

CHARACTERIZATION OF γ -IRRADIATED CRYSTALLINE POLYMERS II ISOTHERMAL CRYSTALLIZATION KINETICS OF γ -RADIATION INDUCED CROSSLINKED POLYAMIDE 1010

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ABSTRACT

Polyamide 1010 is a γ -radiation crosslinkable polymer. After irradiation, it is possible to raise its service temperature up to 240 °C. Network formation greatly changes the crystallization behaviour of the polymer. In the present work, DSC was used to examine its isothermal crystallization kinetics. It is found that in addition to the necessity of more undercooling and the lowering of crystallization rate, the primary crystallization stage of the irradiated polymer is shortened. This effect is more evident with increasing radiation dose and content of enhanced difunctional crosslinking agent. However, the crystallization mechanism of the primary stage is not changed as evidenced by the constancy of Avrami exponent. The lamella end surface free energy σ_e calculated according to Hoffman's equation is very sensitive to γ -radiation. It increases abruptly in 2—3 fold even though the radiation dose is not high enough. The origin of this phenomenon may be accounted for in terms of network structure of the polymer.

Polyamide 1010 (PA1010) is one of nylons specifically produced commercially in our country. In comparison with other polyamides, it features lower moisture absorption and thus higher dimensional stability. The additional hydrocarbon segments in the sebacic acid and decamethylenediamine give the polymer a lower melting point (190 ° vs. 265 °C for polyamide 66). However, by radiation crosslinking, high elastic state can be maintained up to 240 °C without flow^[1]. Thereby not only is its service temperature greatly increased, but it is also possible to be used as a heat shrinkable material. In the previous paper^[2], the use of constant cooling rate crystallization temperature to characterize the γ -radiation crosslinking of PA1010 was discussed. The present work reports the isothermal crystallization kinetics of γ -radiation crosslinked PA1010 and its mechanism.

The isothermal crystallization kinetics of polymer has been the subject of numerous studies^[3]. However, no work concerning the crystallization kinetics of γ -radiation crosslinked polymers and in particular of γ -radiation crosslinked polymers containing difunctional crosslinking agent has so far been published. The purpose of this work is to study the effect of radiation dose and content of crosslinking agent on the crystallization kinetics of PA1010 by using differential scanning

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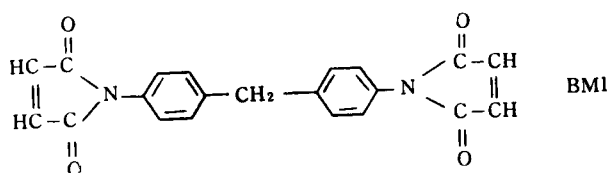
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calorimetry(DSC) technique. The kinetic parameters and surface free energy σ_e of lamella surface were evaluated. A discussion on the relationship between σ_e and the crosslinked structure of the irradiated PA1010 was made.

EXPERIMENTAL

Sample

PA1010 used in this study was a granular commercial product of Jilin Union Chemical Works, Jilin City. The granules were dissolved in hot ethanol under pressure and transformed into powdered sample after precipitation on cooling. The M_n determined by dissolving it in m-cresol was 1.34×10^4 ^[4]. N,N' - bismaleimide-diphenyl methane(BMI) was used as the enhanced crosslinking agent.



After mixing and grinding PA1010 powder with acetone solution of BMI in a mortar and vacuum drying, film sample of ~ 0.5 mm thickness was prepared by compression moulding at 220°C . The BMI contents of the specimens are tabulated in Table 1.

All irradiations were carried out at Co^{60} source in vacuum (1×10^{-3} torr) at room temperature.

