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A NON-ISOTHERMAL TECHNIQUE USING THERMAL X-RAY DIFFRACTION TO FOLLOW THE KINETICS OF POLYMER CRYSTALLIZATION, SOLID STATE PHASE TRANSFORMATIONS AND THE DETERMINATION OF THE LENGTH OF THE CRYSTALLINE SEGMENT*

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ABSTRACT

We previously introduced a non-isothermal technique using TGA to study the kinetics of solid–solid transformations. TGA can only be applied to systems undergoing weight change. For this reason, a technique using Thermal X-ray Analysis (TXA) was developed. The technique involves the determination of the % crystallinity vs. temperature curve and its first derivative. The following equation was derived and found to be applicable.

$$\log\left[-\frac{\mathrm{d}(I_a^c/I_s^c)/\mathrm{d}T}{I_a^c/I_s^c}\right] = \log(Z/a) - \frac{\Delta H^*}{2.3RT}$$

The Klug and Alexander technique for the quantitation of a crystalline compound in a powder mixture using an internal standard was used to determine the crystallinity of each sample studied. The technique was applied to the phase transformation for a semicrystalline, low density, chemically cross-linked polyethylene polymer. The enthalpy for the crystalline–amorphous transformation was found to be 13.2 kcal/equiv. For a high density, non-crosslinked polyethylene, the enthalpy was 20.8 kcal/equiv. A technique to calculate the length of the crystalline segment from the kinetic data was also developed and showed that the crystalline lengths were 65 and 30 Å, respectively.

INTRODUCTION

Quantitative analytical chemistry has great difficulty in distinguishing the chemical identity of the various phases in a mixture, and in determining the precise

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amounts of each phase present. Powder X-ray diffraction analysis, on the other hand, is seemingly the perfect technique for crystalline mixture analysis, since each component of the mixture produces its characteristic pattern independently of the others, making it possible to identify the various components. Moreover, the intensity of each component's pattern is quantitatively related to the amount present. Quantitative X-ray analysis provides the advantage of being specific, and no chemical isolation or treatment of the sample is necessary. Therefore, it can be applied directly to a complex mixture of different crystalline forms of the same compound and in the presence of other diluents[12-29]. In addition, it provides an automatic means for analyzing any changes occurring due to solid interactions or transformations in the mixture.

The application of the powder method to quantitative analysis has been recognized ever since the discovery of this method, but practically no attempts at such analysis were made until 1936 when Clark and Reynolds[1] published a description of a procedure for estimating the amount of silicon dioxide present in mine dust. This work, and other work following, was based upon microphotometric density measurements of X-ray film following exposure. This method of measuring the intensity of diffracted X-ray was highly inaccurate and it was not until the advent of the Geiger Counter Spectrometer[2] that truly quantitative diffractions became possible. Alexander and Klug[3] published an important fundamental paper in which the mathematical relationships pertinent to quantitative diffraction analysis were derived. The paper also described conditions under which standard curves alone could be used, and under which standard curves based on internal standards were required, depending upon absorption effects. This pioneering work stimulated others to use the powder method for quantitative analysis with the result that the literature now abounds with descriptions of procedures and their application of quantitative diffraction to inorganic compounds but only a few to organic compounds.

Christ et al.[4] applied the quantitative diffraction technique to determine sodium penicillin G, while Kumano and Tamura[5] applied it to analyse the α and β forms of the crystals in chloramphenicol palmitate. Papariello et al.[6] investigated the possibility of using quantitative X-ray diffraction to analyse intact tablets. Kuroda and Hashizume[7-11] analysed the active components in ointments and vaginal tablets. Shell[13] and Kuroda et al.[14] showed that the X-ray diffraction technique was useful for the assay of active components in suspensions.

The purpose of this paper is to present a mathematical model derived to study the kinetics of phase transformation from single crystal or powder and polymer crystallization using thermal X-ray diffractometry. The model is a non-isothermal one and involves the use of both the integral curve (of percentage crystallinity change as a function of temperature) and the instantaneous first derivative.

