Available online at www.sciencedirect.com
SCIENCE DIRECT
ELSEVIER
Polymer 46 (2005) 9523–9528
polymer
www.elsevier.com/locate/polymer

Polymer Communication

Mechanism of secondary crystallisation in irradiated and aged ultra high molecular weight polyethylene

D. Barron, C. Birkinshaw*

Department of Materials Science, University of Limerick, Plassey, Limerick, Ireland

Received 14 July 2005; received in revised form 18 August 2005; accepted 25 August 2005

Abstract

Ultra high molecular weight polyethylene has been irradiated in air and aged for 168 months. On melting and recrystallisation in the differential scanning calorimeter a secondary crystallisation event is observed around 80 °C. This event has been studied using isothermal crystallisation and the results analysed using the Avrami equation and the Lauritzen–Hoffman approach. This suggests that during this event growth occurs through regime II kinetics whereby large numbers of surface nuclei form on the substrate, with multiple nucleations acts commencing before the previous ones have finished. It is postulated that this secondary crystallisation event involves the development of a diffuse semi-ordered interface between the well-developed lamellae and the amorphous phase.

Keywords: Ultra high molecular weight polyethylene; Crystallisation; Irradiation

1. Introduction

Ultra high molecular weight polyethylenes (UHMWPE) typically have number average molecular weights of several million, as measured by light scattering, and on cooling from above T_m crystallisation is hindered by limited chain mobility. One of the important uses of these materials is as bearing surfaces in artificial joints and for this application they are sterilised by γ irradiation using received doses of between 2.0 and 5.0 Mrad. The free radical population arising from irradiation causes, amongst other things, time dependent inter-lamellae tie chain scission with a consequent increase in crystallinity and associated mechanical property change on ageing [1–3]. Much recent work has been concerned with establishing radiation conditions which will drive the photochemical processes towards property stabilising cross-linking reactions and away from damaging photo-oxidative scission [4,5], and although many structure-property studies have now been reported with these materials the nature of the crystallisation processes are still not fully understood. Crystals are small and difficult to resolve, with no evidence of spherultic structures being found in melt crystallised materials. In medical applications, particulate wear debris has been identified as a concern [6–9] and generation of debris and long term performance are thought to be influenced by the irradiation and crystallisation conditions, and so the nature of the crystallisation processes are of both technological importance and scientific interest.

Table 1 gives some detail of crystallinity change on irradiation and ageing and Fig. 1 compares melting and recrystallisation curves for control and irradiated aged materials. The small low temperature peak on the recrystallisation curve is always observed in aged irradiated materials and is the subject of examination here. It is not clear whether this peak represents a crystal perfection process or the formation of a second population of crystals, and the objective of this investigation was to see if application of the Lauritzen–Hoffman approach to analysis of this secondary crystallisation could yield useful insight to the process.

The crystallisation kinetics of polymeric materials under isothermal conditions for various modes of nucleation and growth can be approximated by the Avrami equation [10,11].

$$\theta = \exp(-kt^n) \tag{1}$$

Where θ, is the volume fraction not transformed at time t, k is the kinetic rate constant and n is the Avrami exponent. This exponent is related to the nucleation and growth processes and k is a function of nucleation and growth rates and usually follows an Arrhenius relationship with temperature. The equation can be modified to indicate the degree of crystallinity

---

* Corresponding author.
E-mail address: colin.birkinshaw@ul.ie (C. Birkinshaw).

