

Energy dispersive x-ray diffractometry as a tool alternative to differential scanning calorimetry for investigating polymer phase transitions

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Recently, a technique based on energy dispersive x-ray diffraction has been proposed to follow the polymer phase transitions. However, the potentialities of this method were not clear, as well as the experimental conditions in which it is more convenient than differential scanning calorimetry, generally used for the same purpose. In the present letter, the answer to this question is provided. It is shown that the two methods are complementary, rather than equivalent, the heating rate being the relevant parameter to establish which is preferable. The demonstration of this statement is given through the observation of the complex thermal properties of a reference sample studied in both ways at progressively lower heating rates. The connection between such unusual application of x-ray diffraction and the differential scanning calorimetry is discussed in terms of the two possible definitions of entropy. © 2002 American Institute of Physics. [DOI: 10.1063/1.1447317]

The standard method to study the thermal properties of a system undergoing phase transitions is differential scanning calorimetry (DSC) performed by submitting the sample to a temperature ramp. The result of a DSC measurement is a thermogram whose peaks (minima) represent the heat flux absorbed (released) from the system during an endothermic (exothermic) phase transition. However, the heat flux detected in a DSC experiment is just an indirect effect of the phase transition occurring in the sample and no information can be attained on what kind of structural rearrangement took place. A structure-sensitive technique would provide a deeper inspection in the transition phenomena if it could be used to get, as the final result, information similar to DSC. Indeed, the method we propose has these characteristics. It is based on the energy dispersive variant¹ (referred to as EDXD) of the conventional (angular dispersive) x-ray diffraction technique.

It consists of collecting a diffraction pattern by measuring the energy spectrum of a polychromatic x-ray beam scattered by the sample. When phase transitions have to be studied, EDXD has some advantages over the angular dispersive x-ray diffraction technique, which are connected to the higher energy of the photons contained in the polychromatic primary beam. The advantages are an x-ray absorption decrease, an expansion of the accessible q interval in the reciprocal space, and the immobility of the experimental apparatus during data collection. Furthermore, the comparison among the diffraction patterns, which are collected exactly in the same conditions, is very reliable. On the other hand, the main drawback of EDXD, i.e., the decrease of q resolution, is not serious in the case of a system like polymers that produce rather broad diffraction peaks.

The EDXD-based method for phase transitions² was applied to investigate the thermal behavior of a poly [ethylene-succinate] (PES) sample. A collection of diffraction patterns was acquired during the PES sample heating, by irradiating it by a sequence of x-ray “flashes.” The patterns represent snapshots of the evolving system taken in the reciprocal space. Directly from them, a transition coordinate $x(t)$, defined as the fraction of the system mass that has turned into the final phase at time t , can be calculated according to the theory described elsewhere,³ no data processing or corrections for spurious effects being required. In the transition coordinate is concentrated all the information about the sample structural evolution. The use of this method provides an alternative way to investigate the phase transitions, as easy as DSC, since it completely bypasses the difficulties usually connected with x-ray diffraction studies. In the case where the EDXD-polymer transition method (PT) is used, the equivalent of the DSC thermogram curve is represented by the derivative of the transition coordinate.⁴

The connection between the two methods can be explained in terms of the relation between the two definitions of entropy, i.e., in thermodynamics and in statistical mechanics. A peak (minimum) of a DSC thermogram represents the flux of enthalpy absorbed (released) in a phase transition and corresponds to a proportional change of thermodynamic entropy since, during a first order transition, the temperature remains unchanged. On the other hand, according to the ensemble-invariant definition of entropy S in statistical mechanics,⁵

$$S_N = - \frac{k_B}{N!} \int \dots \int f_N^{(N)} \lg[h^{3N} f_N^{(N)}] d\mathbf{r}_1 d\mathbf{p}_1 \dots d\mathbf{r}_N d\mathbf{p}_N,$$

where f is the phase-space density of probability for the system particles. During a transition the part of f representing the (temperature-dependent) moment distribution does not

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change for the same reason as before, and the entropy increase is related to the modification of the system configuration only. Therefore, by using the expansion of entropy in series of the correlation function integrals,⁶

$$S = S^{(1)} + S^{(2)} + \sum_{k>2} S^{(k)}.$$

The first order term (ideal gas contribution)

$$S^{(1)} = Nk_B \left[\frac{3}{2} - \lg(\rho_N \Lambda^3) \right], \quad \text{with } \Lambda = \frac{h}{\sqrt{2\pi k_B T}}$$

is unchanged as well, while the variation of the second order term

$$S^{(2)} = \frac{1}{2} k_B \rho^2 \int \dots \int g^{(2)}(\mathbf{r}_1, \mathbf{r}_2) \lg g^{(2)}(\mathbf{r}_1, \mathbf{r}_2) d\mathbf{r}_1 d\mathbf{r}_2$$

depends on the pair correlation function $g^{(2)}$ only. Since the latter gives the overwhelming contribution to the total entropy change⁶ for insulating materials like ordinary polymers, a probe that is sensitive to $S^{(2)}$ variation is suitable to accurately measure the total entropy change. This probe can be represented by x rays, whose normalized diffracted intensity contains exactly the Fourier transform of the pair correlation function.

