Notes

Enhanced Segmental Mobility at Polymer Surfaces: Thermally Stimulated Current Studies of Crazed Films

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Introduction

In this report we discuss a method for studying the segmental mobility of polymer chains near a free surface and demonstrate that in this region polymer relaxations can be greatly enhanced relative to those characteristic of the bulk. In particular, we have used thermally stimulated depolarization currents (tsc)[1,2] to investigate the polymer mobility within the tiny fibrils of the craze structure; these fibrils are characterized by an inherently large surface to volume ratio and provide an ideal system for studying polymer relaxations dielectrically. Results for crazes grown in films of polystyrene (PS) and its brominated derivative (PBrS) will be discussed. These polymers, which have quite similar craze microstructures yet markedly different dielectric increments, allow the role of dipolar relaxations due to segmental mobility to be distinguished from possible charging phenomena in the tsc experiments.

Recent advances in small-angle X-ray scattering and low-angle electron diffraction methods, in conjunction with bright-field transmission electron microscopy, have yielded detailed quantitative information about the craze microstructure and the mechanism of its formation from a network of entangled and cross-linked polymer chains.[3-10] From these studies a microscopic and in some cases a molecular picture of the craze growth and craze breakdown process is starting to emerge. Nevertheless, an understanding of the physical nature and the viscoelastic properties of the polymer within the craze fibrils remains poor and highly speculative.

Displayed in Figure 1 is a TEM image of a single craze grown in a polystyrene film that shows the prominent features which characterize the craze microstructure. Within an individual craze, the structure consists of an array of small highly oriented and interconnecting polymer fibrils inclined along a direction parallel to the tensile axis; these tiny fibrils span the interfaces of the undeformed polymer. For PS, the volume fraction of polymer within the craze is 0.25; moreover, since the mean craze fibril diameter is 9 ± 1 nm,[3-5] the specific surface area within the craze can be as high as 10^8 m^2/m^3. This enormous surface area has important implications in governing the local topological environment of the polymer chains within the fibrils. For example, if it is first assumed that the chains within the craze fibrils are packed as tightly as they are in the crystalline phase of *isotactic* PS, it can be shown that within a single fibril cross-section each chain is within 4–5 nearest neighbors of a free surface.[3,8] Of course, within the amorphous craze fibrils the density is lower; hence these chains are packed more loosely. The fine dimensions of the craze fibrils also necessitate that a large fraction of the polymer reside at the polymer/air interfacial region; e.g., for an interfacial width of ca. 0.5 nm,[11] the "interface" comprises roughly 20% of the total polymer volume within the ~9-nm-diameter fibril. Because of the segment density gradient across this interface, this interfacial region may be significantly less dense than the bulk polymer, which may permit large-amplitude cooperative motion.

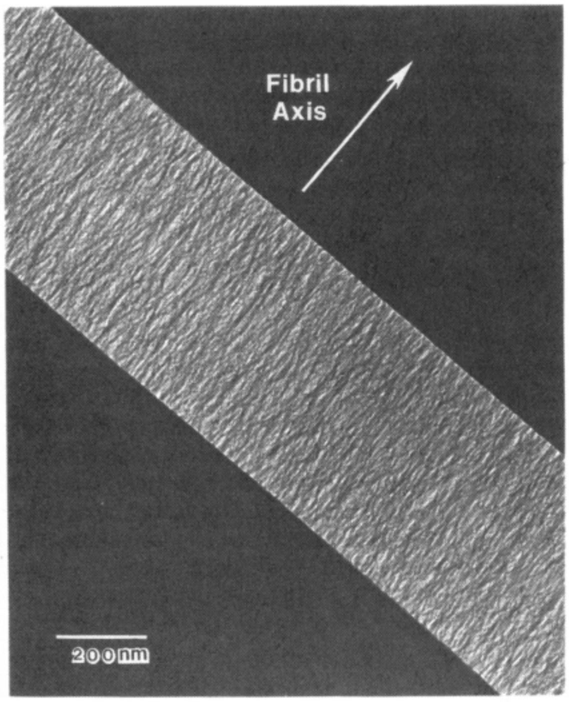

Figure 1. Bright-field transmission electron microscope image of a single craze grown in a thin PS film. The primary direction of the craze fibril axis is shown.