0032-3861/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2005.08.078

Table 1
Crystallinity values for control and irradiated (10 Mrad) UHMWPE

Material	% Crystallinity
Control	47
Irradiated (2 months)	55
Irradiated (168 months)	61

χ, and take into account the induction time to nucleation t_I [12]:

$$\chi = 1 - \exp\{-k(t - t_i)^n\} \tag{2}$$

Although the end result is an over simplification of crystallisation the equation is usually found to represent a good fit with the data. This has been shown to be a consequence of the strong correlation between t_I, the induction time of nucleation, and k and n [13,14]. The kinetic parameters are determined by taking the log of Eq. (1):

$$\log(-\ln(1 - \chi)) = \log k + n \log(t - t_i) \tag{3}$$

Thus, a plot of $\log(-\ln(1-\chi))$ vs. $\log(t - t_i)$ should yield a straight line of slope n and intercept log k if Avrami theory is applicable. Possible values of the Avrami exponent and their relation to various types of nucleation and growth processes are given in standard texts.

Lauritzen and Hoffman have formulated chain-folding kinetics to describe the crystal growth of macromolecules from the melt and these are based on nucleation theory and subsequent growth [14]. The polymer molecule is assumed to have a cross sectional area ab, a surface nucleus of fixed thickness b and height l that is fixed at a specified undercooling and grows along the g direction, where a is the width of the molecule. Overall growth is in the G direction, which is perpendicular to g. The Lauritzen–Hoffman growth rate of polymer crystals is defined by:

$$G = G_0 \exp\left[\frac{-U^*}{R(T - T_\infty)}\right] \exp\left[\frac{-A}{T(\Delta T)f}\right] \tag{4}$$

Where G_0 is a pre-exponential factor containing quantities not strongly dependent on temperature, U^* is a 'universal' constant characteristic of the activation energy of chain motion (reptation) in the melt, R is the gas constant, T is the crystallisation temp, T_∞ is the theoretical temperature at which all motion associated with viscous flow or reptation ceases, A is the nucleation parameter, $\Delta T = T_m^0 - T_c$ the undercooling, T_m^0 is the equilibrium melting temperature, and $f = 2T/\left(T_m^0 + T\right)$, a temperature correction factor.

The crystal growth process involves two steps; the deposition of the first stem on the growth front ('secondary nucleation process') and the attachment of subsequent stems in the chain on the crystal surface ('surface spreading process').

For regime I (rapid substrate completion) each surface nucleation act rapidly leads to a new layer of thickness b and length l at the surface growth front before a new nucleation act occurs. This leads to relatively smooth growth surface over the length L and $G_I = ibL$ where i is the nucleation rate. A from Eq. (4) is thus defined as:

$$A_{(I)} = \frac{4b\sigma\sigma_e T_m^0}{(\Delta h_f)k} \tag{5}$$

Where b is the layer thickness, σ is lateral surface free energy, σ_e is the fold surface free energy, T_m^0 is the equilibrium temperature, Δh_f is the enthalpy of fusion and k is Boltzmann's constant.

For regime II, large numbers of surface nuclei form on the substrate at a rate I and spread slowly at a velocity g.