THEORY

A single crystal has a number of parallel planes, oriented differently from one another, each set having a constant *d* spacing between its parallel planes. Diffraction from any single set of parallel planes is possible when the crystal is properly oriented with respect to an X-ray beam. If a sample consists, not of a single crystal, but of a large number of small crystals packed together with random orientation, all possible orientations of single crystals will be presented to a fixed X-ray beam. When the diffraction occurs at a given 2θ value, it does so because a sufficient number of crystals have the same set of planes whose d spacings correspond to the X-ray beam. The intensity of the diffracted ray is a function of the amount of material so oriented. If truly random orientation is assumed (with minimum preferred orientation), except for absorption effects, the diffracted intensity becomes proportional to what may be termed the specific lattice volume. It is highly significant that when the intensity of a single diffraction peak is measured at a fixed 2θ value, both additive and constructive effects are being measured. This unique fact is the basis for the specificity of quantitative diffraction analysis.

The theory of quantitative X-ray diffraction analysis was authoritatively considered by Alexander and Klug[3]. If we assume that the sample is a uniform mixture of n components with a particular size small enough that microabsorption effects are negligible, and the sample is well packed in such a thickness as to give maximum diffracted intensities with minimum preferred orientation, the intensity of a diffracted beam shall depend on[15] the intensity and wavelength of the incident beam, the crystal structure, i.e. the arrangement of atoms within a unit cell, the volume of the diffracting crystals, the diffraction angle, the absorption of X-ray radiation by the crystals and the experimental arrangement used.

The relationship between the diffracted intensity and the above named factors can be written as

$$I_{(hkl)} = \frac{I_0 cm[F_{(hkl)}]^2 L_p}{\mu} \cdot V \tag{1}$$

where I_0 is the direct-beam intensity, c an experimental constant having the same value for all reflecting planes, μ the linear absorption coefficient, $[F_{(hkl)}]$ the structure factor, which depends on the atomic arrangement in a unit cell (constant for a constant set of planes), V the total volume of the diffracting crystals, L_p the Lorentz polarization factor (constant for a constant set of planes), and m the multiplicity of the reflecting planes, that is, the number of planes in a crystal having identical interplanar spacings.

Since the absorption coefficients of the constituents of the two phases are different, the intensity of a refraction from the (hkl) planes of compound A, I_a, in such a mixture can be expressed by

$$I_a = \frac{k_a V_a}{\mu} \tag{2}$$

where μ is the linear absorption coefficient of the mixture (which is equal to the average value of μ_a and μ_b for two component mixtures of A and B) and k_a is a constant given by eqn. (3) where V_t is the total volume.

$$k_a = I_0 \, cm[F_{(hkl)}]^2 \, V_t L_p \tag{3}$$

Equation (2) predicts that if the linear absorption coefficient is negligable, a plot of I_a versus V_a will yield a straight line. However, in most cases, the linear absorption coefficient is not negligible and the linearity of I_a versus V_a cannot be obtained[12]. Therefore, Alexander and Klug[3] introduced eqn. (4) to solve this problem by adding a fixed amount of internal standard (S) to the mixture.

$$V_a = \frac{k_s V_s}{k_a(1 - V_s)} (I_a/I_s) \tag{4}$$

Where the subscript s indicates the internal standard (S) and the subscript a indicates the phase (component A).

The internal standard has to be properly chosen in order for eqn. (4) to give a straight line. Even though no one compound can meet all the qualifications of an ideal internal standard, one should try to use a standard with a maximum finding of the following characteristics. The diffraction peak is not obscured by matrix peaks and does not interfere with the peaks of the materials to be analysed. Its peaks are of relative height and close to the usable peak of the analysed ingredient. It should be chemically stable and consist of elements of low atomic numbers. It has high crystal symmetry, preferably cubic so that strong but few diffraction peaks are produced and it has a density not too far away from those of the system ingredient in order to maintain the homogeneity in mixing and to use the weight percentage rather than volume percentage in the construction of the calibration curve.

