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Effect of Limiting Chain Mobility on the Yielding and Crazing Behavior of Bisphenol-A Polycarbonate Derivatives

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ABSTRACT: The sub-T_g relaxations of Bisphenol-A polycarbonate (BPA-PC) can be selectively altered by appropriate chemical modification. It is established that these secondary relaxations are responsible for the in-chain cooperative motions of BPA-PC and have profound effects on the deformation behavior of the bulk material. Through investigations of the microdeformation behavior of BPA-PC and alternating block copolymers based on BPA-PC, it is found that the extent of cooperative motion is also influential in activating the disentanglement crazing mechanism at elevated temperatures.

1. Introduction

The present work forms part of a concerted effort using a variety of techniques to understand the nature of the sub-T_g γ-relaxation in Bisphenol-A polycarbonate (BPA-PC), which occurs at about −100 °C, and its relationship to the mechanical properties. The main thesis is that this relaxation involves an in-chain cooperative motion extending across 6−9 repeat units of the BPA-PC homopolymer and that this motion has important consequences for yielding. That the γ-relaxation in BPA-PC should be a cooperative motion has been argued on the basis of dynamic mechanical studies of alternating block copolymers (ABCs) with carefully designed polymer components and block lengths (these will be described in detail in section 1.1). The exact origin of this cooperative motion is still unclear but has been suggested to stem from the hyperconjugation effects along the chain backbone.[1]

A phenomenological link between yielding and sub-T_g relaxations has been established for some polymers (the γ-relaxation in BPA-PC and the β-relaxation in poly(methyl methacrylate) (PMMA), for example). We shall show here that in the case of cooperative motions, the extent of in-chain cooperation, which can be varied by suitable chemical modification, can influence the deformation behavior. It will become evident that neither the linear nor the nonlinear response of polymers such as BPA-PC, at least at moderate temperatures, can be attributed simply to the activation of the motion of specific moieties, such as benzene ring flips, as has sometimes been suggested in the past. Indeed, recent computer simulations of shear yielding in BPA-PC suggest that the molecular origins of yielding involve clusters incorporating several repeat units.[2] It is therefore reasonable to suspect in-chain cooperative motions involving several repeat units to be necessary for yielding.

The behavior of BPA-PC contrasts with that of polymers such as PMMA and polystyrene (PS) in which the sub-T_g relaxations are widely attributed to the motion of side groups that are separated by relatively flexible main-chain bonds. In such cases it is unlikely that any form of strong coupling between the mobile side groups and the main chain exists. This distinction has indeed been suggested as a basis for dividing glassy polymers into two categories—those with stiff main-chain linkages and those with flexible main-chain linkages—which correspond roughly to the division between macroscopically ductile and brittle polymers, respectively. It should therefore be emphasized that the arguments to be developed in what follows for BPA-PC may not be generally applicable to polymers falling into the second category.

An important factor here may be entanglement, since it is known from transmission electron microscopy (TEM) studies of thin films that highly entangled polymers show a much reduced tendency to craze, a mechanism generally associated with macroscopic brittle behavior. A relatively stiff linear polymer will generally have a more expanded conformation than a flexible one, and thus interact more strongly with surrounding chains, leading to a relatively high degree of entanglement.[3] This may be quantified in terms of the entanglement density ν_e, which is obtained by treating the small-strain response in the regime of rubberlike behavior just above T_g by analogy with that of a cross-linked rubber. For BPA-PC, which shows only homogeneous shear deformation in thin films at room temperature, ν_e is about an order of magnitude higher than in PS, which predominantly exhibits crazing.[4] Close to T_g, however, thermally and stress activated chain mobility may relax the entanglement constraints sufficiently in high-ν_e polymers, such as BPA-PC, for crazing to become the dominant deformation, as will be discussed in section 3.1.[5−7]

In bulk samples and particularly at notch tips, geometric constraints on localized yielding, which is a roughly isovolumetric process, create dilatational stresses, which may favor the crazing mechanism, even in high-ν_e polymers. Nevertheless yielding and crazing are observed to coexist both at crack tips (the so-called epsilon zones) and in tensile specimens of BPA-PC. Thus it appears that the stress relaxation associated with yielding can have a shielding effect on crazes, inhibiting rapid craze breakdown and crack propagation. Given the relatively high intrinsic craze stability of high-ν_e polymers, this results in tough and ductile behavior at ambient temperature. However, if the cooperative motions we have argued to be associated with yielding

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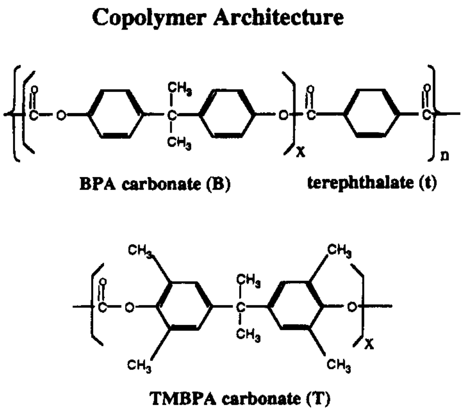

Figure 1. Various blocks used to compose the copolymers of the form $(B_xt)_n$, $(B_xtT_x)_n$, and $(B_xT_x)_n$. The B block is shown here attached to a t block; however, the T block connects in a completely analogous manner.