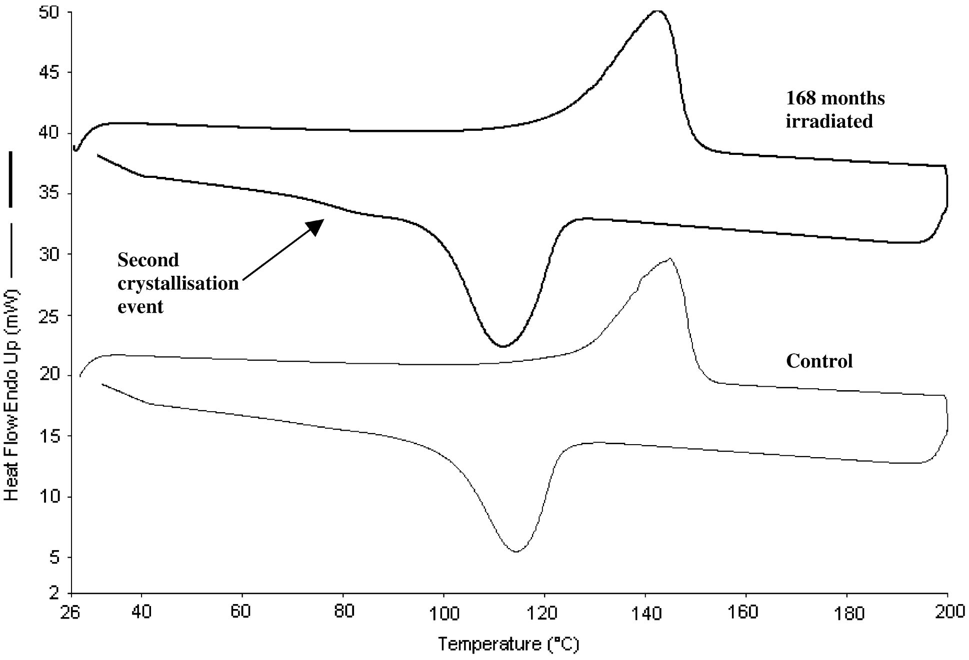

Fig. 1. DSC melt and recrystallisation of control and irradiated and aged for 168 months.

This results in multiple nucleation acts commencing before previous ones have finished. The newly formed surface is rough and uneven on a molecular scale. $G_{\mathrm{II}} = b(2ig)^{1/2}$, that is polymer crystal growth is proportional to the square root of the surface nucleation rate and A is thus defined:

$$A_{\mathrm{II}} = \frac{2b\sigma\sigma_e T_m^0}{(\Delta h_f)k} \tag{6}$$

It can be seen from the previous section that any change in the crystal growth regime present will alter the value of A. Taking the natural log of Eq. (4) results in a linear expression:

$$\ln G = \ln G_0 - \frac{U^*}{R(T - T_\infty)} - \frac{A}{T(\Delta T)f} \tag{7}$$

Therefore, a plot of $[1/T(\Delta T)f]$ against $[\ln G_0 + U^*/R(T - T_\infty)]$ will have a slope of $-A$ and an intercept of $\ln G_0$ [14,16] and the locations of the regimes are clearly illustrated by changes in the slope.

Before determination of any regime present, by means of the Lauritzen–Hoffman plot, the variable G, is estimated in the following manner. Crystal growth from the melt is generally considered to be heterogeneous in nature [15]. It has, therefore, been proposed that a proportionality exists between k, the kinetic constant and G, the linear growth rate, specifically that $k \approx G^{n+1}$ (where n is the Avrami exponent) [16]. While this relationship might not be theoretically demonstrable, it has been found to be a useful method of estimating G and determining the overall trends in the Lauritzen–Hoffmann plots and hence the crystallisation regimes present. The relationship is adapted in the following way:

$$k^{1/(n+1)} \approx G \tag{8}$$

Which leads to:

$$k^{1/(n+1)} = G_0 \exp\left[\frac{-U^*}{R(T - T_\infty)}\right] \exp\left[\frac{-A}{T(\Delta T)f}\right] \tag{9}$$

The isothermal data is plotted according to the Avrami equation. This allows values for k and n to be determined for various crystallisation temperatures. These values are then substituted into Eq. (9). Hoffman found that $U^* = 1500$ cal/mol and $T_\infty = T_g - 30K$ by fitting the crystallisation kinetic data for various polymers [14]. Eq. (9) is then used to create a plot of the general Lauritzen–Hoffman form. This allows any change in the crystallisation regime present to be observed as outlined previously.

2. Experimental

The material used was UHMWPE of molecular weight 3.5 milliong/mol (GUR 1020) and had been compression moulded. Irradiation was carried out in air using a Co60 source at a dose rate of 0.15 Mrad/h to give a received dose of 10 Mrad. Materials were then aged for 7 and 168 months.

A Perkin Elmer Pyris 1 DSC was used for crystallinity measurement and the heat of fusion for UHMWPE taken to be 291 J/g. The sample was heated at a rate of 20 °C/min to 180 °C and then held for 5 min to ensure complete melting, after which it was cooled rapidly (approximate rate 370 °C/min) to the isothermal target temperature. It is then possible to monitor the resulting crystallisation of the polymer as a function of time.

