

CHARACTERIZATION OF γ -IRRADIATED CRYSTALLINE POLYMERS

I. CHARACTERIZATION OF γ -RADIATION INDUCED CROSSLINKED POLYAMIDE 1010 BY CRYSTALLIZATION TEMPERATURE*

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ABSTRACT

The effect of ^{60}Co γ -radiation on plain polyamide 1010 (PA1010 I) and PA1010 containing different amount of crosslinking agent (BMI) (PA1010 II) both in vacuum and in air at room temperature was investigated with DSC. It was found that the crystallization temperature T_c of crosslinked sample determined with DSC at constant cooling rate decreased as the radiation dose increased. The difference between crystallization temperatures before and after crosslinking ($T_{c_0} - T_{c_R}$) is linearly related to the radiation dose for PA1010I. Based on the Charlesby-Pinner's equation an expression was derived $S + S^{1/2} = A + B/(T_{c_0} - T_{c_R})$ where S is the sol fraction, A and B are constants. Since there is evidence that T_c is relative to S only and independent of the way of irradiation, the equation is also applicable to the enhanced γ -irradiation crosslinked PA1010 II. Therefore, determination of T_c of crosslinked polymer by DSC offers a convenient approach to study quantitatively the random and especially non-random crosslinking reaction of crystalline polymer.

INTRODUCTION

It is well-known that crosslinked polymers are infusible and insoluble. The conventional method adopted to characterize such samples is to measure the gel and sol fractions of the crosslinked samples by solvent extraction, and then a quantitative estimation of the ratio of crosslinking to scission of polymer chains is obtained via the Charlesby-Pinner's equation^[1]. However, the measurement of gel content by this method is very tedious and time consuming. Besides, the equation is applicable to random radiation crosslinking only.

Thermal analysis methods have been used by several authors^[2-8] to study the crosslinking of nylon 6 and other polymers. They suggested empirical relationship between glass transition temperature T_g and degree of crosslinking, but quantitative description concerning radiation crosslinking and scission of crystalline polymer in terms of T_c as determined by DSC has not ever been published in the literature.

In this paper the effect of radiation both in vacuum and in air at room temperature was studied on the plain polyamide 1010 (PA1010I) and PA1010 containing different amount of difunctional crosslinking agent, N,N'-bismaleimide-4,4'-diphenyl methane (BMI) (PA1010II). A linear relationship between T_c and radiation dose has been found. Based on this fact, an approach to study quantitatively the random or enhanced crosslinking effect induced by γ -radiation on crystalline polymer is offered.

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EXPERIMENTAL

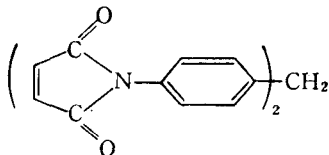
Materials

The PA1010I is a plain polyamide 1010



with $\bar{M}_n = 1.34 \cdot 10^4$ and m.p. 210°C .

PA1010II samples were prepared by mixing dry PA1010 powder with different amount of difunctional monomer N,N'-bismaleimide-4,4'-diphenyl methane (BMI)



Both polyamide samples were moulded at 210 – 230°C into sheets of 0.15 – 0.25mm thick. Samples were subjected to γ -irradiation at room temperature in a ^{60}Co source in vacuum ($1 \cdot 10^{-3}$ torr) or in air. After irradiation, they were annealed at 150°C for 1 hour.

Sol fraction S and gel fraction g were determined by extraction with m -cresol at 50°C .

Thermograms of irradiated samples were determined on a Perkin-Elmer DSC-2C differential scanning calorimeter. Heating and cooling rates were $10^\circ\text{C}/\text{min}$. The precision of temperature readings was $\pm 0.1^\circ\text{C}$.

RESULTS AND DISCUSSION

1. DSC thermogram of irradiated PA1010I and PA1010II

Fig. 1 shows thermograms of PA1010I irradiated in vacuum at room temperature. For the samples of PA1010I irradiated in air and PA1010II irradiated both in vacuum and in air, the trend in change of the shape of the thermograms is similar. With an increase in radiation dose, both melting peaks tend to shift to lower temperature, overlapping gradually, and eventually converging to a single peak. When the melt is cooled at constant rate of cooling, only a single crystallization peak occurs at 450 – 400K , which broadens and shifts gradually to lower temperatures as the radiation dose is increased. The heat of fusion, ΔH_m , and

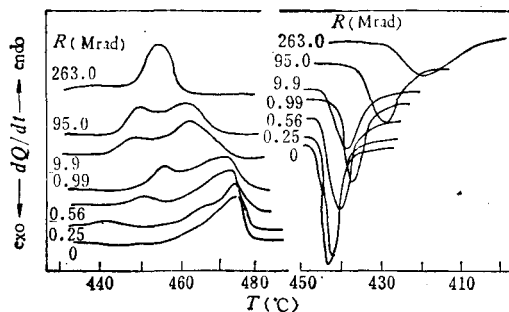


Fig. 1 DSC thermogram of PA1010I irradiated in vacuum

heat of crystallization, ΔH_c , of irradiated PA1010 also decrease with the increase in radiation dose.

