights of the synthesized materials are shown in Table 1. All materials have relatively high molecular weights.

2. Synthesis of Poly[(tetramethyl-Bisphenol A carbonate)-*b*-(Bisphenol A carbonate)s] (Group B). The synthesis and characterization of this series of copolymers has been described in a previous paper.[10] The notation of the synthesized copolymers with all carbonate linkages is generalized in form of B*n*T*n*, where B represents Bisphenol A polycarbonate blocks, T represents tetramethyl-Bisphenol A polycarbonate blocks, and *n* represents the number of repeat units within each block.

3. Processing of Synthesized Polymers. (a) Purification of Synthesized Copolymers. The copolymers were purified to remove the catalysts, low molecular weight oligomers, and other impurities prior to processing. The copolymers were dissolved in CH_2Cl_2 at a concentration of 5% (g/mL) and precipitated from isopropyl alcohol. The volume of isopropyl alcohol used was about twice the volume of the polymer solution. The copolymers were collected by filtration and dried under vacuum at 60 °C for 2 days.

(b) Compression Molding. Large specimens for dynamic mechanical tests and uniaxial tension tests were molded by compression to plaques with a typical size of $75 \times 50 \times 1.5$ mm^3. The plaques were molded in a programmable hydraulic press (Tetrahedron) using the following procedure: The temperature was raised to 80 °C above the glass transition temperature of each polymer, and then the previously dried polymer powder was introduced. The pressure was then raised to 7 MPa to produce thin polymer films. The edges of the films containing bubbles were trimmed off and discarded, and the films were polished to remove residual contaminants such as mold release agents. The films were then washed, dried, and stacked together and then remolded into plaques at temperatures 85 °C above the T_g for each polymer and at 21 MPa. Each molded plaque was cooled to room temperature by quenching the press platens internally with cold water. The molded specimens were slightly yellow or colorless.

(c) Fabrication of Specimens. Specimens for Dynamic Mechanical Tests. Typical specimens used for the dynamic mechanical test were 50 mm long, 12.5 mm wide, and 1.6 mm thick and were cut directly from the remolded sheets. Before the dynamic mechanical measurements, all the specimens were heated above their glass transition temperatures for 15 min to erase their previous thermal histories and then air quenched to room temperature.

Specimens for Uniaxial Tension Tests. Specimens for the tensile tests were fabricated to the configuration specified in ASTM D638, Type V (ASTM, 1984). The surfaces of the specimens were ground and polished to a smoothness of 5 μ-grains. The polished specimens were washed with water and then dried in a vacuum oven at 100 °C for 24 h. The finished specimens were 50 ± 2 mm long, 12.5 ± 0.5 mm wide, and 1.6 ± 0.1 mm thick. The straight part of the narrow gauge section was 10 ± 1 mm long and 3.2 ± 0.1 wide. To erase the previous thermal history, the cut specimens were heated to temperatures 15 °C above their respective glass transition temperatures, held for 15 min, and quenched to room temperature between steel platens with a 1.6-mm spacer before the mechanical measurements were made.

4. Mechanical Testing. (a) Dynamic Mechanical Experiments. The commercial dynamic mechanical tester, Rheometrics RECAP II, was used for testing these large specimens. The instrument is fully automated and used without any modifications. For the purpose of the present experiment this instrument is sufficiently precise and accurate. A stepwise temperature control with a 5 °C dwell interval in each step was used during the measurements. The testing temperature ranged from −160 °C up to the T_g of the copolymers. Data were recorded at multiple frequencies of 0.1, 1.0, and 10.0 Hz. The shear moduli, the shear loss moduli, and the tan δ values were obtained. The purpose of these measurements was to compare the dynamic mechanical behaviors with the macroscopic tensile behaviors of the materials.

(b) Uniaxial Tension Tests. Nominal stresses were calculated from measured loads and the original cross-sectional area. True strains were obtained after conducting an experiment to establish a calibration factor. The calibration experiment was performed using Bisphenol A polycarbonate specimens and a video camera. An experimental session was video-taped and played back to measure the crosshead displacements and displacements in the gauge section. The grip separation was taken as the crosshead displacement, and the gauge section was premarked on the specimen with a pen. An apparent strain (e) was calculated by dividing the instantaneous displacement in the grip separation (ΔL) by the original grip separation (L_0). A true strain (ϵ) was calculated by dividing an instantaneous displacement in the gauge section (Δl) by an instantaneous gauge lengths (l). By plotting the true strains against the apparent strains, the following relationship was obtained:

$$\text{true strain } (\%) = [\text{apparent strain } (\%)][0.26207] - 0.00825$$

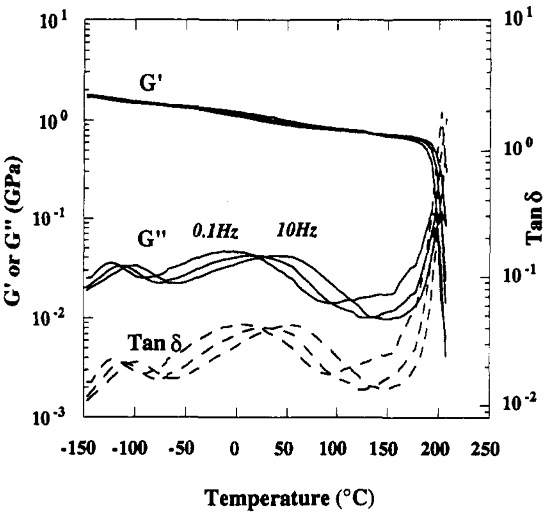

Figure 1. Dynamic mechanical spectra of B3tT3.

The calibration factor obtained was found to be quite reproducible from specimen to specimen and showed little dependence on the strain rate and small fluctuations in sample geometry. This was validated on multiple Bisphenol A polycarbonate and a few copolymer specimens tested at various strain rates. As a result, the same calibration factor was used for all polymers at all strain rates.

The calibration factor obtained above, however, was valid only in the elastic or linear deformation region since a necked zone propagated in favorable conditions beyond the narrow gauge section at large deformations. The values of large strains through yield and up to failure were obtained through the concept of an "effective gauge length". An effective gauge length was obtained by the following relationship:

$$\text{strain rate } (\text{s}^{-1}) = \frac{\text{crosshead speed (in. s}^{-1})}{\text{effective gauge length (in.)}}$$

The effective gauge length was calculated using the instantaneous strain, the instantaneous strain rate, and the crosshead speed. The initial strain rate value was used to calculate the original effective gauge length ($L_{\text{eff},0}$). From $L_{\text{eff},0}$ and the measured crosshead displacement (ΔL), a nominal strain for large deformations was calculated.

III. Results and Discussion

1. Molecular Weight. The number-average molecular weight of each of the synthesized polymers is greater than 27 000 according to the GPC results. On the basis of the chemical structure of the copolymers, we expect that the entanglement molecular weight of these copolymers should be close to that of BPA-PC which is around 2000. Therefore, the molecular weight of the copolymers is significantly higher than their entanglement molecular weight. Although the entanglement molecular weights for the copolymers with short blocks might be somewhat different, they are unlikely to be as much as 10 times higher. The molecular weight is therefore considered to be sufficiently high. This is important because, if the molecular weight is too low, then the material will always proceed to brittle fracture regardless of its molecular mobility.

2. Dynamic Mechanical Measurements. (a) Group A Copolymers (B$n$$tTn$). The dynamic mechanical relaxation spectra of these copolymers are shown in Figures 1–3. All the spectra show two well-separated relaxation peaks. The ones at lower temperatures (~−110 °C at 10 Hz) are due to the relaxation of BPA blocks, while those at higher temperatures (~40 °C at 10 Hz) are due to the relaxation of TMBPA blocks. The two well-separated relaxation peaks demonstrate that the motions of the two

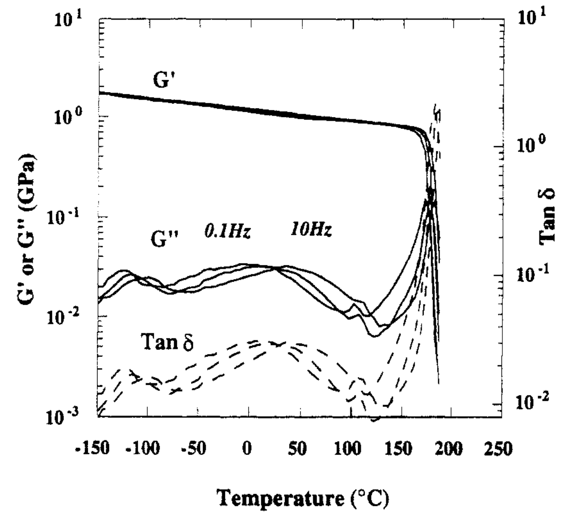

Figure 2. Dynamic mechanical spectra of B5*t*T5.