3. Results and discussion

Figs. 2–4 show that the minor crystallisation peak can be clearly observed using the isothermal crystallisation method and that the size of the peak is a function of ageing time. Fig. 5 shows an isothermal crystallisation series and from this data it is possible to estimate the degree of crystallisation, within this event, at time t.

Avrami plots of the isothermal crystallisation are linear and the exponent is approximately 1.5 at all temperatures suggesting mixed growth and crystallisation mechanisms at each temperature. Non-integer Avrami exponents occur regularly and have been attributed to both the decreasing density within growing spherulites with crystallisation time or to impingement of spherulites, or perhaps in this case

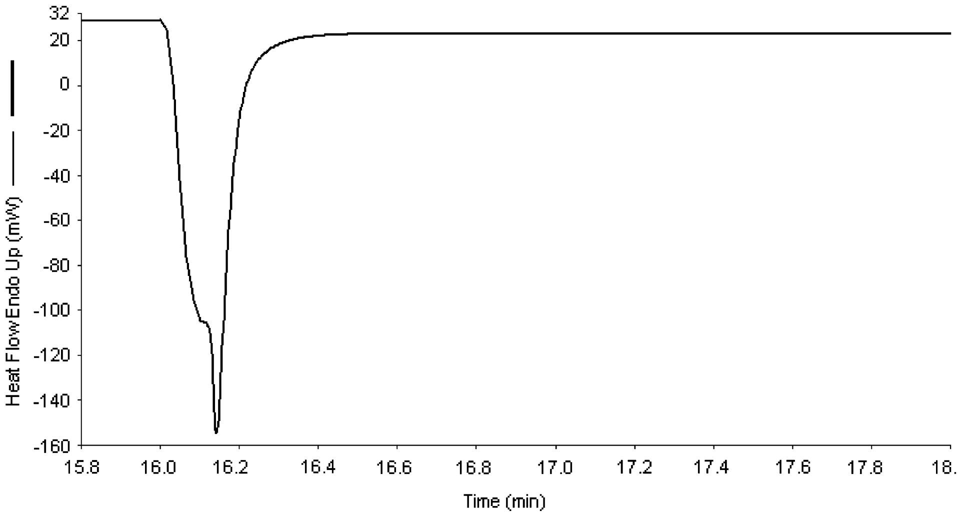

Fig. 2. Isothermal crystallisation trace of control (unirradiated) UHMWPE at 118 °C.