In the case of the use of X-ray to follow the phase transformation

$\text{phase}_1 \rightarrow \text{phase}_2$

and if phase_1 can be followed by measuring the crystalline fraction, V_a, [using eqn. (4)] as a function of temperature, then the rate of phase_1 disappearance can be written as

$$\frac{dV_a}{dt} = -\,kV_a^{t,T} \tag{5}$$

Using eqns. (4) and (5), we get

$$\frac{k_s V_s}{k_a(1 - V_s)} \frac{d(I_a/I_s)}{dt} = -\,\frac{k_s V_s}{k_a(1 - V_s)} k(I_a/I_s)$$

Therefore

$$\frac{d(I_a/I_s)}{dt} = -\,k(I_a/I_s) \tag{6}$$

where k is the specific first-order constant, $(I_a/I_s)^{t,T}$ is the percentage crystallinity of phase_1 in the presence of phase_2 at time t, and temperature T K. A more useful version of this equation for the studies reported in this communication can be obtained by converting the time derivative of the observed change in the phase to the temperature derivative. The results are shown in the equation

$$-\frac{(\mathrm{d}I_2/I_s)^{t,T}}{\mathrm{d}T}=\frac{k}{a}(I_2/I_s)^{t,T} \qquad (7)$$

where a is the heating rate given by $\mathrm{d}T/\mathrm{d}t$.

If the process is considered to be continuous with the X-ray intensity as a function of temperature, and its first derivatives are simultaneously traced on the same recorder, then, under non-isothermal conditions, the calculated % crystallinity, $(I_2/I_s)^{t,T}$, observed at time t, and temperature T, will be given by

$$-\frac{\mathrm{d}(I_2/I_s)^{t,T}}{\mathrm{d}T}=\frac{Z}{a}\mathrm{e}^{-\Delta H^*/RT}(I_2/I_s)^{t,T} \qquad (8)$$

Taking the logarithm of eqn. (8)

$$\log\left[\frac{-\,\mathrm{d}(I_2/I_s)^{t,T}/dT}{(I_2/I_s)^{t,T}}\right]=\log\frac{Z}{a}-\frac{\Delta H^*}{2.303\ RT} \qquad (9)$$

A plot of $\log\{[-\ \mathrm{d}(I_2/I_s)^{t,T}/\mathrm{d}T]/(I_2/I_s)^{t,T}\}$ versus $1/T$ K will yield a linear function for a single process of slope $-\ \Delta H^*/2.303R$ and an intercept of $\log(Z/a)$.

Equation 9 requires that both the integral curve, of the X-ray intensity, as a function of temperature, and the instantaneous first derivative are available. The integral curve could be obtained either by a continuous tracing of the X-ray intensity, at constant 2θ, at a particular heating rate as a function of temperature, or by measuring X-ray intensity of a particular percentage crystallinity at a constant temperature (for the same 2θ) and then plotted to give the integral curve. The integral curve is then differentiated to give its simultaneous derivative. The differentiation could be done simultaneously by specific instrumentation as we measure the X-ray intensity as a function of temperature, by computer fitting, or by glass rod diffraction technique. Care should be taken in the case of computer fitting as a slight deviation could lead into a significant effect on the calculated differential curve. In the case of the construction of the integral curve, the heating rate, a, is a constant value which does not affect the calculated enthalpy, but affects the intercept of the obtained non-isothermal plot.

The equation is not limited to studying the phase transformation but can also be used to study interaction in the solid states.