Table 1 BMI contents of PA1010 samples

Sample	PA1010-1	PA1010-2	PA1010-3
BMI : PA1010 *	0 : 100	1 : 100	2 : 100

* weight ratio

DSC

The isothermal crystallization experiments were performed on a Perkin-Elmer differential scanning calorimeter (DSC-2C) interfaced with a 3600 TADS microprocessor. The temperature readings was calibrated by using standard indium and the precision of the readings was estimated to be better than $\pm 0.1\text{K}$. The

partial areas were evaluated with the software supplied by P-E Coporation(P-E part No:0419 — 0438). Sample weight, 8 — 12mg. At first, the specimen was melted by raising the temperature with a rate of 320K/min to a temperature ca. 20 — 30 °C above its melting point for a period of 5mins. Then the specimen was undercooled rapidly to the predetermined crystallization temperature T_c with a rate of 80K/min. Once T_c was reached the video of the processor began to display crystallization isotherm until the crystallization was completed or until any heat liberated was too small to be detected.

Analysis of the crystallization isotherms

The crystallization-time dependence was analyzed by means of Avrami equation^[5]

$$1 - \frac{X_t}{X_\infty} = \exp(-Kt^n) \quad (1)$$

where X_t and X_∞ are the weight fraction of crystallized material at time t and ∞ . K is the rate constant and n the Avrami exponent. Since DSC measures the rate of evolution of the enthalpy of crystallization(dH_t/dt) as a function of time, it was assumed that the relative extent of crystallization can be expressed by^[6]

$$X_t/X_\infty = \int_0^t (dH_t/dt) dt / \int_0^\infty (dH_t/dt) dt \quad (2)$$

No direct determination of the absolute heat or the degree of crystallinity is required(see Fig. 1)

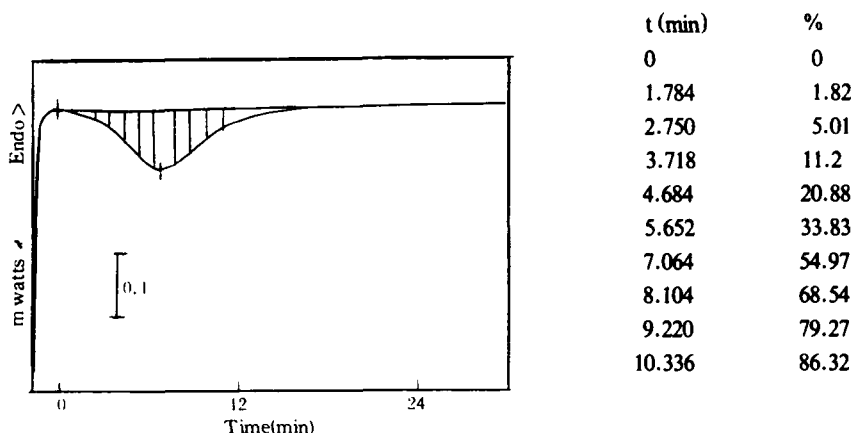


Fig. 1 Schematic illustration for the partial area evaluation of DSC crystallization isotherm

Accordingly, a plot of $\log(-\ln(1 - X_t/X_\infty))$ against $\log t$ is linear with a slope n .

The rate constant K was calculated from the half life time of the crystallization $\tau_{\frac{1}{2}}$ and n

$$K = \ln 2 / \tau_{\frac{1}{2}}^{\frac{n}{n-1}} \quad (3)$$

In order to explore the mechanism of the crystallization, Hoffman's ⁽⁷⁾ radial growth rate equation was used to analyze the relationship between the crystallization rate and the lamella surface free energy

$$G = G_0 \exp(-\Delta F^*/RT_c) \cdot \exp(-4b_0\sigma\sigma_e T_m^0 / \Delta h_f \Delta T k T_c) \quad (4)$$

where G is the radial growth rate, which can be expressed in terms of $K^{\frac{1}{n}}$ or $\tau_{\frac{1}{2}}^{-\frac{n-1}{n}}$; G_0 , a constant; ΔF^* is the free energy of activation for the transport process at the liquid-solid interface; b_0 is the distance between two consecutive monolayer fold planes; σ and σ_e are the lateral and fold surface free energies of the lamella respectively; T_m^0 is the equilibrium melting temperature; Δh_f is the enthalpy of fusion per unit volume; ΔT is the degree of undercooling ($= T_m^0 - T$); R and k are gas constant and Boltzman constant. In equation (4), the first exponential factor is called transference term and the second, nucleation term.

