

Effects of Annealing on Relaxation Behavior and Charge Trapping in Film-Processed Poly(phenylene sulfide)

SHARON XIN LU* and PEGGY CEBE†

Department of Physics and Astronomy, Tufts University, Medford, Massachusetts 02155

SYNOPSIS

The relaxation behavior of poly(phenylene sulfide) (PPS) Ryton™ film has been studied as a function of annealing temperatures, T_a , ranging from 30°C to 140°C. Previously, this type of semicrystalline PPS film was shown to possess a very large fraction of constrained, or rigid, amorphous chains. Here we investigate relaxation of amorphous chains using differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), and thermally stimulated depolarization current (TSDC). DSC studies suggest that annealing causes the as-received PPS film to relax some of its rigid amorphous fraction and increase its crystallinity, for $T_a > T_g$. DMA results show a corresponding increase in the temperature location of the dissipation peak and a decrease in its amplitude when T_a increases above 100°C. Analysis of the TSDC ρ -peak due to injected space charges trapped at the crystal/amorphous interphase provides additional information about amorphous phase relaxation. This peak does not exist in amorphous film, or as-received film, or as-received films annealed at lower T_a . The ρ -peak does exist in cold-crystallized films and as-received films annealed at higher T_a . We suggest that crystallinity is a necessary, but not sufficient, condition for observation of a ρ -peak. In addition to crystallinity, the sufficient conditions for observation of a ρ -peak are existence of (1) a sharp and distinct crystal/amorphous interphase, to provide charge trapping, and, (2) a large fraction of liquid-like amorphous phase, to provide a pathway for charge transport. These conditions are not met in PPS semicrystalline films with very imperfect crystals and large amounts of rigid amorphous phase. In such films, the rigid amorphous phase has, like the crystal phase, a restricted molecular mobility that causes it also to restrict the mobility of space charge. The implications are that film PPS processed with a large amount of rigid amorphous phase chains will have superior barrier properties to the build-up of interfacial space charge. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Poly(*p*-phenylene sulfide) (PPS) is a semicrystalline engineering thermoplastic with excellent properties for use as a matrix in high-temperature composites and electrical insulation. PPS can be processed by many methods, such as compression molding and injection molding and in the form of films, fibers, or composites reinforced with glass fibers. As mo-

lecular structure and relaxation behavior have direct effects on its properties, it is desirable that the initial processing method would have provided the desired structure when it is processed into a final product. Brady¹ first studied the effect of crystallinity on PPS's properties using wide-angle X-ray scattering (WAXS) and differential scanning calorimetry (DSC). Crystal unit cell structure was reported by Tabor et al.² using X-ray scattering of drawn fibers. Later on, extensive research was performed to study PPS's crystallization kinetics, crystal structure, and crystal morphology.³⁻¹⁴ Several earlier reviews^{15,16} and one recent review¹⁷ describe previous research in detail.

One of the interesting properties of PPS discovered by Wunderlich and co-workers is the existence

* Present address: Exxon Chemical Corp., 5200 Bayway Dr., Baytown, TX 77522.

† To whom correspondence should be addressed.

of the rigid amorphous phase (RAP),³ which is that portion of the amorphous phase which does not relax when the temperature is increased above the glass transition temperature (T_g) of the mobile, or liquid-like, amorphous phase during normal DSC scanning. The use of the word *phase* here is not meant to suggest a thermodynamic phase, but rather a region of the material which is subject to different constraints on its mobility. The rigid amorphous phase is suggested to reside near the crystal/amorphous interphase.^{3,18}

The amount of liquid-like amorphous phase, χ_a , has been shown to relate to the heat capacity increment, $C_p(T)$, at the glass transition temperature according to ref. 3:

$$\chi_a = C_p(T)^{sc}/C_p(T)^a|_{T=T_g} \quad (1)$$

where the superscripts "sc" and "a" refer to the heat capacity increments of the semicrystalline sample and the completely amorphous sample, respectively. Then rigid amorphous phase fraction, χ_{ra} , is determined using a three-phase assumption^{3,18,19}:

$$\chi_{ra} = 1 - \chi_a + \chi_c \quad (2)$$

The crystal fraction, χ_c , is determined from the area under melting endotherms or from X-ray diffraction or density measurements. The suggestion that a portion of the amorphous phase in semicrystalline material remains rigid even when heated above T_g is one attempt to describe the structure of a semicrystalline polymer.³ In fact, it is a simplification to treat the material as though it comprised three distinct phases. It is likely that any semicrystalline polymer will exhibit a broad distribution of molecular mobilities within the amorphous phase. Nonetheless, it is very useful to consider the idea of polymer chains of greater or lesser mobility in interpreting the thermal,^{3,18} dielectric,¹⁹ and mechanical properties.

In our laboratory, we investigated the behavior of RAP in PPS using thermal¹⁸ and dielectric measurement.^{19,20} We observed that the RAP formed in PPS relaxes little by little as temperature increases. Since RAP has a restricted molecular mobility, it will influence the ultimate properties that depend on mobility, such as transport, mechanical, and electrical properties. In poly(ether etherketone) polymer, PEEK, Michele and Vittoria found that gas transport properties varied between films containing different amounts of RAP.²¹ The fraction of material impermeable to dichloromethane was equal

to the crystal fraction plus the RAP fraction.²¹ From the standpoint of gas transport, the PEEK crystals and the rigid amorphous fraction behaved similarly.

