폴리카보네이트 공중합체와 블렌드의 인장변형거동

조 재 영[†] · Albert F. Yee*

서울대학교 공업화학과, *Dept. Materials Sci. & Eng., University of Michigan

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Tensile Deformation Behavior of
the Copolymers and Blends of Polycarbonate

Jae Young Jho[†] and Albert F. Yee*

Department of Chemical Technology, Seoul National University, Seoul 151-742
*Dept. Materials Sci. & Eng., The University of Michigan, Ann Arbor, MI 48109 USA
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요약 : 폴리카보네이트를 포함하는 공중합체들과 블렌드의 인장변형거동을 각각의 저온완화거동과 관련하여 조사하였다. 폴리카보네이트와 치환된 폴리카보네이트의 단일 중합체, 블록길이가 다른 공중합체들, 그리고 블렌드의 동적기계적 거동을 여러 진동수에서 측정하고 이들을 여러 변형속도에서 측정한 인장시험 결과와 비교하였다. 완전교대공중합체는 낮은 변형속도에서 연성―취성 전이를 보였으나, 블록의 길이가 충분히 긴 공중합체는 높은 변형속도까지 폴리카보네이트와 비슷한 연성 인장변형 거동을 보였다. 이로서 인장시험의 온도가 저온완화운동의 온도보다 충분히 높고 그 완화운동이 큰 규모의 운동일 경우 그 고분자는 연성 인장변형을 할 수 있음을 실험적으로 확인하였다. 실험결과를 바탕으로 인장항복 과정에서의 완화운동의 역할을 제안하였다.

Abstract : The dynamic mechanical and tensile stress-strain behaviors of the polycarbonate copolymers and blends were investigated, and correlation between their relaxation and mechanical behaviors were examined. The homopolymers, multiblock copolymers with varying block lengths, and blends of bisphenol A polycarbonate and tetramethylbisphenol A polycarbonate were tested; dynamic mechanically at various frequencies, and mechanically at various strain rates. It was observed that a polymer was able to yield and cold-flow when the tension test temperature was sufficiently higher than its secondary relaxation temperature, provided the relaxation involved the cooperative molecular motion of a certain volume of the material. While the alternating copolymer had a ductile to brittle transition at a lower strain rate, the multiblock copolymers with longer block lengths showed ductility comparable to that of polycarbonate up to a relatively high strain rate. Based on the result, an explanation to the role of relaxation in yield process is proposed.

INTRODUCTION

The general recognition of the relation between secondary relaxation and macroscopic mechanical properties is largely based on the fact that tough or ductile polymers have pronounced secondary relaxation peaks at low temperatures in their dynamic mechanical spectra. There is, however, no clear or generally agreed upon understanding on how the secondary

relaxation process affect ductility or toughness: partly because the molecular origins of secondary relaxations are not well understood, and partly due to the lack of materials in which the relaxation behavior and the mechanical behavior are varied systematically.

Bisphenol A polycarbonate (BPA-PC) is one of the most ductile polymers and its dynamic mechanical spectrum exhibits a pronounced secondary relaxation peak. In a previous study,[1] the molecular origin of the secondary relaxation motion of BPA-PC was shown to be a cooperative motion along the chain. In the present paper the correlation between secondary relaxation behavior and ductility of polycarbonates is studied by investigating the tensile deformation behaviors of the copolymers and blends of BPA-PC.

Yield Behavior and Relaxation. The two questions about the correlation between relaxation and yield behavior are if and how the secondary relaxation affects the yield process. One fundamental difficulty is to understand how the relaxation motion determined at low levels of strain could possibly be related to the macroscopic mechanical behaviors usually determined at high levels of non-linear strains. Several investigators proposed the participation of secondary relaxation motion in the yield process based on the Eyring's yield theory.[2,3] Through the observation of the slope changes in the plots of yield stress against strain rate over 6 decades of strain rates at various temperatures (30℃-90℃), Roetling[4] proposed the participation of two yield processes, α and β process. He further suggested that α and β processes are closely related to the glass transition (α) and the secondary relaxation (β), respectively, based on the proximities of the activation energies of the respective processes obtained from dynamic mechanical studies and those found in his yield study.

The same manipulation procedure was applied to the yield behaviors of PVC and BPA-PC.[5,6] Unlike the Roetling's result for PMMA

which showed slope changes for all test temperatures, the PVC and BPA-PC results showed slope changes only at low temperatures, which was attributed to the difference in the location of the secondary relaxations. The secondary relaxation temperatures of PVC (-50℃) and BPA-PC (-100℃) are lower than that of PMMA (25℃; all at 1 Hz). Bauwens[7] went further and suggested that the low temperature yield process and the secondary (γ) relaxation of BPA-PC arise from the same molecular movements, through the estimations of the activation energies and the relaxation strengths using mechanical models. It appears highly probable, through these studies, that secondary relaxation process contributes to yielding somehow: Although assigning a relaxation process directly to a deformation process based on the proximities of the activation energies cannot be easily justified, the activation energies are determined in different strain regimes.

