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DSC, FT-IR, and Energy Dispersive X-ray Diffraction Applied to the Study of the Glass Transition of Poly(*p*-phenylene sulfide)

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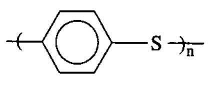
ABSTRACT: The glass transition of poly(phenylene sulfide) (PPS) has been examined by differential scanning calorimetry (DSC), Fourier transform infrared spectroscopy (FT-IR), and energy dispersive X-ray diffraction (EDXD) techniques. All of them evidenced the α transition of the polymer, and the results obtained with the different techniques were found to be consistent when the onset point of the DSC trace is taken. The data were analyzed as a function of the rate of heating, and the activation energy of the phenomenon was calculated by assaying the theoretical model of Barton to fit the experimental data.

Introduction

It is well-known that at $T = T_g$ the physical and mechanical properties of polymeric materials change[1] more or less abruptly depending on the amorphous or semicrystalline nature of the polymer.

The glassy state of matter has recently received great attention by one of the most important and popular scientific journals, *Science* . It has in fact dedicated in 1995 a large space in one of its volumes to a number of review articles[2−6] on the subject, emphasising the different aspects involved. In 1996 Sokolov,[7] in the same journal, has again brought to the attention of the scientific community the importance of understanding the glass transition phenomenon. Although the information on the argument already present in the literature is very copious, its complexity has still left open the field to investigations which make use of more and even more sophisticated experimental and theoretical techniques. The glassy state is indeed a nonequilibrium one and the glass transition temperature appears not to be a thermodynamic parameter, being kinetically affected. Internal stresses are caused to the material by the very rapid cooling necessary for achieving the glass when semicrystalline materials are considered, and in the case of polymers, mechanical tension may originate on the chains which are frozen in their high energy disordered conformational states, typical of the amorphous materials. The tendency to relax toward lower free energy conditions will then be intrinsic to any glassy material. On the other hand the structural and physico-chemical nature of each of them will fundamentally influence their behavior. Particularly relevant, for their technological implications, are the polymeric materials in which the crystallinity is associated with the amorphous state.

For a variety of reasons we have been attracted by PPS, which is a semicrystalline polymer with a backbone of aromatic rings intercalated by S atoms.



Its characteristics of being fusible, soluble, melt processible, chemically and thermally stable, mechanically suitable for high-performance applications, and electrically peculiar for the insulator to semiconductor variation of its properties upon doping by strong oxidizing agents make it one of the most attractive polymers of the day. Therefore the scientific literature has already elucidated its physicochemical properties starting from the early work of Brady[7] in which the differences were reported in the IR spectrum between the amorphous and crystalline state of the polymer. Crystal structure and morphology,[8−12] crystallization kinetics,[13−16] thermal behavior,[17−21] degradation, aging, and curing were also investigated[22] as well as dielectric relaxation[23] behavior, solid state ^{13}C NMR characteristics,[24,25] and electrical properties.[21,26−28] Our interest in PPS was mainly originated by the possibility of investigating quite accurately the structure/electrical properties correlation, which is seriously inhibited in other nonsoluble polymers. However not only did the electrical behavior of such a material appear to be worthy of consideration but also more usual properties related to the chain flexibility found in such a polymer make it a good candidate for a deeper insight.

Therefore part of our efforts was dedicated to the investigation of the IR spectroscopic changes undergone by this polymer upon thermal treatments, particularly near T_g.[29] Those preliminary results have convinced us to deepen our investigation, making also use of the well-established DSC technique and of the more recent EDXD one, in order to acquire both energy flow and structural data.

EDXD allows one indeed to collect spectra in a much shorter time than the usual methods based on angular scanning,[30−32] thus giving structural information on the course of the heating ramp of a thermal investigation. In EDXD, a continuous polychromatic X-ray light is used and the diffracted beam is energy resolved by a solid state detector set at a suitable scattering angle. The modulus of the scattering vector **q**, depending both on the scattering angle 2θ and on the energy **E** of the photons, can be expressed as

$$\mathbf{q}(E,\theta) = K\mathbf{E}\sin\theta \qquad (1)$$

where $K = 1.014$ if the **q** dimensions are in Å^{-1} and the **E** ones are in keV.

The more traditional ***angular dispersive*** (ADXD) technique executes an angular scanning (2θ) of the reciprocal space diffraction pattern originated by the interaction of the X-ray monochromatic radiation with the matter, the photon energy being fixed.

