Chem. Mater. **2000,** *12,* 369−375

Study of the Multiple Melting in Polymeric Materials by EDXD-PT. DSC Compared Application to Poly(ethylene-succinate)

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Received May 17, 1999. Revised Manuscript Received November 10, 1999

An alternative method to DSC, for revealing the thermal dissolution of the phases coexisting in a polymeric sample, is using a structure-sensitive probe, like X-ray diffraction. The problem with this is that it would be necessary to collect many diffraction patterns and to process them using theoretically calculated quantities. Instead, we used a method we developed, which simplifies the experimental procedure in studying phase transitions. It is based on the energy dispersive X-ray Diffraction and results in a curve that represents the evolution of the system under heating. In this paper, we present for the first time a comparison between these two techniques applied to a sample of poly(ethylene-succinate) which shows a multiple melting behavior when subjected to heating. The ability of EDXD applied to phase transitions (PT) to reproduce the complex melting behavior of PES causes one to think that a new tool for these kind of studies, completely independent of DCS, has been found. The potentialities and the merits of EDXD-PT are discussed together with its possible future developments.

1. Introduction

The study of the melting of a semicrystalline polymer sample shows the complexity of the structure and of the thermodynamics of these compounds. Usual micromolecular solids, i.e., solids consisting of aggregates of molecules made by few atoms, are submitted to the phase rule so that the melting process occurs for them at a given temperature if the pressure is unchanged.[1] For polymers, the situation is much more complicated both because of the coexistence of different structures and because of the rearrangement of such structures due to heating.[2] One of the consequences is the multiple melts observed in semicrystalline polymers during a DSC scan. Polymers belonging to this class are isotactic polystyrene,[3] poly(etylene-terephthalate),[4] poly(butylene-terephthalate),[5] Nylons,[6] poly(ether-ether-ketone).[7,8]

The usual procedure adopted in the interpretation of DSC traces consists of assigning to each endothermic peak the dissolution of one component of the spherulitic structure. In this approach, both the number of the coexisting structures and the sequence of the intensities of the cohesion forces that sustain these structures should be known. In fact, the dissolution of structures due to weaker cohesion forces are expected to occur at lower temperatures and, if the sequence of the intensities of these forces is known, the assignment with the endothermic peaks placed at higher temperatures can be done.

However, when the number of endothermic peaks exceeds the assumed number of the structures and when exothermic peaks appear as well, a more complex theory is required to justify these presences. A model based on the rearrangement of the weakest structures dissolved during heating was proposed to explain both:[2] the exothermic peaks would correspond to recrystallization of the molten material and the extra endothermic peaks, to the melting of these new structures.

Although some indirect evidence can be obtained to support this model,[9] the confirmation should come from the application of a method based on the direct observation of the structural changes.

For this purpose, in the paper, the measurements we carried out by DSC are compared with the results obtained through the time-resolved diffraction of the changing sample.

The latter technique consists of the collection of a sequence of rapid X-ray diffraction spectra taken while the sample is melting. Then, using the method briefly

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reported in the following section, the time evolution of the transition coordinate of the system is gained. The modality we adopt to execute the X-ray diffraction is the energy dispersive one, much more suitable of traditional (angular dispersive) for this kind of time-resolved observation. It does not represent a confirmation of the recrystallization model but, nevertheless, it gives further important information. In fact, although it cannot say if a structure is melting and then recrystallizing in an assumed way, yet it is able to show the degree of arrangement in the two phases before and after the transition. On the other hand, it can say also the reverse, namely if any transition—not observable by DSC even using the most favorable scanning conditions—takes place, for instance isoentropic (or almost isoentropic) structural changes involving no (or an undetectably small amount of) heat transfer.

After the comparison of the curves obtained by DSC and EDXD, the results are interpreted according to the above-mentioned recrystallization model. Moreover, to study in which conditions the thermograms better fit the EDXD results, a series of measurements of the variation in the position and in the shape of the DSC peaks have been performed as a function of the crystallization conditions and of the heating rate.

2. The Sample

The polymer we used is a granular sample of PES, poly(ethylene-succinate) (Aldrich Chemical Co., catalog no. 18203-6), having the following stoichiometric unit: $-OCH_2CH_2O_2CCH_2CH_2CO-$.

Its melting temperature, reported on the label, is 108 °C, while the glass transition temperature is −1 °C.

In the fluid state PES is an ionic conductor.[10] All the polymers of this kind show a progressive decrease of the transfer properties during the solidification since the ion mobility is tightly connected to the presence of noncrystallized chains. Hence it is essential to understand how the various coexisting ordered structures are formed or dissolved by cooling or heating. From this point of view the study of the complex multiple melting of PES is particularly interesting. Another reason for choosing it was that the variable-temperature cell for executing real time diffraction measurements works best in the temperature range of PES transition peaks (50−110 °C). Furthermore, PES was studied by other authors who provided a good standard for reference.[9] It represents a suitable test of the reliability of EDXD-PT that was never applied before to a system undergoing a multiple transition.