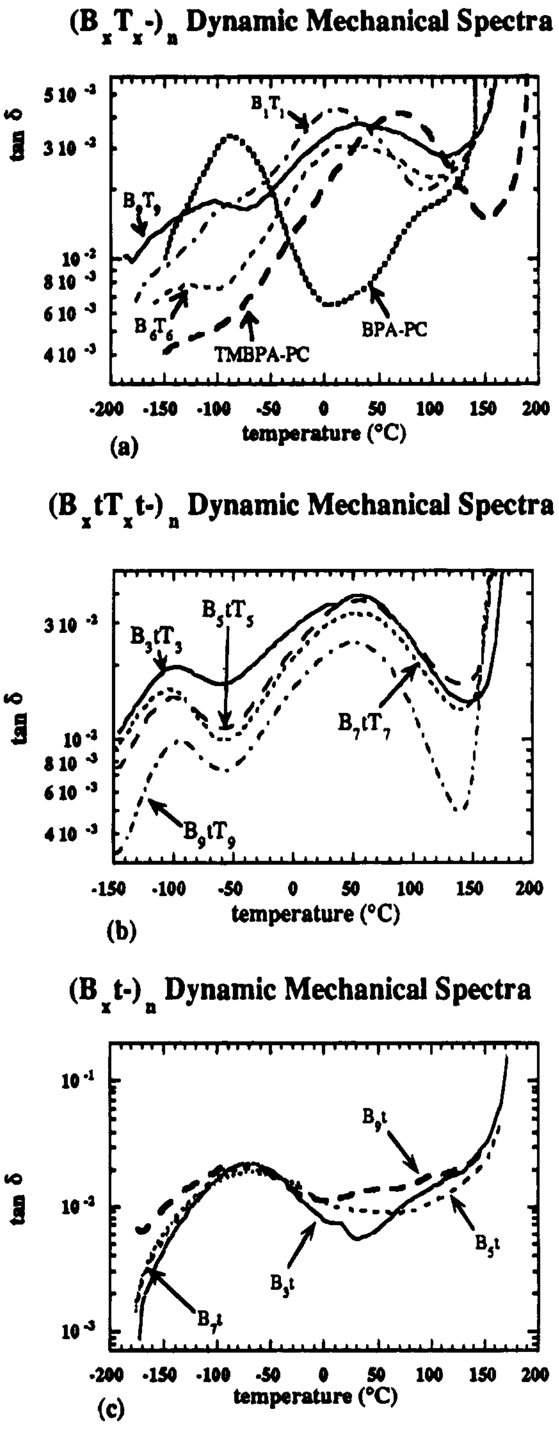

Figure 2. Dynamic mechanical spectra of the three copolymer series. The spectra shown in a–c were obtained from thin-film specimens tested at 11, 10, and 10 Hz, respectively.

are frozen out at ambient temperature as is the case for tetramethyl-Bisphenol-A polycarbonate (TMBPA-PC) (see Figure 2), in which the γ-peak does not occur until 70 °C in the dynamic mechanical spectrum (DMS), the shielding effect described above is no longer effective, and highly brittle behavior is observed. Clearly then, if one can identify the mechanisms linking such chemical modifications to mechanical properties such as the yield stress, one can hope to optimize mechanical performance in tandem with other physical properties such as T_g (for improved thermal stability).

1.1. Evidence for Cooperative Motion in the BPA-PC γ-Relaxation. Jho and Yee[8,9] have copolymerized BPA-PC with TMBPA-PC (abbreviated here to B and T, respectively) to give copolymers of the form $(B_xT_x)_n$, where x is the repeat length in the B and T blocks and n is the overall degree of polymerization (see Figure 1). The homopolymers are known to be fully miscible and the copolymers are neither expected nor observed to show phase separation when combined as a blend. As stated above, the γ-relaxation of the TMBPA-PC homopolymer occurs at a much higher temperature (70 °C) than that of BPA-PC (−100 °C). In the absence of a strong coupling mechanism, two well-separated relaxation peaks should be visible in the dynamic mechanical spectra (DMS) of the copolymers at roughly these temperatures. This type of behavior is already known to occur in blends of the homopolymers, in which the relative peak intensities are found to be proportional to the composition, and the peak temperatures remain unchanged.[10] This indicates that between, or interchain, coupling contributes little to cooperative motion.

In Figure 2 we compare DMS at 11 Hz for the homopolymers and ABCs with various block length x. In $(B_1T_1)_n$ there is strong coupling between the respective relaxations of the homopolymers to give a single broad peak at approximately 10 °C. As x is increased, the single peak broadens and moves to slightly higher temperatures, indicating dominance by the bulkier T groups. However, as x is increased to 6, one sees the emergence of a peak at a temperature close to that of the γ-relaxation peak in pure B. When x is increased to 9, the pure B peak is fully restored, and the pure T peak substantially restored (it remains broader and at a slightly lower temperature than in the homopolymer). This is significant in that the γ-relaxation in BPA-PC can clearly not be assigned to the molecular motion of a single chemical moiety and that the motions responsible for this relaxation must span several repeat units. If this were not the case, the characteristic γ-relaxation of pure BPA-PC would be evident in the DMS of $(B_1T_1)_n$. The results suggest the range of cooperative motion associated with the γ-relaxation to be 6–9 repeat units. It is only when the length of the B blocks is 6–9 repeat units or more than their mobility becomes independent of that of the rest of the chain. For shorter lengths, mobility throughout the B blocks is constrained by coupling to the relatively immobile T blocks.