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If, on the contrary, a polychromatic X-ray light (called "white light" by analogy with the visible radiation) is used, with the θ angle being fixed, the method is named ***energy dispersive*** X-ray diffraction (EDXD). It has some advantages with respect to ADXD and three of them are important in studying kinetic of phase transitions. These are as follows: (a) the reduced acquisition time due to the higher integral intensity of the incident beam, particularly useful in the case of very fast transitions; (b) the static nature of the diffractometer, which has no moving parts while measuring, which makes simpler the experiment as shown later; (c) the fact that the diffracted spectrum is not affected by the intensity fluctuations of the primary beam, the different energies diffracted photons being collected in "parallel". When fluctuation occurs, if it is short enough with respect to the total acquisition period, it has the same effect over all of the energy spectrum, thus leaving unaltered its profile.

The typical energy resolution provided by the solid state detectors (a few hundred electronvolts in the hard X-ray range) is on the other hand sufficient for structural studies.

EDXD allows one to collect a significant portion of the diffracted spectrum simultaneously, thus allowing the real time study of the structure modifications; depending on the time resolution, in situ chemical or physical transformations, phase transitions, reaction kinetics, and transient phenomena may be investigated. The bremsstrahlung radiation produced by conventional X-ray tubes can moreover be used when the process under investigation is not too fast and a high temporal resolution is not required. The isotherm crystallization of PEO[33,34] was in fact studied by EDXD and more recently the kinetics of the solid-state phase transformation of form β to γ of sulfanilamide.[35]

It has to be pointed out that DSC, which is the most common experimental method used to obtain information on the thermal properties of polymeric materials, is not able to detect effects occurring at a very low heating rate as the IR and the X-ray diffraction technique do, but neither gives information on what is going on at the structural level. For this reason we have carried out a quite accurate investigation on the subtle glass transition phenomenon, which is not yet very deeply understood, shown by the PPS polymer, whose limited chain flexibility does not allow one to easily induce a very pronounced amorphous state but does allow it by a definite control of the thermal history.

The activation energy E of the glass transition process may be calculated by means of the equation proposed by J. M. Barton[36]

$$\ln\left(\frac{\Phi}{T_g^{\,2}}\right) = C - \frac{E}{RT_g} \qquad (2)$$

where Φ is the heating rate, C is a constant for a given polymer and T_g is the glass transition defined as the temperature corresponding to the half-life of the process. The relation is valid if the glass transition may be considered to be a simple first-order kinetic process.

The results of our investigation will be discussed afterward.

Materials and Methods

PPS Ryton V-I powder ($\langle M_w \rangle$ 14 000; $\langle M_n \rangle$ 11 000) from Phillips Petroleum was purified from low molecular weight components by a previous treatment in a Soxhlet column with tetrahydrofuran in order to remove all of the low molecular weight species. The samples for all the experiments were prepared by heating them at 300°C for 40 min and then quenching in liquid nitrogen. The temperature over T_m and the residence time in the melt state were chosen so to ensure an optimal rearrangement of the polymer chains, allowing the best loss of the order characterizing the original crystalline phase without significant changes of the chemical nature of the polymer (cross-linking, degradation etc.).

The DSC measurements were accomplished by means of a Mettler TA3000 instrument, equipped with a silver furnace. About 8 mg of quenched sample were heated from 25 to 95 °C at an heating rate ranging from 1 to 35 K/min. All the measurements were carried out under N_2 flow.

IR spectroscopical measurements were accomplished on a Mattson Galaxy 5020 FT-IR instrument working at 1 cm^{-1} resolution. Samples were heated in the temperature range 23−140 °C at a heating rate Φ from 0.05 to 10 K/min using the Specac P/N 21525 variable temperature cell driven by a Hellma P/N 830004 temperature controller. The number of interferograms accumulated for each spectrum was varied according to Φ: 50 for $\Phi = 0.05$, 0.1, and 0.5 °C/min, 25 for $\Phi = 1$ °C/min, and 5 for $\Phi = 4$, 7, 10 °C/min, so that the temperature at the beginning and the end of each spectra did not differ by more than 1 °C. A calibration of the heating cell was carried out for each Φ by means of the following standard organic compounds: diphenil ($T_m = 71$°C), vanillin ($T_m = 82$°C), diphenilethandione ($T_m = 95$°C) and benzoic acid ($T_m = 122$°C).