3. The Experimental Techniques

3.1. Differential Scanning Calorimetry. To perform the thermal investigation of the PES sample, a DSC-7 Perkin-Elmer calorimeter was used. Three different kinds of measurement cycles were carried out to check the influence of the heating rate and of the melting temperature on the thermogram profile.

In the first kind, an amount of PES of 6 mg was subjected to the following thermal treatment (Figure 1)

1. Heating from $T_A = 25$ °C to $T_m = 130$ °C at a rate of 10 °C/min
2. Sample held at T_m for 15 min
3. Cooling at a rate of 200 °C/min
4. Isothermal crystallization at a temperature of reference $T_0 = 50$ °C for 20 min
5. Free cooling to $T_A = 25$ °C

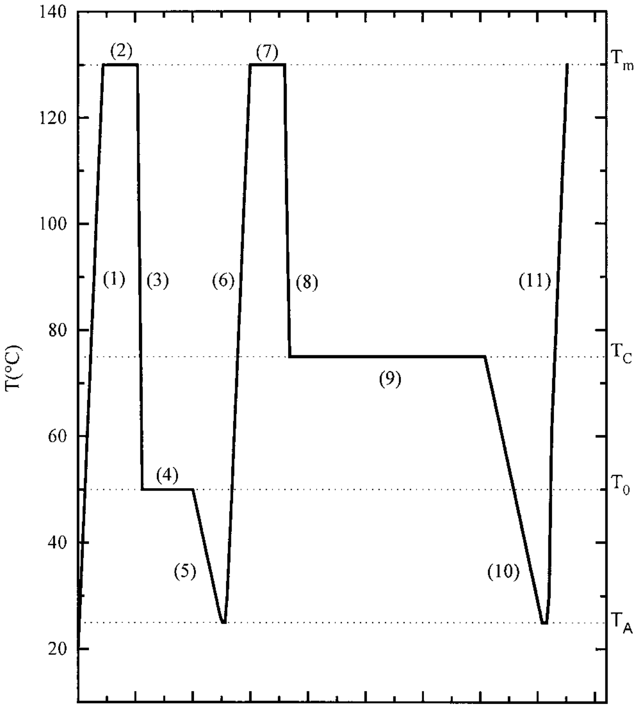

Figure 1. Sequence of the thermic treatments of the sample in the first cycle of DSC measurements as explained in section 3.1. It represents the chronogram of the experiment and the duration of the single operations are not on scale.

6. Heating from 25 °C to 130 °C at a rate of 10 °C/min
7. Melting as in step 2
8. Cooling as in step 3
9. Isothermal crystallization at a temperature T_C for a suitable time depending on T_C (This time can be determined by observing when the X-ray diffractograms do not change any more.)
10. Slow cooling to 25 °C as in step 5
11. New heating as in step 6, collecting the corresponding thermogram

The steps 1−5 are necessary to “reset” the sample, creating a standard reference structure. This can be verified by studying the reproducibility in intensity and position of the peaks in the thermograms associated with step 6 of Figure 1. We observed a relative error less than 1% in the position of the peaks and a relative error of ∼1% on their intensity.

After melting at $T_m = 130$ °C, any residue of the previous crystalline phase is destroyed, since the typical survival time of ordered domains at T_0 is much less than 15 min[11] and the subsequent crystallization has no memory of the preceding one. To demonstrate this statement, a second kind of cycle was performed (see below).

- The first kind of cycle was applied many times to PES, fixing each time a different temperature T_C, so that the whole accessible range of T_C was sampled. The lower limit of this range is found to be around 30 °C (instrumental limit), and the upper limit is about 80 °C, since at this temperature the crystallization is very slow and several days are required to conduct it.
- In the second kind of cycle, the melting at points 6 and 11 was executed at 120 °C, instead of 130 °C, all other parameters being unchanged: the rate of crystal domain consumption increases exponentially with the distance from the melting point. If no remarkable difference from the measurements made during the first kind of cycle is observed, it means that a fortiori the sample is perfectly liquid after melting at 130 °C.