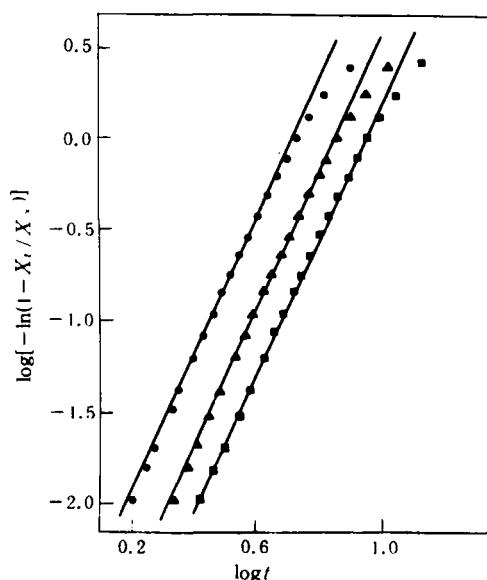


Fig. 2 $\log(-\ln(1 - X_t/X_\infty))$ vs. $\log t$ of unirradiated plain PA1010
 T_c (K) ● 458 ; ▲ 459 ; ■ 460

RESULTS AND DISCUSSION

1. Overall crystallization rate of PA1010 samples

(1) Unirradiated Plain PA1010

Shown in Fig. 2 are the $\log(-\ln(1 - X_t/X_\infty))$ vs. $\log t$ plots of plain PA1010, which was melted at 480K and crystallized at different T_c . It is evident that two processes are present, which could be separated on the time scale. At the primary stage, they are a set of straight lines with nearly the same slope. However, at high X_t/X_∞ , the data deviate from the line due to the onset of the secondary crystallization process. It suggests that the crystallization mechanism is changed. The primary crystallization kinetic parameters of plain PA1010 obtained by linear regression are listed in Table 2.

Table 2 Isothermal crystallization kinetic parameters of unirradiated Plain PA1010

T_c (K)	n	K (min^{-n})	$\tau_{\frac{1}{2}}^{-1}$ (min^{-1})
458	3.83	1.90×10^{-3}	0.214
459	3.84	5.58×10^{-4}	0.156
460	3.77	2.73×10^{-4}	0.125
461	3.73	3.73×10^{-5}	0.072
462	3.75	1.50×10^{-5}	0.057

From Fig. 2 and Table 2, it is noted that with the increase in T_c , crystallization rate is lowered, K decreases by ~ 2 order of magnitude, and $\tau_{\frac{1}{2}}^{-1}$ reduces by a factor of 4 in the range from 458 — 462K. Nevertheless, the value of n are little affected. Their mean value is 3.78 ± 0.06 . This fact indicates that the crystallization temperature has influence only on the crystallization rate, the mechanism of crystallization in the primary stage remains unchanged.

In the light of Avrami's assumption during the derivation of equation (1), n is relevant to the mechanism of crystallization and $n \simeq 4$ means three dimensional homogeneous nucleation^[5], but in the case of the present experimental condition, it is unlikely that homogeneous nucleation would occur^[8,9]. Since crystallization of high polymers is far more complicate than the model for the crystallization of small molecules proposed by Avrami, it is doubtful if a simple Avrami equation alone is capable of specifying the type of crystallization mechanism of bulk polymers. Despite this, however, the Avrami equation is justified as a convenient means to treat the empirical data of crystallization^[10].

(2) γ -Radiation crosslinked PA 1010 :

In the previous paper^[2], it was found that after irradiation, the crystallization

temperature of the irradiated PA1010 decreases with increasing radiation dose, i. e., more undercooling (or higher driving force for crystallization, $\Delta T = T_m^0 - T_c$, where T_c is the lowest crystallization temperature, at which a complete DSC crystallization isotherm could be obtained) is required for the formation of stable nuclei length l^* ^[7], for which the rate of formation of stable nuclei will be a maximum. Fig. 3 shows the relationship between radiation dose for different PA1010 samples and ΔT . Apparently, ΔT increases monotonously with increasing radiation dose.