Here we investigate the properties of PPS initially processed as film and subsequently annealed. We have previously studied the structure of PPS processed commercially as film.¹³ These results showed that there exists a unique orientation of lamellae with respect to the film surface. The crystallographic *a*-axis is preferentially aligned along the normal to the film surface. In addition, the PPS processed as film displayed no glass transition relaxation in normal DSC scanning. This led us to conclude that processed PPS film contains a very large fraction of RAP, nearly 0.63 weight fraction. In the present work, we report the effects of annealing close to the glass transition temperature on the relaxation of film processed PPS. DSC, WAXS, dynamic mechanical analysis (DMA), and thermally stimulated depolarization current (TSDC) are used in this characterization. We find that the rigid amorphous phase acts like the crystal phase in impeding the motion of space charge. When the rigid amorphous phase is relaxed by annealing, space charge mobility is observed. These results have direct implications for the charge transport properties of PPS films used in applications as electrical insulation.

EXPERIMENTAL

The PPS polymer used in this study is Ryton V-1 film, a product from Phillips Petroleum Company, processed by rapid cooling from the melt state. The as-received (AR) polymer is semicrystalline film with a thickness of 75 μm and molecular weight of about 60,000. Some of the AR films were used directly in our study, while the others were annealed in a Mettler FP80 hot stage for 15 min at a certain annealing temperatures (T_a) ranging from 30°C to 140°C, before the experiments. These annealing temperatures were chosen to be well below the onset of melting, as indicated from DSC analysis. For comparison, amorphous Ryton films were also prepared by heating the AR film to 320°C, holding for 2 min to destroy the nucleation seeds, and then quenching the sample into an ice-water bath. Some of these amorphous samples were later cold crystallized at T_a for further study.

The relaxation and melting behavior of AR films were studied using a Perkin-Elmer DSC-4 differential scanning calorimeter. Inside the DSC cell, the AR film was heated from 60°C at 20°C/min to T_a

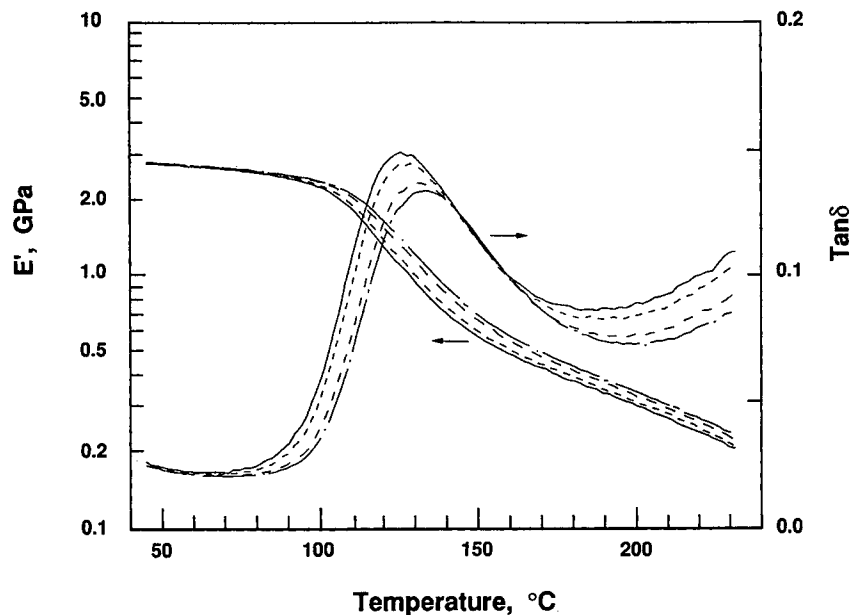


Figure 1 Modulus, E' , and dissipation factor, $\tan \delta$, for as-received (AR) PPS measured at 0.5 Hz (—), 1 Hz (---), 5 Hz (— —), and 10 Hz (- · -).

and held for 15 min. The sample was then cooled at 20°C/min to 30°C. After the temperature was equilibrated, a subsequent rescan was performed at 20°C/min up to the melting temperature. An average sample weight of 8 mg was used in the study, and the temperature and heat flow were calibrated using Indium.

Dynamic mechanical relaxation experiments were carried out on a Seiko DMS 200 system. Both AR and treated AR films were cut into a 5 mm × 10 mm rectangular shape with a cross-sectional area of 0.375 mm². The samples were scanned from 30°C to 220°C at a heating rate of 2°C/min and measured at frequencies of 0.5, 1, 5, and 10 Hz. All the experiments were carried out under nitrogen gas flow of 300 mL/min.

The crystallinity and crystal orientation of the samples were examined using WAXS. A Rigaku RU300 X-ray generator with a diffracted beam graphite monochromator was used to carry out the experiments at room temperature. Copper K_α radiation ($\lambda = 1.54 \text{ \AA}$) was used with a step scan interval of 0.02° and a scanning rate of 2°/min.

The relaxation behavior of PPS films at T_g was studied using the TSDC method. The experiments were performed on our self-designed and self-assembled apparatus.²² All the samples studied were coated with thermally evaporated gold to ensure better contact between the sample and the electrodes. The film was first poled at temperature T_p

for 15 min with a poling voltage of 100 V. Then the sample was quenched to 0°C to freeze in the dipole orientation. After the two electrodes were shorted, the sample was heated at 2°C/min and the current versus temperature data were recorded. Details about our TSDC apparatus were described previously.²²

RESULTS

Dynamic Mechanical Relaxation Study

We have studied the dynamic mechanical relaxation behavior of AR PPS, and AR annealed at temperatures of 30°C, 60°C, 100°C, 120°C, and 138°C. DMA results from the unannealed AR film are shown in Figure 1, as a function of temperature from 40°C to 220°C. Various measurement frequencies are shown by the dotted and dashed curves. Dynamic modulus E' is shown on the left vertical axis, while the dissipation factor, $\tan \delta (= E'/E'')$ is shown on the right vertical axis. In the glassy region from 40°C to 100°C, E' is quite flat with an E' of 1.8 GPa. A drop occurs between 105°C and 160°C, indicating a softening of the material at T_g . After that, E' drops steadily as temperature increases up to 220°C, at which temperature the experiment was stopped. In the dissipation factor, a relaxation peak is observed with a peak maximum temperature (PMT) at 120°C