It is also found that if in-chain motions are decoupled by inserting a terephthaloyl linkage (Figure 1) between the B and T units to give polymers of the form $(B_xtT_xt)_n$, where t is the terephthaloyl linkage,[11] the characteristic relaxations of the constituent homopolymers remain visible in the DMS (see Figure 2), even for block lengths as low as 3 repeat units, with the peak areas being roughly constant for all x (the B to T ratio is 1 for all x). Furthermore, the DMS of ABCs of the form $(\mathrm{B}_x\mathrm{t})_n$ do not vary with x, so that the presence of the t linkages alone has little direct influence on the secondary relaxation peaks. However, one infers from the previous discussion that in the copolymers of the form $(\mathrm{B}_x\mathrm{tT}_x\mathrm{t})_n$ and $(\mathrm{B}_x\mathrm{t})_n$, the range of cooperative motion within the blocks separated by the t units will increase with x, at least for $x < 6-9$.

This may need to be qualified in the light of the observation that 6−9 repeat units corresponds to the generally accepted values for the entanglement molecular weight, M_e, in BPA-PC. This could be taken to suggest that the upper limit to the range of cooperative motion is fixed by the screening effects of the entanglements, in which case the evolution of M_e in the copolymers ought also to be taken into account. In fact, the number of repeat units associated with M_e is found to remain between 7 and 14 repeat units in the $(\mathrm{B}_x\mathrm{t})_n$ copolymers (albeit determined at a temperature at least 20 °C above the glass transition temperature—see section 2). Thus one can only speculate as to whether the extent of cooperative motion would like to extend past 6−9 repeat units but is unable to because of the entanglement restrictions. Although the variation in M_e is too weak to invalidate the conclusions of the previous paragraph regarding the limiting range of cooperativity in BPA-PC, as will be discussed in section 3.2.1, relaxation of entanglement constraints could, at least in principle, lead to increases in the range of cooperativity for relatively long block lengths.

1.2. Cooperative Motion and Yield Behavior. There are two means for analyzing the bulk specimen yield behavior in terms of the cooperative motion. For a first approach, one can consider the mode of deformation as a function of cooperative motion, i.e., whether the macroscopic behavior is brittle or ductile for a given extent of cooperative motion and for a given set of test conditions. In this approach, regimes of brittle and ductile behavior are mapped out as a function of temperature and strain rate, allowing the determination of a brittle to ductile transition temperature as a function of strain rate (or vice versa). Alternatively, one can also investigate quantitative trends in yield stress (in which case test conditions promoting ductile behavior should be chosen). Both techniques were explored here, although the results for each are somewhat incomplete. This is because the copolymers under consideration were synthesized in house, which was both costly and time-consuming, and large quantities of material were not always available. It was thus not possible to perform one uniform set of yield point determinations for all three copolymer homologues. Rather, the trends had to be taken from previous investigations carried out in our laboratory.[11,12,14]

The brittle to ductile transition temperatures (the transitions were relatively insensitive to rate changes) have previously been determined for certain formulations of the $(\mathrm{B}_x\mathrm{tT}_x\mathrm{t})_n$ and $(\mathrm{B}_x\mathrm{T}_x)_n$ copolymers.[11,12] The results show that increasing the extent of the cooperative motion also decreases the temperature of the brittle to ductile transition. The interpretation is that the larger the extent of concerted motion, the "softer" the molecular environment with respect to yielding. Plastic yielding requires diffusional translation of long chain segments in the polymeric network, and such reorganization will be considerably facilitated by cooperative motion.[12]

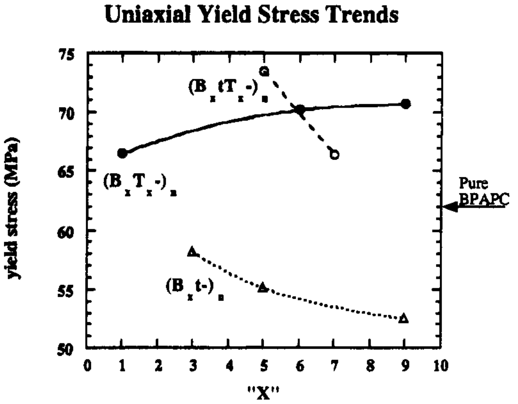

Figure 3. Uniaxial yield stress data for the copolymers as a function of "x", where "x" denotes the block lengths in the nomenclature $(\mathrm{B}_x\mathrm{t})_n$, $(\mathrm{B}_x\mathrm{tT}_x\mathrm{t})_n$, and $(\mathrm{B}_x\mathrm{T}_x\mathrm{t})_n$. All tests reported here were performed at a strain rate of $7.1 \times 10^{-4}\ \mathrm{s}^{-1}$ and ambient temperature.