The above-mentioned phenomenon results from the formation of network structure of irradiated PA1010 and the radiation deterioration on the polymer crystals. With an increase in radiation dose, defects in the crystal region are increased, and more and more chain units are crosslinked. Defects cause shift of T_m to lower temperatures. Crosslinking inhibits the reorganization of crystals and thus multiple melting peaks are reduced to a single peak. Similarly, when a crosslinked melt is cooled at a constant cooling rate, restraint imposed by crosslinks restricts the alignment of polymer chains, leading to the formation of imperfect crystals. Hence, the crystallization peak broadens and shifts to a lower temperature.

2. T_c of irradiated PA1010I and its crosslinked network structure

T_c and the corresponding gel fraction, g , of PA1010I and PA1010II samples irradiated with different amount of radiation dose R both in vacuum and in air are given in Tab. 1. and Fig. 2. As can be seen from Tab. 1, the g values of both sets of samples irradiated in air are lower than that of the corresponding values for samples irradiated in vacuum. It is because of the fact that as a competition process with crosslinking, oxygen can combine with the radicals generated during irradiation, thus the crosslinking between macromolecules by coupling radicals is somewhat inhibited. From curves (1) and (2) in Fig. 2, it shows that the radiation crosslinking of plain PA1010 follows the Charlesby-Pinner's equation for random

Table 1 Relationship between T_c , g and R

R (Mrads)	PA1010I irradiated in				PA1010II irradiated in			
	Vacuum		Air		Vacuum		Air	
	T_c (K)	g (%)	T (K)	g (%)	T_c (K)	g (%)	T_c (K)	g (%)
0	447.0	0	447.0	0	444.0	0	444.0	0
0.05	447.0	0	—	0	—	—	443.0	35.0
0.10	447.0	0	—	0	—	—	443.0	—
0.25	—	0	—	0	443.0	36.4	442.0	35.8
0.56	—	0	—	0	442.0	47.5	442.0	49.3
0.99	—	0	447.0	0	439.0	64.6	—	—
9.90	—	0	—	0	440.0	80.3	438.0	70.4
30.00	444.0	4.2	444.0	7.6	—	—	437.0	76.6
47.5	438.0	48.2	443.0	29.8	—	—	—	—
95.0	438.0	66.5	441.0	50.2	432.0	83.5	432.0	80.9
263.0	420.0	81.6	—	67.7	415.0	87.3	421.0	78.4

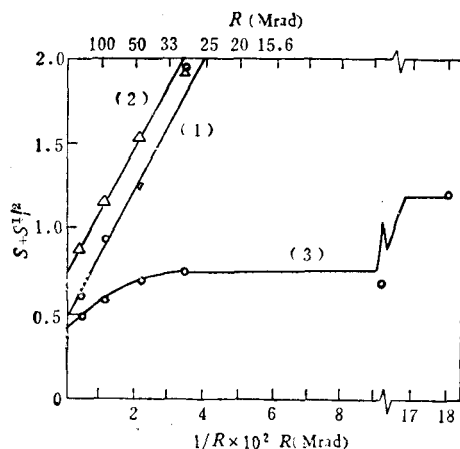


Fig. 2 Plot of $S + S^{1/2}$ against $1/R$ for irradiated PA1010

- (1) PA1010I, irradiated in vacuum,
- (2) PA1010II, irradiated in vacuum,
- (3) PA1010I, irradiated in air.