Besides, the crystallization behaviour of the irradiated samples becomes more complicated, i. e., as compared with those of the unirradiated ones, the primary stage shortens and longer time is required to complete the crystallization process. This phenomenon will be more evident if the sample is subjected to more radiation dose (see Fig. 4 (a) and (b)).

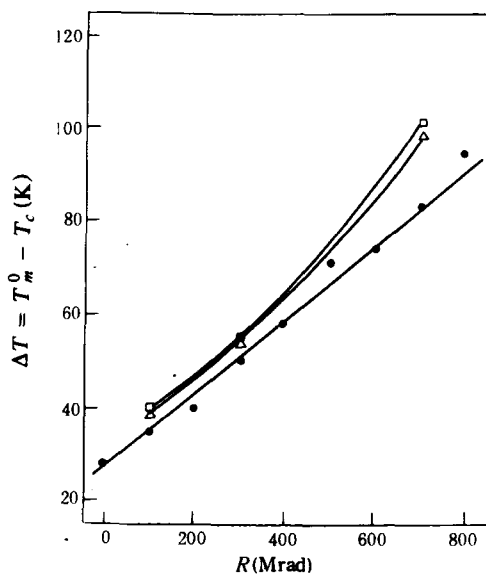
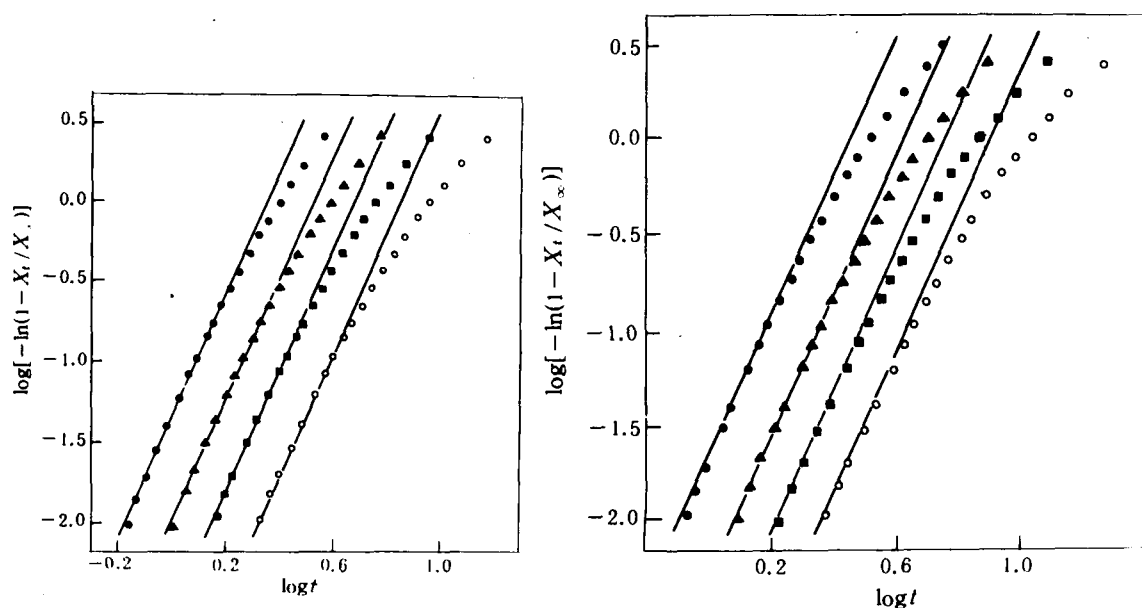


Fig. 3 Degree of undercooling for PA1010 samples subjected to different radiation dose.