However, this equivalence does not imply that there is no difference between DSC and EDXD-PT from the experimental point of view. This can be explained by an elementary example, supposing that the speed of a moving object is to be measured. Two methods are possible for doing this, i.e., to record the value of a quantity directly connected to the speed (for instance, the rotation angle of a tachometer hand) or the positions of the object as a function of time and, then, to calculate its derivative. In principle, the same value of the speed should be provided by both methods, but the errors will generally be different. In particular, in limit conditions, one method can become much more reliable than the other. If the speed to be measured is very low, the quantity connected to the speed will remain almost unchanged with respect to its static value (the hand of the tachometer will almost not move), so that a precise determination of the speed is difficult. Instead, in this condition, the positions of the object can be accurately measured, as well as the value of the speed obtained from deriving it. The same difference applies when the phase change of a system is measured at very low scanning rates. The DSC signal is proportional to a heat flux, namely to a derivative, while diffractograms depict the “instantaneous” arrangement of the system components, like in the case of the positions.

The consequence is that, each time the DSC heating rate is lowered, the heat is released slowly and the difference of temperature between the sample and the reference in the calorimeter becomes small making the thermogram noisy. Instead, by using the EDXD-PT technique at low heating rates, the diffractograms can be collected for longer times, improving the statistics and, consequently, decreasing the error on the transition coordinate derivative. Therefore DSC is recommendable when fast and approximate estimates of the temperature are required; the EDXD-PT, when a slow and precise determination is needed, that is to say, in quasi-iso-

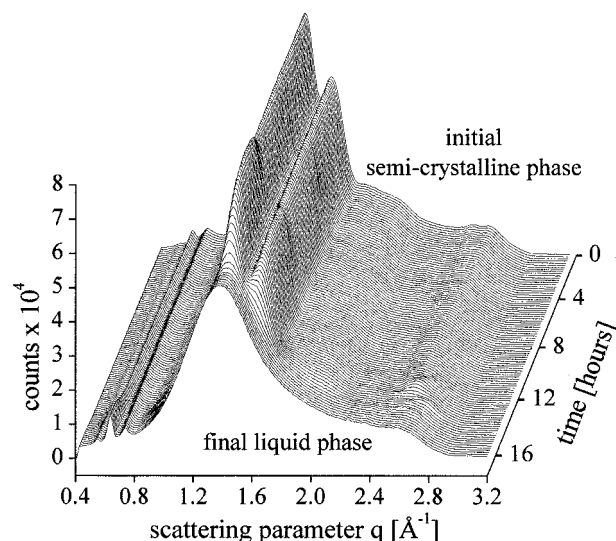


FIG. 1. Sequence of the EDXD spectra. Data refer to the experiment carried out at the heating rate of 0.03 °C/min.

thermal transformations when the thermodynamic equilibrium conditions are approached. From this point of view, the EDXD-PT is an alternative to the precision calorimetric measurements (sometimes improperly substituted by DSC) because of the expense and difficulties associated with them.⁷

The correctness of this discussion was checked by applying the two methods to the PES reference sample. PES is particularly suitable for this purpose, since it belongs to the class of semicrystalline polymers that exhibit the phenomenon of multiple melting upon heating.⁸ In this way, the ability of the EDXD-PT in reproducing the intensity and the position of the various peaks as they appear in the DSC thermogram can be suitably tested.

Sequences of diffraction patterns were collected at the heating rates α [°C/min]=0.03, 0.1, and 1. In Fig. 1, the sequence corresponding to 0.03 °C/min is shown, where the (unprocessed) diffracted intensity is represented as a function of the scattering parameter q (normalized momentum transfer) and of the heating time. In this case, the acquisition time is 33 min for each spectrum. For the other sequences, the collection time was progressively decreased to leave the total number of patterns unchanged: 10 and 1 (min) for 0.1 and 1 (°C/min), respectively. Therefore plots analogous to that in Fig. 1 were obtained for the other heating rates, the difference being the increased statistical noise of the patterns.

In Fig. 1 it can be seen that the main change in the polymer structure upon melting is concentrated in the 1.2–1.6 (\AA^{-1}) range, where the two main crystal reflections finally merge into the broad 1.3 \AA^{-1} peak (while a minor change is visible also around 2.5 \AA^{-1}). However, the method takes into account any variation of diffraction patterns and is able to reveal even small changes not easily detectable by comparing the patterns taken at various temperatures. The peaks in the 0.4–0.8 (\AA^{-1}) range are the fluorescence lines of the W anode x-ray tube and do not depend on the sample structure (therefore not included in data processing).