crosslinking:

$$S + S^{1/2} = \frac{p_0}{q_0} + \frac{1}{q_0 u_1 R} \quad (1)$$

where S is the sol fraction, p_0 the proportion of main chain units fractured per unit radiation dose, q_0 the proportion of monomer units crosslinked per unit radiation dose, and u_1 the number average degree of polymerization before irradiation. According to the basic assumption of random crosslinking^[2], it is also known that

$$q = q_0 R \quad (2)$$

where q is the crosslinking density. From plots of T_c against R for irradiated PA1010 in Fig. 3, it is clear that for PA1010I, irradiated both in vacuum and in air, there exists a fairly linear relationship between T_c and R , and this can be expressed by the following equation:

$$T_{c0} - T_{cR} = KR \quad (3)$$

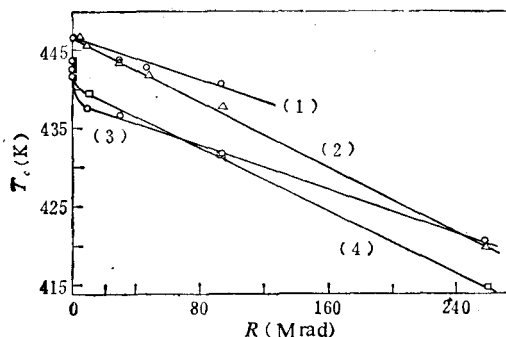


Fig. 3 Variation of T_c with radiation dose R for PA1010

- (1) PA1010I, irradiated in air,
- (2) PA1010I, irradiated in vacuum,
- (3) PA1010II, irradiated in air,
- (4) PA1010II, irradiated in vacuum.

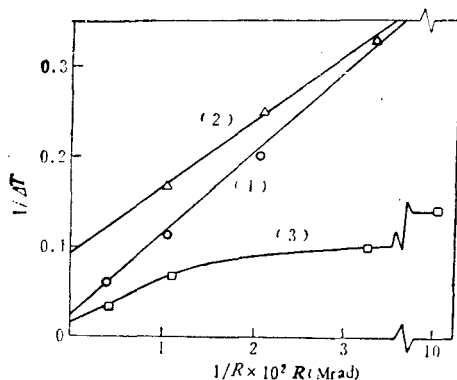


Fig. 4 Relationship between $1/\Delta T_c$ and $1/R$ of PA1010
 (1) PA1010I irradiated in vacuum,
 (2) PA1010I irradiated in air.

where T_{cR} is the T_c of samples irradiated with dose R , T_{c0} , the T_c of the sample before irradiation and K is the slope of the straight line ($K = \Delta T_c / \Delta R$).

By comparing equation (2) with equation (3), it is obvious that q and q_0 are related to $(T_{c0} - T_{cR})$ and K respectively. Therefore, $\Delta T_c (= T_{c0} - T_{cR})$ can be used to characterize the crosslinking density, q .

Plots of $1/\Delta T_c$ against $1/R$ are shown in Fig. 4. For PA1010I, a straight line in the form

$$1/\Delta T_c = H + k/R \quad (4)$$

is obtained. Where H is the intercept when $R \rightarrow \infty$ (i.e. $H = (1/\Delta T_c)_{R \rightarrow \infty}$) and k is the slope. The values of H for PA1010I irradiated both in vacuum and in air are 0.025 and 0.095 respectively.

Fig. 5 is a plot of $S + S^{1/2}$ against $1/\Delta T_c$ for samples PA1010I and PA1010II irradiated both in air and in vacuum. All experimental values are on the same straight line, which can be expressed as

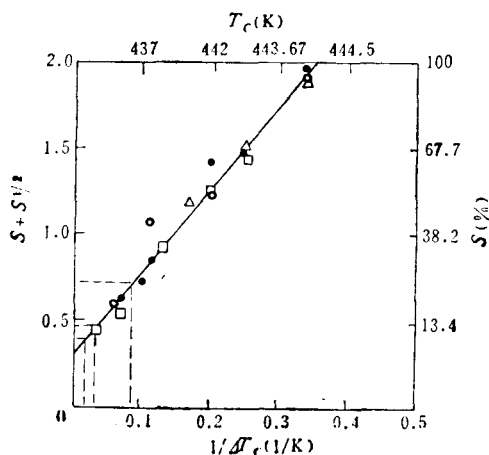


Fig. 5 Plot of $S + S^{1/2}$ against $1/\Delta T_c$

$$S + S^{1/2} = A + B/(T_c - T_{cR}) \quad (5)$$

where A and B are constants. The relationship shown above indicates that T_c or ΔT_c is correlated to S only and is irrelevant to the way of irradiation.