In Figure 3 we compare the tensile uniaxial yield stress values for the various copolymers at room temperature and a deformation rate of $7 \times 10^{-4}\ \mathrm{s}^{-1}$. (The initial slope of the sinusoidal strain input at a frequency of 11 Hz for the DMS measurements is comparable to the deformation rate of $7 \times 10^{-4}\ \mathrm{s}^{-1}$ used in the tensile tests). The incompleteness of this comparison is due both to limited material and to the fact that some of the polymers were not ductile for the chosen test conditions. Nevertheless, it is clear that in the decoupled copolymers ($(\mathrm{B}_x\mathrm{tT}_x\mathrm{t})_n$ and $(\mathrm{B}_x\mathrm{t})_n$), an increase in x, and hence in the extent of cooperative motion, brings about a decrease in the nominal yield stress value. This trend is consistent with the idea that an extensive cooperative motion facilitates yield. In the $(\mathrm{B}_x\mathrm{T}_x)_n$ material, on the other hand, a similar increase in x results in a higher yield stress, which would be inconsistent with the proposed concept of yielding and cooperative motion. However, one must recall that the spectral position(s) of the DMS relaxation peak(s) also vary with x. Although the low-temperature peak characteristic of pure B reappears when x is raised, the temperature of the main peak rises toward that of pure T at 70 °C at the same time. Since this latter relaxation will not be activated at room temperature, the increase of yield stress may therefore be attributed to a loss in mobility of the T blocks as they become longer and decoupled from the more mobile B blocks. In this case the crucial factor is cooperative motion between the B and T blocks, as opposed to the range of cooperativity within the blocks.

1.3. Objectives. The main aim of the present work is to examine the effect of the chemical modifications to BPA-PC described above on microdeformation and, principally, on the competition between crazing and homogeneous shear yielding in the various copolymers, with particular emphasis on $(\mathrm{B}_x\mathrm{t})_n$ and the extent of cooperative motion. The technique used is that of Kramer and Lauterwasser,[13] in which films (<0.5 μm) are bonded to copper grids, strained, and investigated by TEM. This method has the advantage that it uses very little material and allows clear identification of the different types of deformation mechanisms as well as investigation of the internal structure of crazes and other types of deformation zones.

To develop the discussion, we consider first the basic phenomenology of deformation in BPA-PC thin films, followed by the decoupling effect of the t units on the range of cooperative motion in $(B_xt)_n$ and the effect of this on deformation at the macroscopic and microscopic levels. Finally, the combined effects of decoupling and T unit addition in $(B_xtT_xt)_n$ and $(B_xT_x)_n$ on microdeformation are considered in the light of the observations for $(B_xt)_n$.

2. Experimental Section

The synthesis of the various copolymers is described in detail elsewhere[8,11,14] and will not be addressed here, T_g was determined by differential scanning calorimetry (DSC) using the Perkin-Elmer DSC 7. Small disks (7–8 mg) were cut from compression-molded sheets and the T_g determined at a scanning rate of 10 K min^{-1} after a prior heat treatment above T_g. The entanglement molecular weight was estimated from the storage modulus in the rubbery plateau regime just above T_g, using the Rheometrics RMS-80 dynamic mechanical analyzer. The samples were compression-molded disks (25 mm in diameter and 3–4 mm thick), dried at 100 °C under vacuum overnight prior to testing. The testing temperature was varied between T_g + 20 °C and T_g + 60 °C in 5 °C intervals with a frequency scan taken at each temperature. The plateau modulus was then determined from a master curve obtained by shifting along the frequency axis.

2.1. Thin-Film Preparation. Clean glass slides were drawn at a constant rate from a solution in dichloromethane of BPA-PC or the ABCs and the solvent was allowed to evaporate in air, leaving a film approximately 0.5 μm in thickness (the thickness of the resulting film depended on the concentration of the solution and the drawing rate and could be estimated from the interference color of the film in reflected light). The films were allowed to dry on the glass slides for a few minutes before they were floated off onto distilled water and picked up on annealed cooper grids which had been previously dipped in the same solution. The film plus cooper grid was dried in a vacuum oven at 50 °C for 48 h to remove excess water and solvent. In the standard method, a short exposure to dichloromethane vapor is used to bond the film to the grid. However, since this leaves the film in a somewhat ill-defined thermodynamic state, it was chosen here to bond the films to the grids by heating to 10 °C above T_g for 30 s and then air cool back down to room temperature. As with solvent bonding, this also acted to relax the films and to remove any wrinkles. Unless otherwise stated, the films were tested without further heat treatment.

There was some concern that use of solvent casting would lead to crystallization. To obtain an idea of the crystallizing effect of dichloromethane, films cast onto glass slides were held in a dichloromethane vapor rich environment for various times. No attempt was made to quantify the spherulitic growth rates, but spherulites were clearly visible in BPA-PC films by polarized light microscopy after 1 h of exposure to the solvent vapor. In $(B_9t)_n$ films crystallization was slower, with a partially spherulitic microstructure being observed after 6 h. For shorter block lengths, no spherulites were seen in any of the ABCs. Light microscopy was used to verify that the 30 s exposure to a temperature 10 °C above T_g did not induce any crystallization.

Figure 4 contains TEM micrographs of the solvent vapor induced semicrystalline morphology of the BPA-PC and $(B_9t)_n$ films with a well-developed spherulitic structure in the former case and a somewhat indistinct, but essentially spherulitic structure in the latter case. Given the low nucleation density and the long time scale of the spherulite development, it was assumed unlikely that the film preparation method of the previous section would result in artifacts linked to spurious crystallization and that if it did, these would be clearly visible. It is of course also possible that strain-induced crystallization plays a role during plastic deformation or crazing below T_g. However, on the above evidence, this would not appear to be a factor relevant to deformation in the copolymers.