Some investigators attempted to estimate the spatial scale of materials moving at the yield process based on the Eyring flow theory, and to correlate this quantity to the scale of the molecular motion associated with yielding and secondary relaxation. These efforts include the calculation of the 'activation volume' ($V^{\ddagger}$), which is determined by plotting yield stress as a function of strain rate. Since the equations, assumptions, and experimental conditions used by the investigators were different from one to another, the $V^{\ddagger}$ values for one polymer can show discrepancies also. Robertson[8] calculated $V^{\ddagger}$ of BPA-PC as 6.34 nm^3 from the data of tensile yield tests at the temperatures of 0℃ and 25℃. Brady and Yeh[9] calculated the volume between 25℃ and 100℃ as 11.43 nm^3 in tension and 10.62 nm^3 in compression, which showed temperature dependency. In yet another study[10] the volume was estimated as 4.30 nm^3 from a compression experiment at 23℃.

Although it is tempting to correlate $V^{\ddagger}$ to the scale of the motion associated in the sec-

ondary relaxation, a direct correlation would be an oversimplification, if one would recognize the problems like the temperature dependency. After all, activation volume is an imaginary volume which cannot be quantified as a real physical volume: It could be termed a phenomenological manifestation of the scale of molecular motion which occur at yielding. In this context, $V^{\ddagger}$ could be an indication of the ability of a polymer to yield. When the activation volumes of BPA-PC, PMMA, and PS were compared in a study[11], the volume of BPA-PC (10.62 nm^3) was found to be significantly larger than those of PMMA (1. 3 nm^3) and PS (3.0 nm^3). This comparison appears to parallel the comparison of the scale of secondary relaxation motions: The motion of BPA-PC has been characterised as a cooperative chain motion,[1] while the motions of PMMA and PS are known to be motions of groups in a repeating unit.[12] Through the comparison of the activation volumes, the participation of the secondary relaxation motion in the yield process appears to be quite probable, if not evident: Although a direct comparison of the activation energies or the activation volume of the yield process to those of the motion unit of the secondary relaxation should be avoided.

Although the two groups of experimental studies mentioned above showed the participation of secondary relaxation in yield process quite positively, they failed to show the firm experimental proof of the relationship, since direct comparisons of neither the activation energies nor the activation volumes could be justified. In the present paper, this relationship will be tested with the homopolymers, copolymers, and blend of BPA-PC and tetramethyl bisphenol A polycarbonate (TMBPA-PC). These polymers have different relaxation temperatures and strengths, and are expected to have different yield behaviors to provide the support to the relationship. After

the relationship is confirmed, an explanation to the question of how secondary relaxation process can help yield process will be proposed, on the basis of the observed correlation.

Post-Yield Behavior and Relaxation. In most polymers, post-yield behaviors in tensile deformation are observed as the formation and growth of a neck, and necking accompanies two processes in a stress-strain curve, strain softening and strain hardening. According to Vincent[13] who first set a criterion for necking, if a fall in the nominal stress (strain softening) is observed, the first condition for neck formation is met, and the neck will start to form. For the neck to be stable it is further necessary that the necked material be subjected to a strain hardening process. While the true strain softening is defined only in a true stress-strain curve, it is said that strain hardening process may confidently be inferred wherever there is an increase in nominal stress in the plastic deformation regime.[14] The extent of stain hardening could be expressed as ultimate strain or elongation at break, and it is also the measure of toughness in tensile tests.

For strain hardening, a generally accepted molecular process is the straightening out of polymer chains between points of entanglement. This explanation resembles the one for rubber elasticity, and indeed the proposed models for strain hardening is based on rubber elasticity theory.[10,15] One of their conclusions is that the extent of strain hardening would be greatly affected by the chain structure of a polymer, and the subject was studied by Argon and Bessonov[16] with a series of polyimides. In this study, the spacing of natural hinges or the length of stiff unit between rotation correlates closely with the onset of strain hardening. A polymer with longer spacing showed more diffuse strain softening and hardening with reduced plastic strain localiza-

tion. Later Bosnyak and coworkers[17,18] tested this concept with a series of polyestercarbonates with tere- and isophthalic linkages. They also found that a polymer with less coiled structure by virtue of having more terephthalic units showed more diffuse necking behavior. While the role of terephthalic units in the stress drop at necking was explained on the molecular level for this particular polymer,[19,20] the behavior of the polymer after necking was not discussed. In consequence, although these studies clearly shows that onset of strain-hardening is greatly affected by the chain structure, it still is not clear how this behavior affects the extent of strain hardening or elongation at break.

