

Energy dispersive x-ray diffraction and differential scanning calorimetry investigation of the melting behavior of poly(ethylene-succinate) crystallized at low undercooling

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The behavior upon heating of poly(ethylene-succinate) samples crystallized at progressively lower undercooling has been studied. The multiple melting phenomena exhibited by this particular polymer subjected to a temperature ramp were investigated using both ordinary differential scanning calorimetry and an alternative technique, energy dispersive x-ray diffraction applied to phase transition. A critical comparison of the two methods adopted in the melting studies is included. Another application of the energy dispersive x-ray diffraction method, which enables one to distinguish the structural rearrangements that take place on different distance scales, is also described. © 2003 American Institute of Physics. [DOI: 10.1063/1.1589588]

I. INTRODUCTION

Poly(ethylene-succinate) (PES) belongs to a family of polymers that have the interesting property of multiple melting upon heating.¹ In particular, this polymer may exhibit several peaks in the differential scanning calorimetry (DSC) thermogram, up to a maximum of one exothermic and three endothermic peaks. However, the number, position, and height of these peaks is a function of the thermal history of the sample under measurement.² For a particular chemical composition, impurities concentration and crystallization procedure, the peaks of a sample are influenced by:

- (1) the temperature T at which it is melted;
- (2) residence time t at T , with $T > T_m$;
- (3) temperature T_c at which it is recrystallized after melting; and
- (4) the time t_c of residence at T_c .³

When the undercooling $T_m - T_c$ is decreased, the crystallization time t_c increases and an enhanced structural perfection is attained. In this case two effects are observed. The first is that the main peak, which is associated with the most ordered structure,⁴ shifts to a temperature that increases as the undercooling decreases. The second effect is that the peaks related to secondary structures, which are generated when the chain mobility is reduced abruptly, as a result of sample quenching, tend to disappear.

Therefore, the melting temperature of a polymer cannot be univocally determined, since it corresponds to the thermal

history-dependent position of the last endothermic peak. For this reason, T_m can be rigorously defined as the limit position that the highest temperature peak approaches when the undercooling decreases to a vanishingly small value. To evaluate this limit, a series of DSC measurements is usually performed by progressively decreasing the undercooling. The T_m value will correspond to the intersection of two straight lines, the first of which is the linear fit of the highest temperature peak position versus undercooling and, the second, is the line $T_m = T_c$.⁴

By contrast, in this work we have measured the limit value T_m in a more straightforward way, by observing the behavior of the thermogram peaks of a sample crystallized at very low undercoolings. Of course, to observe T_m directly, an infinite t_c would be required. However, a very good approximation consist of crystallizing the sample for such a long time that further prolonging would not produce any significant difference in the value of T_m obtained in this condition. The DSC measurements were supported and complemented by analogous measurements performed using the energy dispersive x-ray diffraction applied to phase transition technique (EDXD-PT),⁵ which is more readily applicable for lengthy experimental procedures. This innovative technique provides similar information to DSC, but is based on the structural rather than on the thermal properties of the melting system.² An original application of the EDXD-PT method, for monitoring the transformation of the polymer on various distance scales, is introduced and discussed for the specific case of a sample crystallized at a suitable temperature T_c (60 °C), and heated at various rates.

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II. EXPERIMENT

A DSC measurement consists of determining the heat flux released or absorbed by a system subjected to heating. The heat flux is associated with an exothermic (heat release) or endothermic (heat absorption) transformation, so it is indicative of a change in the arrangement of the system components. However, this flux is a secondary effect that accompanies structural change, so that DSC is to be considered as an indirect method for determining the transition. In fact, no details can be gleaned from DSC as to the kind of change taking place, since the only information available concerns peak position (transition temperature) and intensity (heat transfer). By contrast, the main feature of diffractometric techniques is that they are structure sensitive and, therefore, diffraction is intrinsically more suitable for studies of this kind. Bearing this in mind, an alternative method has been developed by some of the authors.² It consists precisely of processing the diffractograms collected during the transformation of the system in order to obtain a convenient parameter (transition coordinate x) describing its evolution. The graph of the derivative of x resembles a DSC thermogram, but is potentially more informative. This graph provides a description of the system transformation independently of the DSC and can be used to confirm or, possibly, improve the results obtained from the calorimetric measurement.