In order to ensure the accuracy of the thermal treatment of the samples, all the experiments were accomplished by dispersing the polymer powder in KBr disks, which were, as for the other experiments, first heated at 300 °C for 40 min and then quenched in liquid nitrogen. The amorphous content of the samples was maximized by this method. Temperature during spectral recording was kept constant within ±1 °C. The measurements were accomplished in air, with the CO_2 and H_2O contribution to the absorption peaks analyzed in the present work being negligible.

The samples for the EDXD experiments were prepared according to the above mentioned procedure by heating about 200 mg of polymer at 300 °C for 40 min. They were then quenched in liquid nitrogen. To maximize the rate of heat exchange during measurements, the samples were supported on copper frame. Sample thickness was about 2 mm. The IR experiment's variable temperature cell was employed, keeping the samples under dynamic vacuum. The sample temperature was recorded with a K-type thermocouple held in physical contact with the polymer. The temperature range explored was 25−140 °C, at a heating rate of 0.1 K/min.

The diffraction experiments were carried out by using an X-ray energy scanning diffractometer recently assembled in the Laboratories of the University of Rome[37] on a Seifert & Rich high voltage power supply, whose stability is better then 0.1%.

The equipment is composed of an X-ray generator (water-cooled W target, 45 kV−35 mA), an EG&G solid state detector (ORTEC, model 92X) liquid-nitrogen-cooled ultrapure Ge SSD (energy resolution of about 200 eV at 6 keV) connected to a multichannel analyzer (MCA) with 1024 channels interacting via ADCAM hardware with a personal computer, based on an Intel 286 processor, for the storing of the data collected by the Maestro II (EG&G) software and for their processing by FORTRAN programs,[38] beam collimating system composed of four adjustable width W slits purposely placed to reduce the X-ray beam angular divergence, step motors which, by means of a mechanical setting, guarantee a reproducibility within ±0.001° for the scattering angles, and a sample holder.

The X-ray tube and detector holding arms can rotate in the vertical plane around a common center in order to reach the desired 2θ scattering angle.

The L fluorescence lines present in the 8−12 keV range of the white bremsstrahlung did not affect the measurements, falling outside the region of our interest. Escape peaks from Ge did not perturb significantly the spectra. A preliminary set of measurements was taken to find the angular position corresponding to the maximum scattered intensity. This operation is particularly important if the transition period is short, since it is essential to maximize the signal to noise ratio as far as possible. A suitable diffraction angle can be obtained in the following way. First, some peaks of the diffraction spectrum of the material are located by changing the inclination of the arms: diffraction peaks are related to q_i values in the reciprocal space. From eq 1 it can be seen that if θ is changed, the peak position changes in the energy scale. After this preliminary determination, a better one may be performed by slowly shifting the peak along the multichannel **E**-axis, until the peak coincides with the maximum of the energy spectrum of the incident beam (I_o). In this way the best experimental condition is met for data acquisition, being the observed intensity proportional to I_o. In our case a diffraction angle of 5 degrees, corresponding to $1 < q < 4$ Å^{-1} was chosen, which allowed observation of the main diffraction peaks. The sample is then placed in the rotation center of the diffractometer arms and it is irradiated with a sequence of X-ray flashes.

Our experiments were performed in transmission geometry. During sample heating about 280 spectra were collected. Each spectrum was measured for 200 s. Oxidation and chemical chain rearrangement effects, occurring in sample preparation and the subsequent heating experiment, were excluded by infrared spectroscopy analysis. The amorphous structure of the as-prepared samples was checked before each experimental measurement by comparing their EDXD spectrum to that of a melt-crystallized nonquenched one. These spectra were obtained at room temperature.

Results and Discussion

Since the early studies of Corradini[39] in 1975 the importance of the nonbonded atom interactions in affecting the structural arrangement of the polymeric matter and then its physical properties was recognized. The “Topographic View” of Stillinger[3] on the glassy state today provides a theoretical tool for the understanding of the relaxation processes taking place in the amorphous state as a function of temperature. It points out how the glass transition phenomenon may be interpreted as a “basin-trapping” sequence of processes in which the macromolecules are involved, passing from a conformational minimum to another in the multidimensional configuration space. Inter- and intrabasin relaxations are characterized by different time scales, with the second comparable to those typical of vibrational spectroscopy.