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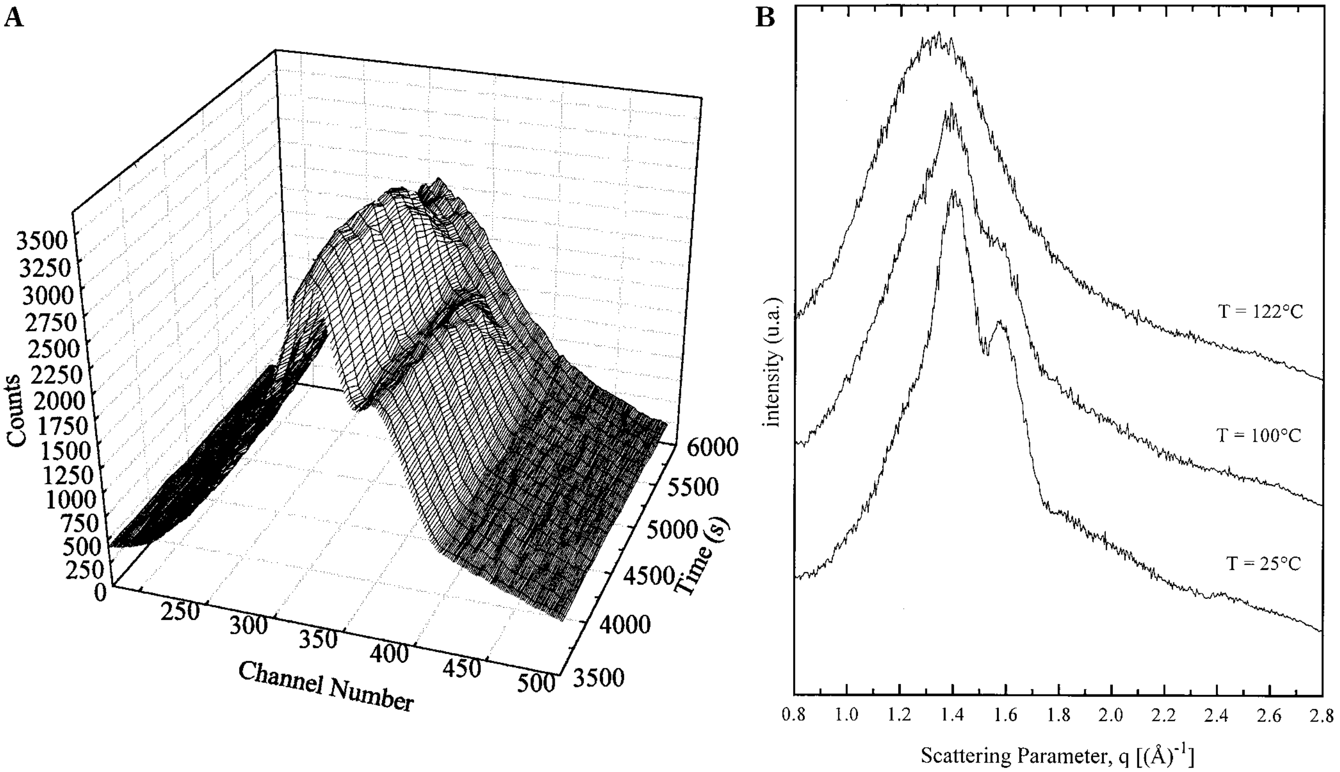

Figure 2. (A) 3-D plot of the time evolution of the EDXD spectra collected during heating of a sample crystallized at $T_C = 57$ °C. (B) Selection of the most significative spectra, collected at the key transition points, of the same sample of Figure 2A. The *x*-axis is now expressed in *q* units. Each spectrum is shifted along the *y* axis by 1000 units with respect to the previous one. The spectra are labeled by their collection temperatures (heating rate 1 °C/min).

- The third kind of cycle is similar to the first, but differing from it in that the heating rate at point 11 was decreased at 1 °C/min, to check also the influence of this parameter on the final results. These are the best conditions of work because, if the heating were too fast, the delay in detecting the thermogram peaks during heating would produce a systematic error on their positions. The disadvantage is that when the heating rate is too slow, the peaks may appear excessively broad and, if not enough intense, hardly detectable. For this reason the amount of sample was increased to 20 mg.

3.2. EDXD Applied to Phase Transitions. The experimental apparatus for the diffraction measurements consists of an energy dispersive X-ray diffractometer[12] at the center of which is placed a variable temperature cell. The polymer is contained in a flat parallel walls holder inside the cell. The X-ray source is an ordinary hot cathode W anode tube working at 45 kV and 35 mA, whose radiation passes through the sample (transmission geometry) after being collimated by a two W slit system. The scattered beam is also collimated in the same way and reaches a solid-state detector where the energy scan is performed. An electronic chain connected to the detector processes the signal coming from it and, finally, a multichannel analyzer digitally reconstructs the energy spectrum of the scattered beam onto a computer screen. The spectrum is collected and automatically stored.

This technique differs from the usual one because the X-ray beam is not monochromatic, but formed by a continuous spectrum radiation (in our case, bremmstrahlung of the X-ray W anode). Although this method implies, as a drawback, the necessity of determining the energy of each scattered photon, on the other hand it boasts several merits.

First, there is no need to changing the scattering angle during the measurement to collect the diffraction pattern. The scan of the reciprocal space is performed by the solid-state detector since a measurement of the intensity of a monochromatic beam scattered at various angles (conventional angular dispersive diffraction) is equivalent to a measurement of a polychromatic beam scattered at a fixed angle (energy dispersive diffraction). In this way, the experimental geometry remains unchanged during the collection, extremely simplifying the instrumental setup and the interpretation of data. In this work measurements are performed at a fixed angle $\theta = 3.5°$, where the main structural peak of the sample is visible. Furthermore, in laboratory X-ray sources, the intensity of bremmstrahlung is much higher than that of fluorescence lines (utilized for angular dispersive measurements) while the average absorption of the sample is lower. This reduces the acquisition times enabling the observation of faster structural transformations. A deeper discussion of this subject can be found in refs 13−17.