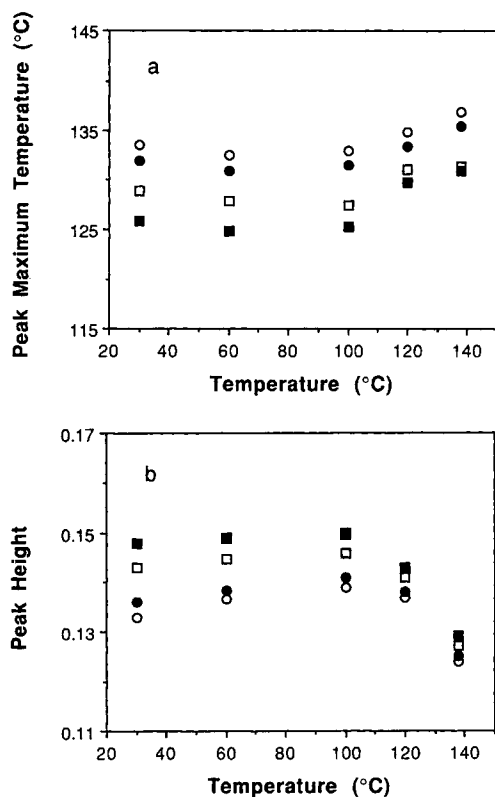


Figure 2 Dissipation factor parameters: (a) Peak maximum temperature, and (b) peak height, for PPS films versus annealing temperatures. Samples were tested at frequencies of 0.5 Hz (■), 1 Hz (□), 5 Hz (●), and 10 Hz (○).

and a peak height (PH) of 0.15 for a frequency of 1 Hz. The peak has an asymmetric shape and starts an upturn after 180°C. A similar upturn in the high-temperature region is also observed dielectrically from our previous study.¹⁹ The reason may be due to the premelting of the imperfect crystals formed during fast processing from the melt.

PMT and PH of $\tan \delta$ represent characteristics of the molecular chain relaxation. These parameters are changed by the annealing treatments performed on the AR film. In Figure 2(a, b), PMT and PH are plotted as a function of annealing treatment temperature for different frequencies. Both PMT and PH are nearly flat until T_a exceeds 100°C; then PMT starts to increase with T_a , while PH decreases. This observation suggests that annealing above T_g pushes the relaxation to a higher temperature and reduces the amount of chain movement, which indicates an overall increase in the chain rigidity. For the same material, PMT increases while PH decreases with increasing frequency. This is consistent

with our intuition that an alternating force at a high frequency activates less polymer chain movement and requires a higher temperature for chains to respond. Our DSC and dielectric relaxation studies of melt and cold-crystallized PPS have shown that annealing at a higher temperature relaxes polymer chains and shifts the relaxation peak to a lower temperature.^{6-8,14,19} This somewhat unusual behavior of the film processed PPS must relate to the polymer's thermal history, which plays an important part in determining how the relaxation is affected by later treatment.

Differential Scanning Calorimetric Study

The relative phase fractions of liquidlike amorphous and rigid amorphous chains in PPS can be deduced from thermal analysis^{3,18,19} according to eqs. (1) and (2). As we have shown in our previous DSC study,¹³ the AR PPS film has unique thermal relaxation properties. This material shows no discernible heat capacity increment at the glass transition temperature in DSC scanning, resulting in a large fraction (almost 40%) of rigid amorphous phase.

DSC experiments were performed on both AR PPS and AR PPS annealed at different T_a to study relaxation and melting behavior. Figure 3 shows a DSC scan of the AR films (curve a), AR film treated at 120°C (curve b), and quenched amorphous PPS for comparison (curve c). A very large difference is observed at T_g between curves a, b, and c, which reflects the fact that AR samples contain a large

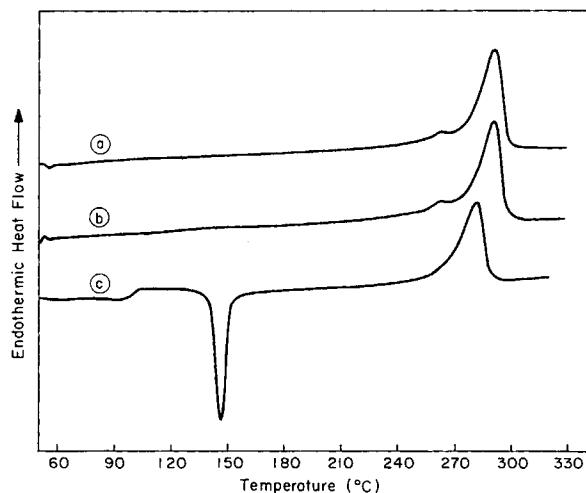


Figure 3 DSC thermogram of PPS films: (a) AR film, (b) AR film annealed at 120°C, and (c) quenched amorphous PPS.

amount of RAP. Little change is observed between curves a and b from ($T_a + 10^\circ\text{C}$) up to the melting temperature. Thus we will plot only the low-temperature part in an expanded scale.

A composite plot of the low-temperature range DSC thermographs of annealed AR films is presented in Figure 4. Here the endothermic heat flow is plotted as a function of temperature during the scan. The treatment temperatures are indicated both by the bars on the curves and the labeled temperatures. The intersections between the dashed lines and the solid curves show the starting temperatures of the glass transition relaxation. Several small endothermic peaks are indicated by the arrows. For the AR sample, we only observe a very shallow exothermic peak just above 100°C . No T_g is found for this material, as we reported previously.¹³ For the sample annealed at 80°C , which is below the T_g of amorphous PPS, we observe a very small step starting at around 95°C , followed by a very shallow exothermic peak around 110°C . This indicates that annealing at 80°C can somewhat relax the material, in the manner of physical aging. However, no crystals can form at this low temperature. As T_a increases to 100°C and above, a small step and a small peak develop, as indicated by the arrows in Figure 4. The intersections between the dashed lines and the solid curves indicate the start of a heat capacity increase. This point stays at almost a constant temperature as the annealing temperature increases from 100°C to 140°C . The heat capacity step comes from the glass transition relaxation and does not change significantly with T_a . It is interesting to note that this heat capacity step does not appear in AR film, from which we concluded that AR contains a very large amount of RAP.¹³ Existence of the heat capacity step in films annealed from a parent AR film suggests that in these annealed films there is some relaxation of the amorphous phase that was originally rigid in the AR parent film.