The effects of temperature and strain rate on elongation at break has not been clearly understood also. A generally accepted explanation is the isothermal – adiabatic transition, which is the result of the competition between the strain hardening and the weakening due to the heat produced by the work of deformation. It was observed that this transition is not greatly affected by ambient temperature,[21] although the rate of heat dissipation would be different at different temperatures. More importantly, it is not clear if the isothermal – adiabatic transition can account for all of observed strain rate dependence of elongation at break. Although it was claimed that, in the isothermal range, strain rate does not affect strain hardening behavior,[14] there seems not to be enough direct experimental results to support this. In elastomers where necking is absent, the effect of strain rate on elongation at break could be predicted by WLF equation.[22] This result suggests that the fracture process is dominated by viscoelastic behavior, and may be predicted by glass transition behavior. However, for most thermoplastics this is contradicted, as pointed out by Ward.[23] Considering all of the factors including temperature, strain rate, and chemical

structure, it appears that post-yield behavior represented by elongation at breat cannot be described in a single model. As a result, it seems difficult to clearly describe how secondary relaxation motion can affect the post-yield behavior.

EXPERIMENTAL

Specimen Preparation. BPA-PC used was a Lexan (General Electric), and TMBPA-PC and the copolycarbonates were synthesized. The syntheses of the polymers were described elsewhere.[24] The structures, molecular weights, and transition temperatures are reported in Table 1. Since direct molding from powder was difficult due to its low bulk density, the powders were first molded into thin films and then remolded to thick specimens. Films with the average thickness of 0.25 mm were molded from the powders, and the surfaces were polished to remove the mold-releasing agent. The films were washed, dried, cut, stacked in a fitted mold, and remolded to a thicker plate. The molding condition used were: at a temperature 50 ℃ above the glass transition temperature of the polymer and at 1,000 psi for film molding; and at a temperature 70 ℃ above and at 10,000 psi for remolding.

Specimens for the dynamic mechanical measuremeents were cut out of a plate to a typical size of 50 mm long, 12 mm wide, and 3 mm thick. Dumbbell-type specimens for the tensile tests were cut and milled to conform with the configuration specified in ASTM D638, Type V. The overall dimensions of a tensile specimen was 50 ± 2 mm long, 12.5 ± 0.5 mm wide, and 1.6 ± 0.1 mm thick: The gauge section had the dimensions of 10 ± 1 mm long and 3.2 ± 0.1 mm wide. The shaped specimens were polished to a smoothness of 15 μm grains, washed and dried. Immediately before the measurements, to erase the previous

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Table 1. Polymers Used in the Tests

Polymer	$[B_x\text{-}T_y\text{-}]^a$		M_n^b	T_g (℃)	T_γ^c (℃)
	x	y			
BPA–PC	m	0	25,900	148	-87
TMBPA–PC	0	n	32,800	200	68
B1T1	1	1	22,400	167	0
B6T6	6	6	32,200	179	-100, 0, 70
B9T9	9	9	22,600	176	-100, 0, 70
Blend	50	50	—	168	-100, 70

^{a} B and T stand for one BPA and TMBPA carbonate repeat units, respectively.
^{b} Number average molecular weight determined by GPC[24].
^{c} Secondary relaxation temperature determined by DMA at 10 Hz.

thermal history, the specimens were heated to a temperatures 15 ℃ above their glass transition temperatures, held for 30 min., and quenched to room temperature between steel platens.

Dynamic Mechanical Measurement. A DuPont Dynamic Mechanical Analyzer (DMA Model 983) was used. To give a typical 0.2 % strain to a specimen, the oscillation amplitude of 0.4 mm was employed for all measurements. Data were recorded at the multiple frequencies of 0.1, 1 and 10 Hz at each 2.5 ℃ temperature step, in this order. For measurements, the first 10 cycles were discarded for equilibration, and the next cycles, the number of which depended on frequency, were recorded. The number of cycles taken were: 4 cycles at 0.1 Hz, 6 cycles for 1 Hz, and 10 cycles for 10 Hz. Five measurements were taken for each frequency and averaged to give one data point at a certain temperature. The flexural storage moduli, the flexural loss moduli, and the tan δ values were obtained.

Tension Test. A servo-hydraulic testing machine (Instron Model 1331) was used with a shoulder-fitting grip specially designed for the micro standard specimens. Tests were performed at crosshead speeds of 0.001, 0.1 and 1 in/sec, which are the strain rates of

7×10^{-4} sec^{-1}, 7×10^{-2} sec^{-1}, and 7×10^{-1} sec^{-1}, respectively, for the specimens used. Since an extensometer which could fit these small specimens was not available, acquiring data for true stress-strain curves was not possible. Nominal stresses were calculated from measured loads and the original cross-sectional area. Strains were recorded based on original gauge lengths and converted to true strains using a calibration factor. Since the deformation outside the gauge section and the slippage at the shoulder region was expected to be excessive especially in the region of large deformation around and after yield, the calibration of the strain seemed to be necessary. The calibration experiment was performed with BPA–PC specimens and a video camera. An experiment session was video-taped, and played back to measure the crosshead displacements and displacements in the gauge section. The complete calibration procedure is described elsewhere.[25] Strain rate and Young's modulus were calculated from the linear portion of nominal stress-true strain curve, which usually was at a few percent strain. Maximum nominal stress was taken as yield stress, and true strain at break was taken as elongation at break.