In order to evaluate the constants A and B , equations (1) and (4) are combined into

$$S + S^{1/2} = p_0/q_0 - H/kq_0u_1 + 1/kq_0u_1 \cdot (1/\Delta T_c) \quad (6)$$

By comparing equation (6) with equation (5), the constants A and B can be expressed in the following forms respectively.

$$A = p_0/q_0 - H/kq_0u_1 \quad (7)$$

$$B = 1/kq_0u_1 \quad (8)$$

$$p_0/q_0 = A + BH \quad (7')$$

In Fig. 5 if the line is extrapolated to $S + S^{1/2} = 2$, a crystallization temperature $T_{c_g} = 444.2\text{K}$ was obtained, which corresponds to the T_c of all PA1010 samples irradiated with the radiation dose for gelation, R_g . Since constants A and B can easily be obtained from Fig. 5 and are the same for all samples, by substituting values of H obtained in Fig. 4 into equation (7'), values of p_0/q_0 for PA1010I samples irradiated both in vacuum and in air was found to be 0.49 and 0.77 respectively. From the slope $B = 1/kq_0u_1$, the values of q_0 can be calculated. Once q_0 is known, the G value for crosslinking, G (c.l.), can be calculated from^[9]

$$G(\text{c.l.}) = 0.48 \cdot 10^6 q_0/w \quad (9)$$

where w is the molecular weight of the monomer unit. Respective values for PA1010I samples are $G(\text{c.l.})_{\text{vac}} = 0.77$ and $G(\text{c.l.})_{\text{air}} = 0.52$. These values are in agreement with the results obtained from Fig. 2 and equation (1), i.e. $(p_0/q_0)_{\text{vac}} = 0.49$, $(p_0/q_0)_{\text{air}} = 0.74$; $G(\text{c.l.})_{\text{vac}} = 0.72$ and $G(\text{c.l.})_{\text{air}} = 0.52$.

3. Enhanced irradiation crosslinking of PA1010II and its characterization in terms of T_c

(1) The presence of BMI in the sample changes the mechanism of crosslinking. The irradiation crosslinking of PA1010II no longer occurs randomly, and does not follow the Charlesby-Pinner's equation (see Fig. 2 curve (3) and equation (1)). The BMI accelerates the crosslinking reaction and leads to non-linear relationship between T_c and R at the beginning (see Fig. 3 curves (3) and (4)). With the increase in radiation dose, BMI is exhausted gradually, and the magnitude of the tangential slope ($K_R = dT_c/dR$) decreases. When R reached a certain value, at which BMI had been completely taken part in the crosslinking reaction, the linear relationship between T_c and R reappeared. In addition, the slope is the same as that of the PA1010I in the same atmosphere (compare curves (1) and (3); (2) and (4) in Fig. 3).

(2) In section 2, it has already been indicated that T_c or ΔT_c is correlated with S only and is irrelevant to the way of irradiation, i.e. equation (5) governs both random and enhanced radiation crosslinking. Therefore, for enhanced systems, the $\hat{T}_{c_g}$ value is also equal to 444.2 K. As T_{c_g} is known, the values of R_g of various crosslinking systems can be estimated from T_{cR} vs. R curves. Fig. 6 illustrates the relationship between T_{cR} and R of samples with different ratio of BMI to PA1010. The estimated values of R_g for various systems are given in Tab. 2. Because BMI facilitates the formation of network structure, R_g shifts to lower dose

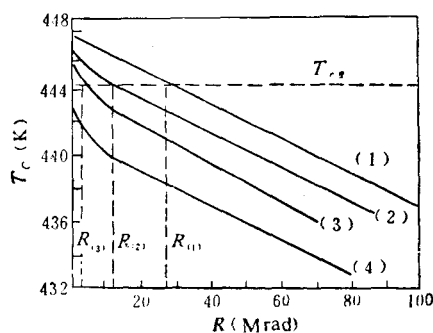


Fig. 6 The T_{cR} vs. R curves of PA1010II irradiated in vacuum

- (1) BMI/PA1010-0/100,
- (2) BMI/PA1010-2.5/100,
- (3) BMI/PA1010-5/100,
- (4) BMI/PA1010-10/100.

Table 2 BMI content of PA1010II and estimated R_g

BMI/PA1010 ($\times 100$)	5	2.5	5.0	10.0
R_g (Mrads)	28	13	4	very small

with the increase in BMI/PA1010 ratio.

(3) Estimation of G values for enhanced irradiation crosslinking.

In the case of random irradiation crosslinking, the crosslinking yield or G (c.l.) value is usually given by the following equation (10):

$$G(\text{c.l.}) = 0.48 \cdot 10^6 / R_g \bar{M}_w \quad (10)$$

where R_g is the gelation dose, obtained via the Charlesby-Pinner's relation, and $\bar{M}_w$ the original weight average molecular weight. For enhanced crosslinking, some workers have still estimated the G value by means of equation (10). This is rather inadequate, because, in the presence of multifunctional group monomer, G (c.l.) value is a function of the amount and consumption of the monomer, any single value of G (c.l.) for the system is unsuitable. Therefore, the estimated value of G (c.l.) by means of equation (10) for enhanced system is merely an average value before R_g is reached.