● PA1010-1; △ PA1010-2; □ PA1010-3

The comparison of Fig. 2 with Fig. 4 shows that the discrepancy between them reflects the structural complexity of irradiated samples. For unirradiated PA1010-1, it is a linear macromolecule, and its chemical structure is homogeneous. Thus crystallization of PA1010-1 is simpler, and in the whole crystallization process, primary stage predominates (more than 90%). On the other hand, irradiated samples consist not only of the more dispersed linear molecules due to γ -degradation, but also of the branched and crosslinked molecules resulting from the action of γ -radiation. These structurally highly nonhomogeneous macromolecules possess their own specific crystallization behaviour. Thereby the irradiated sample shows a rather broad crystallization process. For example, with increasing radiation dose, the content of crosslinked network, and thus the restriction imposed by crosslinks on the motion of network chains increases. As a result, the "tailing effect" in the secondary stage becomes more pronounced. Listed in Table 3 are the crystallization kinetic parameters of PA1010-1 samples irradiated with different amount of radiation dose.

Fig. 4 Avrami plot of γ -irradiated PA1010-1

(a) 300 Mrads

 T_c (K)

● 437 ▲ 438 ; ■ 439 ; ○ 440

(b) 700 Mrads

 T_c (K)

● 404 ; ▲ 406 ; ■ 408 ; ○ 410

Table 3 Isothermal crystallization kinetic parameters of γ -irradiated PA1010-1

R (Mrad)	T_c (K)	n	K (min^{-n})	$\tau \frac{1}{2} \text{ (min}^{-1}\text{)}$
100	452	3.84	2.62×10^{-1}	0.776
	453	3.76	4.45×10^{-2}	0.482
	454	3.71	5.02×10^{-3}	0.265
300	437	3.75	4.74×10^{-2}	0.489
	438	3.77	1.07×10^{-2}	0.331
	439	3.77	2.85×10^{-3}	0.233
	440	3.70	6.70×10^{-4}	0.153
500	416	3.68	1.82×10^{-3}	0.199
	417	3.71	7.26×10^{-4}	0.157
	418	3.78	2.67×10^{-4}	0.125
700	404	3.75	2.11×10^{-2}	0.394
	406	3.79	4.68×10^{-3}	0.267
	408	3.69	1.54×10^{-3}	0.191
	410	3.70	4.47×10^{-4}	0.137

Apparently, for irradiated PA1010-1 samples, the temperature at which

isothermal crystallization would occur decreases rapidly with the increase in radiation dose. However, Avrami exponent n remained nearly unchanged. On the other hand, for a given irradiated sample, the effect of T_c on the value of K and $\tau_{\frac{1}{2}}^{-1}$ were the same as that of the unirradiated PA1010-1.

(3) PA1010 containing BMI :

Fig. 5 shows the Avrami plots for irradiated samples containing BMI (PA1010-3). As to sample PA1010-2, its crystallization behaviour is quite similar to PA1010-3.