RESULTS AND DISCUSSION

Equivalent Frequency and Strain Rates. To correlate relaxation and tensile property, it appears necessary to find a relationship between the frequency of dynamic mechanical test and the strain rate of tension test. Although the overall strain regimes and the modes of stress are totally different, strain rates at the very first part of the two tests may be compared where both strains are in the elastic range. Since dynamic mechanical tests probe the molecular motions which are thermally activated at the test temperature, if the strain rate of the tension test is compara-

ble to the frequency of the dynamic mechanical test, then the molecular motion detected by dynamic mechanical tests is expected to be available at the start of the tensile test.

If the strain is plotted as a function of time for the dynamic mechanical test and for the tension test, the former would be a sine curve and the latter a straight line in linear deformation region. As shown in Fig. 1, the initial straining part, with rising strain, of the strain-time curve of the dynamic mechanical test with the typical 0.2% strain amplitude at the frequency of 10 Hz has the comparable slope to that of the tension test with strain rate of 7×10^{-2} sec^{-1}. Although this is certainly a rough estimation and should be confined to a very small strain region, one might expect that if a molecular motion is detected, by a dynamic mechanical test at 10 Hz, to be available at room temperature, that motion is also available in tensile test at 7×10^{-2} sec^{-1} at room temperature. For example, the secondary relaxation motion of BPA-PC is expected to be available in a room-temperature tension test with the strain rate of 7×10^{-2} sec^{-1}, since the secondary relaxation peak is located at -87 ℃ at 10 Hz. With the same method of comparison, the strain rates of 7×10^{-4} sec^{-1}, 7×10^{-2} sec^{-1}, and 7×10^{-1}

Fig. 2. Stress–strain curves of the polymers at the strain rate of 7×10^{-4} sec^{-1}.

Fig. 3. Stress–strain curves of the polymers at the strain rate of 7×10^{-2} sec^{-1}.
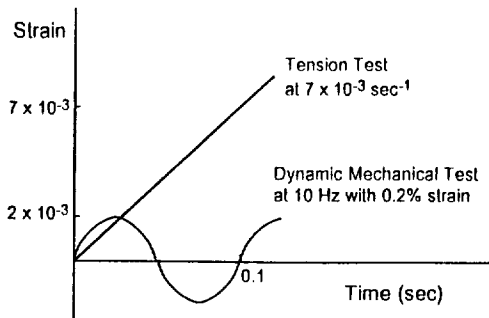

Fig. 1 Comparison of strain increments in tension test and dynamic mechanical test showing the equivalence of the two tests in the early stage of the straining.
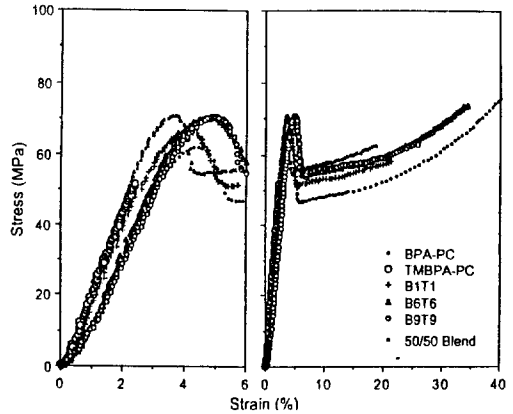

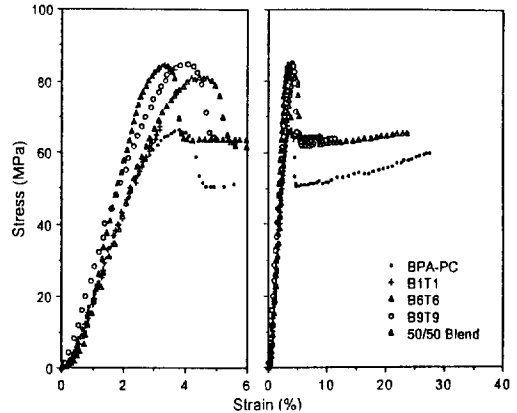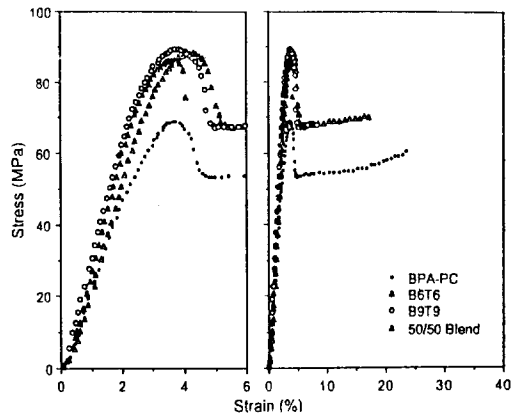**Fig. 4.** Stress–strain curves of the polymers at the strain rate of 7×10^{-1} sec^{-1}.