The accessible range of temperature for the cell is 20−250 °C. The thermal treatment to which the sample was subjected is the same as the third type of DSC cycle (section 3.1). The detecting system of the diffractometer was set up to automatically collect and store X-ray spectra of the radiation scattered by the sample while its temperature was increased at the heating rate of 1 °C/min. The temperature is measured by a thermocouple inserted in the sample in a way that it does not intercept the radiation. It enables a real time check of the heating rate. The result is a sequence of ~100 spectra describing the system evolution from 20 °C and increased by 1 °C/min. It is like a movie of the evolving system submitted to heating, whose frames are snapshots taken in the reciprocal space.

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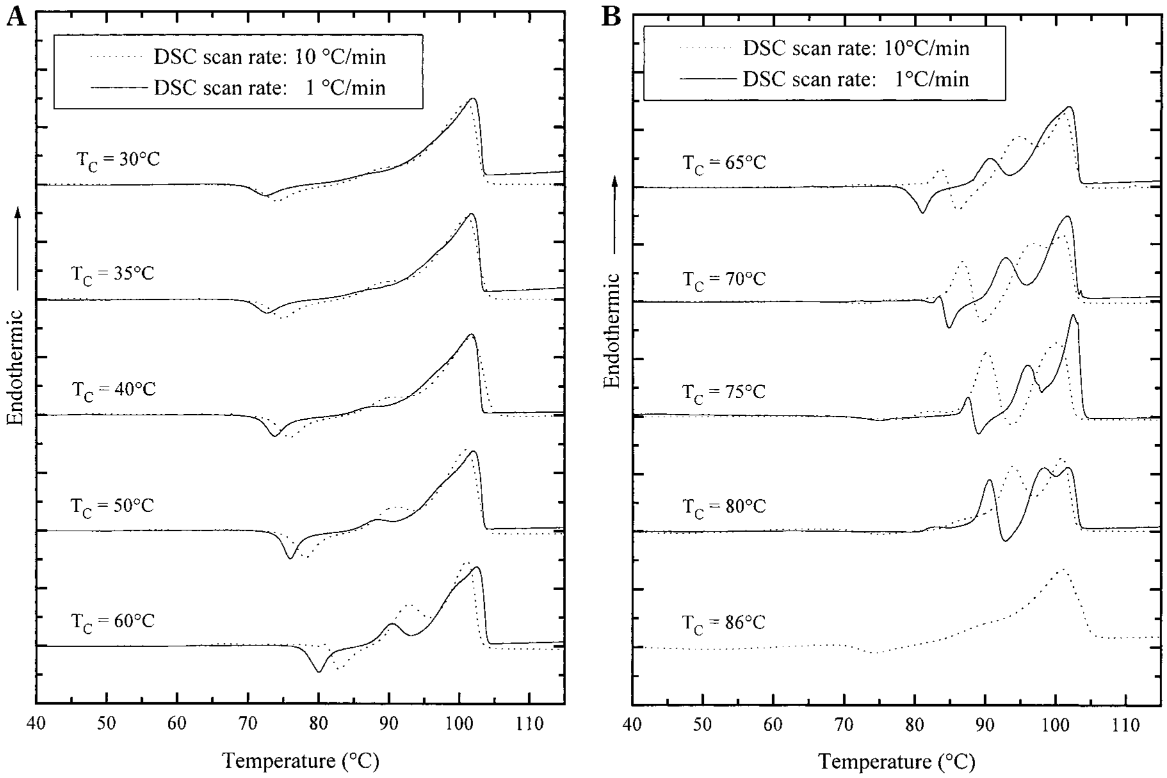

Figure 3. (A and B) Sequence of DSC spectra taken during step 11 in Figure 1 for various choices of T_C. A comparison is shown among the spectra collected when the sample is heated at a rate of 10 °C/min (dotted line) and of 1 °C/min (solid line).

In Figure 2A is shown, as an example, a three-dimensional plot of the time evolution of the EDXD spectra collected during heating of a sample previously crystallized at $T = 57$ °C. For clarity, only spectra in the temperature range 70 °C−110 °C are plotted; a temperature increase of 1 °C corresponds to a time range of 60 s. In Figure 2B we show three spectra of the evolving system at the key transition points: the relation between the scattering parameter and the channel index (chn), or energy (keV), is

$$q[\text{Å}^{-1}] = 1.014E[\text{keV}] \sin \theta$$

4. Results and Discussion

4.1. DSC Measurements. It is known that the behavior of a semicrystalline polymer during melting is determined by its lamellar structure which, in turn, depends on the thermodynamics and kinetic conditions of crystallization. Since there are no remarkable differences between the thermograms collected at 120 °C and 130 °C, modifications of the thermogram peaks are expected only by changing T_c and the heating rate.