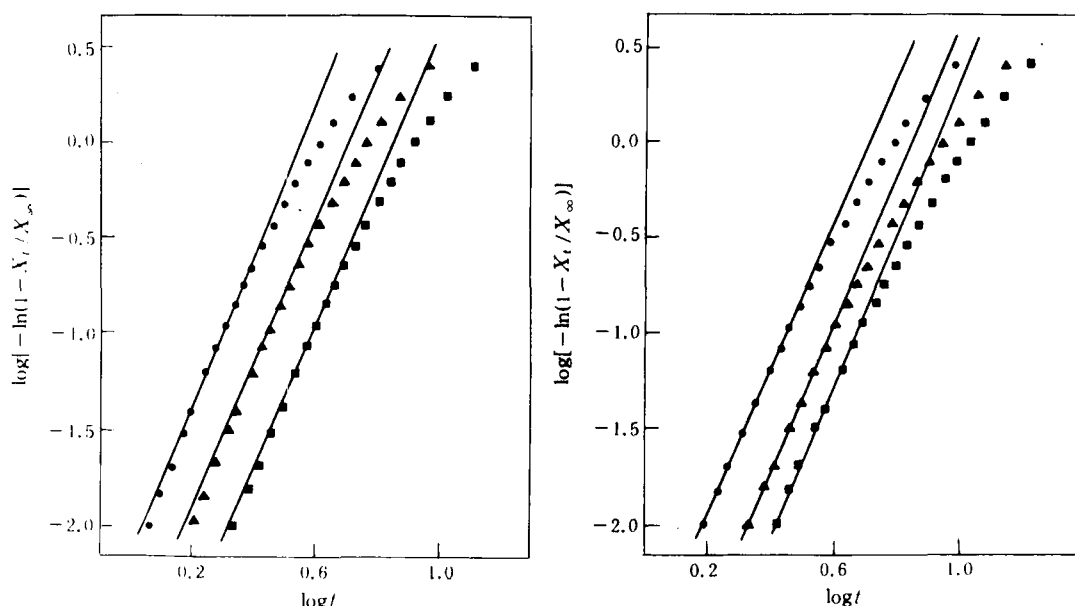


Fig. 5 Avrami plot of γ -irradiated PA1010-3

(a) 300 Mrads

T_c (K) ● 432 ; ▲ 433 ; ■ 434

(b) 700 Mrads

T_c (K) ● 388 ; ▲ 390 ; ■ 392

By comparing with Fig. 4, the addition of BMI leads the data points to deviate from the Avrami straight line at much lower dose. Besides, on the same dose level, there would be more ΔT with more BMI content (see Fig. 3). In Table 4, the isothermal crystallization parameters for samples PA1010-2 and -3 are listed.

In Table 4, it is noted that the addition of BMI accelerates the formation of crosslinked network. Therefore as compared with the plain PA1010 the presence of BMI causes the drastic lowering of T_c , K and $\tau_{\frac{1}{2}}^{-1}$. The effect is more pronounced with increasing BMI content. Nevertheless, the value of n is still unaffected. It indicates that for PA1010, neither γ -irradiation nor the addition of enhanced crosslinking agent BMI would influence the mechanism of crystallization. However, it should be emphasized that the value of n is derived merely from the primary stage, i.e., the stage conformed to the linear portion of Avrami plot. It is believed that in this stage, crystallization mechanism in all of the three case (plain, γ -irradiated,

Table 4 Isothermal crystallization parameters of γ -irradiated samples containing different amount of BMI

Sample	R (Mrad)	T_c (K)	n	K (min^{-n})	$\tau_{\frac{1}{2}}^{-1}$ (min^{-1})
PA1010-2	100	448	3.76	1.38×10^{-1}	0.651
		449	3.72	3.26×10^{-2}	0.440
		450	3.73	7.74×10^{-3}	0.300
		451	3.72	7.74×10^{-4}	0.161
	300	433	3.72	9.40×10^{-3}	0.315
		434	3.83	1.10×10^{-3}	0.186
		435	3.73	2.59×10^{-4}	0.121
		438	3.76	7.62×10^{-6}	0.048
	700	388	3.79	2.00×10^{-3}	0.214
		389	3.71	1.76×10^{-3}	0.200
		390	3.79	9.25×10^{-4}	0.174
PA1010-3	100	447	3.78	1.03×10^{-1}	0.604
		448	3.75	2.17×10^{-2}	0.397
		449	3.85	2.49×10^{-3}	0.232
	300	432	3.77	7.31×10^{-3}	0.299
		433	3.73	2.13×10^{-3}	0.212
		434	3.74	6.16×10^{-4}	0.153
	700	388	3.69	1.98×10^{-3}	0.204
		390	3.73	6.04×10^{-4}	0.151
		392	3.77	2.79×10^{-4}	0.126

and irradiated in the presence of BMI) remains unchanged, but as shown in Figs. 2, 4 and 5, γ -irradiation and the addition of BMI would increasingly shorten the primary stage and lengthen the secondary stage, which is usually proportional to the first power of logarithm time. Therefore, the "tailing effect" is more pronounced with the increase in radiation dose and the content of BMI.