Experimental Section

Nearly monodisperse atactic polystyrene (PS) having number-average molecular weight M_n = 1 860 000 and a polydispersity index of 1.05 (equal to the ratio of the weight-average to number-average degree of polymerization) was used in this study. An aliquot of this PS sample was brominated using the procedure described by Kambour and Bendler.[12] Bromination under these conditions has been shown to occur exclusively on the aromatic ring and in the para position, resulting in PBrS. Uniform films, ca. 50–100 μm thick, were prepared by casting from a solution of polymer (either PS or PBrS) in methylene chloride. The films were dried by slowly raising the temperature in an oven (under N_2) to 20 °C above T_g and holding for ~1 h. Subsequently, the samples were physically aged at a temperature 10 °C below T_g and then cooled to room temperature. Highly crazed samples were produced by bending the films slowly in tension. The tsc results presented here were obtained by sandwiching the polymer films (area 15–25 mm^2) between two pieces of thin gold foil which were found to produce good contacts. The sample areas for each spectra are given in the figure legends.

A tsc spectrometer (Solomat Instruments, Stamford, CT) was used to investigate the dielectric relaxation behavior of crazed

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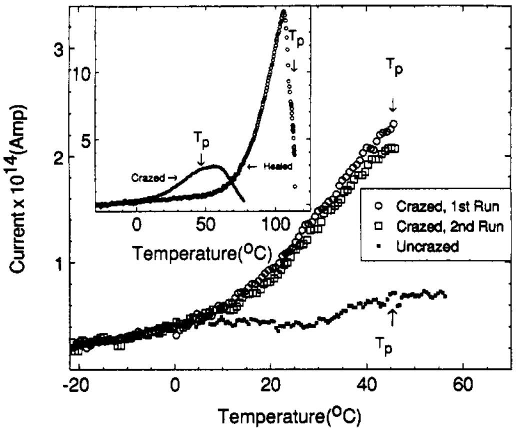

Figure 2. tsc spectra for a crazed sample (○), a repetitive run (□), and an uncrazed (■) PS film polarized at the temperatures indicated by the arrows. A significant enhanced signal is seen for the crazed samples at a temperature as low as 5 °C. For these runs the polarization field was E = 2000 kV/m and the sample area was A = 15 mm^2. Shown in the inset are spectra taken for a crazed (□) and fully healed film (○); the spectrum for the healed sample reveals a complete suppression of the enhanced relaxation and a T_g at 105 °C.

and uncrazed samples. Measurements were made with a sample cell flushed three times with 1.1 bar of high-purity He (grade 5.5, 99.9995%). Between the flushing stages the cell was evacuated to ~10^{-4} mbar. The tsc experiment consists of two steps:[1,13] (1) alignment of dipoles by applying a polarization field E (~2000 kV/m) for 2 min at the polarization temperature T_p and then keeping the field applied while cooling at 20 °C/min to the "freezing" temperature T_0 and (2) with E = 0 and the sample short circuited, subsequent measurement of the depolarization current due to a change in dielectric constant caused by the reorientation of dipoles in the polymer chain, as the temperature is increased at a constant rate. The results are similar to low-frequency (10^{-2}–10^{-4} Hz) ac dielectric permittivity measurements.[1]