In Figure 3A,B the DSC curves taken at the rate of 10 °C/min are compared with those corresponding to the rate of 1 °C/min (step 11 in section 3.1).

To discuss the experimental results it must be taken into account that this kind of polymers shows behaviors which are sometimes different from those expected for the ordinary ones. For instance, the presence of so many peaks in the DSC traces and the variation of their positions and intensities are not fully accounted for by using ordinary models.[18a]

Therefore, to explain the observed characteristics, ad hoc hypotheses will be required.

To gain useful information on thermal behavior of the polymer, a systematic analysis of DSC peaks intensity and position have been performed by changing the crystallization temperature and the scan rate. The procedure adopted consists of fitting each DSC peak with various Gaussian functions, by changing the fit procedure (the limits of the fit and the constrains on it): the value assumed is the mean of the values obtained and the experimental error is their standard deviation.

The first endothermic peak is visible only in thermograms of samples that had been crystallized at $T > 60$ °C. Increasing T_C, it becomes more intense and shifts linearly toward higher temperatures. This may be explained by assuming that this peak is associated with secondary structures that develop in the crystalline lattice when the main crystallization process is already in progress. They would consist of chains that arrange themselves inside the residual spaces contained in the lattice of the main lamellas. At low T_C (up to about 60 °C), the crystallization is so fast that the sudden reduction of the chains' mobility prevents the development of these structures and the corresponding peak is not present in the thermogram. At higher T_C, the peak appears at rather low temperatures showing that these crystals are rather imperfect. In fact, the amorphous chains are hindered by the presence of preexisting lamellas that confine them and reduce their ordering ability. With an increase of T_C above 60 °C, the peak shifts toward higher T, indicating a progressive perfecting of the structure that requires a stronger thermal excitation to be destroyed.

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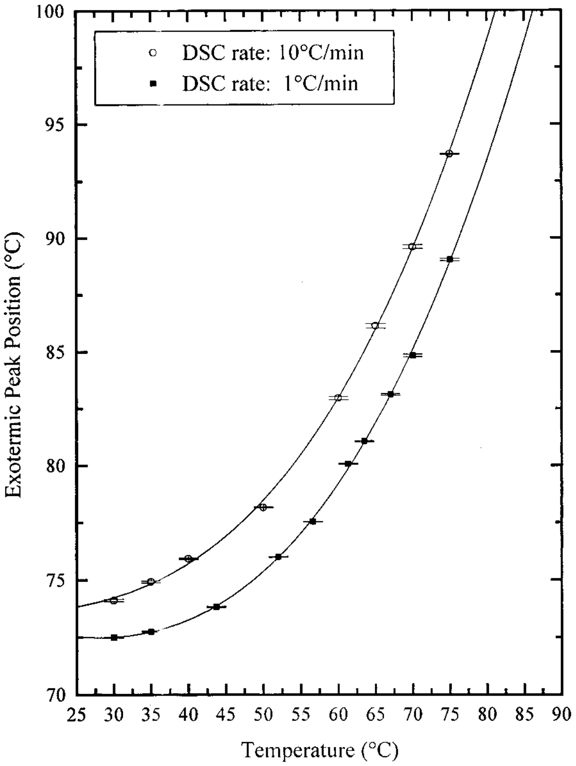

Figure 4. Positions of the exothermic peak vs T_C estimated from DSC thermogram related to step 11 in Figure 1. The third-order polynomial fits represent eye guides. The experimental points taken at a heating rate of 10 °C/min are plotted by using open symbols; those taken at a rate of 1 °C/min, by solid symbols.

The exothermic peak is associated with a structural reorganization process during heating. The amorphous material, which was trapped in the crystalline structures (or also produced by the dissolution just described), reaches favorable thermodynamic conditions for crystallization. When T_C is increased, this peak moves to higher T with a trend that is weakly increasing at the beginning and almost linear after (Figure 4). The recrystallization process is more efficient for higher values of the undercooling $\Delta T = T_m - T_C$ and seems to have a maximum within the explored range of temperatures (Figure 5). An interpretation may be that the maximum coincides with the fastest crystallization rate, occurring approximately at $(T_m - T_g)/2$, which induces the trapping of the largest amount of amorphous material available for re-crystallization.

The second endothermic peak can be put in connection with the breaking of the main crystalline matrix. Changes of the peak positions with T_C are shown in Figure 6. Approaching T_C, an increment of the peak intensity is observable (Figure 7), which may be correlated to the amount of crystallinity of the sample. In fact, the structural order is expected to improve by reducing the undercooling ΔT, because the crystallization rate decreases so that the polymers have a longer time and a higher mobility to arrange in a regular configuration.