In Fig. 2, the transition coordinates are plotted as a function of temperature. By definition, their value is 0 when the sample is in the initial semicrystalline state and 1, when the melting is concluded. Decreasing the heating rate, the $x(T)$

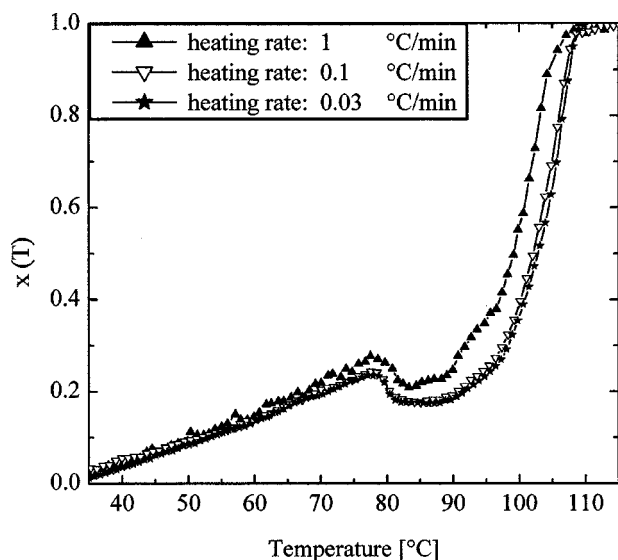


FIG. 2. The $x(T)$ curves plotted as a function of temperature at the various heating rates.

profiles tend to collapse on an asymptotic curve that represents the quasistatic melting process in reversible thermodynamic conditions. The derivatives of $x(T)$ (connected with time derivatives through the heating rates) are drawn in Fig. 3 and compared with the corresponding DSC thermograms, except for 0.03 °C/min because this rate is below the sensitivity of standard calorimeters. As expected theoretically, the trend of the statistical noise in the two kinds of curves is opposite, showing the antagonist behavior of the two techniques.

From $dx(T)/dT$ plots, a progressive disappearing of the endothermic peak with increasing α can be noted at about 88 °C. In fact, such effect seems to be already suggested by the DSC thermogram at 0.1 °C/min, but the critical working conditions for a DSC make this observation uncertain. In the literature,⁹ the intensity of this peak was related to the melting of a lamellar structure formed under suitable crystallization conditions. The present finding may suggest that the appearance of this peak is not a consequence of the crystallization conditions only but, rather, the result of the combined effects of crystallization and of the heating procedure to which the sample is submitted during the measurement. If so, in order to minimize the perturbation on the system, the necessity of investigating samples with these characteristics at heating rates lower than those generally used in DSC

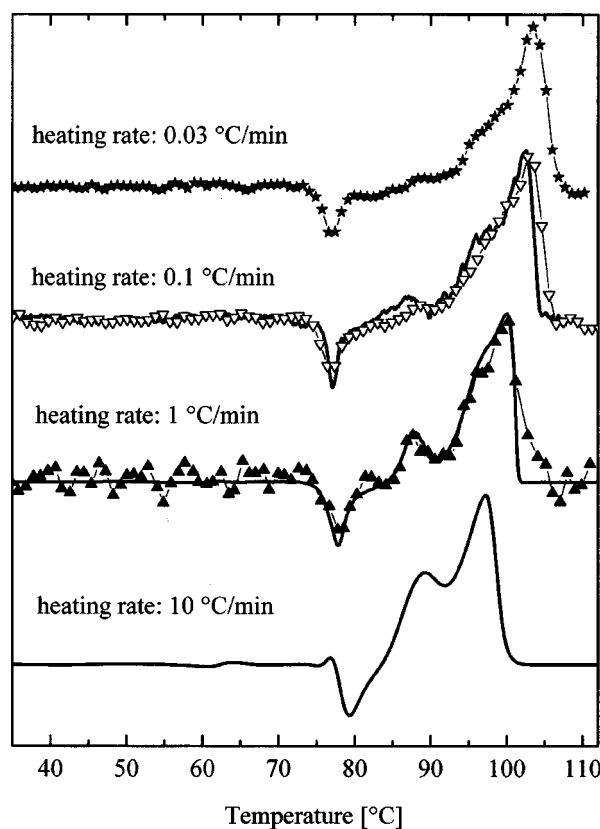


FIG. 3. Comparison between DSC thermograms (lines) and $dx(T)/dT$ curves (lines+symbols) as a function of temperature at each heating rate.

scans becomes evident. From this respect the EDXD-PT technique appears as a promising candidate to perform high accuracy phase transition studies.

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