2. Linear growth rate and lamella surface free energy

In order to further explore the detailed crystallization mechanism of different PA1010 samples the overall growth rate is converted into G through the relationship $G \propto K^{1/n}$ and equation (4) is modified in the following form

$$1/n \cdot \log K + E_D / 2.303RT_c = A + B \cdot 10^3 / T_c \Delta T \quad (5)$$

where E_D corresponds to ΔF^* in equation (4), A is a constant and slope $B = (4b_0 \sigma \sigma_e T_m^0 / 2.303 \Delta h_f \cdot k) \cdot 10^{-3}$. According to the empirical relationship proposed by Mandelkern^[11], E_D can be expressed in terms of T_m and T_g

$$E_D / R = 5.3 \cdot T_m^2 / (T_m - T_g) \quad (6)$$

By plotting $1/n \cdot \log K + E_D/2 \cdot 303 R T_c$ of all of the three samples against their respective $10^3/T_c \cdot \Delta T$, a set of fairly straight lines were obtained. As an example, the plot of equation (5) for unirradiated PA1010-1 sample is shown in Fig. 6.

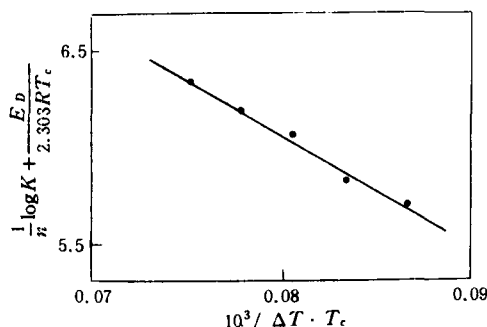


Fig. 6 The plot of $1/n \cdot \log K + E_D/2 \cdot 303 R T_c$ against $10^3/T_c \Delta T$ for unirradiated PA1010-1 sample.

That the data fit to Eq. (4) suggests that the crystal growth proceeds heterogeneously by two dimensional secondary nuclei, which is the fundamental assumption proposed by Hoffman during the derivation of the equation. From slope B , the value of $\sigma \sigma_e$, the product of lateral and lamella surface free energy can readily be evaluated if other parameters are known. In the previous work^[1], it is known that $T_m^0 = 487\text{K}$, $\Delta H_m^0 = 244\text{J/g}$, $\rho_c = 1.135\text{g/cm}^3$, $\Delta h_f = \Delta H_m^0 \cdot \rho_c = 276.9\text{J/cm}^3$. On the other hand, $T_g = 42^\circ\text{C}$ (315K) was determined by the temperature dependence of linear expansion coefficient examined on a Perkin-Elmer TMS-2 Thermomechanical Analyzer. As to b_0 , a Rigaku Denki D/Max-IIB diffractometer was used to determine the diffraction angle 2θ of (010)/(110) plane of a highly crystallized unirradiated PA1010 sample and the measured value is 23.8° , which corresponds to $b_0 = 3.74\text{\AA}$.

Substituting data listed in Table into equation (5) and calculating the slope of the straight line by linear regression, we got the value of $\sigma \sigma_e$ of PA1010 to be $704.6\text{ erg}^2/\text{cm}^4$. A similar treatment of the data listed in Table 3 and 4 also gave the values of surface free energies of irradiated and enhanced γ -radiation crosslinked samples (see Table 5). In the table, the value of σ_e was calculated based on the Hoffman's empirical relation⁽⁷⁾ i.e., $\sigma = \alpha \cdot \Delta h_f \cdot b_0$, $\alpha = 0.1$; $\sigma = 10.36\text{ erg/cm}^2$.

As shown in Table 5, σ_e increases with increasing radiation dose and the content of BMI. According to Eq. (4), if ΔF^* remains constant, at the same T_c , an increase in σ_e results in the decrease of the probability that a surface nucleus will reach critical size. That is why irradiated and BMI enhanced crosslinked samples require more undercooling in order to cause the crystallization to occur. In addition, the lowering of the crystallization rate K and $\tau_{1/2}^{-1}$ can also be attributed to the increase of σ_e .

