

THE EFFECTS OF IRRADIATION ON THE THERMAL PROPERTIES OF SEMI-CRYSTALLINE POLYAMIDES*

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ABSTRACT

Irradiation crosslinking of semi-crystalline polyamides was performed by high energy electrons with various dosages. It is known that the melting behavior of the polymers after irradiation is a complex phenomenon. In company with the wide angle X-ray diffraction and DSC data of irradiated and unirradiated polyamides it is possible to develop the local order and perfection of the crystallinities slightly which resulted from introduction of intermolecular crosslinking in amorphous region, including in amorphous-crystalline interface and crystalline defect regions due to irradiation. It can be explained that slight increase of melting temperature (T_m) and heat of fusion (ΔH_f) with increasing dosage for both of higher crystallinity nylon 4 and nylon 6. For irradiated lower crystallinity nylons, in contrast, the T_m and ΔH_f decrease obviously with increasing dosage. In this case, radiation crosslinking "freeze in" the pre-existing morphology, and then the prevention for reorganization during heating is a dominant effect. The T_m from the second melting for all of the samples were depressed, corresponding with Flory theory. Therefore the crosslinks imposed on the molecules restrained the molecular mobility, and that not only depresses the crystallinity but also increases the imperfection of crystallites when the radiated polymer melted and then recrystallized. These are also reflected in the depression of heat and entropy of fusion as well as the appearance of double melting peaks on the DSC thermograms.

INTRODUCTION

High energy irradiation effects on most of commercial polymers in solid state have been widely investigated. They consist of modifications of structural and physical properties, which depends on chemical structure and morphology of the polymers and on the radiation conditions^[1]. The principal radiochemical and physical effects produced in semicrystalline polymers include crosslinking, chain scission, local ordering and perfection or imperfection of crystallites as well as the transition of crystalline forms, etc. They were reflected in the changes of the thermal and morphological properties.

For polyamides, present experimental evidence on nylon 6 has shown that the crosslinking is the dominant reaction and the degree of crosslinking increases with increasing dose of radiation under ambient conditions and in inert atmosphere with lower dose level.

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Furthermore, crosslinks were localized preferably in the amorphous phase and the crystal structure of the sample remained virtually the same^[2]. The effect of radiation on thermal properties of polyamides has received little attention in the past. As far as we know such information about nylon 4 has not yet been published anywhere. Recently we reported that radiation crosslinking for nylon 4 and nylon 6 up to 80 Mrad doses might "freeze in" the existing morphology. The increase of glass transition temperature and depression of the incremental change in heat capacity at T_g with increasing radiation doses have been observed for both of nylon 4^[3] and nylon 6^[4]. The present work will investigate the effect of radiation on the melting and crystallization behaviors for different crystallinity nylon 4 and nylon 6.

EXPERIMENTAL

Sample preparation

Polypyrrolidone (nylon 4, Chevron Research Co.) and polycaprolactam (nylon 6, Polyscience Inc.) films with thickness of 0.1–0.2 mm were obtained from dried granules by compression molding. The molding was performed at 273°C (3°C above the melting temperature) for nylon 4 and 250°C (30°C above the melting point) for nylon 6 respectively with the granules pressed between two pieces of aluminum foil, thickness 15 μ m, by using a mold release agent VYDAC 525 (DuPont Co.). Amorphous and low crystallinity samples were fused at molding temperature and then quenched in liquid nitrogen or air as quickly as possible. Samples of higher crystallinities were made by annealing at different periods of time in a mold block at 200°C for nylon 4 and 190°C for nylon 6 after melting. After molding, all samples were rigorously dried under high vacuum and then stored under phosphorous pentoxide at least 10 days before further treatment and measurement.

Crystallinity measurements

Wide angle X-ray spectroscopy and density measurement were used in crystallinity determination for nylon 4 and nylon 6 respectively. WAXS profiles were recorded using a Siemens D 500 wide angle diffractometer employed in the symmetric transmission mode with Ni filtered $\text{CuK}\alpha$ radiation. It is judged that amorphous scattering curve intersects the background scattering at the lower and upper diffraction limits of diffraction angle (2θ) of 10° and 35°. The maximum intensity occurs at $2\theta = 20^\circ$ ^[5]. The diffraction trace of partial crystalline nylon 4 has two crystalline peaks occurred at $2\theta = 20.5^\circ$ and 24° corresponding to the reflection

Table 1 Crystallinity of samples

Sample code	A	B	C	D
Nylon 4*	12	25	46	60
Nylon 6**	3.5	14.2	34.5	48.3

* From wide angle X-ray measurements

** From density measurements

from 200 and 002 planes of α -crystal. The percentage crystallinity of nylon 4 samples was calculated^[6] and shown in Table 1.