However, two ways are available to collect a diffractogram, namely the energy dispersive (EDXD) and the angular dispersive (ADX) mode, the former proved more suitable for conducting time-resolved *in situ* diffraction measurements of the melting polymer. Indeed, no movement is required in EDXD during data collection, which simplifies the experimental setup, and the photon energy is higher than that of the usual monochromatic beam utilized in ADXD, reducing x-ray absorption effects.

On the other hand, the major drawback of EDXD, namely its poorer resolution, does not pose a problem since the diffraction peaks of a polymer, even in its semicrystalline phase, are so wide that further minor broadening becomes insignificant. In the section dedicated to EDXD, a brief outline of the technique is provided. A more detailed discussion is reported elsewhere.⁵⁻⁷

A. Sample preparation

Since the polymer structure is dependent upon its thermal history, all the samples were prepared following the same procedure, schematically shown in Table I. This consisted of melting the PES sample (Aldrich Chemical Co. Catalog No. 18203-6 with specified nominal T_m of 108 °C) at 130 °C for a pre-established time (15 min). Next it was crystallized at 50 °C for 30 min and remelted at 130 °C for another 15 min. Finally, the sample was quenched at the crystallization temperature T_c and kept at this temperature for a time t_c .

Polymers do not have a unique crystalline structure and the arrangement of the chains may vary. To describe this phenomenon, polymers are usually said to suffer memory effects.^{8,9}

The earlier described procedure was adopted to minimize such memory effects and to reproduce the same initial

TABLE I. Thermal treatment steps of the PES sample. Both the initial (T_1) and final (T_2) temperature, together with the time (Δt) required for each step are indicated

Step	Operation	T_1 (°C)	T_2 (°C)	Δt (min)
1	Heating	25	130	12
2	Melting	130	130	15
3	Cooling	130	50	3-4
4	Crystallization	50	50	30
5	Heating	50	130	10
6	Melting	130	130	15
7	Cooling	130	T_c	3-4
8	Crystallization	T_c	T_c	t_c
9	Heating	25	130	90
10	Cooling	130	25	120

conditions each time a new measurement was executed. In fact, a polymer melted at a given temperature, even if far higher than its T_m , retains some residual microcrystals in the liquid phase. The abundance of these microcrystals depends on the polymer structure prior to melting, since higher degrees of crystallinity require higher temperatures and longer times to achieve complete melting. The microcrystals that survive (incomplete) melting act as catalysts in the subsequent crystallization and influence the resulting structure.⁸ Thus, it is necessary to first create a reference structure (steps 1-4 in Table I) such that, once the sample has been kept at a fixed melting temperature T (step 2) for a fixed time t , the abundance of microcrystals is expected to be the same so that quenching always occurs in the same conditions (steps 7 and 8).

B. DSC measurements

A DSC-7 Perkin-Elmer calorimeter was used for the thermal study of the PES sample, as reported in Table I.

The DSC measurements were performed at the following T_c : 73, 75, 78, 80, 82, 84, 86, 88, and 90 °C at a temperature heating rate of 1 °C/min (Table II).

To achieve reasonable intensity in the DSC peaks, about 20 mg of sample was used for each measurement.

TABLE II. Crystallization temperature (T_c) explored, together with the time required for complete crystallization (t_c) and the experimental technique adopted.