For the isothermal condition, the integration of eqn. (5) gives eqn. (10).

$$\ln(I_2/I_s)=-\ kt+\ln(I_{\mathrm{obs}}^{t=0}) \qquad (10)$$

From eqn. (10), a plot of $\ln(I_2/I_s)$ versus time will yield a straight line with a slope equal to the rate constant, $-k$. This process should be repeated at different temperatures. The van't Hoff plot ($\log k$ versus $1/T$ K) should be constructed to obtain the enthalpy for the phase transformation involved in the temperature region of the isothermal studies.

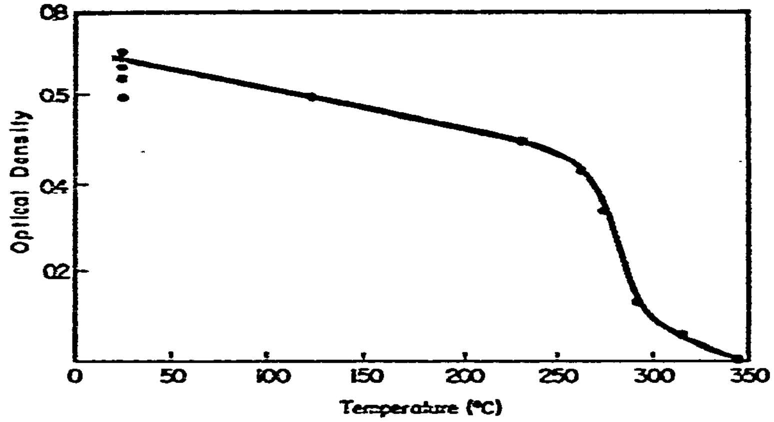


Fig. 1. Reflection intensity of the layer line (*hkl*) vs. temperature in a single crystal of barium sodium niobate. The disappearance above 300 °C shows the change in translational symmetry which occurs along (001) at the ferroelastic transition.

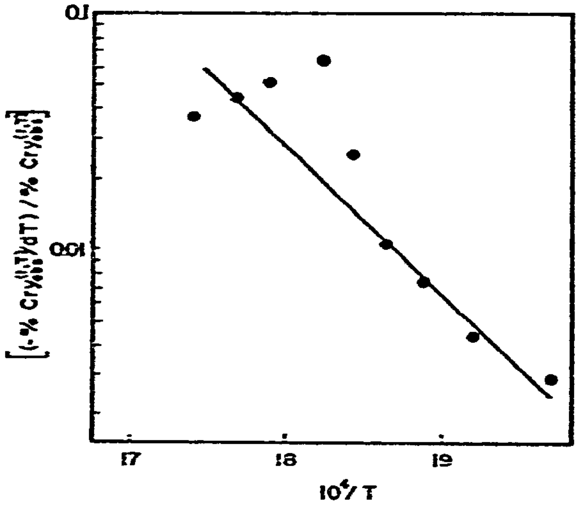


Fig. 2. Non-isothermal plot of ferroelastic transition of barium sodium niobate from single crystals.

RESULTS AND DISCUSSION

The kinetics of the ferroelastic transition of barium sodium niobate from single crystals using thermal X-ray diffraction

Burgent and Toledano[16] studied the ferroelastic transformation of barium sodium niobate from a single crystal, mounted in a goneometer parallel to the (001) plane using a Weissenberg camera, as a function of temperature. The sample was heated by dry nitrogen gas and the temperature was probed by a copper–constant thermocouple positioned about 1 mm from the crystal. The ferroelastic transformation of barium sodium niobate from orthorhombic to tetragonal involving the symmetry change 4mm → mm2 is given in Fig. 1. Figure 1 shows the reflection intensity along the (001) plane versus temperature in a single crystal of barium sodium niobate. This