Table. 2. Elongations at Break of the Polymers at Various Strain Rates and Corresponding Relaxation Temperatures

Polymer	$\varepsilon_{ult}(\%)$ ($\dot{\varepsilon}=7\times10^{-4}s^{-1}$)	$T_{\gamma}(°C)^a$ (0.1Hz)	$\varepsilon_{ult}(\%)$ ($\dot{\varepsilon}=7\times10^{-2}s^{-1}$)	$T_{\gamma}(°C)^a$ (10Hz)	$\varepsilon_{ult}(\%)$ ($\dot{\varepsilon}=7\times10^{-1}s^{-1}$)	$T_{\gamma}(°C)^b$ (100Hz)
BPA-PC	40.0	-107	27.5	-87	23.5	-75
TMBPA-PC	-(2.4)^c	31	$-^d$	68	$-^d$	90
B1T1	21.4	-15	-(3.2)^c	16	$-^d$	34
B6T6	34.4	-120	25.7	-100	17.1	-90
B9T9	25.9	-120	11.3	-100	8.0	-90
50/50 Blend	18.9	-120	9.0	-100	-(4.0)^e	-90

^{a} Temperature of the lowest secondary relaxation peak determined by DMA at the given frequency.
^{b} Temperature of the lowest secondary relaxation peak estimated using the activation energies obtained from DMA and the frequency - temperature relationship.
^{c} Failed in brittle manner (Brittle strain).
^{d} Not tested.
^{e} Failed right after the yield.

sec^{-1} are equivalent to the frequencies of 0.1 Hz, 10 Hz, and 100 Hz, respectively.

Yield Behavior of the Polymers. The ability of a polymer to yield with the imposed stress is proposed to be due to the availability of the low temperature secondary relaxation motion at the test temperature. Since all the tension tests were carried out at room temperature, we will discuss the availability at room temperature. The stress–strain curves of the polymers at the strain rates of 7x10^{-4} sec^{-1}, 7x10^{-2} sec^{-1}, and 7x10^{-1} sec^{-1} are shown in Fig. 2, 3, and 4, respectively. The dynamic mechanical results of the polymers are shown in the Fig. 5 through 8. For comparison and correlation, the results of the tension and the dynamic mechanical tests are tabulated in Table 2 using the concept of equivalent frequency and strain rate described above.

BPA-PC and TMBPA-PC are the two extremes exhibiting ductile and brittle deformations, repectively. BPA-PC showed ductile behavior even at a very high strain rate of 7x10^{-1} sec^{-1}, while TMBPA-PC showed brittle behavior even at a quite low strain rate of 7x10^{-4} sec^{-1}. For BPA-PC, the secondary relaxation peak temperatures are in the range from -107°C (0.1 Hz) to -75°C (100 Hz) depending on frequency. The molecular motions

responsible for this peak is expected to have been thermally activated at these temperatures below room temperature. This motion should, therefore, also be available for the stress in tension tests with the strain rates used in the present experiments. In TMBPA-PC, however, the secondary relaxation motion is not available at room temperature. Even for the lowest strain rate the secondary relaxation peak temperature would be 31°C at the equivalent frequency of 0.1 Hz. Although a portion of the motion appears already activated at room temperature by virtue of the relaxation peak, the majority of the motion
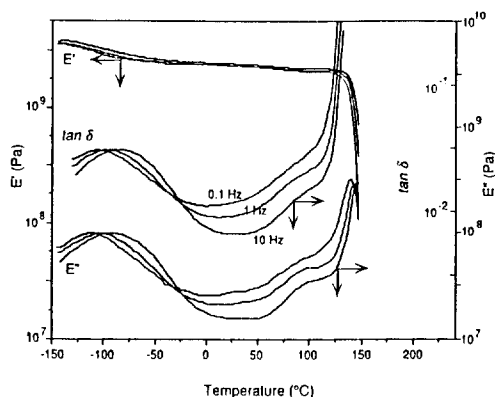

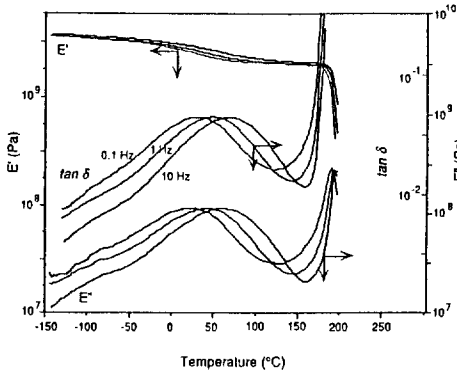**Fig. 5.** DMA result of bisphenol-A polycarbonate at the frequencies of 0.1, 1, and 10 Hz.