IR Analysis. The relaxation movements of the polymer chains involved in the glass transition give rise to well-evidenced calorimetric, dynamomechanical, and dielectric relaxation effects. On the other hand the infrared technique has not been, until now, so often employed in studying such a phenomenon. The infrared intensities of the matter in the condensed phase depend on the Boltzman factors, density, and refractive index. However slope variations of the intensity as a function of temperature were observed at T_g in a few cases.[40−45] In a preceding paper we have already shown that also in the case of PPS such an effect has been observed[29] for absorptions falling in the regions 1100−1000 cm^{-1} and 850−800 cm^{-1}. They were assigned[46] to the asymmetrical stretching of the S−Phe−S bond, in plane C−H bending (1100−1000 cm^{-1}), and out of plane C−H bending (850−800 cm^{-1}). Figure 1 shows a FT-IR spectrum of the previously quenched polymer, in which the aforementioned spectral regions are evidenced.

Anomalous dispersion effects due to the particle size of the dispersed sample are revealed by the shapes of the strong bands under investigation. However such a specular reflectance contribution may be considered to be constant over the temperature range explored and to be of little significance in our case, as the particle size is not seriously affected by the thermal treatment across T_g.

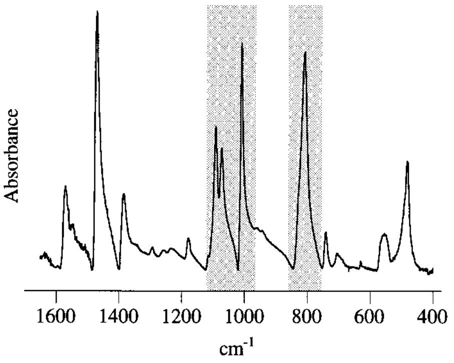

Figure 1. FT-IR spectrum of quenched PPS.

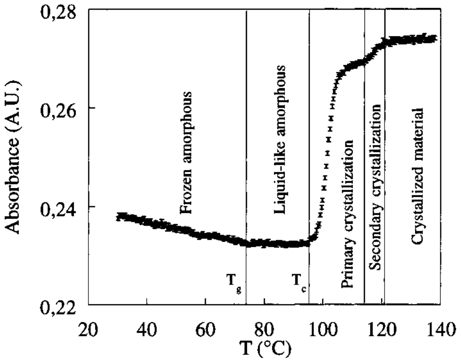

Figure 2. Absorbance variation of the peak at 1091 cm^{-1} as a function of temperature ($\Phi = 0.1$ K/min).

According to Brady[8] this spectrum reveals the presence of a high amount of amorphous material in the shapes of the peaks at 1091 and 1072 cm^{-1} (ν_{asym} (S−Phe−S)), 1009 cm^{-1} ($\delta_{\mathrm{i.p.}}$ (C−H)) and 809 cm^{-1} ($\delta_{\mathrm{o.p.}}$ (C−H)). We have then followed the absorbance changes with temperature in those regions. Figure 2 shows all the figures collected up to 140 °C for the peak at 1091 cm^{-1}. As can be seen the complex thermal behavior of the polymer is fully evidenced by the heating trace which may be separated into five different regions. The first two distinguish the frozen and liquidlike amorphous state of the polymer across T_g, while the other three concern its crystallization processes, which will be discussed in a future paper, which is in preparation.

As far as the amorphous state is concerned, by following the spectral evolution in the temperature range 30−90 °C only small absorbance decrease in the overall spectrum may be observed, but a careful inspection of the slopes taken for the peaks at 1091, 1009 and the shoulder at 825 cm^{-1} as a function of temperature reveals an inflection in correspondence of $T = T_g$.

Figure 3 shows the results obtained using an heating rate of 0.5 K/min. Such an effect decreases as the heating rate increases.

The data were obtained after base line flattening at 754, 846, 1020, and 1124 cm^{-1}. As may be seen, the peak at 1072 cm^{-1}, probably arising from a breakdown of the selection rules, does not reveal any slope change but only the absorbance variation due to temperature.

The inflection point was considered meaningful according to the criterion suggested by Hannon and Koenig:[40] all n data points were consecutively divided in two sets, taking the first m and the remaining $n - m$ points, with $3 \geq m \geq n - 3$. Slopes and standard

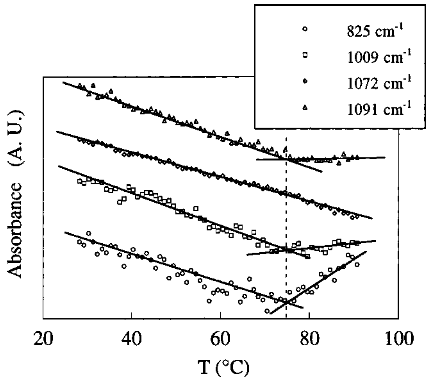

Figure 3. Absorbance variation of the peaks at 1091, 1072, and 1009 and the shoulder at 825 cm^{-1} as a function of temperature ($\Phi = 0.5$ K/min).