Density measurements were carried out at 25°C using a density gradient column filled with heptane/carbon tetrachloride mixture (dried by 5Å molecular sieve in advance). Values recorded for density represent an average from three determinations. Based on the density values of the 100% amorphous and 100% crystalline nylon 6, the crystallinity of nylon 6 samples was obtained and shown in Table 1. Determination also indicated that there is no significant change in crystallinity during storage.

Crosslinking

Irradiation crosslinking of the dry films was performed with 3.0 meV and 30 milliamp beam current from a Dynamatron Accelerator (Radiation Dynamic Inc.) with dose from 10 to 80 Mrad at room temperature during the irradiation process.

After irradiation, solubility was assessed using formic acid, m-cresol and absolute ethyl alcohol saturated with calcium chloride respectively at room temperature. Observed results after 2 weeks were shown in Table 2.

Table 2 Solubility of radiated nylon 4 and nylon 6 in various solvents at room temperature

Sample	Solvent	Radiation doses, Mrad						
		30		55		70		
Nylon 4	Formic acid	Soluble						A little gel
	m-Cresol							Gel
Nylon 6		10	20	30	40	60	80	
	Formic Acid	Soluble		Soluble after 2 weeks	Gel			
	m-Cresol	Soluble	Soluble slowly	Gel				
	C ₂ H ₅ OH with CaCl ₂							

Calorimetry

The melting temperature and heat of fusion of all the sample were measured calorimetrically using a Perkin-Elmer Differential Scanning Calorimeter DSC-2, programmed at a heating rate of 20°C/min with approximately 5 mg of sample. Value of melting temperature was taken as the maximum on the enthalpy versus temperature curve. Each sample was then crystallized from the melt in the DSC at a constant cooling rate of 40°C/min until the temperature reached 270K, then run again.

RESULTS AND DISCUSSION

Crosslinking and solubility

It is well known that irradiation was connected only with networks for which the change in chemical composition can be ignored. Many studies in which nylon 6 was crosslinked by high energy irradiation have been published^[2,7,8]. The suggested mechanism was based on the formation of a radical on the methylene adjacent to the nitrogen atom of the amide link when nylon 6 was irradiated, and crosslinking or chain scission occurs^[7]. It was exhibited that under ambient conditions and in vacuum or inert atmosphere the degree of crosslinking increases with increasing irradiation dose up to a certain level of irradiation for nylon 6. Although some degradation did occur, noted in these studies by a slight yellow coloration, crosslinking is still the dominant reaction, as observed in the change of solubility and thermal properties, which will be mentioned below. Furthermore, experimental evidence has shown that crosslinking takes place primarily in the amorphous phase, as well as in the folding surface of crystallinities for nylon 6^[2] and for polyethylene^[9] at lower doses of irradiation. The scarcity of crosslinks inside the crystal lattice at relatively low doses has been ascribed to carbon atoms on adjacent chains in lattice being too far apart, and to the lattice being too rigid at room temperature. For the interchains in amorphous region, the crosslinks formed easily.

It has been known, nylon 4 and nylon 6 are soluble in formic acid and *m*-cresol at room temperature. In addition, nylon 6 is also soluble in absolute ethyl alcohol saturated with CaCl_2 . The solubility of radiated nylon 4 and nylon 6 with various doses was summarized in Table 2. For nylon 6, the loss of solubility appeared at 20 Mrad and gel was observed clearly at 30 Mrad in *m*-cresol and ethyl alcohol at room temperature. In formic acid these doses are at 30 Mrad and 40 Mrad respectively. The little difference of solubility between formic acid and other solvents perhaps can be attributed to the hydrolysis of crosslinks in formic acid in longer observed period. For nylon 4 the dose for starting crosslinking is higher than that of nylon 6. The onset of insolubility for irradiated nylon 4 is at doses of the order of 70 Mrad.