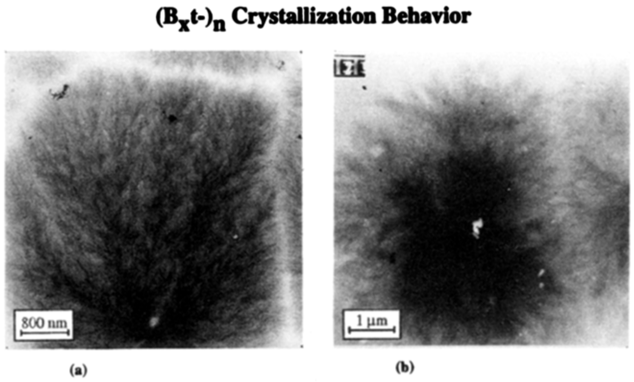

Figure 4. Solvent-induced crystallization in thin films of BPA-PC (a) and $(B_9t)_n$ (b). The spherulitic structure developed in the BPA-PC after 1 h of exposure to the solvent vapor, while exposure times of 6 h produced only a partially spherulitic structure in $(B_9)_n$.

2.2. Tensile Testing. Tensile tests of the thin films were carried out by stretching the copper grids in a Polymer Laboratory Minimat miniature tensile test apparatus equipped with an environmental chamber. Unless otherwise state, the strain rate was 5 × 10^{-4} s^{-1}. This rate was on the same order of magnitude as the rate used for the uniaxial tensile tests performed in the previous investigations.[11,12,14] In addition, this deformation rate was also chosen so as to be comparable to the initial deformation rate in a strain cycle of the dynamic mechanical measurements used in these works (although we do not suggest comparisons between the linear and nonlinear deformation processes). The deformation process was monitored in-situ using an Olympus BH2 stereomicroscope. TEM was then employed to identify the deformation mechanism.

3. Results and Discussion

3.1. Microdeformation in BPA-PC. Previous studies of the deformation behavior of thin films of BPA-PC have indicated both crazing and shear deformation to be possible depending on the temperature and deformation rate.[15,16] The active mode of deformation may be argued to depend on which mechanism exhibits the lower critical propagation stress (S_c for crazing and S_{DZ} for shear) as given by the following relations:[5]

$$S_c \sim \sigma_f^{1/2}(\gamma + \nu_e d_e f_d/2)^{1/2} \tag{1}$$

$$S_{DZ} \sim \sigma_f(T)(\dot{\epsilon})^{1/n} \tag{2}$$

(σ_f = flow stress, γ = van der Waals surface energy, ν_e = entanglement density, d_e = entanglement spacing, f_d = force to overcome entanglement constraints, $\dot{\epsilon}$ = strain rate, n = stress exponent). It is generally found that the temperature and strain rate dependence of the flow stress reflects that of the yield stress σ_y, and indeed the term σ_f of eq 2 is often replaced with σ_y (the two quantities will henceforth be assumed interchangeable).

A strong case has also been made for the existence of two distinct mechanisms of crazing: disentanglement and scission crazing. Scission crazing involves the breaking of chains to accommodate the geometrically required entanglement loss during fibril formation[4] and is favored by low temperatures and high deformation rates. Disentanglement crazing invokes the frictional sliding of chains to account for entanglement loss and is thus expected to be favored by low molecular weights, low deformation rates, and the relatively high molecular mobility associated with elevated temperatures.[5–7,17,18] In BPA-PC thin films, where some form of diffuse shear deformation generally dominates at moderate deforma-

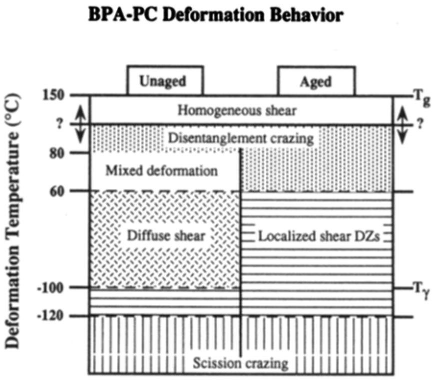

Figure 5. Comparison of the thin-film deformation behavior as a function of temperature in BPA-PC for a strain rate of 4 × 10^{-4} s^{-1}.

tion rates and room temperature, increasing the temperature results in a transition to crazing. In films of BPA-PC physically aged at $T_g - 20$ °C overnight, this manifests itself as a transition from highly localized shear deformation zones (DZs) when the temperature is raised to about 80 °C,[15] with lower strain rates and molecular weights resulting in a reduction in the transition temperature, consistent with the disentanglement model.

Similar trends, summarized in Figure 5, occurred in the unaged films of BPA-PC studied here, although they were less well defined. At room temperature we observed patches of diffuse homogeneous shear deformation rather than highly localized DZs, but when the temperature was raised to a critical value T_{SC}, there was a transition to localized deformation. At temperatures immediately above T_{SC}, DZs and crazing were observed to coexist. A reasonable explanation for this is that S_{DZ} and S_c are similar in this temperature regime, whereas in aged film S_{DZ} is much higher than S_c[19] (physical aging is known to increase σ_y and S_{DZ} shows a stronger σ_y dependence than S_c). As the temperature was raised further above T_{SC}, crazing became the dominant deformation mode with a final transition to homogeneous deformation just below T_g (as T approaches T_g, σ_y begins to drop very rapidly). No evidence was obtained from selected-area electron diffraction for strain-induced crystallization in BPA-PC, even at high temperatures and low strain rates.

The possibility of scission crazing at subambient temperature is also implicit in the above picture and was confirmed by the observation of features such as that shown in Figure 6a. Optically, there was a marked transition from diffuse shear to localized deformation at −100 °C, corresponding to the γ-peak in DMS (Figure 4). However, TEM examination suggested crazes such as shown in Figure 6a do not occur until −110 °C, and even at this temperature, continued to be in competition with localized DZs.