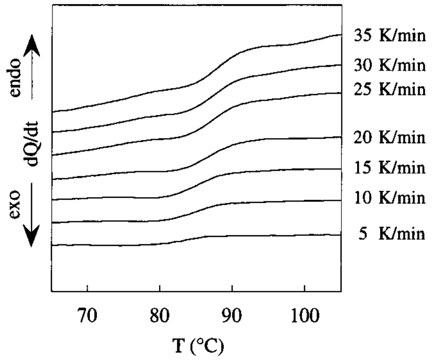

Figure 4. DSC traces recorded for the quenched PPS samples at different heating rates.

Table 1. Absorbance Variations Found at T_g for the IR PPS Spectral Lines Affected by the Glass Transition

spectral line (cm^{-1})	$Abs_{max} - Abs_{min}$ (arbitray units)	absorbance % variation
825	3.8 10^{-3}	1.86
1009	9.6 10^{-3}	1.91
1072	1.67 10^{-2}	6.20
1091	8.4 10^{-3}	2.64

deviations of best least-square lines were calculated for every set of data. The results were then compared with the standard deviation σ of the slope of the best least-squares line (BLSL) calculated using all data points. The transition was considered to occur if two lines of one set were found with a slope differing by more than $\pm\sigma$ from the slope of the BLSL. The transition temperature corresponds to the intersection point of the two straight lines having the minimum percentage standard deviation in slope.

It must be noticed that the observed changes were small and that they may mainly be recognized in the absorbance value. Table 1 gives the values of these variations.

As may be seen the major effect involves the 1072 cm^{-1} peak, although in this case no variation in slope is observed. However frequency shift and peak shape variations may not be excluded, and they are, at the moment, under careful investigation. Their presence would imply a variation at T_g of the intermolecular force field contributing to the vibration.

DSC Analysis. Figure 4 shows the DSC traces recorded for the quenched PPS samples at different heating rates.

Apart from the variation of onset and inflection point of the curves with heating rate, i.e. T_g, ranging between 82.9 and 87.6 °C, which will be better evidenced in Figure 9, an additional feature may be distinguished in the higher heating rate curves. A small and relatively large endothermic peak, centered at nearly 80 °C, appears before the glass transition temperature, which could be associated with low-energy chain rearrangements. These aspect will be better evidenced in the following discussion of the EDXD results.

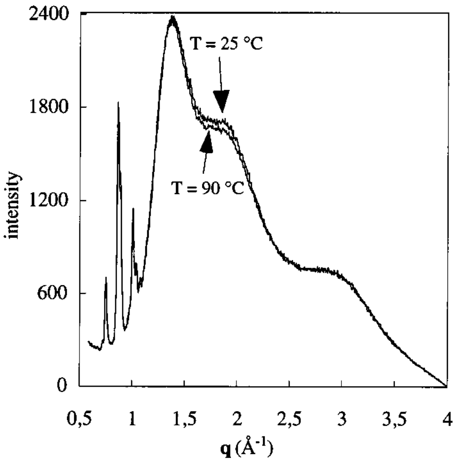

Figure 5. EDXD diffraction spectra of quenched PPS when measured at room temperature and at $T = 90 \pm 1$ °C.

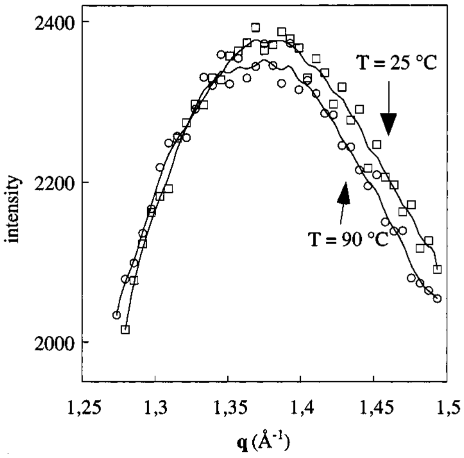

Figure 6. EDXD intensities measured at $T = 25$ and 90 °C for the peak at $q = 1.38$ Å^{-1}.