T_c (°C)	Method	t_c (h)
73	DSC	15
75	DSC	15
78	DSC	15
80	DSC/EDXD	15
82	DSC	40
84	DSC	40
86	DSC/EDXD	62
88	DSC/EDXD	92
90	DSC	100
92	EDXD	120
95	EDXD	288

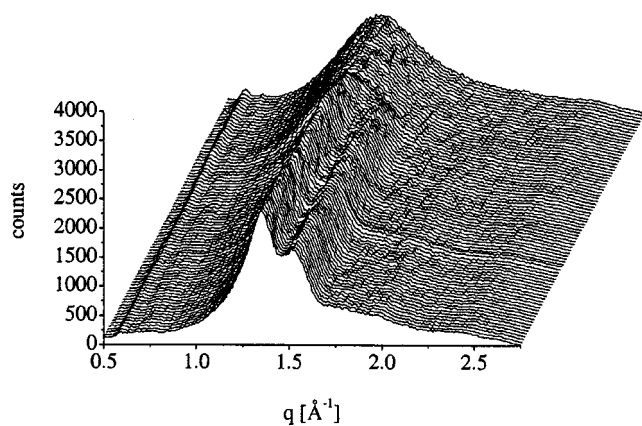


FIG. 1. 3D plot of the time evolution of EDXD spectra recorded during heating of the sample (step 9 in Table I) crystallized at $T_c = 80^\circ\text{C}$. The whole process requires 90 spectra, each taking 60 s, i.e., making a total of 90 min.

C. EDXD measurements

In the present EDXD study, the nonmonochromatized (white) bremsstrahlung spectrum emitted by a W-anode x-ray tube impinges on the polymer sample. The diffracted intensity is recorded with an ultrapure germanium solid-state detector (EG&G-Ortec, model GLP/10180), placed at a fixed diffraction angle. The energy spectrum of the diffracted radiation is reconstructed using a multichannel analyzer. Consequently, in this case, instead of fixing the energy of the primary beam and performing an angular scan (ADX), the deflection angle is fixed and the energy is scanned (EDXD).

Since the scattering parameter q is proportional to the photon energy ($q = \alpha E \sin \vartheta$, where $\alpha = 1.014 \text{ \AA}^{-1} \text{ keV}$, E is the photon energy, and 2ϑ is the fixed scattering angle), the observed radiation energy spectrum directly represents the diffraction pattern.¹⁰

This method proved to be very effective for conducting diffraction experiments during structure evolution of polymer systems and/or if access to the sample is hampered, for instance when complex and cumbersome devices are used.

III. RESULTS AND DISCUSSION

The EDXD-PT method consists of recording a series of diffraction spectra of the evolving structure of the system under study. The experimental set up comprises an energy dispersive x-ray diffractometer¹¹ fitted with a variable temperature chamber, in which the sample is subjected to thermal cycles. After step 8 in Table I, the temperature ramp is initiated (step 9), simultaneously irradiating the sample with a series of white x-ray “flashes” of fixed duration. As the EDXD technique does not require scattering angle scanning, experimental geometry can be kept unchanged during the measurement.

Every 60 s a diffraction spectrum of the polymer during heating is recorded. The temperature of the sample is measured by a thermocouple device, in this way is possible to know its temperature at each time. By processing the collected spectra, an example of which is given in Fig. 1 in the form of a three-dimensional (3D) map, the transition coordi-