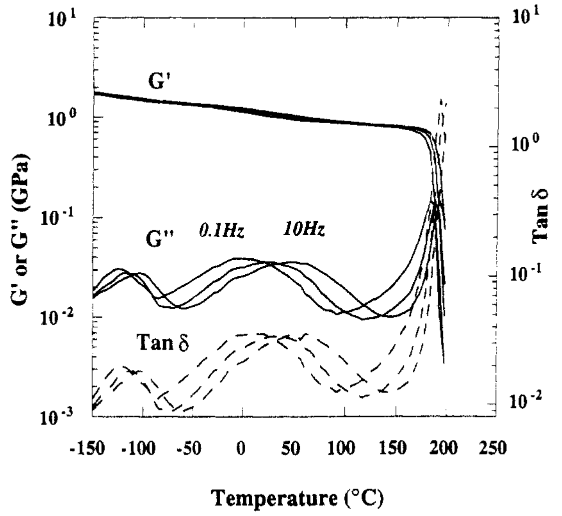

Figure 3. Dynamic mechanical spectra of B7*t*T7.

types of blocks are decoupled. These results are consistent with those previously obtained from thin film specimens,[9] and thus the materials synthesized using the simplified scheme described here are suitable for our purpose, i.e., for studying the relationship between relaxation behavior and tensile properties. All the copolymers have glass transition temperatures of about 200 °C. The dynamic mechanical spectra also show that these copolymers have very good modulus retention at elevated temperatures, which is desirable for practical applications.

(b) Group B Copolymers (B*n*T*n*). The dynamic mechanical relaxation spectra of group B copolymers have been reported in our previous paper.[12] The alternating copolymer, B1T1, has a single γ-relaxation peak due to the cooperative relaxation of the two different types of comonomers. As the block length increases from 6 to 9, the characteristic γ-relaxation peaks of Bisphenol A polycarbonate and tetramethyl-Bisphenol A polycarbonate begin to reappear. However, the relaxation peak due to the cooperative motion of the junctions between the two types of blocks remains.

3. Uniaxial Tension Tests. (a) Onset of Cooperative Motion and Correlation with Yielding. To correlate the dynamic mechanical relaxation of a polymer with its tensile deformation behavior, it is useful to find a relationship between the frequency of the dynamic mechanical measurement and the strain rate of the tensile test. Although the overall strain magnitudes involved in each of the tests and the modes of stress may be totally different, nevertheless the strain rates at the beginning of the two types of tests where the strains are in the linear viscoelastic range may be compared. In fact, this comparison is necessary to explain the participation of the secondary relaxation motion in the tensile yield behavior, since, for a motion to contribute to the macroscopic deformation behavior, it must presumably be thermally activated already at the appropriate time scale and temperature. The dynamic mechanical tests can be used to determine these important parameters.

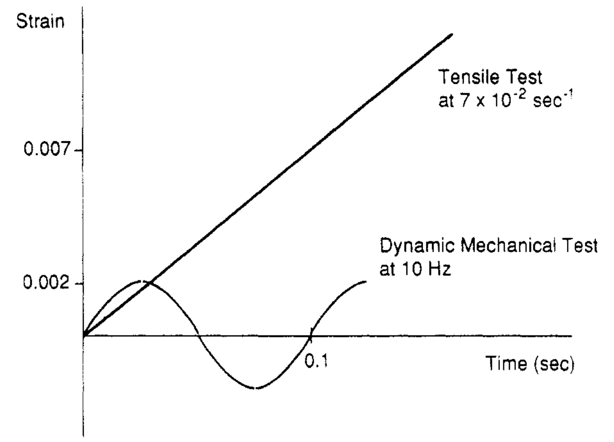

Figure 4. Equivalent frequencies of dynamic and tensile tests.

Table 2. Equivalent Frequenices for the Strain Rates in Tensile Tests

crosshead speed (in./s)	strain rate (s^{-1})	equivalent frequency (Hz)
0.001	7×10^{-4}	0.1
0.1	7×10^{-2}	10
1	7×10^{-1}	100
impact	70	10 000

Figure 4 schematically shows the strain imposed on the material as a function of time. The strain history used in the dynamic mechanical test is a sinusoid with a peak-to-peak amplitude of 0.4% and a frequency of 10 Hz. One of the strain rates employed in the tensile test was 7×10^{-2} s^{-1}, and the strain–time curve for this strain rate is represented by the straight line in the figure. Obviously, the strain rates of the two types of tests are comparable in the initial region. Although this comparison is only approximate and is valid in the region of very small strains, one might expect that, if a molecular motion is detectable by the dynamic mechanical test at 10 Hz, at, say, room temperature, then that motion is also available in the tensile test at strain rates up to 7×10^{-2} s^{-1} at the same temperature. For example, the secondary relaxation motion of BPA-PC is expected to be available in a room-temperature tensile test with the strain rate of 7×10^{-2} s^{-1}, since the secondary relaxation peak is located at −100 °C at 10 Hz. The same method of comparison is applied to other strain rates. The results are listed in Table 2.