Melting behavior of irradiated nylon 4 and nylon 6

The melting behavior for first melting of crystalline polymers after irradiation is a complex phenomenon. The different alteration of the melting properties has been known for irradiated polyethylene^[9,10] polypropylene^[11] poly-1-butene^[12] and isotactic PMMA^[13]. As shown in Figs. 1,2 and 3, the melting temperature and heat of fusion are approximately unchanged for high crystallinity nylon 4 and nylon 6 after irradiation. Exactly, a slight increase of melting temperature and heat of fusion with increasing doses can be found for high crystallinity nylon 4 and nylon 6. X-ray diffractograms of the high crystallinity samples of nylon 4 and nylon 6 with various doses were illustrated in Fig. 4 and Fig. 5. A small γ -crystalline peak of unirradiated sample can be observed in Fig. 5, and it disappeared with increasing doses for nylon 6. Furthermore, though no significant change in crystallinity from X-ray data, the ratio for the peak intensity of the α reflections $200(\alpha_1)$ and $002,202(\alpha_2)$, and the resolution of these two peaks were altered with radiation. Similar situation also took place in

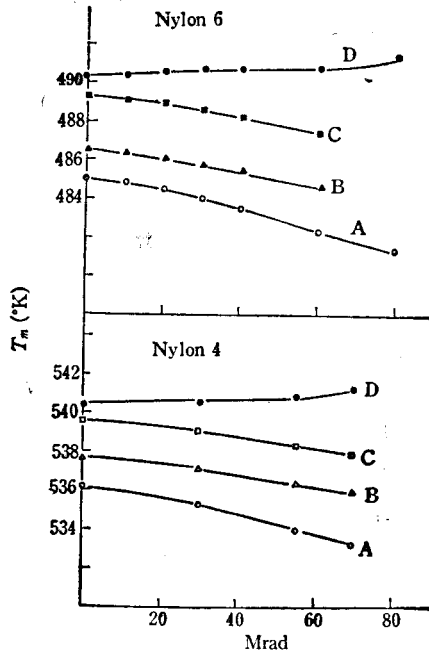


Fig. 1 The melting temperatures of irradiated nylon 4 and nylon 6 measured from the first melting after the irradiation
A,B,C and D represent the crystallinity of samples, see Table 1

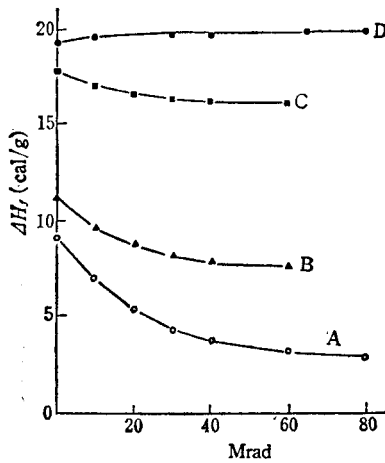


Fig. 2 The heat of fusion of irradiated nylon 4 measured from the first melting after the irradiation

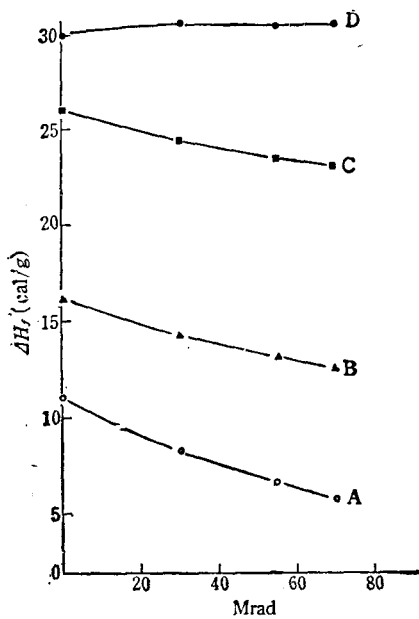


Fig. 3 The heat of fusion of irradiated nylon 6 measured from the first melting after the irradiation