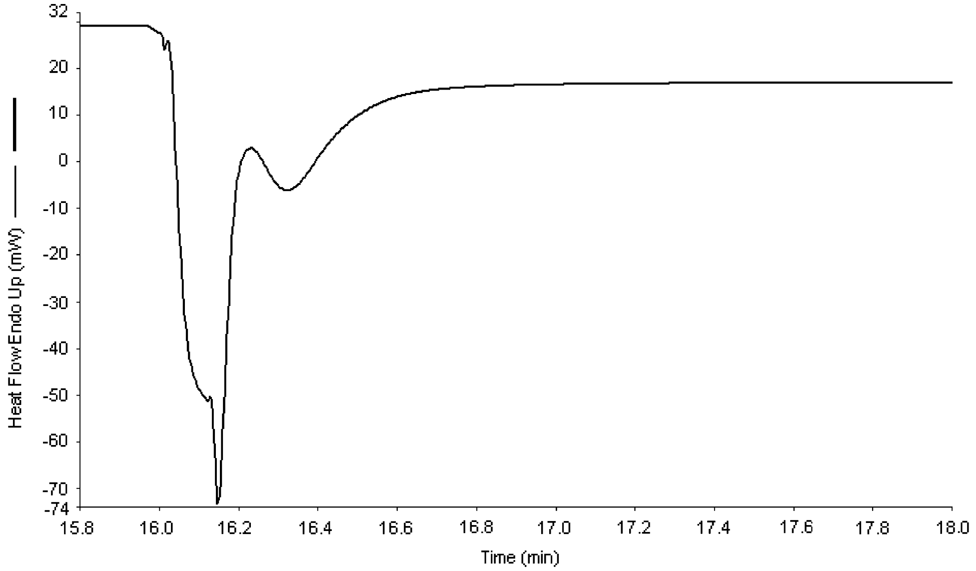

Fig. 3. Isothermal crystallisation trace of UHMWPE at 118 °C, irradiated (10 Mrad) and aged 7 months.

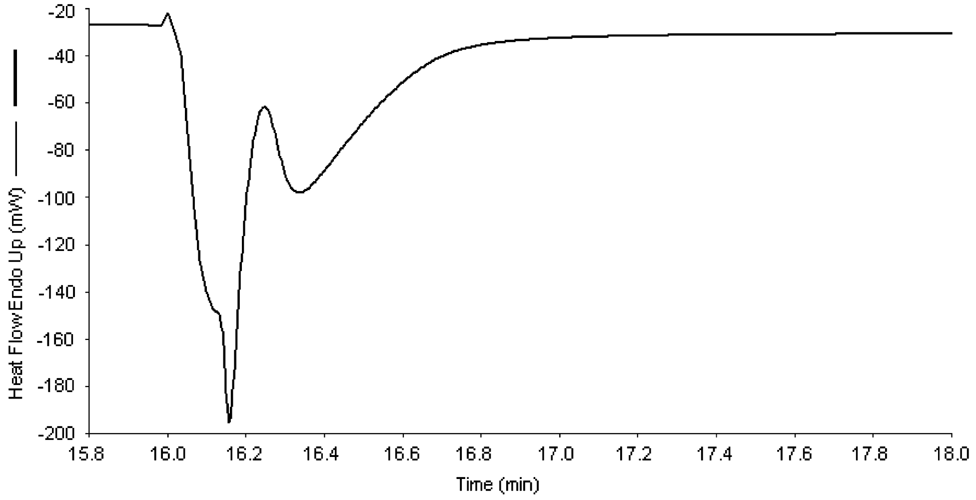

Fig. 4. Isothermal crystallisation trace of UHMWPE at 118 °C, irradiated (10 Mrad) and aged 168 months.

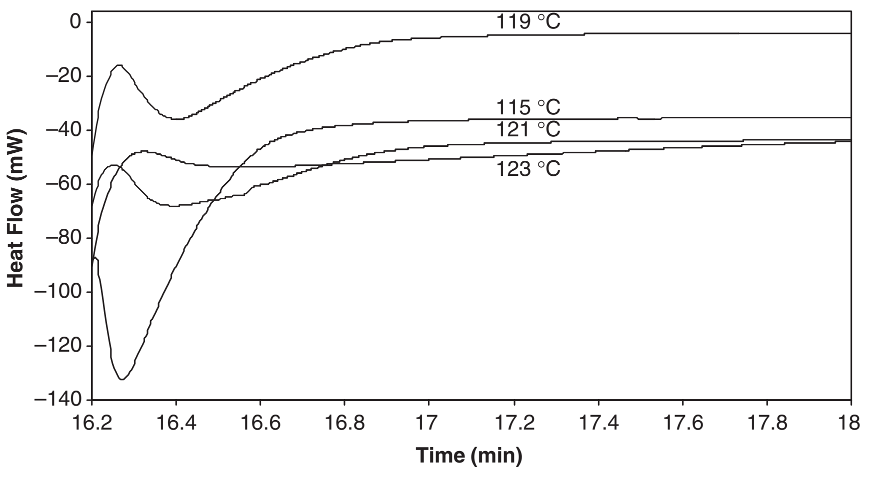

Fig. 5. Isothermal crystallisations of the minor crystallisation peak of irradiated UHMWPE aged 168 months.