Each tsc scan represents a convoluted spectrum of the dielectrically active relaxations excited between T_p and T_0. Integrating the area under a typical tsc curve (as shown in the inset in Figure 2) gives the dielectric increment ($\Delta\epsilon$) for the sum of the processes in the temperature range examined;[1] viz.:

$$\Delta\epsilon = \frac{1}{E\epsilon_0}\int_{t_0}^{\infty}\frac{j}{A}\,dt \qquad (1)$$

where $\epsilon_0 = 8.854 \times 10^{-12}$ F/m is the permittivity of vacuum, t_0 is the time at which the depolarization scan was started, j is the measured current, and A is the sample area (ca. 20 mm^2). In previous studies, $\Delta\epsilon$ obtained from an integration of the tsc relaxation peak has been shown to agree within a factor of 2 with that obtained from ac dielectric experiments.[2] As will be described below, for PS and PBrS, we too have found a similarly satisfactory agreement in the values of $\Delta\epsilon$ determined with these two techniques.

Results and Discussion

Typical tsc scans for a crazed (○) and an uncrazed (■) PS film are shown in Figure 2. In both cases the samples were polarized from T_p = 45 °C down to T_0 = −30 °C with E = 2000 kV/m; then, with the field turned off, the depolarization current was measured at a heating rate of 7 °C/min from T_0 to T = 45 °C. For the uncrazed film the recorded tsc curve is flat and essentially featureless, consistent with a low degree of mobility for a bulk polymer at $T \ll T_g$. In marked contrast, however, the tsc spectrum for the crazed sample exhibits a strong increase in the depolarization current above the baseline at a temperature of 5 ± 5 °C. This increase reveals the presence of significant polymer mobility at a temperature nearly 100 °C below the nominal glass transition temperature of PS! Evidence that the enhanced relaxation in the crazed film can be studied without modifying the craze fibril structure is also shown in Figure 2. The second spectra for the crazed sample (□) was taken immediately after the first using the same experimental parameters. Under these conditions, a near identical spectrum was obtained, indicating that no significant craze healing occurred within this temperature range and the short time period necessary for the poling.

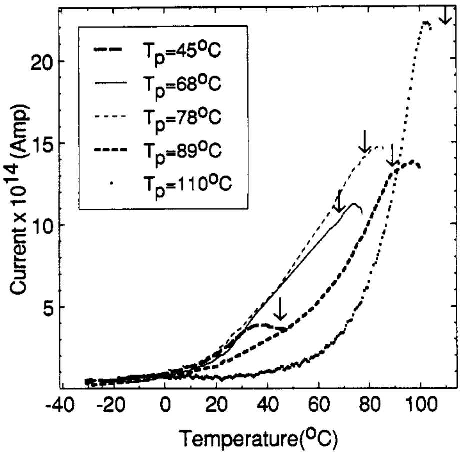

Figure 3. Series of tsc spectra for a crazed sample of PS successively polarized at T_p = 45, 68, 78, 89, and 110 °C; the bulk T_g of PS is 105 °C. This film was polarized with E = 2000 kV/m and had an area of 25 mm^2.

On the other hand, healing and coalescence of the craze microstructure were found to have marked effects on the enhanced relaxation. Shown in the inset in Figure 2 are tsc spectra for a crazed sample before and after annealing at 140 °C for 10 min. Such annealing (i.e., above T_g) is known to result in a complete healing of the craze fibril structure.[3,14] As shown, the tsc spectrum for the healed sample was found to exhibit a complete disappearance of the enhanced signal; moreover, it is equivalent to that obtained from a never crazed sample, which has a glass transition at 105 °C. (The apparent drop-off in the depolarization current above T_p for the crazed sample is an artifact of the original poling procedure; i.e., the excitation field was only applied at T < 45 °C.)