EDXD Analysis. We decided at this point to investigate the PPS glass transition by using a more suitable technique for the observation of structural variations, i.e., energy dispersive X-ray diffraction. As already stated this technique reveals all its potentiality when it is needed a very fast collection of diffraction information, as it is the case when the diffracting material is subjected to a temperature ramp. Figure 5 shows the EDXD diffraction spectra of quenched PPS when measured at room temperature and at $T = 90 \pm 1$ °C.

It can be seen that, beside the fluorescence peaks of the tungsten anode at 0.75, 0.87, and 1.01 Å^{-1}, three other peaks appear which are approximately centered at q values of 1.38, 1.90, and 2.91 Å^{-1}. Although small, the difference between the two spectra is easily distinguished, mainly in the q region between 1.5 and 2.0 Å^{-1}. With a more careful analysis, the peak at 1.38 Å^{-1} shifts at lower q values by raising the temperature, as shown in Figure 6.

Figure 7 shows the difference spectrum obtained by subtracting that recorded at $T = 90$ °C to the one obtained at room temperature (25 °C) which evidences

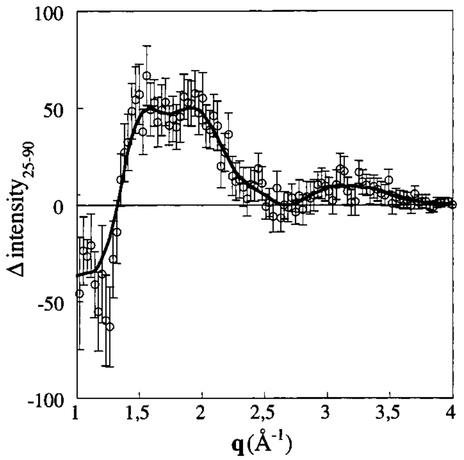

Figure 7. EDXD difference spectrum ($I_{25°C} - I_{90°C}$).

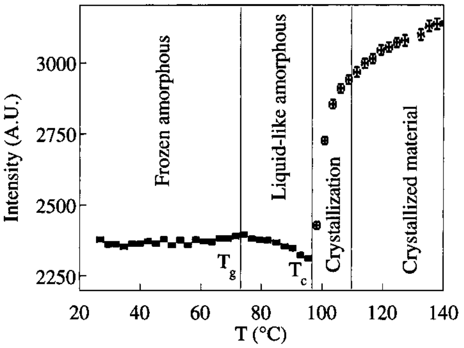

Figure 8. EDXD intensity variation measured in the q range 1.37−1.39 Å^{-1} as a function of temperature in the overall interval explored between 25 and 190 °C (Φ = 0.1 K/min).

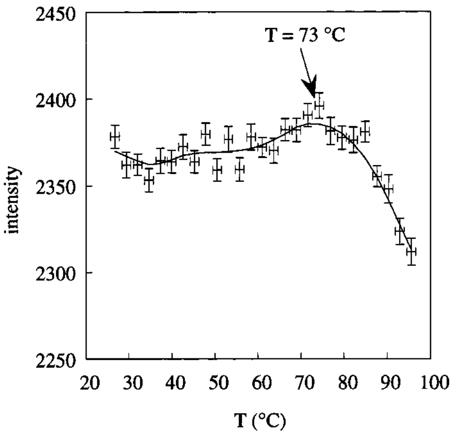

Figure 9. Total EDXD intensity measured in the q region 1.37−1.39 Å^{-1}.

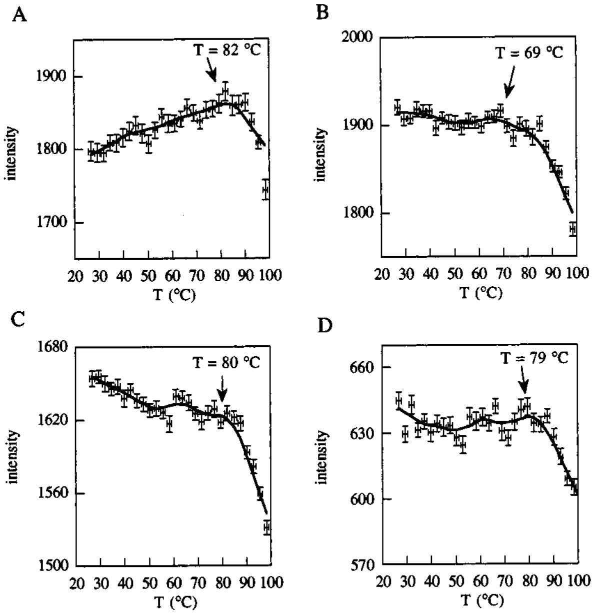

Figure 10. EDXD intensity variation measured at q = 1.25 Å^{-1} (inset A), q = 1.56 Å^{-1} (inset B), q = 1.95 Å^{-1} (inset C), and q = 3.11 Å^{-1} (inset D).

the more prominent deviations at q = 1.25, 1.56, 1.95 and 3.11 Å^{-1}, with the first being negative and the others positive.