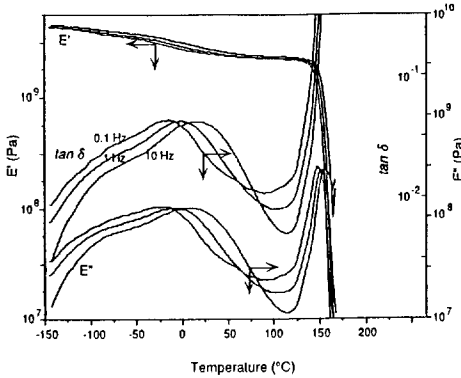**Fig. 6.** DMA results of tetramethylbisphenol-A polycarbonate at the frequencies of. 0.1, 1, and 10 Hz.

Fig. 7. DMA results of the alternating copolymer of BAP and TMBPA polycarbonate at the frequencies of 0.1, 1, and 10 Hz.
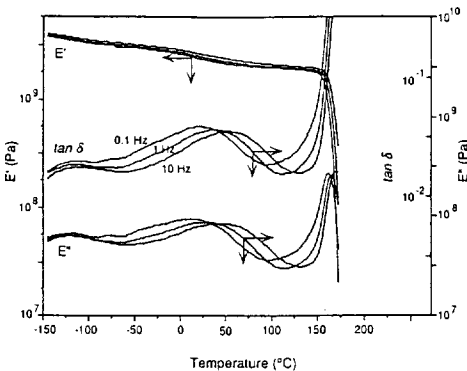

Fig. 8. DMA results of a multiblock copolymer of BPA and TMBPA polycarbonate with the block lengths of 9 at the frequencies of 0.1, 1, and 10 Hz.

would be activated above room temperature. As a result, TMBPA-PC shows brittle behavior at room temperature for all the strain rates of this experiment. An aspect of the correlation between secondary relaxation and yield behavior might be drawn here: A certain amount of well-developed secondary relaxation motion is required to respond the initial stress and to be further relaxed and eventually to yield. In other words, the presence of a secondary relaxation peak at a temperature sufficiently below the testing temperature is necessary for a polymer to be ductile at that temperature. This proposition is tested with the copolymers and one of the blends of the two polymers where the relaxation and mechanical properties vary systematically.

At the lowest strain rate of 7×10^{-4} sec^{-1}, all the copolymers and the blend showed ductile deformation behavior. The alternating copolymer (B1T1) which has the highest secondary relaxation peak among the copolymers at -15℃ at the equivalent frequency of 0.1 Hz shows ductility. This temperature is much below room temperature, and, as shown in Fig. 7, the major portion of the peak is located below room temperature. It appears, therefore, that the amount of secondary relaxation motion activated at room temperature is just enough to trigger the process leading to yield. For the multi-block copolymers with average block lengths of 6 and 9 (B6T6 and B9T9), as shown in Fig. 8, the secondary relaxation motion of BPA units are restored, and the relaxation peaks are located at about the same temperature as the peak for BPA-PC. Despite the relatively small relaxation strengths compared to that of BPA-PC, since the cooperative nature of the motion of BPA units are restored, these copolymers show ductile behavior. A miscible blend with 50/50 composition also shows ductility at this strain rate: As in the multi-block copolymers, the extent of the cooperative motions appears to

be sufficient to cause ductility at this strain rate.

At the strain rate of 7×10^{-2} sec^{-1} (equivalent frequency of 10 Hz), the alternating copolymer failed in a brittle manner. The secondary relaxation temperature of B1T1 at this strain rate is 16℃ or only 10 degrees below room temperature. A sufficient amount of the relaxation motion to lead the yield process does not exist at a temperature below room temperature. The same motion which enabled the ductility at a lower strain rate, as shown in Fig. 7, shifts to a higher temperature and becomes unavailable due to the higher strain rate. In the multiblock copolymers and the blend, despite again the small peak intensities, ductile behavior is observed by virtue of the low temperature cooperative motions available.

At the strain rate of 7×10^{-1} sec^{-1} (equivalent frequency of 100 Hz), only the multiblock copolymers show ductility. The blend ruptures immediately after the yield point is reached, despite that the block copolymers and the blend have the secondary relaxation peaks at the similar temperatures with similar intensities. An explanation to the question why the blend is more brittle than the multiblock copolymers cannot be clearly made at this point with the limited amount of data. The difference could be due to the motion of the interlinking part in the copolymers. The interlinking part is a part of the multiblock copolymer chain where BPA and TMBPA carbonate blocks are connected: The motion of this part produce a dynamic mechanical peak at around 0℃ at 10 Hz as in the alternating copolymer.[1] It is possible for this motion to contribute to the ductility of the copolymers, although it may not cause ductility by itself at this strain rate. The other possible explanation concerns the contribution of interchain interaction, which is much hindered in the blend due to the different neighboring

chain species. Both of the explanations cannot be justified at this point without more experimental results.