The stress–strain curves of BPA-PC and TMBPA-PC are shown in Figures 5 and 6, respectively. These are two good examples of a ductile and a brittle polymer (at the given temperature and strain rate): BPA-PC exhibits ductile behavior at a very high strain rate of 0.7 s^{-1}, while TMBPA-PC exhibits brittle behavior even at the relatively low strain rate of 7×10^{-4} s^{-1}. For BPA-PC the secondary relaxation peak occurs in the temperature range from −112 °C (0.1 Hz) to −80 °C (100 Hz) depending on the frequency. Since this temperature range was determined dynamic mechanically at very small strains, the molecular motion responsible for this peak can safely be assumed to have been thermally activated at room temperature. Thus, this

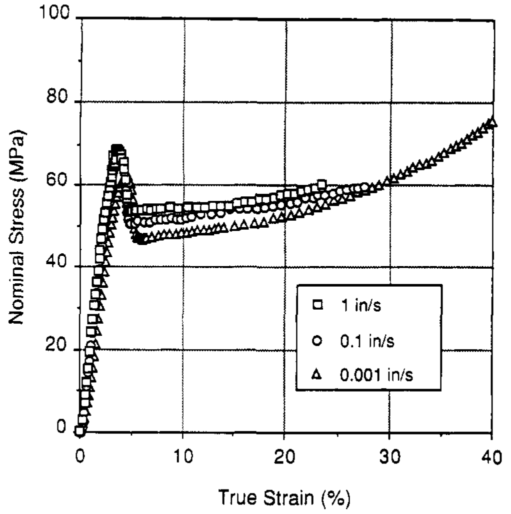

Figure 5. Stress–strain behaviors of Bisphenol A polycarbonate at room temperature.

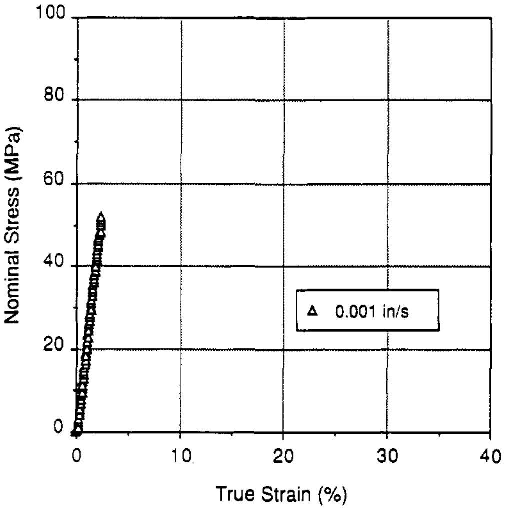

Figure 6. Stress–strain behavior of tetramethyl-Bisphenol A polycarbonate at room temperature.

motion should be available in tensile tests with the strain rates in the present experiments.

In TMBPA-PC, on the other hand, the secondary relaxation motion is not available at room temperature. Even at the lowest strain rate (7×10^{-4} s^{-1}) the secondary relaxation peak temperature would be at 31 °C at the equivalent frequency of 0.1 Hz as revealed by the dynamic mechanical analyzer results.[11] Although a portion of the motion is already activated and available at room temperature due to the breadth of the relaxation peak, it appears not to be large enough to be able to respond to the external stress. Actually, the portion of the relaxation motion available at room temperature is expected to be quite small, as will be discussed later. As a result, TMPBA-PC exhibits brittle behavior at room temperature.