The difference at q = 1.25 Å^{-1} is mainly due to the shift of the peak at 1.38 Å^{-1}, while the others arise from a decrease of the intensity measured at higher temperature.

In Figure 8 we show the intensity change measured in the q range 1.37−1.39 Å^{-1} as a function of temperature in the overall interval explored between 25 and 190 °C. The aforementioned q region corresponds to the intensity maximum in the EDXD spectra. As may be seen, as in the case of the IR analysis, different regions may be distinguished. The first one is relative to the heating of the frozen amorphous polymer, the second to the heating of the liquidlike amorphous after T_g, and the third to the crystallization process followed by the region of subsequent annealing of the crystallized polymer.

In the present work we intend to discuss the EDXD spectrum changes which have been observed on heating the sample up to 95 °C at Φ = 0.1 K/min, before the crystallization starts. Figure 9 illustrates the results obtained by considering the total radiation intensity measured in the q region 1.37−1.39 Å^{-1}, where the largest positive differences have been observed in the EDXD intensity, as shown in Figure 7.

Such a plot is evidence of an intensity drop at $T \approx 73$ °C, which could be taken as indicative of the glass transition. However the information given by the overall intensity may be considered as due to the integral of all the short-range rearrangements of the chains. A more careful analysis of what was going on in the correspondence of the largest deviations in the difference spectrum revealed a more complex pattern. In Figure 10 we show the diffracted X-ray intensity variation measured within the region shown in Figure 7, at q = 1.25, 1.56, 1.94, and 3.11 Å^{-1}.

The curve fitting was calculated by applying the locally weighted least-squares method, the fraction of the data population considered during smoothing being fixed at a value of 33%. As may be seen, the intensity trend varies differently with the q value. The intensity drops are found within a quite wide range of temperature, the lowest temperature intensity drop being that observed at q = 1.56 Å^{-1} corresponding to $T \approx 69$ °C, while in the other cases it arises around $T \approx 80$ °C.

One would have expected that, because of the specific volume increase with temperature, the scattered intensity would continuously decrease in absence of structural rearrangements. On the contrary the slope of the curve in the first temperature interval in Figures 8, 9, and 10 (A) shows an intensity increase, followed by a drop that we attribute to the α transition of PPS. This may be interpreted as due to the sum of the density changes and structural aforementioned rearrangements. Movements of chain segments of different length may be activated at unlike temperatures, the lowest of which

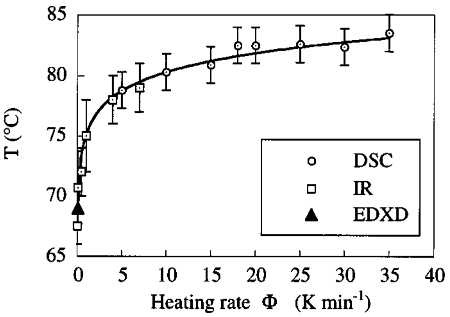

Figure 11. Dependence on heating rate of T_g onset, as measured by means of IR, DSC, and EDXD.

could be regarded as the onset of the glass transition process. Then the drop in intensity observed at $T = T_\alpha = 69 \pm 1$ °C could be attributed to the polymer softening. The coincidence of the T_α transition seen in EDXD with the T_g value obtained in the IR experiments for the same heating rate is striking, as will be better seen later on.

Without deepening, at the present stage, the discussion on the structural meaning of the results obtained, which will need a Fourier transform computation of a larger set of diffraction data also taken at a small angle, it seems possible to infer that local rearrangements of the PPS chains in the short range are induced at the polymer softening, as indicated by the reversed trend of the intensity variation measured at $q = 1.25$ Å^{-1}. On reaching the T_g, an higher concentration of scattering vectors falling within the range 1 Å^{-1} < q < 3 Å^{-1} is induced, corresponding to a "more ordered" structure (the vector length distribution becomes sharper). Such a structure then becomes able to undergo larger movements, producing the sudden specific volume increase at $T = T_g$, possibly affecting wider scattering vectors that have not yet been measured.

Another point which will need a deeper investigation is the apparent complexity of the intensity curves, which seem to subtend some shoulder at a temperature lower than T_g.