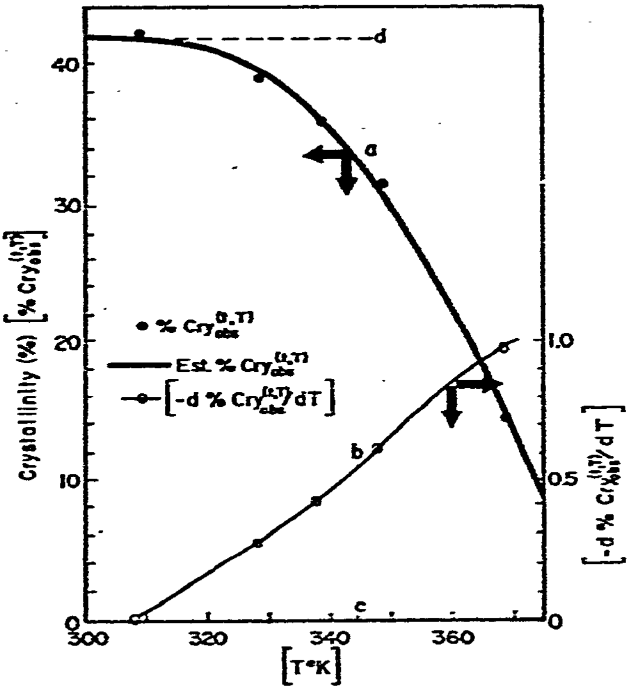


Fig. 3. Thermal X-ray data of low density cross-linked polyethylene (XLPE) phase transformation and its first derivative curve.

integral curve was differentiated by the diffraction glass rod technique and from the integral curve, its instantaneous derivative and eqn. (9), Fig. 2 was obtained. Figure 2 shows the non-isothermal plot of the ferroelastic transformation of barium sodium niobate obtained according to eqn. (9). The plot shows a linearity between the left-hand side logarithmic form of eqn. (9) and $1/T$ at low temperatures (up to 270°C). Above that, deviation from linearity was observed. The calculated enthalpy for the phase transformation of the first segment was 14.5 kcal/mole which agrees with the value obtained from data by Toledano and Schneck[17], analyzed by a hybrid form[18] of eqn. (9), for the same phase transformation using optical measurement.

Kinetics of polymer crystallization

Low density chemically cross-linked polyethylene (XLPE) and high density polyethylene were used as model compounds to study this system. The percentage crystallinity of XLPE was determined at temperatures from 35 to 95°C by X-ray crystallography with a Philips X-ray diffractometer and copper radiation. The 110 and 200 crystalline reflections and amorphous scatter were recorded. The reflections were resolved into Gaussian peaks and converted to intensities. The data were then computer fitted according to a polynomial regression program and the instantaneous differential curve was obtained. Figure 3 shows a plot of percentage crystallinity as a function of temperature, its computer fit, and the first derivative of the produced curve. The first derivative is considered to be the simultaneous derivative.

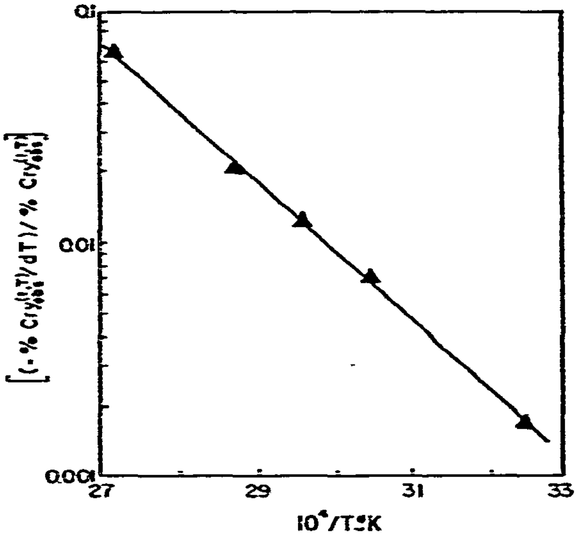


Fig. 4. Non-isothermal plot of low density cross-linked polyethylene (XLPE) phase transformation (crystalline phase to amorphous phase).