The activation volumes were estimated for the polymers that yield at all strain rates. Since $V^{\ddagger}$ is dependent on the method of modification of Eyring equation and its determination requires other parameters like internal friction factor, the estimation of the actual value was not attempted. Instead the volumes are compared to the $V^{\ddagger}$ of BPA-PC. As shown in Fig. 9, by estimating from the slopes of the yield stress vs. log[strain rate] plots, the activation volumes of B6T6, B9T9, and the blend are all about one-third of that of BPA-PC. The difference parallels the smaller relaxation strengths of the copolymers and the blend. We propose that this effect is due to the presence of stiffer non-relaxing TMBPA component in the copolymers and the blend. These polymers might not be as ductile as BPA-PC under other testing conditions.

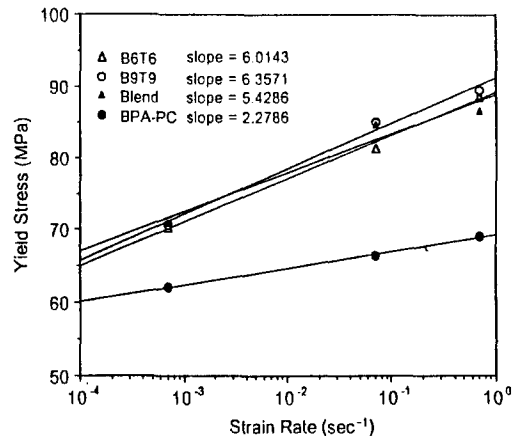In summary, only the multi-block copolymers besides BPA-PC were able to yield up

Fig. 9. Plots of the yield stress as a function of log[strain rate] for the polymers that yield. The larger the slope is, the smaller the activation volume is, since activation volume is inversely proportional to the slope of this plot according to Eyring theory.

to a high strain rate of 7×10^{-1} sec^{-1}. This is a result of having low temperature secondary relaxation motion of BPA units which is equivalent to the motion of BPA-PC including inter-chain interaction. The alternating copolymer has the ductile to brittle transition at a strain rate where the equivalent peak temperature approaches to the test temperature. The activation of secondary relaxation motions at a sufficiently low temperature appears necessary for the motion to effectively contribute to ductility. This is revealed by comparing the behaviors of the alternating copolymer and the blend, which has the ductile to brittle transition at a higher strain rate. In consequence, there appears to be a direct correlation between secondary relaxation motion and ductility.

Role of Secondary Relaxation in Yield Process. The question now is how secondary relaxation motion helps a polymer to yield. No rigorous explanation has been given yet. Explanations by directly comparing activation energies or activation volumes of a yield process to those of the secondary relaxation was discussed and deemed problematic. In addition, the question of how the small strain dynamic mechanical behavior could help the large strain yield behavior has not been answered yet. A speculative explanation is proposed based on the nature of glassy state and the result of the present experiment.

It is well known that glasses, including glassy polymers, do not possess long range order, and the structure is considered to be rather heterogeneous. It is also well known that an imposed stress can be released through the stress relaxation in the linear viscoelastic range. The question is how a large stress could be relaxed in the nonlinear viscoelastic range and how it could be related to the secondary relaxation. As stress is applied to a glassy polymer, it is not evenly distributed in the system because of heterogeneities in

the glass. Instead, some regions bear larger stress than others, and respond differently. Goldstein[26] proposed that the stress applied to a heterogeneous system is distributed through a local 'molecular rearrangement' of initially stressed 'molecular elements' of the material. As other rearrangements occur elsewhere, they will be restressed, becoming capable of further rearrangements. He concluded by stating that his theory needed detailed molecular description, even though his explanation is phenomenologically correct. We propose the secondary relaxation as the molecular process he needed: the 'molecular elements' to be the part of the polymer chain which undergoes the secondary relaxation, and the 'rearrangements' be the actual secondary relaxation motions. Now the question is whether the secondary relaxation motion is able to respond to the imposed stress.

In fact, the possibility of the participation of secondary relaxation motions in early stages of deformation has been previously proposed. Boyd and coworkers[27] proposed that secondary relaxation motion is responsible for the nonlinearity which is observed at the very early stage (less than 1% of strain) of a stress-strain curve, and for the secondary relaxation to repond to a very small strain it must be of considerable volume. Robertson and Patel[28] observed that anelastic strain is developed at the very early stage of deformation and rapidly becomes dominant. They also pointed out that secondary relaxation motions can cause the anelasticity, and the sensitivity of anelastic response is greater if the moving segment is larger, based on the Eyring theory. The secondary relaxation motion of BPA-PC has been characterized to be a cooperative motion of several repeating units and a multiple number of chains, eventually containing a movement of a volume of material. The motion therefore is thought to be able to respond to the imposed stress. In conse-

quence, the secondary relaxation motion of BPA-PC is expected to be able to respond to the initially imposed stress and redistribute the stress to other parts of the material through structural rearrangements (motions), and the rearranged structure is ready for further stresses.