While the heat capacity increase occurs at the same temperature location regardless of T_a , the small endothermic peak, indicated by the arrows, shifts as T_a increases. As T_a increases, the endothermic peak increases to about ($T_a + 10^\circ\text{C}$). In many polymers either cold crystallized from the glassy state or melt crystallized from the melt state, there usually exists such an endothermic melting peak several degrees above T_a in addition to the dominant melting peak appearing at higher temperature.⁶⁻⁸ The origin of the low-temperature peak has been studied extensively^{7,8} and is generally considered due to the melting of the crystal lamellae

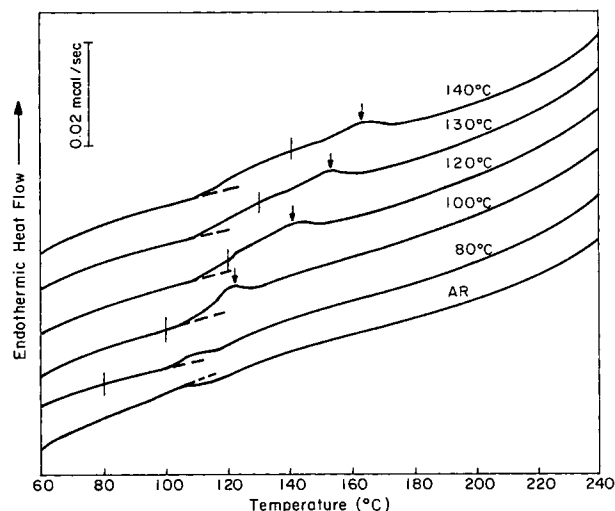


Figure 4 Expanded view of the lower-temperature regime of DSC thermograms for PPS AR film, and AR films annealed at the temperatures represented by both the labeled temperatures and the vertical markers. The arrow marks the position of the observed small endothermic peak.

formed at T_a . Thus, the results indicate that AR PPS has the ability to crystallize when the annealing temperature is above T_g . To summarize, the DSC study shows that AR PPS film is able to relax some of its RAP fraction and recrystallize when annealed at a temperature T_a , above T_g . To confirm this idea, we performed a TSDC study on PPS since this technique is very sensitive to amorphous phase relaxation.

Thermally Stimulated Depolarization Current Study

TSDC has been used quite widely in studying the relaxation behavior of amorphous and semicrystalline polymers and their blends.²³⁻³⁶ This technique probes the depolarization current of the oriented dipoles aligned under the electric field and frozen by the quenching process. It provides detailed information about relaxation of the amorphous phase. In the TSDC experiments, the films first need to be poled at T_p . We observe that poling the sample at T_p also anneals the sample. Since no difference was found in our DSC and WAXS study on samples annealed with or without the electric field, we assume that the electric field has no effect on the crystal structure of the samples. The electric field merely orients the dipoles of the amorphous phase. Therefore, the AR films were used directly in our TSDC

study and the samples were annealed as well as poled at T_p .

Figure 5 presents a composite plot of the TSDC spectra of AR PPS films poled at different temperatures (82°C, 94°C, 105°C, 116°C, and 128°C). The currents have been offset by 0.75 pA for clarity. At 0°C, all currents were zero. The arrows indicate the temperatures at which the samples are annealed as well as poled. When the sample is annealed and poled at 82°C, a current peak maximum temperature (PMT) at 95°C is observed. The peak is quite broad with a current peak height (PH) of 0.6 pA. As T_p increases to 94°C, a much stronger depolarization current shows up with a PH of 2.2 pA and PMT of 98°C. In both cases, the observed PMTs are higher than the poling temperatures. When the sample is poled at 105°C, the PH reduces to 1.6 pA and the PMT increases to 102°C. This peak also shows less symmetry compared with the previous two peaks, and the peak full width at half maximum (FWHM) covers a much broader temperature range. When the sample is poled at 116°C, we observe two peaks overlapping with each other. One looks as though it has been reduced from the 105°C poled peak, with a PMT around 105°C and a PH around 0.85 pA. The second is merged with the previous peak and has an approximate PMT at about 120°C and PH of 0.8 pA. Two current peaks appear again when the sample is poled at 128°C. This time the first peak current is further reduced to 0.4 pA with the PMT about the same as the previous one. The second peak increases in both height and maximum position and is hidden under a steeply rising current. This steeply rising current is observed for all the other samples. The origin of this peak is considered as a complex TSDC phenomenon and has been attributed to the increased conduction of the sample at high temperature.^{37,38}

When a polymer is poled at T_p , the electric field will orient those dipoles which are able to align themselves along the field. Therefore, as long as there exist amorphous dipoles that can be activated at a higher temperature, the higher the poling temperature, the more the dipoles will be activated and the stronger the depolarization current will appear. At the same time, as we have mentioned earlier, the PPS sample is also annealed when it is poled inside the TSDC cell. Thus both the annealing effect and the poling temperature effect need to be considered when we interpret the data.