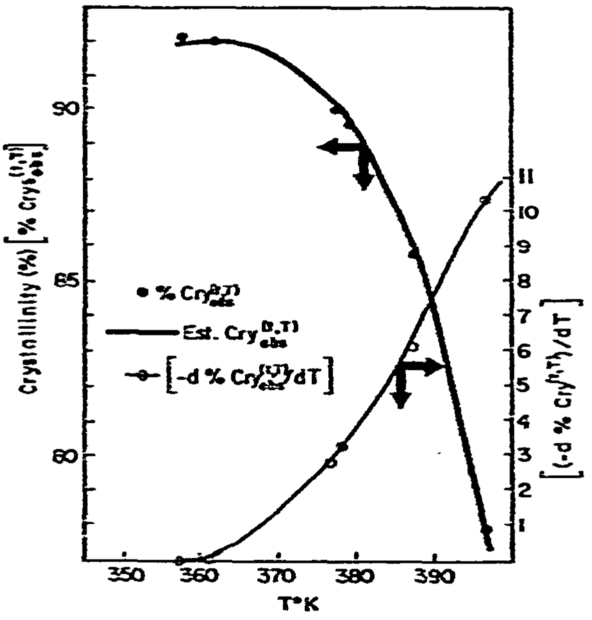


Fig. 5. Thermal X-ray data of high density polyethylene phase transformation with its first derivative curve.

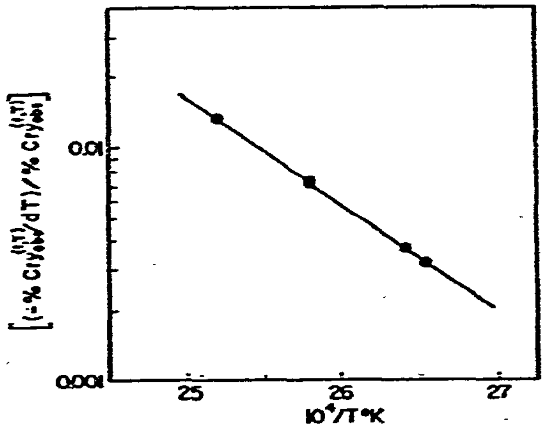
From Fig. 3, the percentage crystallinity at point a is $(I_a/I_s)^{t,T}$ and its first derivative at point b is given by bc, $\mathrm{d}(I_a/I_s)^{t,T}/\mathrm{d}T$. This procedure is repeated across the graph, and the value of $\{[\mathrm{d}(I_a/I_s)^{t,T}/\mathrm{d}T]/(I_a/I_s)^{t,T}\}$ is plotted on semilogarithmic paper versus $10^4/T$. Figure 4 shows the non-isothermal plot of chemically cross-linked polyethylene (low density and semicrystalline). The calculated enthalpy of the crystalline to amorphous phase transformation obtained from Fig. 4 is equal to 13.2 kcal/cryst. equiv.

Figure 5 shows the change in the percentage crystallinity of high density polyethylene as a function of temperature and its computer fit as well as its instantaneous first derivative obtained by differentiating the produced *n*th polynomial equation. The change in the percentage crystallinity as a function of temperature was obtained from Richardson[19] using dilatometric measurement. From both the integral curve and the instantaneous first derivative curve in Fig. 5 and eqn. (9), the non-isothermal plot was obtained as shown in Fig. 6. The calculated enthalpy of transformation in this case was found to be 20.8 kcal/cryst. equiv.

It should be noted that, in the case of polymer decrystallization or crystallization, we are following the change in the configuration of the crystalline polymer to the amorphous form and the crystalline equivalent in our term will refer to the weight (g) of the stretched, linear, planar, crystalline segment. The ability to follow the crystallinity of the polymer can be important in characterizing the physical properties of that polymer as it will yield the kinetic parameters of these phase transformations. In addition, it will give insight to the length of the crystalline segment which can be an important parameter for the rate of polymer breakdown for a crystalline, biodegradable polymer.