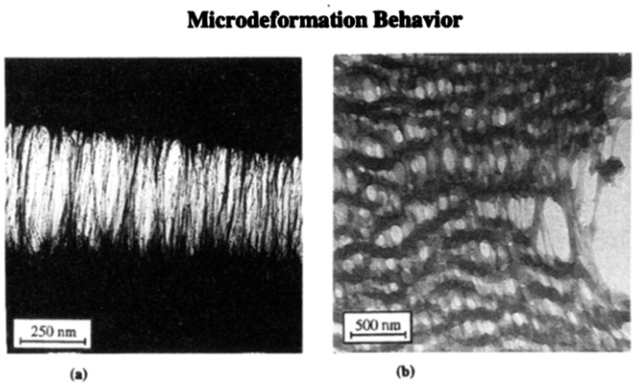

Figure 6. Thin-film deformation microstructure in BPA-PC (a) and $(B_3t)_n$ (b) at −110 and 150 °C, respectively. Note the well-developed fibrils typical for scission type crazes in the low-temperature deformation of (a) as well as the type-II reminiscent, cavitational yielding in the high-temperature deformation.

Table 1. Materials Parameters for $(B_xt)_n$ Materials

x	M_e	T_g (°C)
3	2219	171
5	3565	164
7	2902	164
9	2547	160
BPA-PC	1810	154

3.2. $(B_xt)_n$ Alternating Block Copolymers. 3.2.1. Basic Characterization. The entanglement molecular weights (M_e) determined for the $(B_xt)_n$ alternating block copolymers are shown in Table 1, along with the glass transition temperatures. The observed variations in M_e were not expected to result in significant changes in crazing behavior (M_e enters the relation for S_c through the terms ν_e ($\nu_e = \varrho N_a/M_e$) and d_e ($d_e = k(M_e)^{1/2}$), giving an overall dependence on $M_e^{-1/4}$). It is nevertheless interesting to note that the changes in M_e with block length were nonmonotonic. Starting with BPA-PC, there was an initial rise in M_e with decreasing block length, but M_e fell again as the block length decreased below 7, suggesting that two or more competing factors are responsible the degree of entanglement.

As discussed in the Introduction, the M_e in BPA-PC is roughly equivalent to 6−9 repeat units, that is, the same number of units as associated with the γ-relaxation, which suggests that entanglements may be acting to restrict longer range cooperative motion. If the effect of adding the t linkages is to increase chain flexibility, this may relax entanglement constraints,[3] accounting for the initial rise in M_e. Indeed, both group additive predictions[20] and light scattering experiments[21] do suggest that adding t linkages increases the flexibility. Thus if M_e rises, for block lengths longer than the range of cooperativity in the BPA-PC homopolymer, the range of cooperativity may increase on the addition of the t linkages. However, for shorter block lengths (below 7, say), where decoupling by the t units begins to restrict the range of the γ-motions, it is possible that the effective chain stiffness (from the localization of the motion) and thus the degree of entanglement will begin to rise again, explaining the decrease in M_e observed here for small x. This interpretation differs from that of Prevorsek and De Bona,[22] who argued addition of t units to result in a monotonic increase in stiffness with x. However, these authors considered much larger t contents than those for which we have observed the peak in M_e, i.e., $9 > x > 3$.

3.2.2. Bulk Yield Stress. The DMS of the different $(B_xt)_n$ copolymers revealed almost identical sub-T_g spectra, with similar peak positions and intensities, and a slight monotonic increase of the T_g peak temperature for increasing t contents. However, as shown in Figure 7, the uniaxial yield stress was highest in BPA-PC, with a drastic drop on initial addition of t linkages, followed by a monotonic increase back toward the yield stress of BPA-PC as x was reduced further. An increase in yield stress with decreased cooperative motion (decreased x) is consistent with the idea of cooperative motion facilitating yield. However, it is not clear why the yield stress of BPA-PC was so high in comparison with those

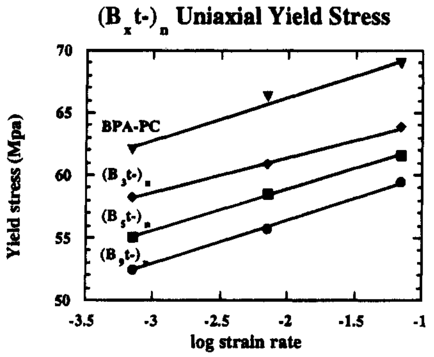

Figure 7. Uniaxial yield stress trends for the $(B_xt)_n$ copolymers as a function of strain rate at ambient temperature. Note that for the initial addition of terephthalate the yield stress drops markedly but then increases back toward pure BPA-PC for continued terephthalate additions.

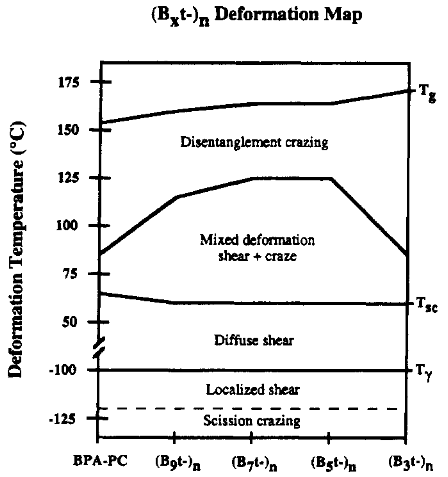

Figure 8. Deformation behavior of the $(B_xt)_n$ copolymers as compared to BPA-PC at various temperatures. All tests were performed at a strain rate of 2 × 10^{-4} s^{-1}.

of the copolymers. One could speculate that the drop on going from BPA-PC to $(B_9t)_n$ was due to an increase in cooperativity owing to relaxation of entanglement constraints as discussed at the end of section 3.2.1, with continued terephthalate additions (toward $(B_3t)_n$) restricting the cooperativity and thus raising the yield stress. However, this would not explain why BPA-PC had a higher yield stress than $(B_3t)_n$, the latter in which cooperativity should be severely reduced.