When the sample is poled at 82°C, which is about 10°C below the amorphous PPS T_g , not much amorphous phase is able to orient along the electric field

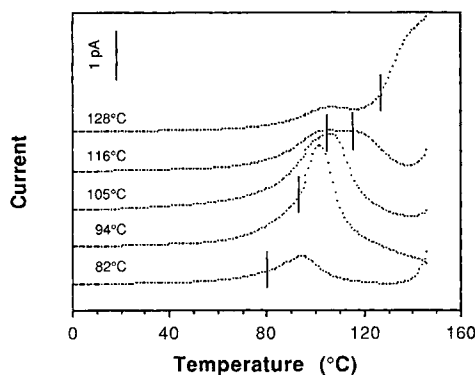


Figure 5 TSDC current versus measurement temperature for PPS AR films poled at 82°C, 94°C, 105°C, 116°C, or 128°C. The poling temperature for each curve is also indicated by the vertical markers.

direction. This sample shows a broad and small relaxation current peak with PMT quite far away from the T_p . As T_p increases to 94°C, more amorphous phase is able to be poled, and the TSDC spectrum shows about four times stronger relaxation peak height. However, PMT is still higher than the T_p , which indicates that not all the available dipoles from the amorphous phase have been activated at this poling temperature. When the poling temperature increases to 105°C, T_p is found to be slightly higher than the PMT. At the same time, the PH is reduced and the peak FWHM is broader. These observations suggest that the annealing increases the chain rigidity and the poling process is able to activate more dipoles.

When T_p further increases to 116°C and 128°C, two peaks are observed. We consider the first peak to be due to the dipole relaxation as its PMT is around 105°C and does not change much with T_p . It is observed that the PH, as well the area underneath the peak (PA), decreases with increasing T_p when the sample is poled above 105°C. As PA is directly proportional to the number of dipoles in the amorphous phase, the amount of amorphous phase may have decreased through the formation of crystals, as we have seen from DSC. At the same time, we have to keep in mind that the formation of the crystals may broaden the relaxation time distribution of the amorphous phase,^{13,19} which is suggested by the smaller yet broader peak.

From the TSDC spectra, we observe the formation of a second peak when the sample is poled at 116°C and 128°C. The origin of this peak comes from the release of the charges formed at the crystal/amorphous interphase, the so-called ρ -peak. This

peak has been observed in other semicrystalline polymers.^{26,36} The reason it was not observed during the low-temperature poling may be the extremely rough and ill-defined interphase between the amorphous phase and crystalline phase. Rough interphases are likely to be formed during the fast cooling process when the PPS film was originally produced and become less rough after annealing at higher temperature. To confirm our idea, the following TSDC experiments have been performed on the quenched amorphous and cold-crystallized PPS films.

A TSDC experiment was performed on the quenched amorphous PPS film, and the result is shown in Figure 6. The film sample is evaporated with Au and poled at 92°C. A strong relaxation peak occurs at 82°C with a PH of 7 pA. The shape of the peak is quite asymmetric and shows common features which have been reported for amorphous polymers.³⁹ The peak is the result of dipole relaxation. The lower T_g observed here compared to that from DSC is due to the lower heating rate.^{26,36} During the testing, the amorphous film begins to crystallize. As no crystals were originally in the polymer, no ρ -peak is observed at the higher temperature. The only feature seen at high temperature is the high-rising current.

We also studied PPS samples cold crystallized at $T_c = 120^\circ\text{C}$ and 200°C , where these samples were annealed at T_c after heating from the quenched amorphous state. The same experimental conditions were adopted except that the samples were poled at 120°C since higher T_g values are expected for semicrystalline polymers. We present the results for $T_c = 200^\circ\text{C}$ and 120°C in Figures 7(a) and 7(b), respectively. Two peaks are observed besides the steeply rising current (not shown). For T_c

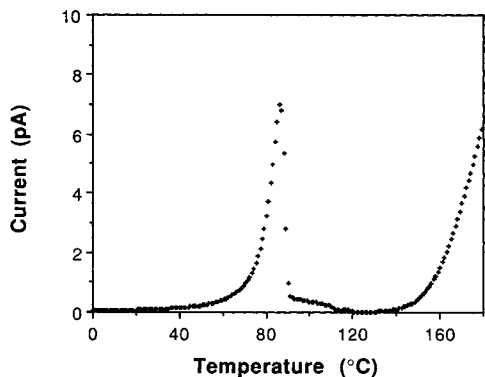


Figure 6 TSDC current versus temperature for quenched amorphous PPS poled at 92°C .

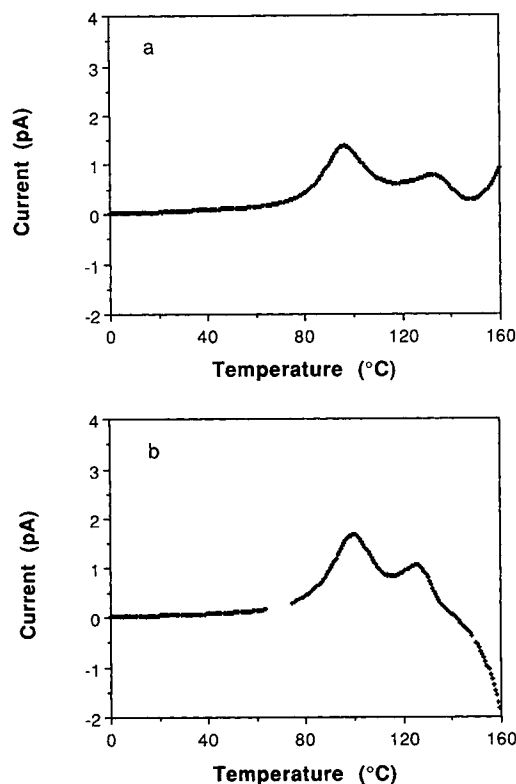


Figure 7 TSDC current versus temperature for PPS cold crystallized at (a) $T_c = 200^\circ\text{C}$, and (b) $T_c = 120^\circ\text{C}$.