The final question is how the material responds to further stressing and eventually yields, and what is the role of secondary relaxations at this stage. In his yield theory, Robertson[29] proposed a structural change upon the application of stress. He also argued that, by introducing disorder into the polymer, the bond flexing indirectly causes the volume to dilatate, and at yield a structural state characteristic of the liquid some temperature above the glass transition is reached. Yee and coworkers[30] proposed the strain level – temperature equivalence in relaxation behavior, which can explain the softening of the material by straining effectively. It was experimentally shown that approaching either the yield strain or glass transition temperature produces nearly the same relaxation behavior. Both Robertson's and Yee and coworkers' theories describe the yield point as a point where the material relaxes as if it were at (or above) the glass transition temperature, enabling flow. Although the glass transition scale motion is certainly involved at the yield point, it is hard to imagine that such a large scale motion is activated before yield, at lower temperatures or strain levels. Since there is no reason why the molecular element should response to the stress with a large scale motion when smaller scale motion is available, there must be a smaller scale motion which is readily available at glassy state, and we propose the secondary relaxation motion to be this motion. Although it is not clear, at this point, how the secondary relaxation motion responds to a larger strain, it is evident that the motion participates in the re-

laxation process and helps the material to yield up to the yield point where the glass transition scale motion takes over.

Post – Yield Behavior. As discussed before, it is not immediately evident that there should be a correlation between post – yield behavior and secondary relaxation. This is in a sense natural if one recognizes that glass transition scale motion takes over the deformation process at the yield point. In addition it has been shown that post – yield behavior is partly governed by viscoelastic properties. Other factors such as the isothermal – adiabatic transition and molecular weight also affect post – yield behavior. Therefore, the observed post – yield behavior of the polymers is discussed as it is. All the specimens that were able to yield showed necking and a drop in the nominal stress (strain softening) after yielding in their stress – strain curves. Specimens drawn at the lowest strain rate showed a marked increase in the nominal stress (strain hardening) at high strains, while hardening at higher strain rates was less than significant. It is not evident that these softening and hardening reflect true strain softening and hardening processes, since no true stress – strain data were obtained due to the small size of the specimens. But, it is believed so, especially since true strain softening and hardening have been observed in the calibration tension test of BPA – PC. Also the minimal criterion for strain softening and hardening was met as discussed before.[14]

The elongations at break, the ultimate strain where a specimen failed, of the polymers obtained are tabulated in Table 2. It appears that the elongations at break are greatly affected by the strain rate. It is not clear if or where the isothermal – adiabatic transition occurred. Since the strain rate of 7×10^{-1} sec^{-1} is quite high, it is likely that the transition had already occurred. If it had occurred

and does account for all the strain rate dependence of the elongation at break, then the observed values of elongation at break for two of the three strain rates would be close to each other. This was not the case. Rather, the elongation at break seemed to be inversely proportional to the logarithm of the strain rate. This result suggests either that the isothermal – adiabatic transition had not occurred or that factors other than the transition affect the elongation at break. Further analysis of this subject is not possible with the data obtained. The other factor discussed before, i. e., the effect of chain structure, is not expected to play a significant role in determining the elongation at break. Although it is certain that TMBPA units will change the chain stiffness, the change in terms of persistence length is not expected to be as significant as in the case of polyestercarbonate for which the effect is extensively studied.[17,18]

Besides BPA – PC, only the multi-block copolymers are ductile with substantial elongation ot break at all strain rates covered. While the elongation at break of B6T6 is comparable to that of BPA – PC, that of B9T9 is substantially lower. It is not clear why this should be the case. One potential reason for that would be the lower molecular weight of B9T9 compared to that of B6T6 (Table 1). It was proposed that molecular weight greatly affects the brittle strength and thus ductile – brittle transition shifts.[21] However, neither the brittle stress nor the ductile – brittle transition are expected to affect the elongation at break as long as the material yields. Also, since the molecular weight of the copolymer appears to be much higher than the molecular weight between entanglements of BPA – PC ($\sim 2,400$[31]), attributing the difference in elongation at break to the difference in molecular weight is hard to justify. The other possible reason would be the difference in the length of TMBPA blocks in-

corporated in the chains. It is possible that the longer stiff TMBPA blocks in B9T9 restrict the chain motions in drawing process. Also, the 50/50 blend, which possesses TMBPA – PC homopolymer chain, shows a smaller elongation at break than other polymers. However, at this time, when even a description of the molecular process accompanying drawing is not clearly understood, it is impossible to describe how the stiff TMBPA block would affect the post – yield behavior.

The toughness of B6T6 as measured by the area under the stress-strain curve is remarkable. Compared to BPA-PC, even though the elongation at break value is smaller, the yield stress and the stress in the strain hardening region are larger. The toughness, in a tensile sense, is comparable to that of BPA-PC. In addition, the modulus and yield stress as well as the glass transition temperature (179°C) of B6T6 are all higher than those of BPA-PC. As a result this copolymer may be a answer to the effort to develop a stiffer, more heat-resistant polymer without losing the ductility of BPA-PC.

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