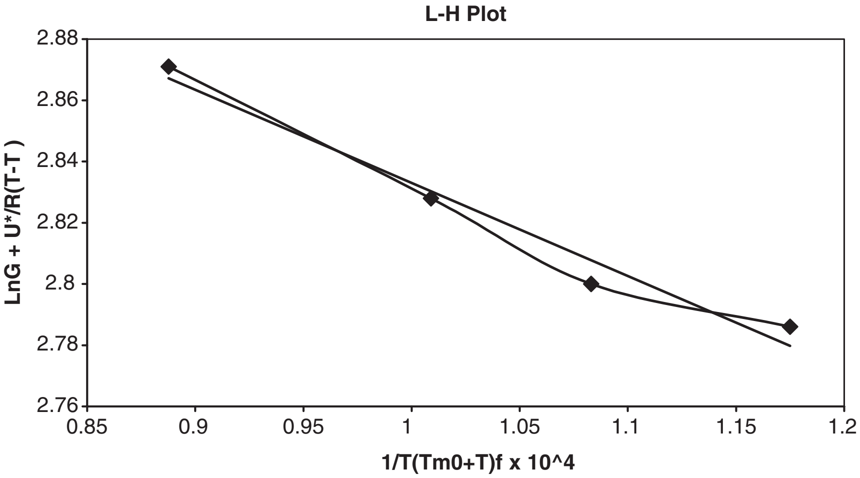

Fig. 6. *L–H* plot for second crystallisation event in UHMWPE irradiated (10 Mrad) and aged 168 months.

impingement of the growing lamellae, as spherulites are not seen in UHMWPE.

Using T_g and T_m^0 values from published experimental data [17,18], and estimating *G* using the kinetic constant *k*, Lauritzen–Hoffman plots can be prepared using the equations outlined above and this is illustrated in Fig. 6. For this second crystallising event the data predominantly follows a linear trend over a broad range of crystallisation temperatures, which suggests that Lauritzen–Hoffman theory is a suitable tool with which to examine the crystallisation kinetics.

It is possible to obtain an indication of whether crystallisation is regime I or regime II using the Lauritzen–Hoffman *Z*-test [14,18]. The *Z*-test equation is:

$$Z = \frac{iL^2}{4g} \tag{10}$$

Where *Z* is a dimensionless quantity, *L* is the substrate length and *a* is the fold width parallel to the growth face. *Z* can be approximated by:

$$Z \approx 10^3 \left(\frac{L}{2a}\right)^2 \exp\left[\frac{-X}{(T\Delta T)}\right] \tag{11}$$

For regime I, $X=A$, and $Z \leq 0.01$. For regime II, $X=2A$ and $Z \geq 1$. The value of *A* is determined from the slope of the *L–H* plot and substituted in to Eq. (11). Thus possible values of *L* are calculated for each regime. It is generally found that one regime will produce acceptable values of *L*, whereas the other will present unrealistic values. In this case for regime I, *L* was determined to be ≥ 23 μm and for regime II to be ≤ 2 μm, which is a more reasonable substrate length compared to the former, Lauritzen [18] stated that for low density polyethylene, using the '*Z*'-test equation the substrate length approximated to 1.4 μm. It is, therefore, possible to conclude, that during this secondary crystallisation event in irradiated and aged UHMWPE, growth occurs according to regime II kinetics whereby large numbers of surface nuclei form on the substrate, with multiple nucleation acts commencing before the previous ones have finished. The newly formed surface is rough and uneven on a molecular scale.

Intuitively this seems a reasonable result as the temperature of the event being studied is well below T_m^0 and nucleation events can be presumed to be abundant. The question remains as to the location of the process being studied, as to whether it is occurring as a separate crystallisation event occurring within the amorphous phase or is a growth process occurring on the surfaces of existing crystallites. There is some NMR data [19] to suggest that the crystal amorphous boundary region in these materials is large and diffuse, and this encourages a presumption that the event studied is a growth process on the surface of previously formed crystals. This will lead to such a semi-ordered boundary zone.