$= 200^\circ\text{C}$, the first peak appears at 95°C , while for $T_c = 120^\circ\text{C}$, the peak appears at 100°C . Our previous study^{6,13,19-21} has shown that amorphous material is more constrained by crystals when the sample is crystallized at lower T_c because of the lower chain mobility. Thus, the relaxation peak shifts slightly to a higher temperature when T_c is lower. Both low-temperature peaks have a broad peak shape which is similar to those we observed in the AR samples. The difference in the peak shapes compared with that of the amorphous sample is due to the broad distribution of dipole relaxation times and the effects of the rigid amorphous phase. A distinct second peak, the ρ -peak, shows up in both samples with a PMT at about 134°C for $T_c = 200^\circ\text{C}$, and 125°C for $T_c = 120^\circ\text{C}$. The sample crystallized at lower T_c possesses a larger amount of RAP and a coarse interphase because of the higher chain rigidity.^{6,13,19-21} The less perfect the interphase, the less strong will be the interfacial polarization. Therefore, charges will be released more easily at a higher temperature, resulting in a shift in the second peak to a lower temperature for lower T_c .

DISCUSSION

Special Relaxation Behavior of AR PPS Film

When PPS experiences isothermal melt crystallization, as Chung and Cebe^{7,8,14} have found, constraints on crystal growth become severe after spherulitic crystal impingement and only secondary crystals can form in the interlamellar region. The existence of the crystals previously formed almost makes it impossible to form new crystals at a temperature below the annealing temperature. In our case, AR PPS films are processed by general film processing methods, in which the material is cooled quickly from the molten state. During this fast-cooling process, the films experience nonisothermal crystallization, in which the number density of nucleation sites increases and crystal growth rate decreases as temperature drops. This process puts severe constraints on the amorphous chains such that almost all the uncrystallizable material is considered to be rigid amorphous phase. This amorphous material does not relax when subsequently heated to T_g .¹³

The crystals formed during the rapid film processing show very small spherulites and poorly defined interphases due to the short time given for the crystals to grow.¹³ Therefore, quite different relaxation behavior is observed in this material compared to that seen in the melt-crystallized PPS. Although the amorphous phase does not show any relaxation at T_g , it is able to crystallize at a higher temperature. The very shallow exothermic peaks we observed for AR film and the AR film annealed at $T_a = 80^\circ\text{C}$ (Fig. 4) come from the crystallization of these rigid amorphous materials. The quick crystallization process results in the formation of short-range order in the amorphous phase. When the temperature is increased above T_g , the amorphous material gains mobility and crystallizes to form some small imperfect crystals. Since the primary crystal structure has already developed during the cooling process, the constraints on this amorphous phase are very high. Only a very small amount of amorphous material was able to form crystallites. Some rigid amorphous material is also able to relax, as shown from DSC. In addition, previously formed imperfect crystals now have a chance to form better crystals and better crystal/amorphous interphases.

The study of mechanical properties of PPS was first reported as a function of crystallinity by Brady.¹ Brady observed that an increase in polymer crystallinity was accompanied by a decrease in tensile

strength. He suggested that this behavior came from the modest molecular weight effect and slightly crosslinked nature of the PPS. In this work we have used DMA to investigate the effect of annealing on the mechanical relaxation properties of AR films. No significant difference is found in the modulus because of the small amount of crystallites formed on annealing. However, an increase in the relaxation PMT and a decrease in the PH are observed as a function of increasing treatment temperature. This suggests that a smaller amount of amorphous phase chains may experience more constraints on their motion, leading to higher T_g . This also implies that if we anneal a fast-cooled polymer material above its T_g , a small amount of crystals will form, which will both increase the relaxation temperature and improve the mechanical properties. As a matter of fact, commercial processing of PET bottles is carried out in a similar way. To obtain the clarity of the amorphous material and the rigidity of the semicrystalline material, PET is first fast cooled from the melt and then reannealed above its T_g . Therefore, small imperfect crystals will form which do not scatter too much light yet provide excellent rigidity to handle the weight of the liquid.

TSDC ρ -Peak and Interphase Roughness

TSDC has been used to study many semicrystalline polymers.^{26,36} A common feature observed in TSDC spectra is the interphase relaxation peak seen right above the polymer glass transition peak. It has been proposed that this ρ -peak is due to the release of the injected space charges trapped at the crystal/amorphous interphase during poling. In this work we hope to describe the unique feature of the ρ -peak and its possible correlation with the amorphous phase mobility, which has been suggested to be an important factor in determining the relaxation of liquid-like amorphous phase.¹³

From our TSDC study, we gain the following observations. First, no ρ -peak appears in the amorphous sample since no crystals exist during poling. Therefore, there is no crystal/amorphous interphase. Sauer et al.²⁶ observed a peak after the α -relaxation peak when they studied PEKK, and they attributed it to the spontaneous reorientation of amorphous phase into crystallites. Second, a ρ -peak appears in the cold-crystallized PPS samples. Third, the ρ -peak does not show up in the AR sample and AR samples annealed at lower temperatures. However, when the AR samples were annealed at a higher temperature, the ρ -peak appears again. From these observations,