In the study on the isothermal crystallization of γ -radiation crosslinked crystalline polymer, it is usually necessary to compare the crystallization rate of irradiated samples with different degree of crosslinking at the same crystallization temperature. Since the degree of undercooling required for different sample is different, this comparison is in general experimentally impossible. If σ_e is known and assuming ΔF^* is constant, by using Eq. (4), the ratio of crystallization rate can be

Table 5 Surface free energy of different PA1010 samples

Sample	R (Mrad)	$\sigma \sigma_e (\text{erg}^2/\text{cm}^4)$	$\sigma_e (\text{erg}/\text{cm}^2)$
PA1010-1	0	704.6	68.0
	100	1707.3	164.9
	200	2119.4	204.6
	300	2565.5	247.7
	400	3006.7	290.3
	500	3550.8	342.9
	600	3382.4	326.6
	700	3723.4	359.5
	800	3917.4	378.3
PA1010-2	100	1789.8	172.8
	300	2751.7	265.7
	700	3966.3	383.0
PA1010-3	100	2016.6	194.7
	300	2855.1	275.7
	700	4336.6	418.8

approximated by the following expression

$$G_1/G_2 = \exp(4b_0 \sigma T_m^0 (\sigma_{e2} - \sigma_{e1}) / \Delta h_f \cdot \Delta T \cdot k \cdot T_c) \quad (7)$$

where σ_{e1} and σ_{e2} are the surface free energies of sample 1 and 2.

σ_e is the isothermal work required to form 1 cm² of lamella end surface. The more regular the surface, the lower the value of σ_e . Hoffman^[7] calculated the value of σ_e of adjacent reentry fold surface of polyethylene crystal to be $\sim 50 \text{ erg}/\text{cm}^2$, which is somewhat the same as that of the value $\sim 55 \text{ erg}/\text{cm}^2$ obtained by his isothermal crystallization experiment. As to the "switch board" model proposed by Flory^[13], considering the fold surface being very rough with loops of various length due to random reentry and entanglements, Hoffman assigned a higher value of $150 \text{ erg}/\text{cm}^2$. In comparison with polyethylene the value $\sigma_e = 68.0 \text{ erg}/\text{cm}^2$ for plain PA1010 in the present work is fairly reasonable. However, once crosslinked by γ -irradiation, σ_e increases abruptly in 2—3 fold as shown in Table 5. From the viewpoint of the network structure of crystallizable macromolecule, it is conceivable, that only those chains with appropriate length between crosslinks is capable of taking part in the formation of crystalline lamella, while crosslinks and those chains adjacent to them must inevitably be excluded from the crystalline lattice. As a result, the disorder or randomness is greatly increased. If the crosslinking density is extremely high, the bundellike crystal or fringed micelle might be formed^[12]. This is ascertained by the fact that an extraordinary high value of σ_e are given for samples containing BMI. Owing to the bulkness of BMI molecule, the disorderliness of the crystal end surface would be even more serious than that of the "switch board" model.

In summary, network formation by γ -irradiation greatly changes the crystallization characteristics of PA1010. In addition to the necessity of more undercooling and the lowering of the rate of crystallization, the primary crystallization stage is shortened and the secondary stage lengthened, resulting in a very long "tailing effect" in the overall crystallization process. While the addition of the difunctional crosslinking agent is beneficial to the formation of crosslinks, the inhibition of crystallization is increasingly evident with the increase in BMI content. The origin of this phenomenon is due to the presence of crosslink which interferes with a part of chains into the crystalline lattice, leading to the formation of irregular crystal end surface. The randomness of the surface increases the surface free energy σ_e , and decreases the probability of critical size nucleus formation.

Keywords

γ -Irradiation ; Crosslinking ; Polyamide 1010 ; Isothermal crystallization .

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