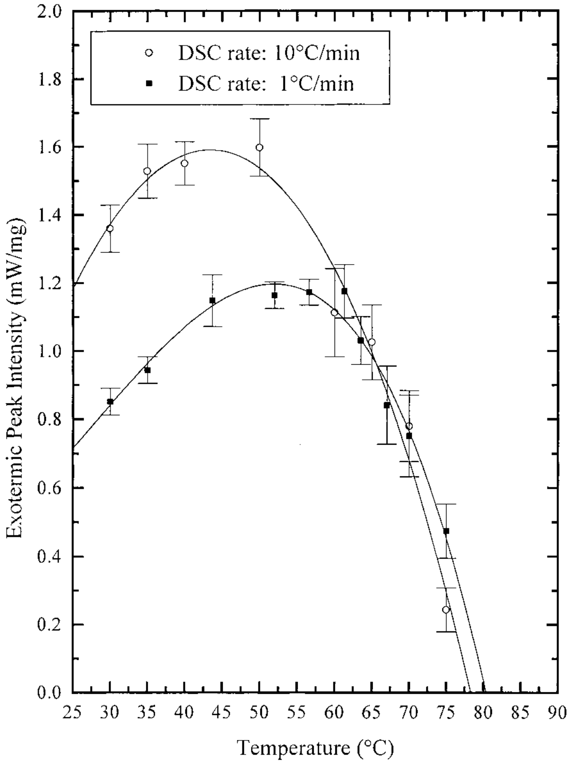

Figure 5. Intensity of the exothermic peak vs T_C for the same thermogram as Figure 4. A third-order polynomial fit of the experimental data is drawn as before. The convention on the symbols is as in the preceding figure.

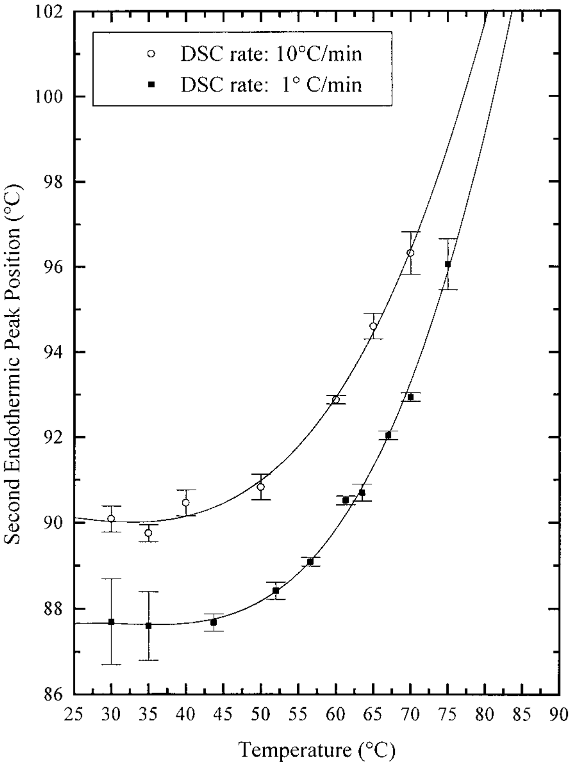

Figure 6. Positions of the second endothermic peak vs T_C fitted by a third-order polynomial for the same thermogram as Figure 4. The symbols are as in Figure 4.

The position of the third exothermic peak does not seem to be influenced by T_C. However the study of its intensity as a function of T_C could not be performed because it shows an asymmetrical shape. This suggests that it may hide another unresolved secondary peak, which reveals the presence of a structure more complicated than that originally supposed. The following section shows how it may be possible to overcome this limit of DSC.

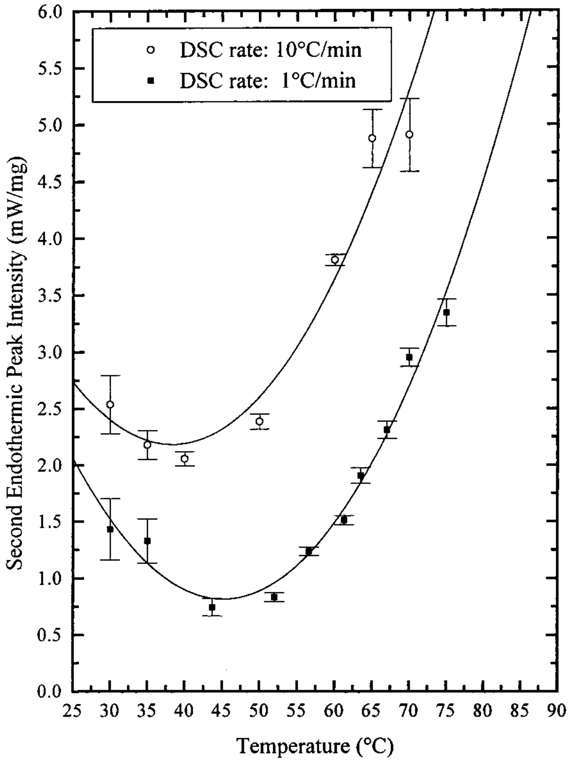

Figure 7. Intensities of the second endothermic peak vs T_C fitted by a third-order polynomial for the same thermogram as Figure 4. The symbols are as in Figure 4.