To monitor the gradual onset of craze fibril healing in PS, a series of tsc spectra were taken at T_p = 45, 68, 78, 89, and 110 °C and are shown in Figure 3. At the heating and cooling rates used here, each scan required approximately 40 min to complete, including a 2-min anneal at T_p. (In each case, the tsc scan was stopped at approximately 10 °C past T_p in order to retain the craze structure as much as possible before continuing with the next run.) For the freshly crazed systems the depolarization current was observed to increase sharply at ~5 °C owing to the onset of a strong dielectric relaxation at that temperature. Moreover, the relative strength of the depolarization current, as well as the temperature at which a peak in the tsc spectrum occurred, was observed to increase with increasing T_p until T_p = 89 °C. Since only dipolar processes below T_p are excited, the effect of polarizing at a successively increasing temperature is to fractionally polarize a larger part of the overall relaxation. This type of fractional excitation is a general feature of tsc and is not unique to these systems.[1] However, the drop in the enhanced signal for the scan with T_p = 89 °C is unique to this system and is due to the partial craze healing that occurs rapidly at this temperature.[3] Finally, this same sample was healed at 30 °C above T_g for 10 min to induce complete coalescence and then poled with T_p = 110 °C. Again, the tsc curve obtained from the fully healed sample

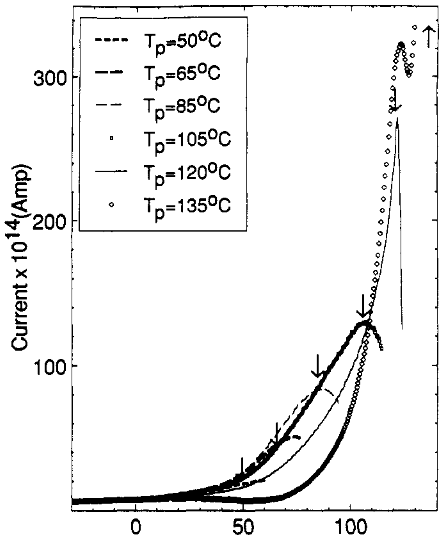

Figure 4. Series of tsc spectra for a crazed sample of PBrS successively polarized at T_p = 50, 65, 85, 105, 120, and 135 °C; the bulk T_g of PBrS is 123 °C. This film was polarized with E = 2000 kV/m and had an area of 20 mm^2.

Table I

	ϵ'_∞(PS)[a]	$\Delta\epsilon$(PS)	ϵ'_∞(PBrS)[a]	$\Delta\epsilon$(PBrS)
ac dielectric	2.52	0.04	3.14	1.25
tsc		0.056		1.4

[a] The absolute value of the dielectric constant on the low-temperature side of T_g (or at infinite frequency) is given here.

reveals that all of the low-temperature relaxations are suppressed, similar to that seen in the inset in Figure 2.

An analogous series of tsc experiments were performed on crazed samples of PBrS; spectra taken with T_p = 50, 65, 85, 105, 120, and 135 °C are shown in Figure 4. Here, too, tsc revealed a pronounced polymer mobility in the craze fibrils, in this case starting at T = 10 ± 10 °C. Moreover, similar to the behavior observed in the crazed PS samples, the strength of the signal was found to increase with increasing T_p, up to T_p = 105 °C. For experiments run above this poling temperature, i.e., where healing effects are pronounced, the magnitude of enhanced low-temperature relaxation was found to be significantly reduced. Following complete healing of the crazes, effected by taking the sample 30 °C above T_g for a 10 min, the subsequent tsc spectrum taken with T_p = 135 °C revealed that all of the low-temperature relaxations were greatly suppressed. Now the only observable peak corresponds to the glass transition at 123 °C, as indicated in Figure 4.

It is evident from Figures 3 and 4 that the larger dipole moment in PBrS produces more than an order of magnitude increase in the absolute intensities of the depolarization current. Independent characterization of the dielectric strength of the glass transition in uncrazed samples of PS and PBrS was performed by using ac dielectric spectroscopy. These values of $\Delta\epsilon$ (shown in Table I) are consistent with those calculated from a peak integration of the tsc data using eq 1; in both cases, $\Delta\epsilon$ in PBrS was found to be ~30 times larger than in PS.