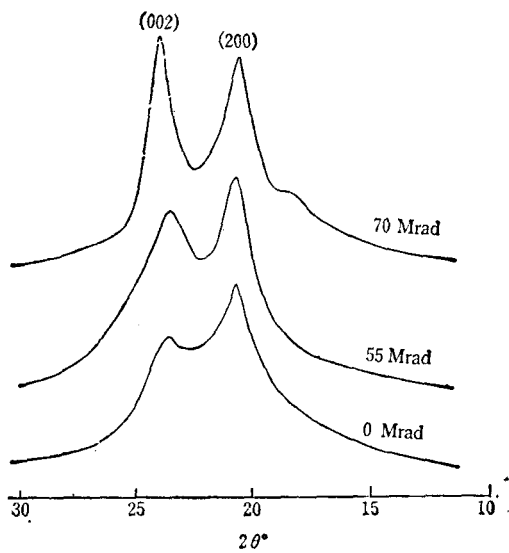


Fig. 4 The wide angle X-ray diffractograms of the irradiated nylon 4

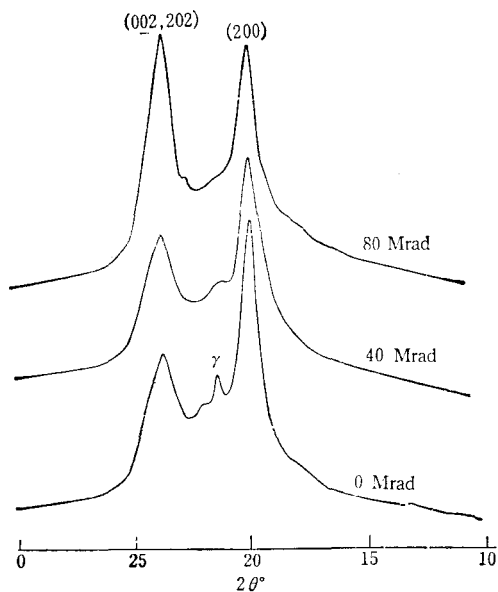


Fig. 5 The wide angle X-ray diffractograms of the irradiated nylon 6

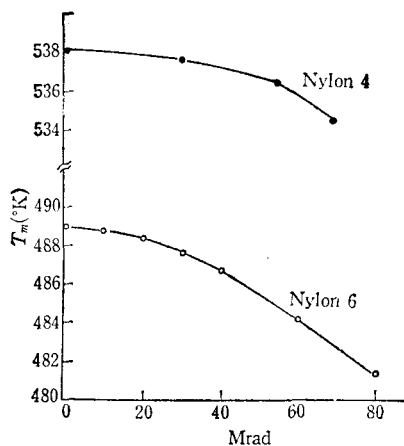


Fig. 6 The melting temperatures of irradiated nylon 4 and nylon 6 measured from the second melting after the irradiation

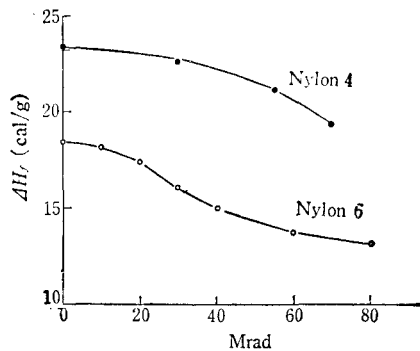


Fig. 7 The heat of fusion of irradiated nylon 4 and nylon 6 measured from the second melting after the irradiation

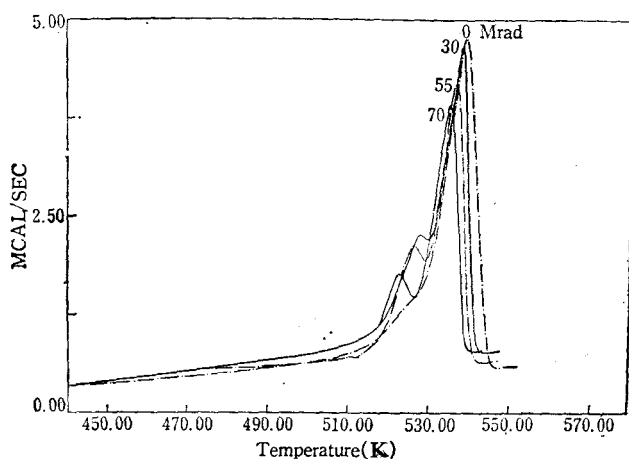


Fig. 8 The DSC curves of irradiated nylon 4 measured from the second melting after the irradiation

nylon 4, as shown in Fig. 4. It has been indicated that the ratio and resolution of α_1 and α_2 peaks for nylon 6 related to the crystalline lateral order, including the lattice perfection, etc.^[14]. Noted that the swelling treatment of nylon 6 increases the local order and lattice perfection based on the above alternation of X-ray patterns. The analogy of the behaviour between swelling and irradiation treatment has been observed from the similar qualitative results in the change of X-ray profiles. However, it is possible to develop the local order and perfection of the crystallinities slightly by irradiation which resulted in the introduction of intermolecular crosslinks in amorphous region, amorphous crystalline interface and crystalline defect region, that may be applied to explain the result which show a very little increase of melting temperature and heat of fusion with increasing doses for both of high crystallinity nylon 4 and nylon 6, as shown in curve D, Fig. 1 and Figs. 2, 3. Gee^[15] also noted the increase of heat of fusion for irradiated nylon 6 up to dose of 200 Mrad and that was attributed to the ordering process of crystallites. Recently, similar results have been obtained for irradiated ultrahigh molecular weight polyethylene with melting temperature and heat of fusion increase after irradiation without change in average crystalline lamellar thickness, and that was speculated as due to the enhancing of the degree of crystalline perfection^[16].