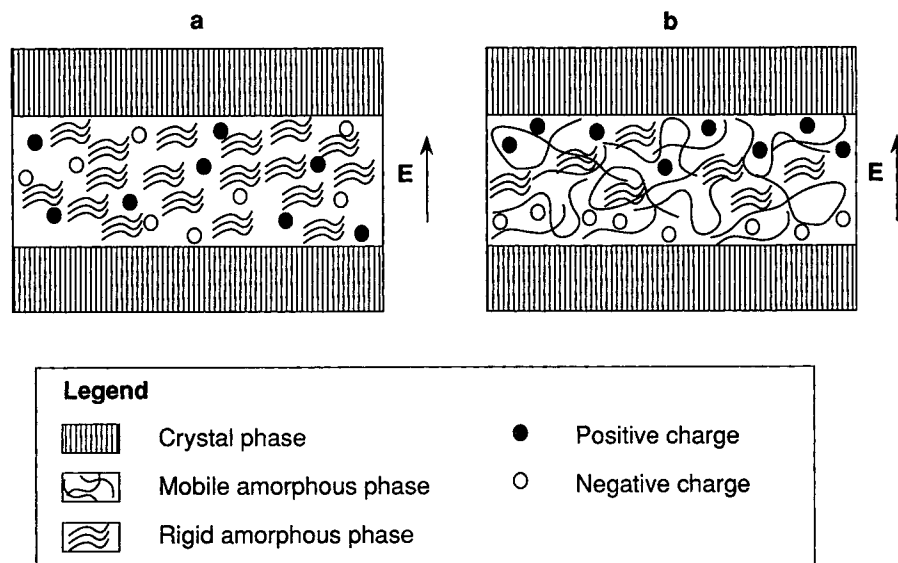


Figure 8 Sketch of example crystal/amorphous phase structures and trapped charges during poling by an electric field, E . (a) The entire amorphous fraction consists of rigid amorphous phase. Charge motion through the rigid amorphous phase is impeded. No ρ -peak is observed. (b) A portion of the amorphous phase is mobile at the poling temperature. Charges are able to move through the amorphous phase and become trapped at the crystal/amorphous interphase. Upon heating, a ρ -peak is observed.

we conclude that the ρ -peak is likely to appear in PPS samples in which the crystals and the amorphous phase have different mobilities. This occurs in samples with a large amount of mobile amorphous phase and a small amount of rigid amorphous phase. Conditions favoring the observation of a ρ -peak are those such as high-temperature isothermal annealing.

The correlation between the glass transition behavior and the crystal/amorphous interphase of PPS has been reported by our group.¹³ We suggest that the reason that the original AR film is unable to relax at T_g during DSC scanning may be that the highly imperfect crystals have constrained the amorphous phase. Since the ρ -peak has been considered to be the result of the released charge at the interphase, this peak provides us with information about the interphase and about the relative mobilities of the crystal and amorphous phases. For AR film and AR films annealed at the lower temperatures, little amorphous phase relaxation at T_g is observed, indicating restricted mobility. Charge transport through the rigid amorphous phase should be impeded. Confirming this idea, no ρ -peak is observed in these samples from TSDC, indicating that few charges, if any, build up at the interphase.

On the other hand, for AR films annealed at the higher temperatures and for cold-crystallized PPS,

DSC thermographs show observable heat capacity steps at T_g leaving the signature of the long-range cooperative motion. There is a larger fraction of mobile amorphous phase and smaller fraction of RAP in these samples. Mobility through the amorphous phase should be improved, and indeed TSDC scans show strong ρ -peaks because of the release of the interphase charges. These observations support our idea that there is a strong correlation between the amorphous phase mobility and the ρ -peak.

Figure 8 depicts two extreme cases in which charges are (a) barely able and (b) very able to move to the crystal/amorphous interphase during poling. In Figure 8(a), all the amorphous phase is RAP, which, like the crystals, has reduced mobility. Under an applied field, charges are scarcely able to move to the interphase. This sample will show no ρ -peak, in spite of a reasonably large degree of crystallinity. This is the case seen in Figure 5, for $T_p = 82^\circ\text{C}$ and 94°C . In Figure 8(b), there is a smaller amount of RAP and a correspondingly larger amount of mobile amorphous chains. The mobile amorphous chains are considered to have formed from the relaxation of the RAP during poling when the poling temperature is above T_g . Charges move easily to the interphase, where they become trapped during poling. They are released at higher temperature, creating the ρ -peak. Such is the case in Figure 5, for T_p

= 116°C and 128°C, and also in Figure 7 for both cold-crystallized samples.

Furthermore, the PMT of the ρ -peak also provides more information regarding the interphase. PPS cold crystallized at a higher T_a contains less RAP, has more mobile amorphous phase, and therefore has well-defined crystal/amorphous interphases. Differences in mobility between the crystals and the amorphous phase cause space charge to move through the amorphous phase but become stranded at the crystal/amorphous interphase. The better interphase (i.e., one which is sharper and smoother) will hold charges at the interphase more strongly and release them at a higher temperature. Therefore, we observed that the PMT of the ρ -peak appears at a higher temperature when T_a is higher. For AR samples, no ρ -peak occurs because of the ill-defined interphase and the more nearly similar crystal and amorphous phase mobility formed during the rapid cooling process. When AR samples are annealed at temperatures above T_g , the interphase gets more regular and the ρ -peak appears. As T_a increases, the ρ -peak shifts to a higher temperature.

CONCLUSIONS

Film processed Ryton™ PPS films have been investigated using DSC, DMA, and TSDC. Unique relaxation properties are observed in these films. A small amount of crystals is able to form when the temperature is above T_g , while at the same time, some formerly rigid amorphous phase is able to relax. Annealing pushes the dynamic mechanical relaxation $\tan \delta$ to a higher temperature and reduces the amount of mobile chains.

Our TSDC results suggest a correlation between the interfacial relaxation peak, ρ -peak, and molecular mobility and the crystal/amorphous interphase. Crystallinity is a necessary, but not sufficient, condition for the observation of a ρ -peak. To observe a ρ -peak, charges must be separated during poling, they must become trapped at the crystal/amorphous interphase, and they must become mobile during thermally stimulated depolarization. These properties of trapped charges relate to the mobility of the amorphous chains themselves, which contribute to charge mobility and to the existence and perfection of the crystal/amorphous interphase. The ρ -peak exists in cold-crystallized films and as-received films annealed at higher T_a , both of which have an increased fraction of mobile amorphous phase and better crystal/amorphous interphases. No ρ -peak is

seen in amorphous samples (having no crystal/amorphous interphase), or as-received film, or as-received films annealed at lower T_a (having too small a mobile amorphous phase fraction and very imperfect interphases). In the semicrystalline films showing no ρ -peak, the rigid amorphous phase has, like the crystal phase, a restricted molecular mobility that causes it also to restrict the mobility of space charge. The implications are that film PPS processed with a large amount of rigid amorphous phase chains will have superior barrier properties to the build-up of interfacial space charge.