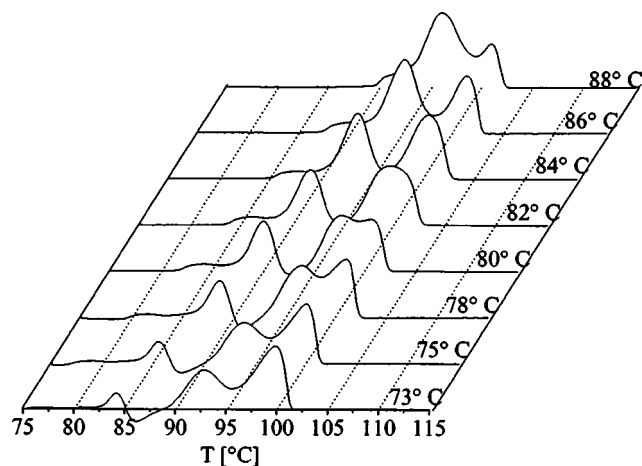


FIG. 2. DSC thermograms for step 9 of thermal cycle (Table I), after crystallization at the indicated T_c ($^\circ\text{C}$). DSC scan rate is $1^\circ\text{C}/\text{min}$. The thermogram for the sample crystallized at 90°C is not shown.

nate $x(T)$ can be obtained. It represents the transformation stage as a function of temperature and is calculated through the relation

$$x(T) = \frac{I(T) - I(T_1)}{I(T_2) - I(T_1)},$$

where $I(T)$ is the average intensity diffracted by the sample when it is at temperature T , and T_1 (T_2) is the initial (final) temperature of the ramp.

Such coordinate contains the structural information about the sample. As mentioned earlier, by calculating its derivative $dx(T)/dT$, a graph similar to the DSC thermogram can be obtained. The theoretic equivalence of the two methods, discussed in detail elsewhere,^{2,12} is associated with the relation between the two possible definitions of entropy, namely the thermodynamic (Carnot) and the statistical mechanics (Boltzmann-Gibbs) definition, and can be summarized as follows. In the former instance (Carnot), a peak (minimum) of the DSC thermogram is the rate of enthalpy released (absorbed) during a first-order phase transition and, since the temperature remains unchanged, it corresponds to a proportional change in entropy. Alternatively, in the Boltzmann-Gibbs approach, a diffractogram represents the Fourier transform of the pair correlation function $g(r)$, which describes the system configuration. According to the statistical mechanics definition of entropy, the entropy change during the transition is related to the modification of the system configuration only, since the moment distribution is constant if the temperature does not change, and can be obtained by recording the $g(r)$ (i.e., the diffractogram) modifications.

As a consequence, both the DSC and the EDXD-PT methods probe the entropy variation and must provide correlated results. Measurements of the melting process were performed using the EDXD-PT technique on samples crystallized at five T_c : 80, 86, 88, 92, and 95°C , at the same temperature ramp as for the DSC measurements ($1^\circ\text{C}/\text{min}$) (see Table II).

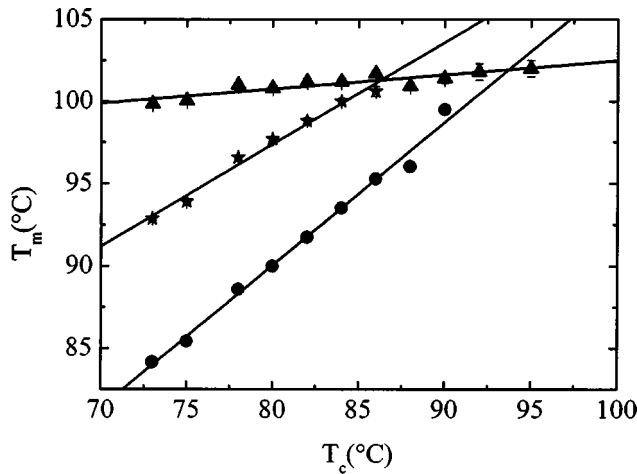


FIG. 3. Melting temperature of the first (circle), second (star), and third (upturned triangle) endothermic peak vs crystallization (T_c) temperature. Temperatures were deduced from the peak position of the corresponding DSC thermogram. A linear fit of the experimental points is shown in each case.