The melting behavior of radiated lower crystallinity nylon 4 and nylon 6 is quite different from that of high crystallinity samples. It can be observed that the melting temperature and heat of fusion decreases obviously with increasing doses in Fig. 1 and Figs. 2, 3. It has been known, for low crystallinity polyamides there is a strong morphological change, i.e. further crystallization and reorganization occurs around the glass transition temperature during heating on DSC scan. Therefore the melting temperature and heat of fusion calculated from DSC curve become higher than the original. As mentioned, the irradiation crosslinking could "freeze in" the pre-existing morphology for further crystallization during heating^[3,4]. It results in the decrease of melting temperature and heat of fusion of irradiated low crystallinity

nylon 4 and nylon 6 with increasing doses. Though the local ordering which was caused by the crosslinking as mentioned above still existed, however, the observation of the decreasing of melting temperature and heat of fusion for low crystallinity samples is due to the compensatory effects and the hampering of reorganization is a dominant effect in this case.

In addition, in comparison with nylon 4, the tendency of the depression of melting temperature and heat of fusion for nylon 6 is stronger than that of nylon 4 as shown in Figs. 1—3. It can be explained that there is more crosslinks in irradiated nylon 6 at the same dose, because the gelation dose for nylon 6 is less than that of nylon 4 which has been noted in the above section. Melting behavior of nylon 4 and nylon 6 after radiation, fusion and melt crystallization.

Melting temperature from the second melting in a crosslinked polymer is lower than that of uncrosslinked materials. This melting temperature depression can, according to Flory^[17], be understood as a result of a reduction of the concentration of segments of length suitable for crystallization due to the existence of the crosslinks:

$$\frac{1}{T_m(X)} - \frac{1}{T_m(0)} = \frac{R}{\Delta H_u} X$$

where $T_m(X)$ and $T_m(0)$ are the equilibrium melting temperature of the crosslinked and uncrosslinked polymer respectively, ΔH_u the heat of fusion per mole of chain unit, R is the gas constant, and X is the fraction of crosslinked chain units. However, the crosslink restrains the molecular mobility, and that not only depresses the crystallinity, but also increases the imperfection of crystallites when the irradiated polymer melt and then recrystallized. These are also reflected in the depression of heat and entropy of fusion. The depression of melting temperature and heat of fusion with increasing doses for radiated nylon 4 and nylon 6 was shown in Fig. 6 and 7 respectively. Similar phenomenon has also been noted for polyethylene^[11] etc. in low level radiation.

In addition, the depression of melting temperature and heat of fusion for nylon 6 from the second scan at the same doses is more than that for nylon 4, it means there are more crosslinks in irradiated nylon 6 than that in nylon 4 based on the solubility results. From the DSC thermograms, as illustrated in Fig. 8 for nylon 4, it can also be found that there is a smaller low temperature melting peak, and the peak increases oppositely with increasing doses. Present reports indicated that the phenomenon of double melting peaks of nylon 6 during DSC process is due to the partial melting and recrystallization of original crystallites at the moment of thermal scanning. The low melting temperature peak corresponds to the melting of imperfect crystallites, and the higher melting temperature peak corresponds to the melting of better organized crystallites^[18]. Such results from thermograms also exhibit that the crystallization and reorganization are prevented because of crosslinking by irradiation for nylon 4 and nylon 6 at present condition.

Finally, on the investigation of thermal properties of low density polyethylene at high irradiation doses, it was known that if irradiation causes the chain scission and reducing the molecular weight, the crystallinity measured from heat of fusion in DSC thermograms at second scan after irradiation might increase due to the increasing of molecular mobility^[19]. But in our studies, the results, shown in Fig. 6 and Fig. 7 are contrary to that. However,

it showed no significant scission took place at lower doses used in this work for nylon 4 and nylon 6.

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