The stress-strain behaviors of the copolymers are shown in Figures 7–9. The average strain rate for these specimens is 7×10^{-4} s^{-1}. The equivalent frequency of dynamic mechanical tests for this strain rate is 0.1 Hz according to the discussion above. At this low crosshead speed, all the copolymers exhibit ductile behavior. The alternating copolymer (B1T1) has a prominent secondary relaxation peak at −15 °C at 0.1 Hz. This temperature is some 40 °C below room temperature, and the major portion of the relaxation peak area is located below room temperature. It appears that the amount of secondary relaxation motion activated at room temperature is just enough to lead to yielding. At the strain rate of 7×10^{-2} s^{-1} (equivalent to the frequency of 10 Hz), the alternating copolymer failed in a brittle manner. The secondary relaxation temperature of B1T1 at this strain rate is 16 °C. These observations clearly demonstrate the importance of the locations of secondary relaxation peaks. The motion of the alternating copolymer was characterized to be a mixed motion of the BPA and TMBPA units, a motional unit inherently stiffer than that of BPA-PC. Because of this stiffness, the relaxation peak is located at a much higher temperature than that in BPA-PC, consequently brittle failure is

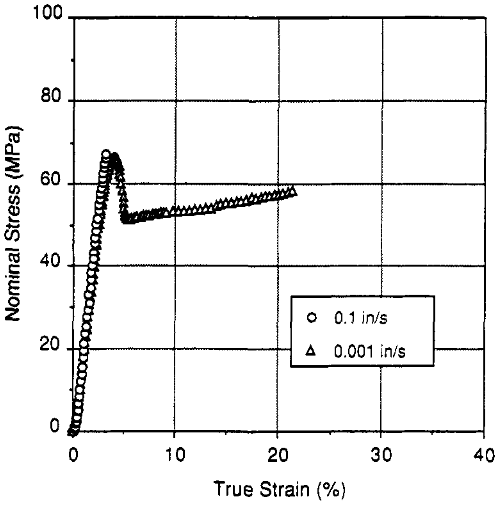

Figure 7. Stress–strain behavior of BT at room temperature.

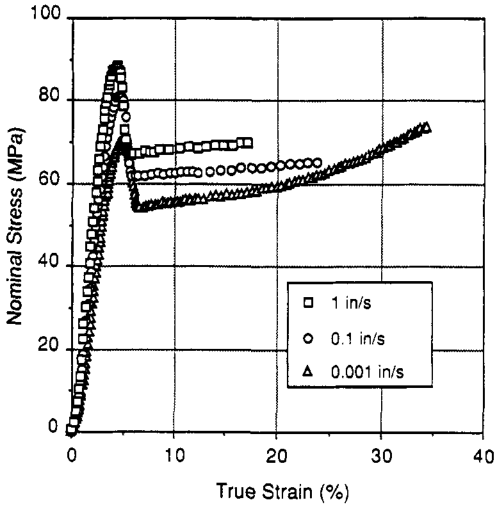

Figure 8. Stress–strain behavior of B6T6 at room temperature.

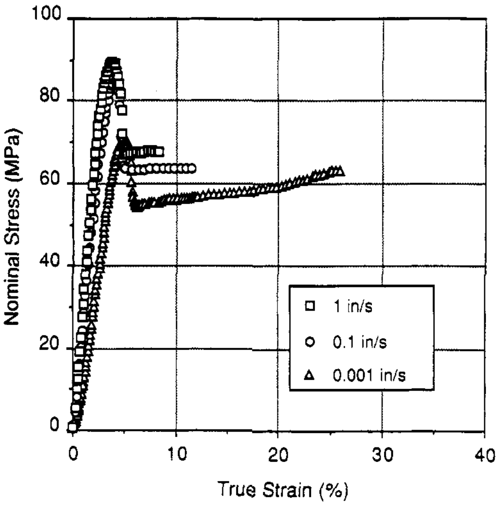

Figure 9. Stress–strain behavior of B9T9 at room temperature.

observed. For the multiblock copolymers with average block lengths of 6 and 9 (B6T6 and B9T9), the relaxation motions of the BPA units are restored and are located at about the same temperature as the peak for BPA-PC. In these copolymers, despite the relatively low relaxation strengths compared to that of BPA-PC, the motion of the BPA units is sufficient to cause the copolymers to exhibit ductile behavior at a wide range of strain rates (Figures 8 and 9). In addition, the relaxation motions of the interlinking part of the chains, which occur at a temperature similar to that of the alternating copolymer, may be able to contribute to the yielding of the copolymers, because these motions favor yielding in the alternating copolymers at this strain rate.