The DSC thermograms collected for the different crystallization temperatures are shown in Fig. 2. As was to be expected, T_c was observed to influence peak intensity and position. In particular, increasing T_c , the peaks shift toward higher temperatures, indicating that a higher thermal energy is required to dissolve the polymer crystalline structure. According to the lamellar PES model,¹³ each endothermic peak

is associated with a different kind of lamellae within the polymer semicrystalline phase, so that the melting behavior can be interpreted as an increase of the crystalline regularity of the structures. Moreover, the peaks corresponding to weaker structures tend to gradually disappear when T_c is increased.

This tendency is shown in Fig. 3, where the positions of the peaks are plotted versus T_c . Two limit temperatures can be extrapolated from the patterns of the first and second endothermic peaks at around 94 and 86 °C, respectively. Above these temperatures, the lamellae of the first and second kind are no longer produced during quenching and a single peak, relative to the only lamellar structure still present in the crystallized polymer, can be observed.

In order to obtain the transition parameter $x(T)$, series of diffraction patterns measured by EDXD-PT (of the kind in Fig. 1) were recorded during polymer melting. The derivative of $x(T)$ calculated from the diffraction patterns of Fig. 1 ($T_c = 80$ °C) and, analogously, from those recorded during melting of samples crystallized at 86, 88, 92, and 95 °C have characteristics similar to the corresponding DSC thermograms. Figure 4 shows the comparison between $dx(T)/dT$ and the thermogram of the samples crystallized at 80, 86, and 88 °C. The agreement is satisfactory, despite the experimental differences between these two techniques. Figure 4 also gives the $dx(T)/dT$ plots of the two remaining samples. These were measured in order to confirm that only a single peak is going to survive at such high crystallization tempera-

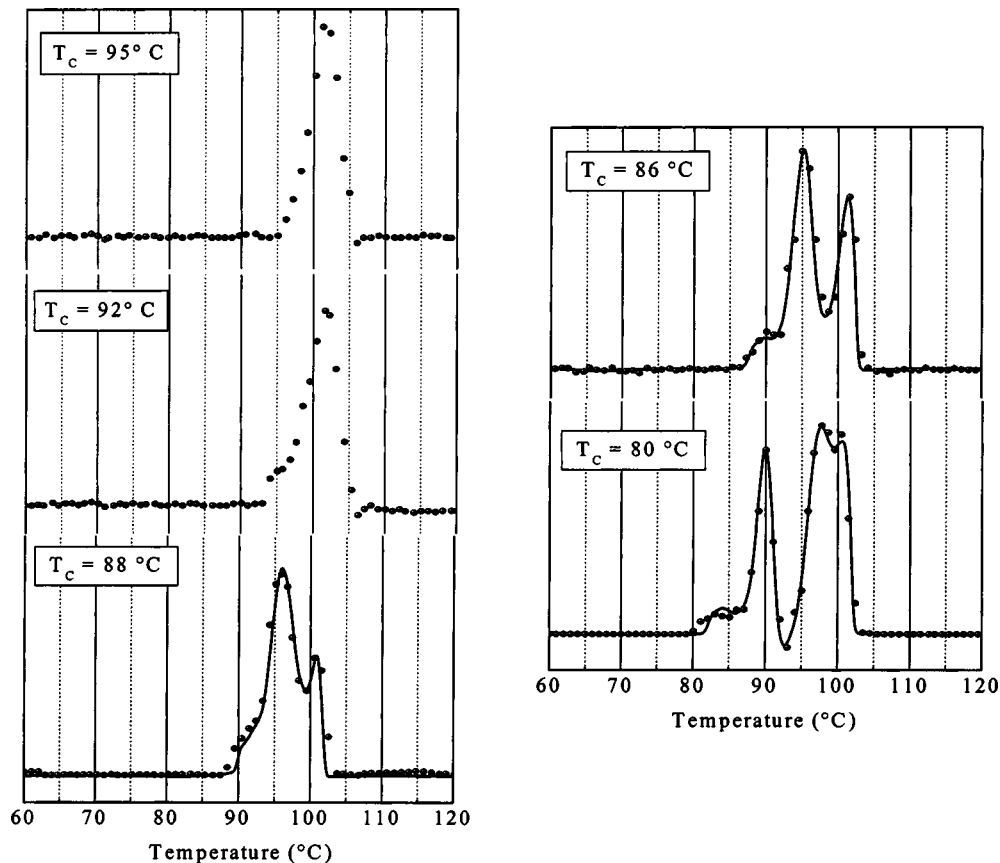


FIG. 4. Comparison of DSC (line) and EDXD (solid circles) measurements for the series of indicated T_c . EDXD data were slightly smoothed for a better understanding.