The tsc spectra of the enhanced relaxation observed in crazed samples of PS vis-à-vis PBrS indicate that the relaxation in the craze fibrils is dipolar and not simply a charging phenomena, such as the Maxwell–Wagner (M–W) effect.[2,15] It should be emphasized that while brominating PS has a marked effect on $\Delta\epsilon$, the microstructure and the fibril dimensions of the crazes produced in PS and PBrS were found to be nominally the same. This larger dielectric strength in PBrS was found not only to increase the magnitude of the tsc signal through the glass transition but similarly to increase the tsc signal of the enhanced relaxation. Additionally, at a comparable $T_g - T$, the magnitudes of the enhanced signals in PS and PBrS were found to roughly scale with the magnitude of the glass transitions of the respective materials. Such a scaling would be expected for a dipolar process but would not be the case for interfacial charging effects. The reason for this important conclusion is as follows: the absolute values of the dielectric constants for PS and PBrS (shown in Table I) are about the same, indicating that potential M–W type charging due to the porous nature of the crazed system should be similar in magnitude for PS and PBrS.[16] Moreover, if anything, the relative contribution of M–W charging would be expected to be much more prevalent for the tsc spectra of crazed PS (Figure 3), because there the overall signal is weaker. However, within the experimental uncertainty, no evidence for charging effects was observed.

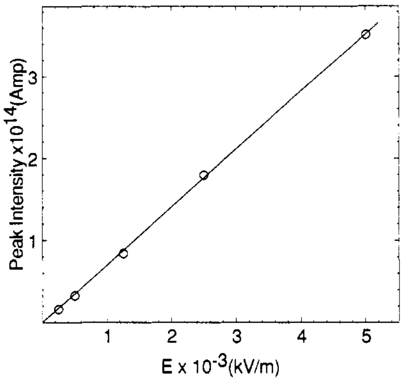

Figure 5. Plot of peak intensity versus E (kV/m) for a crazed PS sample polarized at T_p = 30 °C.

Still another test to determine whether the depolarization current stems from a dipolar process (i.e., due to a dielectric relaxation of polymer chain segments) or from potential charging effects is to perform repetitive runs as a function of polarizing field strength.[1,2] For a dipolar process, the magnitude of the depolarization current should scale linearly with the applied field (E), whereas for a process which is not perfectly efficient (e.g., charge injection or electrode polarization), no such scaling is observed. Indeed in all of the crazed samples examined (both PS and PBrS), a linear dependence was observed; shown in Figure 5 is a typical plot of peak intensity versus E obtained at T_p = 30 °C for a crazed PS sample. These data provide further support for our interpretation that the enhanced relaxation is a dipolar process.

It is also worthwhile to compare our tsc results to the previous indirect observations of an enhanced polymer chain mobility within the craze fibrils. The most compelling of these studies revealed that PS craze fibrils can coalesce at temperatures well below T_g.[3] This coalescence, as deduced from changes in the low-angle electron diffraction patterns of the craze microstructure, produced a marked increase in the magnitude of the mean craze fibril diameter. Yang and Kramer[3] also showed that the coalescence rate increased strongly with increasing temperature above T = 75 °C. Nevertheless, even at room temperature, freshly crazed samples were found to exhibit appreciable fibril coalescence after 10 days. Qualitatively similar results were independently observed in macroscopic samples;[17] in those experiments the fading of interference colors on freshly produced fracture surfaces suggested that craze healing was occurring. It should be noted, however, that measurements of craze healing are only sensitive to the gross (irreversible) changes in the fibril microstructure. That is, for coalescence to occur, the mobility must be pervasive enough to allow polymer (segment) diffusion. The tsc results reported here reveal significant segmental mobility at temperatures well below that for which rapid healing can be measured and also allow the effects of thermally induced healing to be quantitatively investigated.