It is worth noticing that the reversibility of the aforementioned phenomena has been carefully checked. It came out that if the 90 °C threshold is not overcome, the EDXD intensity variations previously described were found to be reproducible, thus avoiding the doubt of a possible incipient crystallization of the material.

The Overall View. Figure 11 shows how the T_g varies as a function of heating rate, by taking into account all the experimental data collected by means of the different techniques that we have employed. The results obtained by DSC, IR spectroscopy, and EDXD are plotted on the same graph, showing that they may be interpolated by the same curve if the onset temperature for the DSC experiments is taken as representative of the glass transition. It is worth stressing such a result, as the question of the criteria to be used to recognize T_g in DSC experiments is still open. Our results seem to strongly indicate that the onset of the Δc_p should be taken as indicative of the transition.

It must be noticed that the heating rate ranges explored by the above-mentioned techniques are contiguous and complementary. For $\Phi < 5$ K min^{-1}, the DSC trace becomes noisy and does not allow us to detect the glass transition phenomenon, while for $\Phi > 7$ K min^{-1} the IR spectra do not show appreciable variations of the absorbance value corresponding with T_g.

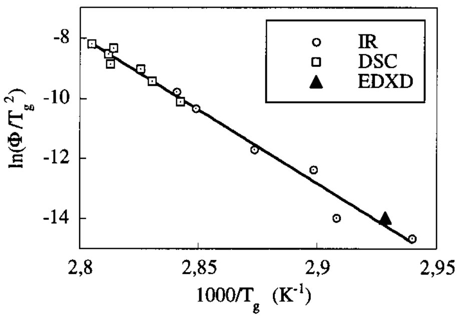

Figure 12. Dependence of $\ln(\Phi/T_g^2)$ as a function of $1/T_g$, according to the Barton theoretical model, as measured by means of IR, DSC, and EDXD.

The dependence of $\ln(\Phi/T_g^2)$ as a function of $1/T_g$, according to the theoretical model proposed by Barton (eq 2), is shown in Figure 12. The slope of the best fit linear interpolation gives an activation energy $E_a = 97 \pm 3$ kcal/mol.

Conclusions

As in the case of poly(ethylene terephtalate), polystyrene, polyacrylonitrile, and PVC[40–45] the IR intensity changes observed in our study could be accounted for in terms of density variation with temperature, related to the thermal expansion. As is well-known, density indeed exhibits a linear temperature dependence. Moreover the effects observed by IR may also be due to changes of refractive index, which is related to the dielectric constant of the material and then to the dipole moment. On the other hand the conformational changes, undergone by the material in going from the frozen amorphous state to the softened one through the glass transition, could also affect the measured absorptivity in the presence of frequency shift. However it seems difficult, at the moment, to correlate the observed absorptivity variations with conformational changes of the PPS chain as well as with 180° flipping of the aromatic rings, as was demonstrated by Gomez and Tonelli with ^{13}C NMR studies.[25] On the contrary, small amplitude librations of the phenyl rings could start the chain reorganization process which brings us to the crystallization of the amorphous part of the sample in the solid phase. Such molecular motions could affect the resonance of the sulfur electrons with the aromatic ring, leading to a change in the electron delocalization and modification of the dipolar momentum. Another contribution may be due to the relaxation of the internal stresses caused to the chain by the quenching process, which may set up mechanical tension on the disordered polymer chains. A new frequency distribution within the individual band could then be obtained, leading to a small IR peak shape modification which cannot be excluded in our case, where the limited flexibility of the PPS chain would reduce the importance of the effect. On the other hand, the significance of the limited PPS flexibility is also evident in the thermal studies of Wunderlich,[47] which found a particularly low rigid amorphous content in the quenched PPS samples. Intramolecular effects, connected with the specific volume variation, may be questioned, although they could contribute to the local dipole moment variation.

EDXD has proved to be very powerful in detecting structural rearrangements of the PPS chain during heating and in evidencing its glass transition, although at the present stage it is not possible to derive any structural model. However, throughout the study of the structural function obtained by recording the data in a wider scattering angle range, it will be possible to elucidate the underlying molecular processes involved. We have also anticipated in the present work the finding of a double crystallization process of PPS from the solid amorphous, which will be discussed together with its kinetic features in a forthcoming paper.

The onset of the glass transition seems to be more suitable for monitoring the phenomenon, being less affected by the different heat conduction conditions which can be met with the different experimental techniques.

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