A model for the determination of the length of the crystalline segment

The kinetic method we described before, which follows the phase transformation of crystalline to amorphous polymer system, provides a crystalline equivalent enthalpy, ΔH_1, (i.e. the enthalpy per crystalline equivalent in which the crystalline equivalent can be defined as the effective crystalline length within the polymer). On the other hand, adiabatic calorimetry provides the specific enthalpy, ΔH_2, for this



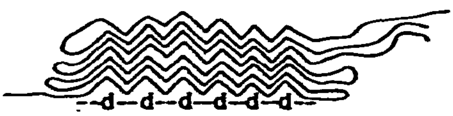


Fig. 6. Non-isothermal plot of high density polyethylene phase transformation.

Fig. 7. Schematic diagram of fully extended, planar zigzag conformation of a polymer crystallite.

TABLE 1

SUMMARY OF THE KINETIC ENTHALPY AND SPECIFIC ENTHALPY FOR LOW DENSITY CROSS-LINKED POLYETHYLENE (XLPE) AND HIGH DENSITY POLYETHYLENE

	ΔH_1 (cal/cryst. equiv. wt.)	ΔH_2 (cal/g)
XLPE (low density)	13,200	21
PE (high density)	20,800	72

transformation (cal/g). Therefore, using these two enthalpies, one could determine the weight of the crystalline segment, W_s, as given in eqn. (11).

$$W_s = \Delta H_1/\Delta H_2 \tag{11}$$

From the morphology of polyethylene[20], it is well understood that the polymer is present in fully extended, planar, zigzag conformation and crystallizes from melt either in fringed micelle[21], lamellae sharp folds, switch-board model, loose loops with adjacent reentry or a combination of several features[22, 28]. All these models have one thing in common, that the polymer chains are precisely alike over distances corresponding to the dimensions of the crystallites. Figure 7 presents a sketch of one of these crystallities to develop our model which accounts for the lengths of the crystalline segments. As shown in Fig. 7, for every *nd* Å length increase or decrease, *n* (Equiv. wt.) will crystallize or decrystallize (where *d* is the distance between every two alternating carbon atoms within polyethylene and *n* is the number of *d*'s in the crystalline segment). From eqn. (11), the number of the equivalent weights, *n*, in the crystalline equivalent is given in eqn. (12) and the length of the crystalline segment is given in eqn. (13).

$$\mathrm{n} = \frac{(\Delta H_1/\Delta H_2)}{\text{Equiv. wt.}} \tag{12}$$

$$\text{length of cryst. segment} = \frac{(\Delta H_1/\Delta H_2)d}{\text{Equiv. wt.}} \tag{13}$$

Table 1 shows the summary of the kinetic enthalpy and specific enthalpy for both low density XLPE and high density polyethylene obtained from Figs. 4 and 6. Using these data and eqn. (13), it was found that for XLPE

$$\text{length of the cryst. segment} = \frac{2.9122(13200)}{28\ (21)} = 65\ \text{Å}$$

and for polyethylene

$$\text{length of the cryst. segment} = \frac{2.9122(20800)}{28\ (72)} = 30\ \text{Å}$$

The value of *d* was calculated from the geometry of polyethylene, assuming that the length of the C–C bond is 1.54 Å and the angle between C–C–C is 109°.

It is apparent that eqn. (13) will provide the determination of the length of the crystalline segment and therefore we could monitor the length as a function of the experimental condition. This, in turn, will provide a good way for characterizing the physico-chemical properties of the polymer.

In summary, we have extended our mathematical approach introduced[23–26] to follow the kinetics of polymer crystallization and phase transformation using thermal X-ray analysis. In addition, we were able to introduce a new technique to calculate the length of the crystalline segment in a polymer. This is important as we feel that, not only will it be used as a physico-chemical parameter, but also it will provide (from the pharmaceutical point of view) a control of the drug release from a drug-biodegradable polymer system.

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