It is sometimes said that the ability of a polymer to yield depends on the existence of a secondary relaxation due to the main chain. This can easily be shown to be not true. Polystyrene, which has no prominent secondary relaxation of any kind, nevertheless yields in compression as long as the molecular weight is sufficiently high. This is presumably because the externally imposed stress can activate certain plastic processes that will eventually culminate in yielding.[13] The higher the stress, the greater the spatial scale of segmental activation (i.e., volume of molecular segments). Thus, the stress activation process is most likely to be nonlinear. Bearing this in mind, we propose that the role played by relaxation in the polymer solid is to facilitate the stress activation. In other words, segments of chains that are already mobile become even more mobile with the application of stress. In this sense we propose that the mobile segments act as molecular scale lubricants, and stress activation causes a larger and larger number of segments to participate in this process. This notion is consistent with our previous observation that nonlinear strain accelerates relaxation in much the same manner as increasing the temperature[14] and with some aspects of the theories of yielding proposed by Eyring,[18] Bauwens,[8] Robertson,[19] and Argon.[20]

It is important to note that, in glassy thermoplastics subjected to uniaxial tension, an alternative deformation process, i.e., crazing, is always available to compete against shear yielding,[21,22] which is necessary for macroscopic ductile behavior. Crazing will occur if the molecular weight is sufficiently high to stabilize the craze fibrils[15] and if shear yielding does not occur more easily at that particular deformation rate and temperature. In such a case the material will deform macroscopically in a brittle manner. This point needs to be made because presumably TMBPA-PC will shear yield if the stress state does not allow crazing to occur, e.g., in compression, irrespective of the existence of relaxation processes.

(b) Scale of In-Chain Motion and Yielding. To study the effect of the scale of in-chain cooperative motion on yielding in these materials, we performed uniaxial tension tests on the group A block copolymers (B*nt*T*n*) at a moderate strain rate, 7×10^{-4} s^{-1}, at room temperature. As shown by their dynamic mechanical spectra, the motions of Bisphenol A and tetramethyl-Bisphenol A blocks are both activated at room temperature for all the copolymers studied. Also, the in-chain correlation between the Bisphenol A carbonate blocks and tetramethyl-Bisphenol A carbonate blocks is decoupled by the presence of terephthalate linkages. This allows us to elucidate the effect of block length or the scale of in-chain cooperativity on tensile yielding behavior. These results are shown in Figure 10. Both B5*t*T5 and B7*t*T7 are able to yield and exhibit ductile failure. B3*t*T3, however, failed in a brittle manner at this strain rate. Since all the materials have similar thermal histories, T_g's, and molecular weights, the most probable reason for such a dramatic change in the stress–strain behavior is the change in the block lengths and, hence, the scale of in-chain cooperative motion. Therefore, we conclude that, besides the activation of a relaxation, having a large-scale cooperativity is highly beneficial for producing ductile behavior in the copolymers.

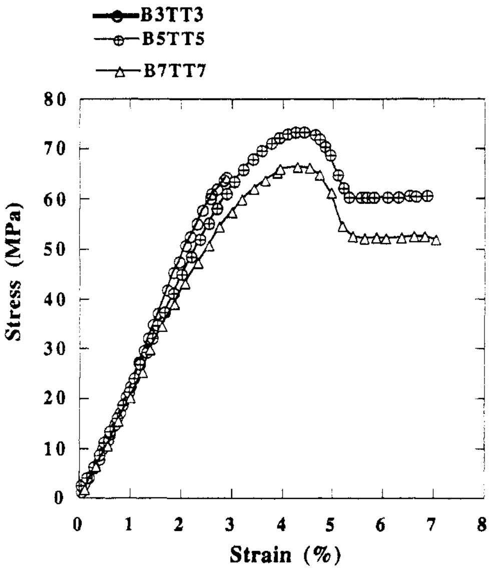

Figure 10. Effect of block length on ductility (testing strain rate = 7×10^{-4} s^{-1}).

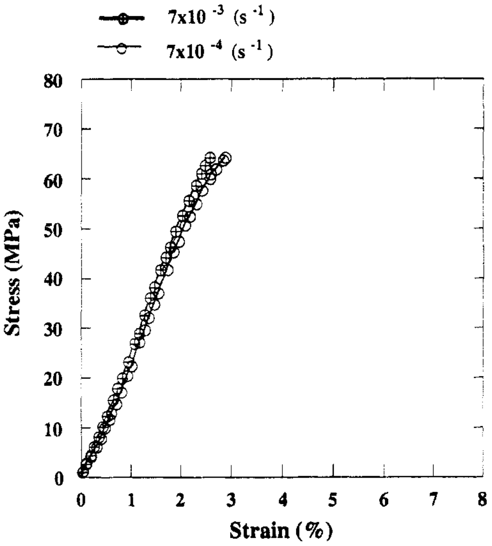

Figure 11. Stress–strain behavior of B3*t*T3 at room temperature.