As mentioned above, the relationship between S and T_{cR} for samples PA1010I and PA1010II is both governed by equation (5). In order to show the peculiarity of the enhanced crosslinking, it is better to express the slope B in equation (5) in terms of K_R or dT_c/dR of curves (3) and (4) of Figure (3) in the low radiation dose range. Rearranging equation (4), we obtain

$$T_{cR} = T_{c0} - (1/(HR + k)) R \quad (4')$$

Since $H \ll 1$, and $k \gg 1$, when the radiation dose R is low, HR is negligible in comparison with k , i.e.

$$T_{cR} \doteq T_{c0} - \frac{1}{k} \cdot R \quad (4'')$$

By comparing equation (4'') with equation (3),

$$K \approx 1/k \quad (11)$$

Therefore, equation (8) can be expressed as

$$B \approx K/q_0 u_1 \quad (12)$$

Although the value of B in equation (5) is the same in both cases, for enhanced systems, K varies with dose R (i.e. varies with the consumption of the difunctional monomer, or $K_R = dT_e/dR$, see Fig. 3). Thereby we express equation (8) as

$$B = K_R/q_{0R} u_1 \quad (13)$$

where q_{0R} is a dependent variable of K_R , and is a function of monomer concentration. As the K_R values for different R can be obtained from experimental results, the corresponding q_{0R} values can readily be given by above equation. By means of an expression analogous to equation (9), we obtain:

$$G(c.l.)_R = 0.48 \cdot 10^6 q_{0R}/w \quad (14)$$

The G values relevant to different radiation dose R can thus be calculated. The $G(c.l.)_R$ values for PA1010II (BMI/PA1010=10/100) for different R are given in Tab. 3 and Fig. 7.

Table 3 $G(c.l.)_R$ values for enhanced irradiation crosslinked PA1010

R (Mrads)	1	2	4	5	7	10	30	50
Irradiated in vacuum	4.81	3.02	1.87	1.51	1.22	0.859	0.737	0.737
Irradiated in air	6.79	4.59	3.08	2.04	1.38	0.669	0.517	0.517

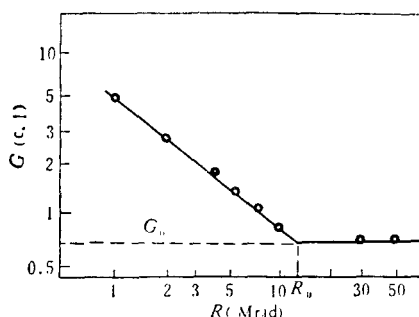


Fig. 7 $\log G$ against $\log R$ curve of PA1010II irradiated in vacuum

The above results indicate that for enhanced irradiation crosslinking of PA1010II, $G(c.l.)_R$ is a function of the effective concentration of BMI. With the increase in R , the concentration of BMI will be lowered due to its participating in crosslinking, thus the $G(c.l.)_R$ value is decreased. When BMI is completely exhausted, the crosslinking will proceed randomly again, $G(c.l.)_R$ approaches a definite value even though R is further increased. For example, when R is greater than 10 Mrads, and PA1010II is irradiated in vacuum, $G(c.l.)_R$ approaches 0.74; if it is irradiated in air, $G(c.l.)_R$ approaches 0.52. These values are nearly the same as the values for PA1010I irradiated in the same atmosphere.

The results shown in Fig. 7 can also be expressed in the form

$$G(c.l.)_R = G_0(R_0/R)^{-\alpha} \quad (15)$$

where G_0 is the $G(c.l.)_R$ value in the random crosslinking region (± 0.74); R_0 , the minimum dose (± 13 Mrads) with which $G(c.l.)_R$ reaches a constant value; α , the slope of the curve (± -0.74). Equation (15) is valid in the $R < R_0$ region only, since, when $R \geq R_0$, $G(c.l.)_R \equiv G_0$. By means of the above equation it is possible to estimate the instantaneous $G(c.l.)_R$ values for lower doses. For example, $G(c.l.)_R \pm 27$ when R is 0.1 Mrad; $G(c.l.)_R \pm 147$, when R is 0.01 Mrad, and so on.

In summary, the crystallization temperature of irradiation crosslinked PA1010 samples determined by DSC at a constant cooling rate is a characteristic value of crosslinking. It correlates with sol fraction only and is independent of the way of crosslinking. Based on the Charlesby-Pinner's equation, an analogous expression was derived, and by means of which, a convenient approach to study quantitatively the radiation crosslinking reaction of crystalline polymers was offered.

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