This research was supported by the Petroleum Research Fund of the American Chemical Society. The authors thank Phillips Petroleum Company for providing the PPS Ryton™ samples, and Professor C. Lacabanne for helpful discussions about the TSDC technique.

REFERENCES

1. D. J. Brady, *J. Appl. Polym. Sci.*, **20**, 2541 (1976).
2. B. J. Tabor, E. P. Magre, and J. Boon, *Eur. Polym. J.*, **7**, 1127 (1971).
3. S. Z. D. Cheng, Z. Q. Wu, and B. Wunderlich, *Macromol.*, **20**, 2802 (1987).
4. L. C. Lopez and G. L. Wilkes, *Polymer*, **29**, 106 (1988).
5. L. C. Lopez, G. L. Wilkes, and J. F. Geibel, *Polymer*, **30**, 147 (1989).
6. J. S. Chung and P. Cebe, *J. Polym. Sci., Polym. Phys. Ed.*, **30**, 163 (1992).
7. J. S. Chung and P. Cebe, *Polymer*, **33**, 2312 (1992).
8. J. S. Chung and P. Cebe, *Polymer*, **33**, 2325 (1992).
9. A. J. Lovinger, F. J. Padden, and D. D. Davis, *Polymer*, **29**, 229 (1984).
10. A. J. Lovinger, D. D. Davis, and F. J. Padden, *Polymer*, **26**, 1595 (1985).
11. J. D. Menczel and G. L. Collins, *Polym. Eng. Sci.*, **32**, 1264 (1992).
12. G. L. Collins and J. D. Menczel, *Polym. Eng. Sci.*, **32**, 1270 (1992).
13. P. P. Huo, J. S. Chung, and P. Cebe, *Polym. Composites*, **13**, 346 (1992).
14. P. Cebe and J. S. Chung, *Polym. Composites*, **11**, 265 (1990).
15. L. C. Lopez and G. L. Wilkes, *J. Macromol. Sci., Rev. Macromol. Chem. Phys.*, **C29**, 83 (1989).
16. J. F. Geibel and R. W. Campbell, "Poly(phenylene sulfide)s," in *Comprehensive Polymer Science*, Vol. 5, G. C. Eastmond, A. Ledwith, S. Russo, P. Sigwalt, Eds., Pergamon Press, Oxford, UK, 1989.
17. P. Cebe, *Polymers and Polymer Composites*, **3**, 239 (1995).
18. P. P. Huo and P. Cebe, *Colloid Polym. Sci.*, **270**, 840 (1992).

19. P. P. Huo and P. Cebe, *J. Polym. Sci., Polym. Phys. Ed.*, **30**, 239 (1992).
20. P. P. Huo and P. Cebe, *Macromol.*, **25**, 902 (1992).
21. A. Michele and V. Vittoria, *Polym. Comm.*, **32**, 232 (1991).
22. S. X. Lu, Ph.D. thesis, Massachusetts Institute of Technology, 1995.
23. B. B. Sauer and P. Avakian, *Polymer*, **33**, 5128 (1992).
24. J. J. del Val, A. Alegria, J. Colmenero, and J. M. Barandiaran, *Polymer*, **27**, 1771 (1986).
25. A. Bernes, D. Chatain, and C. Lacabanne, *Polymer*, **33**, 4682 (1992).
26. B. B. Sauer, P. Avakian, H. W. Starkweather, and B. S. Hsiao, *Macromol.*, **23**, 5119 (1990).
27. W. Brostow, B. K. Kaushik, S. B. Mall, and I. M. Talwar, *Polymer*, **33**, 4687 (1992).
28. B. B. Sauer and B. Hsiao, *J. of Polym. Sci.: Polym. Phys.*, **31**, 917 (1993).
29. B. B. Sauer, P. Avakian, and G. M. Cohen, *Polymer*, **33**, 2666 (1992).
30. B. B. Sauer, R. Beckerbauer, and L. Wang, *J. of Polym. Sci.: Polym. Phys.*, **31**, 1861 (1992).
31. T. Tanaka, S. Hayashi, S. Hirabayashi, and K. Shibayama, *J. Appl. Phys.*, **49**, 2493 (1978).
32. A. Chafai, D. Chatain, J. Dugas, C. Lacabanne, and J. Vayssie, *J. Macromol. Sci., Phys.*, **B22**(5&6), 633 (1983).
33. I. M. Talwar, H. C. Sinha, and A. P. Srivastava, *Thin Solid Films*, **113**, 251 (1984).
34. J. P. Dechesne, J. Vanderschueren, and F. Jaminet, *J. Pharm. Belg.*, **39**, 341 (1984).
35. M. Mourgues-Martin, A. Bernes, C. Lacabanne, O. Nouvel, and G. Seytre, *IEEE Trans. Elec. Insulation*, **27**, 795 (1992).
36. S. X. Lu, P. Cebe, and M. Capel, *J. Appl. Polym. Sci.*, **57**, 1359 (1995).
37. J. van Turnhout, *Thermally Stimulated Discharge of Polymer Electrets*, Elsevier, Amsterdam, 1975.
38. J. van Turnhout, *Polym. J.*, **2**, 173 (1971).
39. Braunlich, P., *Thermally Stimulated Relaxation in Solids*, Springer-Verlag, Berlin, 1979.

Received August 21, 1995

Accepted December 27, 1995