To examine the effect of block length on the brittle-to-ductile transition temperature, two copolymers, B3*t*T3 and B5*t*T5, were tested in tension at different temperatures and strain rates. It was found that B3*t*T3 undergoes brittle failure even at very low strain rates at room temperature, as shown in Figure 11. The brittle-to-ductile transition temperature for this copolymer must therefore be somewhere above room temperature. At 60 °C, the material yields at low strain rates (7×10^{-4} s^{-1}), while at a high strain rate (7×10^{-2} s^{-1}) it exhibits brittleness. We conclude that B3*t*T3 has a brittle-to-ductile transition temperature near 60 °C. (Since the effect of temperature is much greater than that of strain rate in these copolymers, we are able to give a single transition temperature for the range of strain rates tested.) As the temperature was increased to 90 °C, B3*t*T3 was able to yield at all available strain rates. The transition can be illustrated in terms of a deformation map (Figure 12).

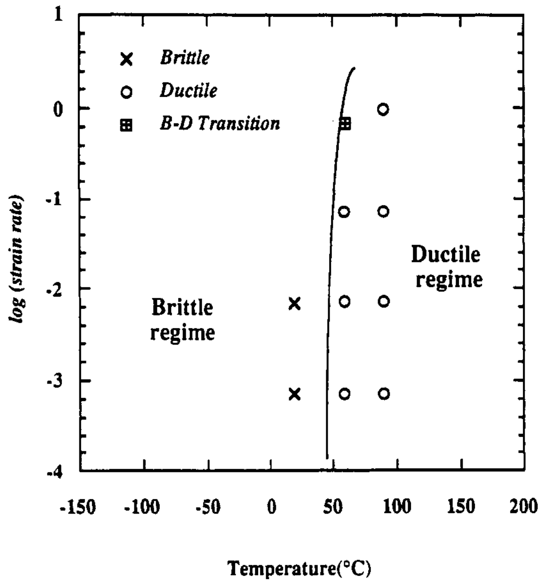

Figure 12. Deformation map of B3*t*T3.

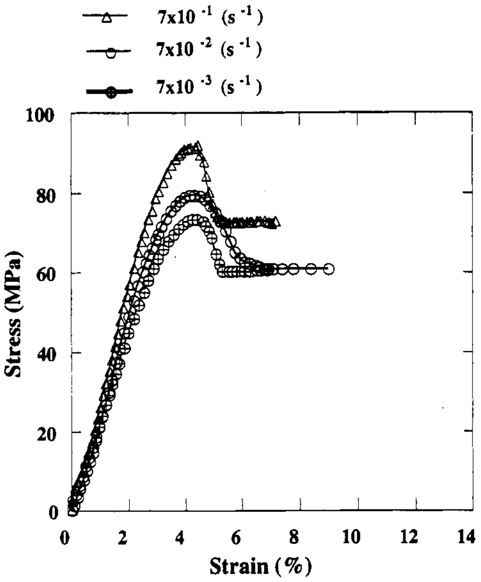

Figure 13. Stress–strain behavior of B5*t*T5 at room temperature.

At room temperature, B5*t*T5 undergoes ductile failure at all available strain rates (Figure 13), indicating that it has a lower brittle-to-ductile transition temperature than that of B3*t*T3. Tests were performed at lower temperatures to determine the brittle-to-ductile transition temperature of this copolymer. The material was ductile at all available strain rates at −20 °C. Brittle failure was found at high strain rates at −40 °C. These results are summarized in the deformation map for B5*t*T5 (Figure 14).

The results of this study also show that the in-chain cooperative motion has to couple with interchain interactions under large deformations. For B3*t*T3, the temperature has to be raised to 60 °C in order to have the copolymer yield at moderate strain rates. We noted that at this temperature all the secondary relaxations are fully activated. B5*t*T5, however, has a brittle–ductile transition temperature at −40 °C, which is approximately the conjunction point of the two relaxation peaks. At −40 °C, the motion of Bisphenol A blocks is fully activated, while the tetramethyl-Bisphenol A blocks are nearly immobile. The large-scale motion of the Bisphenol A blocks (this time involving five repeat units instead of three) on provide a "softer" environment for the tetramethyl-Bisphenol A blocks, and thus it is easier for them to become activated, i.e., flow when the mechanical stress is sufficiently high.