4.2. EDXD-PT Measurements. The peaks of DSC are connected to structural transitions that involve absorption or release of (latent) heat. This is based on the proportionality, at a constant pressure, between this heat (enthalpy variation) and the entropy change due to the microscopic rearrangement of the polymer chains. However, this technique has some intrinsic and some practical limits.

First, it is not a direct measurement of the change in structure, but rather, the detection of a macroscopic effect produced by the change. Transitions between two different structures having comparable entropies would produce modest heat fluxes and would hardly be observed in this way. Samples having complicated crystalline structures may have such problems. Second, the time of detection of the heat flux depends on the experimental arrangement as well as on the conduction properties of the sample. This limits the resolution of the thermogram and the ability of distinguishing two consecutive transitions.

A solution to this problem is offered by EDXD-PT technique, whose final aim is similar to DSC. It consists of a method[13,17] to measure the time evolution of a transition coordinate $x(t)$, which summarizes the state of the system at a given instant t. The $x(t)$ curve was calculated by following the transformation of the peaks in the 1.3−1.6 Å^{-1} q interval (Figure 2B), which corresponds to structural changes in the distance range of about 4−5 Å. The derivative of $x(t)$ gives a plot analogous to the DSC thermogram (Figure 8). Practically $x(t)$ is calculated by comparison of diffraction patterns collected during the transformation of the system (suitably normalized if the system changes its density) as it is described in section 3.2. In this way the complicated problem of extracting the structure factor $S(q)$ is bypassed: the information contained in $S(q)$ is used without calculating it explicitly. Mathematical details can be found in ref 13.

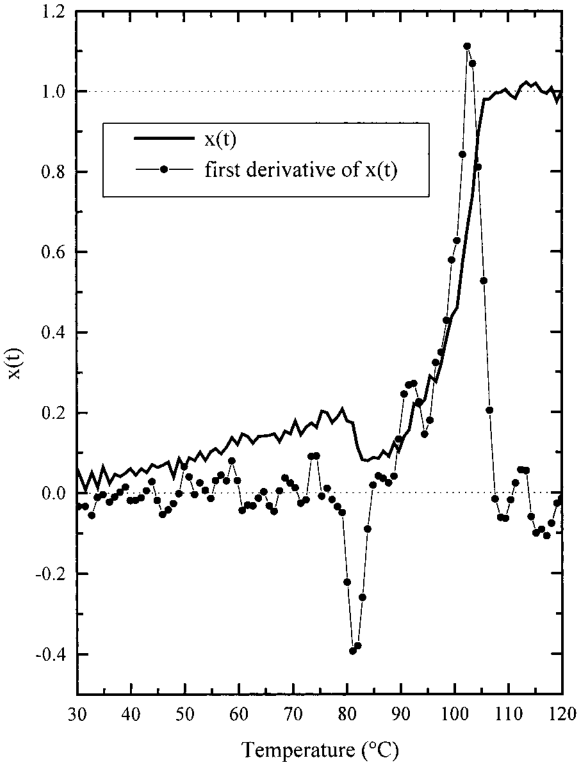

Figure 8. $x(t)$ plot, obtained from EDXD measurements (Figure 2A,B), vs temperature (solid line) and its first derivative (line + symbol). Numerical values on y axis are referred to $x(t)$.

Here it is worth showing in simple terms the qualitative connection between the DSC thermogram and the diagram obtained by plotting dx/dt as a function of time.

A DSC thermogram represents the rate of enthalpy transfer between the system and the environment during a transition and, in constant pressure transformations, enthalpy and entropy are proportional. Now, according to the information theory, entropy can be expressed in terms of the radial distribution function $g(r)$.[19] The latter, in turn, is proportional to the Fourier transform of $S(q)$ that is contained in the diffraction patterns used to obtain $x(t)$.

Therefore, this is the link: once the time evolution of the structure-dependent quantity $x(t)$ is observed by X-ray diffraction, this derivative $\dot{x}(t)$ must behave as the heat transfer rate represented by the DSC thermogram.

In Figure 9A−C a comparison between DSC and EDXD-PT diagrams is shown. The agreement appears to be satisfactory. The EDXD-PT curves seem to reveal an even more complex behavior than that expected according to the before-mentioned recrystallization model.