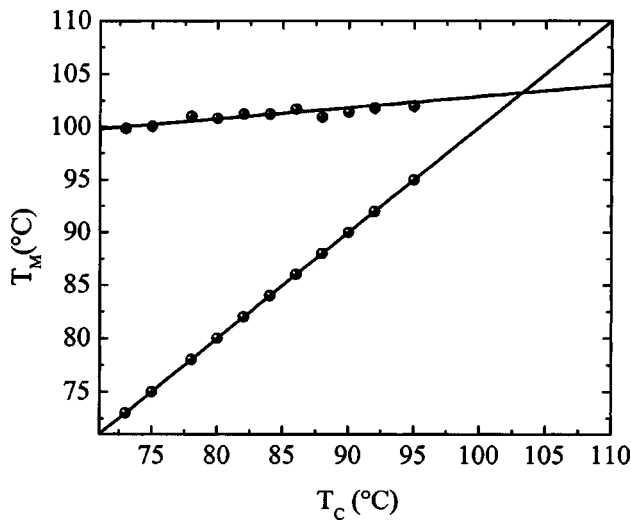


FIG. 5. Extrapolation of the polymer's theoretical melting temperature T_m .

tures (low undercooling). In the latter two cases, DSC measurements proved difficult to conduct because of the length of time required to achieve complete crystallization (Table II). By contrast, at very low undercooling ($T_c=92, 95\text{ }^\circ\text{C}$), EDXD-PT turned out to be an effective technique for investigating the melting behavior in a temperature range closer to the nominal T_m . In this way, the extrapolation error was reduced, thus increasing the accuracy in determining actual T_m , which was experimentally found to be about 103–104 °C (Fig. 5), appreciably lower than the nominal value (108 °C).

One advantage of the EDXD-PT over the DSC technique, discussed in a previous letter,¹² is its greater accuracy at low heating rates $\dot{T}(t)$. Indeed, the noise in DSC thermograms increases when $\dot{T}(t)$ is decreased. Conversely, as EDXD-PT is based on diffractograms collection, its performance is enhanced at lower $\dot{T}(t)$ since, under these conditions, acquisition time can be extended. For this reason, EDXD-PT is more reliable when phase transitions in qua-

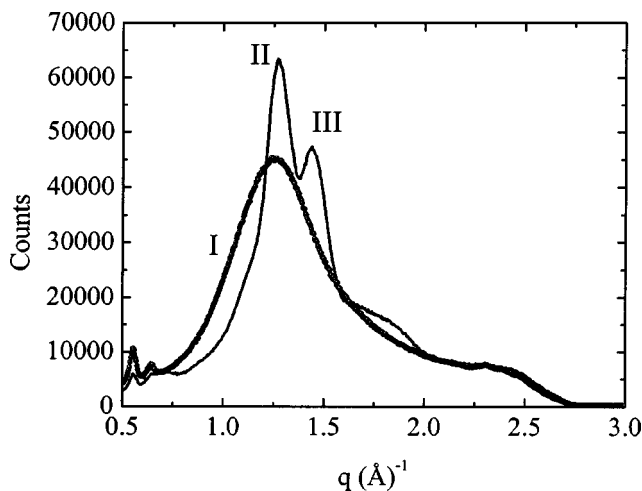


FIG. 6. Selection of first and last EDXD spectra. The q zones where the most significant intensity variations take place are labeled I, II, and III.

