Effects of Irradiation on the Melting and Crystallization Behavior of Ethylene Polymers with Different Thermal History

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ABSTRACT: Ethylene polymers, including HDPE, Ziegler–Natta-catalyzed LLDPE (Z–N LLDPE), metallocene-catalyzed LLDPE (m-LLDPE), and LDPE were thermally treated by different procedures, that is, quenching, slow cooling, and thermal segregation. These PE samples, having different thermal histories, were then irradiated with various doses, that is, 0, 13, 35, and 70 Mrad, by gamma ray using a ^{60}Co radiation source. The melting and crystallization behaviors of these irradiated samples were studied by a differential scanning calorimeter (DSC). The effects of the thermal histories and irradiation on the polymers were evaluated by their melting temperatures (T_m), crystallization temperatures (T_c), and heat enthalpies (ΔH) in the heating and cooling scans. The results indicated that irradiation affects the samples having different thermal histories in different ways. The effects of the dosage on each kind of sample are discussed. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 88: 536–544, 2003

Key words: irradiation; melt; crystallization; polyethylene (PE)

INTRODUCTION

High-energy irradiation modification of polymers in the solid state has been widely investigated and commercially applied. Irradiation can affect the chemical and physical properties of polymers, mainly through the reactions of chain scission and crosslinking.[1–10] For ethylene polymers, generally, at a low dose (lower than 20 Mrad), the main reaction caused by irradiation is chain scission in the amorphous region. The broken tie molecules are then incorporated into the crystal lamellae, which results in an increase of crystallinity due to the improvement of the chain mobility.[11–13] With an increasing irradiation dosage, crosslinking takes place significantly in the amorphous fraction and on the lamellar surface. The crystallinity slightly decreases due to the high concentration of defects in the crystal lattice. The mechanical properties will be strengthened by the formation of the network within the polymer.[14,15] If the irradiation dose is even higher, the formed polymer networks will be gradually destroyed and degraded.[7]

Irradiation plays different roles in the different fractions for a semicrystalline polymer. Keller et al. pointed out that the crosslinkages are formed in the amorphous region or the crystal-folded surface of the polyethylene (PE) single crystal, but it is absent in the crystal lattice because the distance between chains is larger than is required for crosslinking.[16] Therefore, Klein et al. considered that the efficiency of crosslinking is relevant to the degree of intermolecular contact, and chain scission is unimportant in isotropic PE, but significant for highly drawn PE fibers.[3]

Recently, Hutzler et al. reported both isothermal and nonisothermal crystallization kinetics of ethylene polymers after irradiation.[17] The results indicated that the crystallization rate decreases caused by the crosslinking of the polymers. The thermal and mechanical properties of LLDPE crosslinked with gamma radiation were examined by Krupa and Luyt using DSC, TGA, SEM, and tensile experiments.[18] The results indicated that the trace of the second DSC heating scan is different from that of the first one, the thermal stability assessed by TGA was increased after irradiation, and the mechanical properties were affected in different ways. Djokovic et al. reported the influence of irradiation on the stress relaxation of LLDPE and brought forward a two-process model to explain the result obtained.[19] In this article, the coop-

TABLE I
Fundamental Characterization Results of the Samples

Samples	$M_n \times 10^{-3}$ (g/mol)	M_w/M_n	SCB/1000C	T_m (°C)	X_c (%)
HDPE	303	2.5	—	134.3	73.6
LLDPE-1	116	4.6	18.3	123.7	34.5
LLDPE-2	145	2.0	13.2	119.3	35.0
LDPE	27.0	2.9	—	106.6	35.2

erative effects of thermal history and irradiation on the melting and crystallization behaviors of different ethylene polymers were assessed in detail.

EXPERIMENTAL

The samples used in the work were ethylene polymers including HDPE, Ziegler–Natta (Z–N LLDPE), m-LLDPE, and LDPE. HDPE and LDPE were obtained from the Beijing 2nd Reagent Factory (Beijing, China) and the Yanshan Petroleum Co. (Beijing, China), respectively. Z–N LLDPE (LLDPE-1) and m-LLDPE (LLDPE-2) were supplied by the Panjin Petroleum Co. (Panjin, China) and the Exxon Co. (Houston, TX), respectively. The characteristic parameters of these samples are listed in Table I. The molecular weight and molecular weight distribution were measured by gel permeation chromatography (GPC) using a PL GPC210 instrument operated at 160°C with dichlorobenzene as the eluant and at a flow rate of 10 mL/min. The instrument was calibrated with polystyrene standards. The branching degree (SCB) was calculated from the ^{13}C-NMR spectra recorded on a Bruker DMX-300 NMR spectrometer in a 10% solution of 1,2,4-trichlorobenzene (TCB) at 125°C. The calculation was performed according to the literature.[20] Differntial scanning calorimetry (DSC) was operated on a Perkin–Elmer DSC4 instrument with a heating rate of 10°C/min in N₂. The calculation of crystallinity was based on the heat of fusion of 273 J/g for the perfect PE crystals. Isotropic sheets of PE samples were prepared by compression molding at 150°C and 2 MPa for 10 min, followed by quenching in air at room temperature.

Sheets of the PE samples were thermally treated in the following ways:

Quenching: The samples were heated to 150°C and maintained for about 10 min to eliminate their thermal history, then quenched in a refrigerator to cool as soon as possible.

Slow cooling: The samples were heated to 150°C to eliminate their thermal history and then were chilled to room temperature at a cooling rate of about −5°C/min.