As is usual in polymers, when a characteristic is measured using different methods, slightly different results are found.[18b] However, in this case, what matters is not the absolute measure of a given characteristic, but its variation in order to detect the onset of a phase transition. Since this variation is due to a structural change of the system, the structural-dependent quanti-

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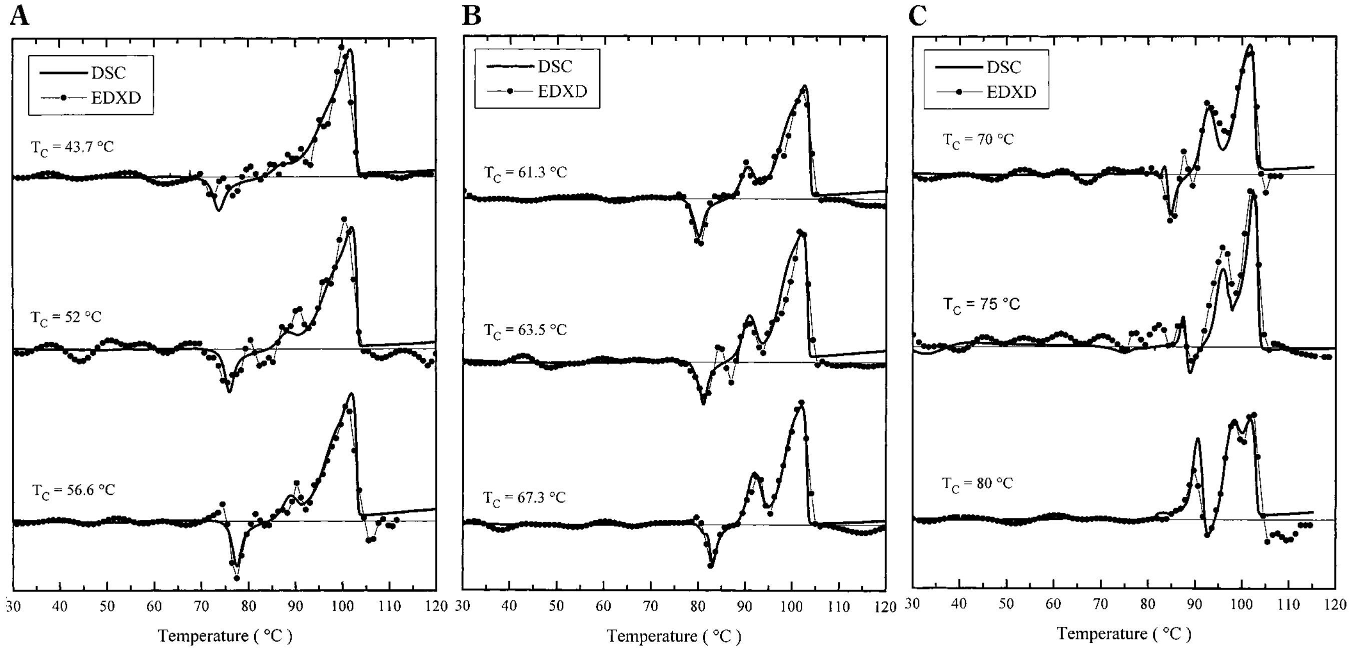

Figure 9. (A−C) Comparison between DSC thermograms (solid line) and first derivative of $x(t)$ (line + symbol) for various choices of T_C.

ties (like enthalpy of transition and structure factor) are also expected to change accordingly. Of course, the amount of the change of each quantity may be different, but the onsets must be simultaneous (apart from delays in detection). As a consequence, if we consider two diagrams describing the change rate of two different quantities of the system, peaks corresponding to the same transition in the two diagrams may have different intensities but the same position on the time axis.

Once the substantial equivalence of DSC and EDXD-PT is stated, some advantages of the latter method can be shown.

First, the problems in DSC measurements, which occur when the change of enthalpy (entropy) during the phase transition is small, are overcome. In fact, different structures, even if they have similar entropies, can be readily distinguished by X-ray diffraction.

Second, DSC is based on a macroscopic collective effect which involves the whole sample, while EDXD-PT is based on local properties of the system and various zones can be defined: variations in the high q zone of the reciprocal space qualitatively correspond to changes in the short-range arrangement of the sample and vice versa. Therefore, it is possible to observe if the transition involves short-, medium-, or long-range changes and, if these all happen, their sequence.

Then, the time resolution of EDXD-PT technique can be tuned by varying the sampling time of the diffraction pattern (spacing of the experimental points in the $x(t)$ plot) and increasing the intensity of the incident beam to reduce the noise-to-signal ratio. However, DSC is constrained by the time required for the heat transfer which cannot be changed and which is rather long for the bad thermal properties of polymers.

Conclusions

We showed how the EDXD-PT technique provides a new tool for the investigation of the phase transitions even when they are complicated by the simultaneous presence of several changing structures. From the comparison with DSC, it is possible to affirm that the single steps of a multiple transition can be correctly identified by using the EDXD-PT. Improvements are likely to be expected by optimizing the experimental conditions and by using a brighter source of X-ray. EDXD-PT seems to be a practical way to check if the behavior of this kind of systems is even more complex than that observable by traditional calorimetric methods and, therefore, if new models of polymer transitions should be devised to interpret the experimental evidence.

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