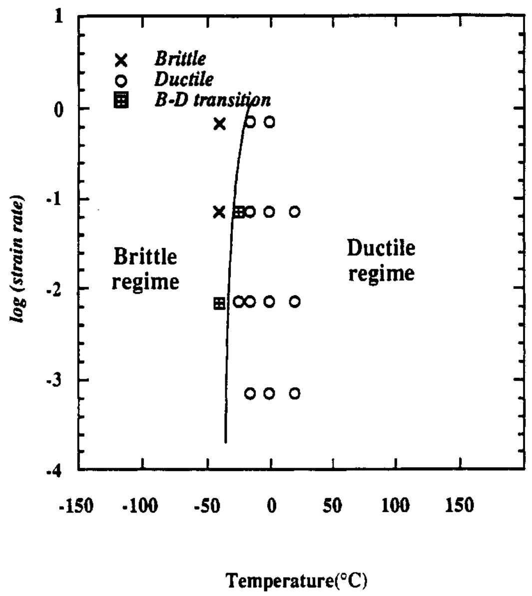

Figure 14. Deformation map of B5*t*T5.

Another important hypothesis that can be drawn from the correlation between secondary relaxation and yield behavior might be proposed here. Apparently a certain amount of well-developed relaxation motion is required for the "lubrication" effect to respond to the initial stress in a significant fashion, i.e., causing the stress to relax rapidly. This appears to be necessary for the stress to be further relaxed and eventually cause the material to yield. In other words, for a secondary relaxation to be effective in "lubricating" the stress-activated relaxation process, its occurrence at a temperature sufficiently below the testing temperature is necessary but not sufficient, as we just demonstrated. Since, as characterized in our previous work,[10],[11] the secondary relaxation motions of these polymers are all highly cooperative, by comparing the yield behavior of these polymers, a correlation between the location of the secondary relaxation temperature and ductility could be developed.

The idea that large-scale cooperative motion can increase the rate of relaxation of the material is supported by the results of our recent study on the microscopic structure of Bisphenol A polycarbonate block copolymers.[17] In this study, terephthalate units acting as flexible linkages were inserted into BPA-PC at regular intervals. (Note that there are no tetramethyl-substituted BPA-PC blocks in this series.) Positronium annihilation lifetime spectroscopy (PALS) was employed to study the possible changes in the packing and the dynamics due to the modification of the main chain. The result shows that when *n*, the number of BPA repeat units between terephthalate linkages, was raised from 3 to 9, the size of the nanometer-sized holes sampled by *o*-positronium within the copolymers remained constant, while the hole density increased rapidly up to the point where $n = 7$ and then leveled off thereafter. A comparison between the PALS results and bulk density data suggests the holes are mainly dynamic in nature. Thus, the dynamic "free volume" of the material increases as the scale of in-chain cooperative motion increases. The increase in dynamic fluctuation is generally beneficial for the material to relax the external stress.

IV. Conclusions

The contributions of large-scale cooperative relaxation to inducing ductile behavior in polymers may be due to the following combinations of factors: (1) large-scale intrachain coupled relaxation, and (2) consequent intermolecular interaction which allows neighboring chains to act together to relax the stress arising from a deformation. The deformation is thus prevented from becoming localized. Our results show that the availability of large-scale main-chain cooperative motion is beneficial for ductile yielding. When the scale of in-chain cooperative motion is small, as in the case of B3*t*T3, a higher temperature is needed in order to have the copolymer yield at moderate strain rates even though at this temperature all the secondary relaxations are activated. We believe that this is the case where the terephthaloyl linkages in B3*t*T3 limit the intrachain coupling. The mobile BPA blocks cannot increase the mobility of the bulky tetramethyl-Bisphenol A units even at large strains. Although the BPA blocks are still able to undergo cooperative motion, the scale of it is not large enough to drive the less mobile tetramethyl-Bisphenol A units through interchain interactions. In contrast, B5*t*T5, which has only BPA segments activated at room temperature, is very ductile. It has a brittle-ductile transition temperature at −40 °C which is the conjunction point of the two relaxation peaks. At −40 °C, all BPA blocks are fully activated and the tetramethyl-Bisphenol A blocks are nearly immobile. Still, the large-scale BPA block motion (this time involving five repeat units instead of three) can provide a relatively soft environment for the tetramethyl-Bisphenol A blocks. Thus it is easier for them to undergo a diffusional motion under the mechanical stress. Tetramethyl-Bisphenol A is a very brittle material at room temperature. B5*t*T5, however, is ductile even at −40 °C. These facts should attract a great deal of interest for industrial applications. Such results demonstrate that we are able to synthesize ductile materials without sacrificing high-temperature performance.

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