3.2.3. Microdeformation. The microdeformation behavior of $(B_xt)_n$ is compared with that of BPA-PC in Figure 8. For the localized to diffuse deformation transition at temperatures near the γ-relaxation peak, the behavior for all the polymers was as for BPA-PC. T_{SC} (the diffuse shear to mixed deformation transition temperature) also varied little with x, the main variation being in the range of mixed deformation above T_{SC}, which was relatively narrow in both BPA-PC and for small x. This is explicable in terms of the changes in σ_y described in section 3.2.2; the materials with the highest yield stresses exhibited a reduced regime of mixed deformation, since yield is less competitive with crazing (cf. eqs 1 and 2).

If T_{SC} represents the onset of disentanglement as has been suggested for BPA-PC, a rough criterion for crazing might be that the force to disentangle a chain, f_d, falls below the chain scission force of about 2 × 10^{-9} N (given the strong temperature dependence generally assumed for the mobility, it is reasonable to assume that disentanglement will become competitive with both scission crazing and shear at about the same temperature, even if the scission crazing stress is somewhat higher than S_{DZ}).[23] It has been argued that for forced disentanglement[5,17,18]

$$f_d \sim (M/M_0)^{\alpha} v \zeta_0 \qquad (3)$$

where ζ_0 is a monomeric friction coefficient, v is the disentanglement rate, and $\alpha \sim 1$. Unfortunately, it is not clear how to obtain or even estimate ζ_o for the copolymers in the glassy state. Values of ζ_0 estimated for temperatures well above the T_g using empirical chemical group additive rules[20] suggest the t linkages would not have a profound effect on disentanglement, and it seems reasonable to assume that this would be true of values of f_d given by eq 3 below T_g. A serious objection to this approach is that classical theory appears to rule out all forms of disentanglement in the glassy state. However, as suggested by Kramer and Berger[18,24] and supported by recent measurements of a decrease in T_g with film thickness in thin films,[25] the paradox might be resolved by assuming chains in the vicinity of a free surface (the active zone in a craze for example) to have much higher mobilities than those in the bulk.

Bearing in mind such reservations, the overall conclusion to be drawn from this section is that given their similar M_w and the relatively minor changes in T_g, M_e, and the t content as x was increased, the observation of little variation in the high-temperature crazing behavior of the $(B_xt)_n$ polymers suggests cooperativity to have little direct influence in this case. On the other hand, the changes in the extent of the regime of mixed shear and disentanglement crazing above T_{SC}, which were mainly due to changes in σ_y, are thought to be associated with changes in the range of cooperative motion.

Since T_{SC} remained approximately constant, in spite of the rises in T_g, in $(B_3t)_n$, which has the highest T_g, there was a particularly extended temperature regime relative to the T_g of disentanglement crazing. Within this extended regime, as the temperature rose and the strain rate was decreased, the characteristics of the craze deformation changed markedly. The crazes took on the "flame" shape usually associated with DZs and the craze body resembled a perforated sheet (Figure 6b). This was a gradual transition. Figure 6b shows deformation at 150 °C and $d\epsilon/dt \sim 5 \times 10^{-7}$ s^{-1}, which was an extreme case. The voiding appeared to be a post-drawing phenomenon similar to the Type-II crazing observed in bulk BPA-PC close to T_g.[26] That the voids nucleated in rows perpendicular to the principal stress axis is expected from the form of the biaxial stress field around an isolated void. It is less clear why material separating the rows of voids was relatively undeformed, whereas the deformation ratio of the material separating voids within the rows was large at these temperatures (presumably because of disentanglement). The resemblance of the feature shown in Figure 6b to Type-II crazing is also interesting in that Type-II craze behavior can be induced in BPA-PC by adding low-M_w diluents that plasticize T_g but antiplasticize the sub-T_g relaxations.[26] We have argued here that it is precisely these sub-T_g relaxations (γ) which are responsible for the cooperative motion. Hence, there are some potentially interesting correlations relating diluent systems, cooperative motion, and deformation behavior which could be investigated in this context.

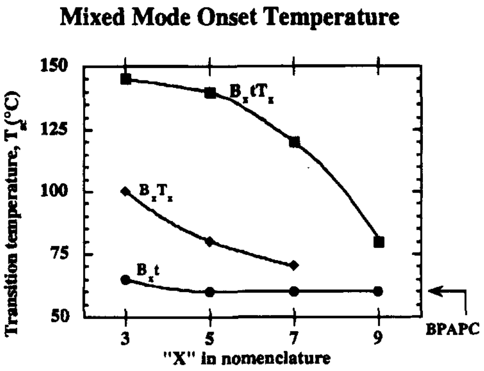

Figure 9. Comparison of the onset of craze deformation at various temperatures for the three different copolymer series.