Finally, while the tsc experiments indicate that the segmental mobility of the polymer chains within the craze fibrils is greatly enhanced relative to the bulk, the precise origin of this mobility is less clear. As discussed above, both the loss of topological constraints on the chains within the fibril[18] and the sizable fraction of the polymer segments which reside in the surface region of the fibril are believed to be responsible. However, which, if either, of these factors is dominant is not known at this time. It may be expected that future studies exploring the dependence of the enhanced mobility on the craze fibril diameter[5] as well as studies on polymers with largely different T_g's (to investigate whether the onset temperature for the enhanced mobility scales with the nominal bulk T_g) will shed insight on this problem.

Conclusions

Thermal stimulated current depolarization was used to investigate dielectric relaxations in crazed and uncrazed films of PS and PBrS. For highly crazed samples of both polymers a significantly enhanced dielectric signal was found at temperatures nearly 100 °C below the bulk T_g. Partial healing of the crazed samples, by heating to temperatures 10–20 °C below T_g, was found to markedly decrease the magnitude of the enhanced low-temperature relaxation. Additionally, for fully healed crazes a complete disappearance of this relaxation was found. The enhanced mobility of the polymer segments within the small (ca. 9-nm diameter) craze fibrils is believed to be due to the close proximity of these chains to a free surface.

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References and Notes

(1) van Turnhout, J. *Polym. J.* **1971**, *2*, 173.
(2) van Turnhout, J. *Thermally Stimulated Discharge of Polymer Electrets*; Elsevier: Amsterdam, 1975.
(3) Yang, A. C.-M.; Kramer, E. J. *J. Polym. Sci., Part B: Polym. Phys.* **1985**, *23*, 1353.
(4) Brown, H. R. *J. Polym. Sci., Part B: Polym. Phys.* **1983**, *21*, 483.
(5) Berger, L. L. *Macromolecules* **1989**, *22*, 3162.
(6) Kramer, E. J.; Berger, L. L. *Adv. Polym. Sci.* **1990**, *91/92*, 1.
(7) Henkee, C. S.; Kramer, E. J. *J. Polym. Sci., Part B: Polym. Phys.* **1984**, *22*, 721.
(8) Passaglia, E. *J. Phys. Chem. Solids* **1987**, *48* (11), 1075.
(9) Kambour, R. P.; Kopp, R. W. *J. Polym. Sci., Part A-2* **1969**, *7*, 183.
(10) Trassaert, P.; Schirrer, R. *J. Mater. Sci.* **1983**, *18*, 3004.
(11) Sauer, B. B.; Walsh, D. J., to be submitted to *Macromolecules*.
(12) Kambour, R. P.; Bendler, J. T. *Macromolecules* **1986**, *19*, 2679.
(13) Lacabanne, C.; Chatain, D.; Monpagens, J. C. *J. Appl. Phys.* **1979**, *50*, 2723.
(14) Wool, R. P.; O'Connor, K. M. *Polym. Eng. Sci.* **1981**, *21*, 1970.
(15) van Beek, L. K. H. *Prog. Dielectr.* **1967**, *7*, 69.
(16) The possible contribution of interfacial charging effects to the measured depolarization signal was estimated by using a Maxwell–Wagner model of ellipsoids of one dielectric (air) immersed in a second dielectric (polymer) (eqs 3.32–3.34 in ref 15). While these calculations show that Maxwell–Wagner effects could largely contribute to the enhanced tsc signal in the crazed systems, such interfacial charging effects cannot explain the differences in the tsc spectra for crazed samples of PS and PBrS.
(17) Kambour, R. P. *J. Polym. Sci.* **1964**, *2*, 4165.
(18) At temperatures well below T_g, the formation of the surfaces of the craze fibrils is known to accompany a significant decrease in the molecular weight of the polymer chains; e.g., for a PS with $M_w \sim M_n = 1\,800\,000$, the number-average molecular weight of the polymer in the fibrils is reduced to $\sim$40 000 (see ref 6).