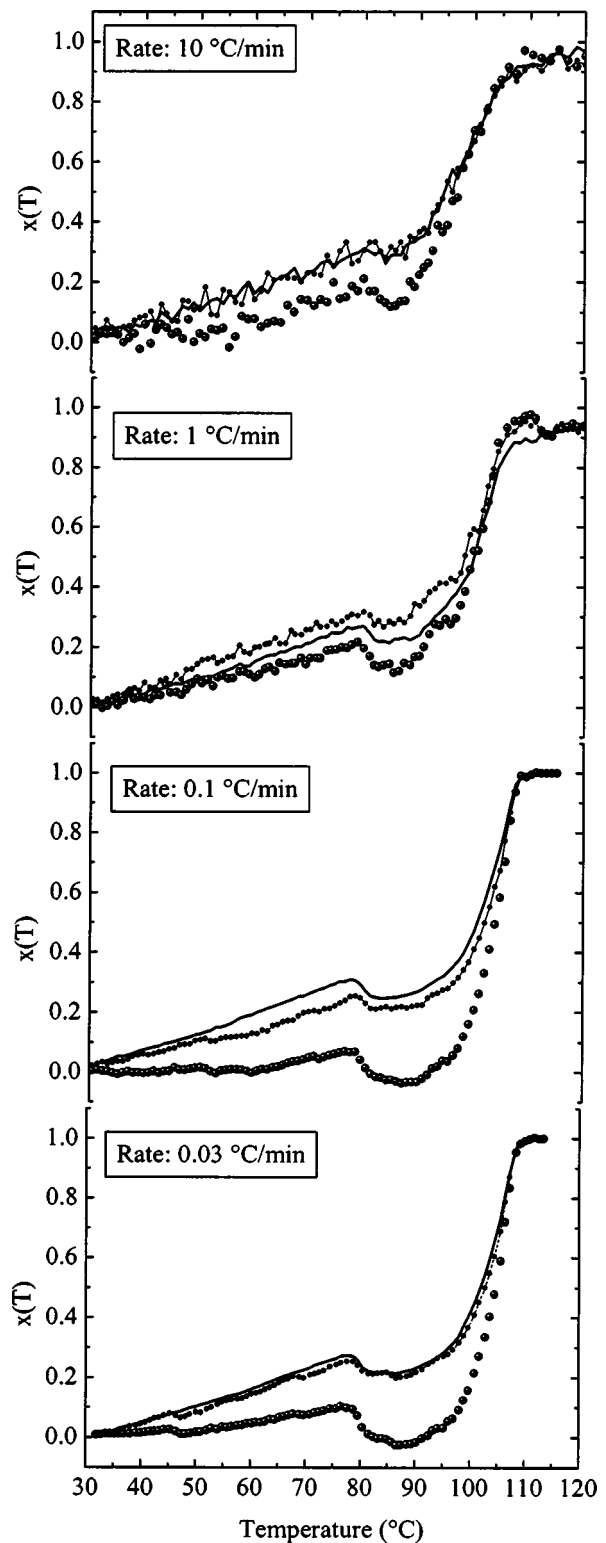


FIG. 7. Comparison of $x(T)$ curves obtained for zone I (solid line), zone II (open circles), zone III (line+circles) at heating rates indicated. Steps present in the small T range of graphs recorded at 0.03 °C/min are due to N_2 filling of detector.

sithermodynamic equilibrium, i.e., vanishingly small $\dot{T}(t)$, are to be studied.