3.3. $(B_xtT_xt)_n$ and $(B_xT_x)_n$ Alternating Block Copolymers. The DMS and bulk deformation behavior of $(B_xtT_xt)_n$ and $(B_xT_x)_n$ were briefly discussed in the Introduction, but we shall recall the essential points here. For low x, $(B_xT_x)_n$ exhibits one broad γ-peak at about 10 °C, with an increase in x leading to the restoration of two separate peaks for the constituent B and T blocks. In $(B_xtT_xt)_n$, as with $(B_xt)_n$, increasing x does not change the spectral position or relative intensities of the sub-T_g relaxations. Hence for $(B_xtT_xt)_n$ and $(B_xt)_n$, increasing x increases the extent of cooperative motion, whereas for $(B_xT_x)_n$ a similar increase also changes the degree of activation (at a given temperature).

Microdeformation maps for thin films of $(B_xtT_xt)_n$ and $(B_xT_x)_n$ (both homologues have $M_w \sim 10^5$ and $T_g \sim 200$ °C) are given in Figure 9 showing the onset of disentanglement crazing as a function of composition. It is proposed that in the presence of the T blocks, a fully activated γ-relaxation is necessary, but not sufficient, for disentanglement crazing in BPA-PC, since the extent of the cooperative motion associated with the γ-relaxation also appears to play an important role in high-temperature crazing. This may be seen by considering Figure 9 in the light of the DMS. In $(B_xtT_xt)_n$, the onset of crazing showed a considerable dependence on the block length. When x was small, much greater thermal stimulation was needed for the crazing mechanism to operate, which is an indicator to the role of cooperative motion, since both the DMS and the materials parameters (T_g, M_w) were similar for all the compositions. Increasing the block lengths in $(B_xT_x)_n$ also appeared to facilitate crazing. However, for a given x, T_{SC} fell roughly between that of $(B_xT_xt)_n$ and $(B_xt)_n$. This can be understood in terms of the decoupling effect of the t linkages. In $(B_xtT_xt)_n$, mobilization of the bulky T blocks depended predominantly on the thermal environment and the applied stress, since the t linkages inhibit in-chain coupling with the relatively mobile B blocks. However, in $(B_xT_x)_n$, the B blocks were directly coupled to the T blocks, and it is reasonable to assume the motion of the B blocks to assist in mobilizing the T blocks.

Within the framework of the disentanglement model for crazing, since the t units alone had a relatively minor effect on T_{SC}, if the effective monomeric friction coefficient were a truly additive property, one might expect disentanglement to remain substantially independent of x in the polymers containing T units, since the proportion of T units remains roughly constant. On the present evidence however, the coupling of B and T units and the lubricating effect of long-range B motions for large x, which facilitate mobilization of the T blocks, also appear to promote disentanglement.

It might be tempting to account for the high-temperature transition to crazing as being a consequence of the onset of localized deformation on the molecular level. Certainly, in a macroscopic sense crazing is considered localized, whereas shear is perceived to be a large-scale deformation mode. However, the results strongly suggest full activation of the chains to be necessary for high-temperature crazing (consistent with the disentanglement mechanism). Simple shear deformation, on the other hand, persists even when all the sub-T_g relaxations are not activated, so that at the molecular level, crazing is a less localized process than shear. Studies of PMMA–glutarimide random copolymer systems, in which the β-relaxation process needs to be completely activated for crazing to dominate at high temperature, appear to corroborate this idea.[27] For PMMA, the β-relaxation can be attributed to the motion of the ester side groups, although Yee and Takemori[28] and Spiess *et al.*[29] found this side group motion to be coupled to the main chain, with its activation inducing a main-chain wiggling motion. However, regardless of whether the sub-T_g motions are main chain or side group in nature, the conclusion is the same; it appears that the entire molecule needs to be activated for disentanglement to be observed. Futhermore, the predominance of localized DZs in aged films deformed at ambient temperature shows that while localized deformation may be a necessary condition for crazing, it is not a sufficient one. On the other hand, disentanglement may also be available as a relaxation mechanism for material undergoing plastic drawing, reducing work hardening, and hence provoking the transition to localized deformation in unaged BPA-PC. In this scenario, the onset of disentanglement crazing and the diffuse to localized shear transition would both be manifestation of the same basic phenomenon.

4. Conclusions

It has been demonstrated that by changing the extent of in-chain cooperative motion, the deformation behavior of BPA-PC can be significantly altered, and this affects both the yield stress and toughness. The consequences of such modifications for thin-film microdeformation behavior have also been examined, with emphasis on the competition between shear yielding and high-temperature crazing. For BPA-PC containing t linkages inserted every x repeat units along the chain, and in which cooperative motion was limited when $x < 6-9$, the yield stress rose with decreasing x in this regime. Since the secondary relaxations were well activated at room temperature, the temperature of the shear to disentanglement crazing transition, T_{SC}, was relatively unaffected, although lowering the yield stress led to an expanded regime of mixed shear and crazing just below T_g. If, on the other hand, the cooperative motions were frozen out from the polymer chain at ambient temperature, as is the case of those copolymers containing the relatively immobile TMBPA-PC blocks, disentanglement crazing became more difficult, requiring greater thermal stimulation than for BPA-PC. In such cases disentanglement was facilitated both by increasing the range of cooperativity (increasing the block length) and by strong coupling between the BPA-PC and the TMBPA-PC blocks. That mobilization of both types of block was necessary for high-temperature crazing is consistent with the disentanglement mechanism, which requires concerted motion along the whole of the polymer chains.

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