References

[1] Birkinshaw C, Buggy M, Daly S, O'Neill M. Effect of [gamma] radiation on the physical structure and mechanical properties of ultrahigh molecular weight polyethylene. J Appl Polym Sci 1989;38(11):1967–73.
[2] Birkinshaw C, Buggy M, Daly S, O'Neill M. Mechanism of ageing in irradiated polymers. Polym Degrad Stab 1988;22(3):285–94.
[3] Bhateja SK, Deurst RW, Martens JA, Andrews AH. Radiation induced enhancement of crystallinity in polymers. Macromol Chem Phys 1995; C35(4):581–659.
[4] McKellop H, Shen F, Lu B, Campbell P, Salovey R. Development of an extremely wear-resistant ultra high molecular weight polyethylene for total hip replacements. J Orthop Res 1999;17(2):157–67.
[5] Muratoglu OK, Bragdon CR, O'Connor DO, Jasty M, Harris WH. A novel method of cross-linking ultra-high-molecular-weight polyethylene to improve wear, reduce oxidation, and retain mechanical properties: recipient of the HAP Paul Award. J Arthroplasty 1999;16(2):149–60.
[6] Harris WH. The problem is osteolysis. Clin Orthop 1995;311:46–53.
[7] Kurtz SM, Muratoglu OK, Evans M, Edidin AA. Advances in the processing, sterilization, and crosslinking of ultra-high molecular weight polyethylene for total joint arthroplasty. Biomaterials 1999;20(18): 1659–88.
[8] Bradford L, Kurland R, Sankaran M, Kim H, Pruitt L, Ries M. Early failure due to osteolysis associated with contemporary highly cross-linked ultra-high molecular weight polyethylene. A Case Report. J Bone Joint Surg Am 2004;86(5):1051–6.

[9] Goldman M, Gronsky R, Ranganathan R, Pruitt L. The effects of gamma radiation sterilization and ageing on the structure and morphology of medical grade ultra high molecular weight polyethylene. Polymer 1996; 37(14):2909–13.
[10] Avrami M. Kinetics of phase change I. J Chem Phys 1939;7:1103–12.
[11] Avrami M. Kinetics of phase change II. J Chem Phys 1940;8:212–24.
[12] Cimmino S, DiPace E, Martuscelli E, Silvestre C. Syndiotatctic polystyrene: crystallization and melting behaviour. Polymer 1991;32: 1080–3.
[13] Binsbergin FL, De Lange BG. Heterogeneous nucleation in the crystallization of nucleated polypropylene. Polymer 1970;11:309.
[14] Hoffman JD, Davis GT, Lauritzen Jr JI. The rate of crystallization of linear polymers with chain folding. In: Hanney NB, editor. Treatise on solid state chemistry. NY, USA: Plenum Press; 1976. p. 467–614.
[15] Wunderlich B. Macromolecular physics. NY, USA: Academic Press; 1976 [chapter 6].
[16] Duff S, Tsuyama S, Iwamoto T, Fujibayashi F, Birkinshaw C. The crystallisation of blends of syndiotactic polystyrene and polyphenylene ether. Polymer 2001;42:991–1000.
[17] Shen FW, McKellop H, Salovey R. Morphology of chemically crosslinked ultra high molecular weight polyethylene. J Biomed Mater Res 1998;41(1):111–9.
[18] Hoffman JD, Frolen LJ, Ross GS, Lauritzen JI. On the growth rate of spherulites and axilites from the melt in polyethylene fractions: regime I and Regime II crystallization. J Res Nat Bur Std 1975;79A(6):671–99.
[19] O'Neill P, Birkinshaw C, Leahy JJ. Ageing characteristics of γ irradiated ultra-high molecular weight polyethylene. International conference on ageing studies and lifetime extension of materials, Oxford 1999.