A further peculiarity of the EDXD-PT method, not outlined in the past, is to be mentioned. It is that, even when the information obtained by EDXD-PT and DSC are of compa-

rable quality, namely at intermediate heating rates (in the present case about 1°C , see Fig. 4), the former can probe more deeply into the phase transition process. Indeed, as discussed earlier, the similarity of the two methods is due to the fact that the heat flux released by the sample in DSC and the modification in the diffraction pattern in EDXD-PT are both associated with the rearrangement of the constituents of the sample. But in DSC, the overall effect of these rearrangements can be observed in its entirety, since the heat emission is due to the contribution of any kind of change occurring during the phase transition. Instead, the various q zones distinguishable in the EDXD diffractograms are related to different distance ranges in the direct space. For instance, the modification of a diffraction pattern for small values of q indicates changes occurring preferentially at long interchain distances and vice versa. Therefore, another advantage of EDXD-PT is its ability to distinguish the structure transformation of the system at different distance ranges. In fact, by analyzing the variation of the diffracted intensity in different q zones during the phase transition, the velocities of rearrangements taking place at different scales can be monitored. In Fig. 6, three q zones are indicated, where the differences between the initial and final diffractograms are more pronounced. Despite the vicinity of these three zones, analysis using the EDXD-PT technique revealed a slight difference in the corresponding transition co-ordinates $x_i(T)$, $i = \text{I,II,III}$. In Fig. 7, the different behaviors are plotted versus heating rate for a sample crystallized at 60°C . The figure demonstrates that, for this kind of analysis too, EDXD-PT performance is significantly enhanced when heating rates are lowered, i.e., approaching the ideal quasistatic transformation, since the calculated $x(T)$ functions are smoother and their measurements are more reliable. Analysis of the $x(T)$ curve at $\dot{T}(t)$ of $0.03^\circ\text{C}/\text{min}$, indicates that the system undergoes a transformation that, at the intermediate distances, has a characteristic time that differs significantly from that at the shorter and longer distances (which show similar behavior). Indeed, observing Fig. 8 where $d[x(T)]/dT$ at $\dot{T}(t) = 0.03^\circ\text{C}/\text{min}$ is plotted, the highest (deepest) peak (minimum) belong to the curve obtained by analysis of intermediate distances. In this way, the capability of the EDXD-PT method in distinguishing the contribution to the overall entropy of transformations taking place at various distance-scales is shown.

Although these results should be considered as preliminary for the applications of EDXD-PT, the technique seem to be a promising tool for studying polymer transition kinetics.

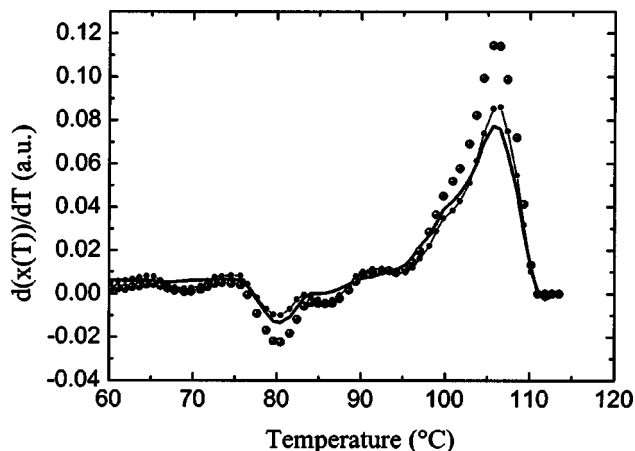


FIG. 8. First derivative of $x(T)$ corresponding to heating rate of $0.03^\circ\text{C}/\text{min}$. Symbols have the same meaning as in Fig. 7.

IV. CONCLUSIONS

We have conducted an investigation of the melting behavior of poly(ethylene-succinate) after crystallization progressively closer to its melting point. The problem of obtaining a quasihomogeneous structural phase, when the polymer is crystallized near to melting temperature, has been examined with the aid of the energy dispersive x-ray diffraction technique applied to phase transition. Critical comparison with the conventional differential scanning calorimetry technique, has pointed to the advantages of this method in selectively determining the transformation kinetics occurring on different scales.

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