Thermal segregation: The samples were heated to 150°C to eliminate their thermal history and then were thermally segregated using the successive self-nucleation and annealing (SSA) method as described in the literature with a temperature width of 5°C and then maintaining them 30 min at each temperature.[21]

Every kind of thermally treated sample sheet obtained above was differentiated into four groups: the unirradiated one and the irradiated ones with doses of 13, 35, and 70 Mrad, respectively. The irradiation resource was gamma radiation of Co-60 at the rate of 1.5 Mrad/h. All the irradiation experiments were operated in a vacuum at room temperature.

All the samples then experienced three DSC scans: a first heating scan with a rate of 10°C/min, a cooling scan of −10°C/min, and a second heating scan of 10°C/min. The peak melting temperature (T_m), the peak crystallization temperature (T_c), and the heat enthalpy (ΔH) were recorded, respectively.

The gel content of each irradiated sample was determined by extraction with boiling xylene for 24 h and drying in a vacuum at 50°C for another 24 h. The results obtained are listed in Table II.

TABLE II
Gel Contents (wt %) of Samples After Thermal Treatment and Irradiation

| Samples	Quenching				Slowly cooling				Thermal segregation			
	Irradiation doses (Mrad)											
	0	13	35	70	0	13	35	70	0	13	35	70
HDPE	0	62	72	83	0	22	60	75	0	27	55	72
LLDPE-1	0	69	90	88	0	70	89	86	0	64	88	84
LLDPE-2	0	50	81	93	0	57	86	91	0	54	85	92
LDPE	0	75	82	90	0	74	84	89	0	75	84	89
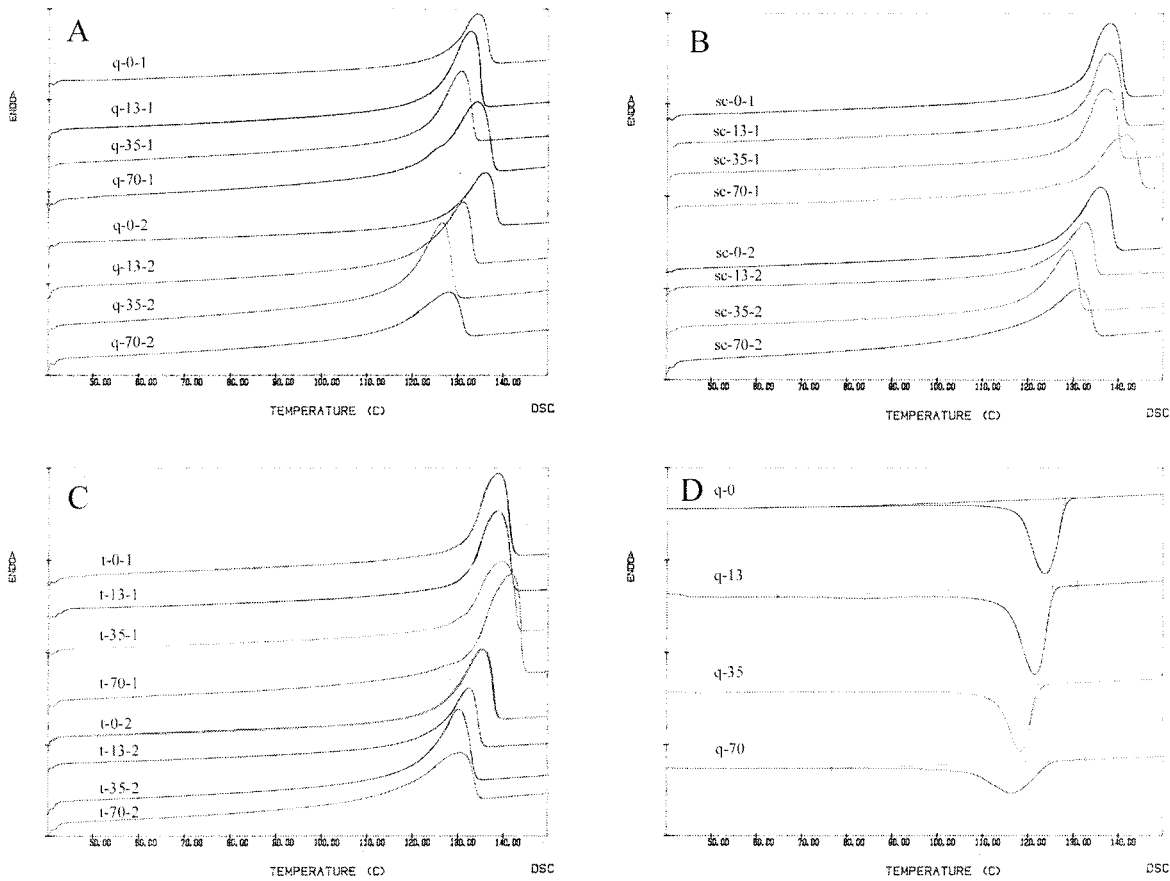
Figure 1 DSC curves of HDPE treated with different thermal history and irradiation dose. (A–C) Heating traces of the samples treated by quenching (q-), slow cooling (sc-), and thermal segregating (t-), respectively. The marks –1 and –2 represent the first and the second heating scans. (D) Cooling traces of the quenched sample: –0-, -13-, -35-, and –70- are the irradiation doses.

RESULTS AND DISCUSSION

HDPE

The results of the DSC scans of HDPE with a certain thermal history and irradiation are shown in Figure 1. There is only one melting peak for the thermally seg-

regated sample (denoted as t- in the figures) due to a few branched chains and a quite fast crystallization rate. The variations of T_m, T_c, and ΔH are plotted in Figure 2. It can be seen that the T_m and the ΔH of the slowly cooled (denoted as sc- in the figures) and the thermally segregated polymers are higher than those
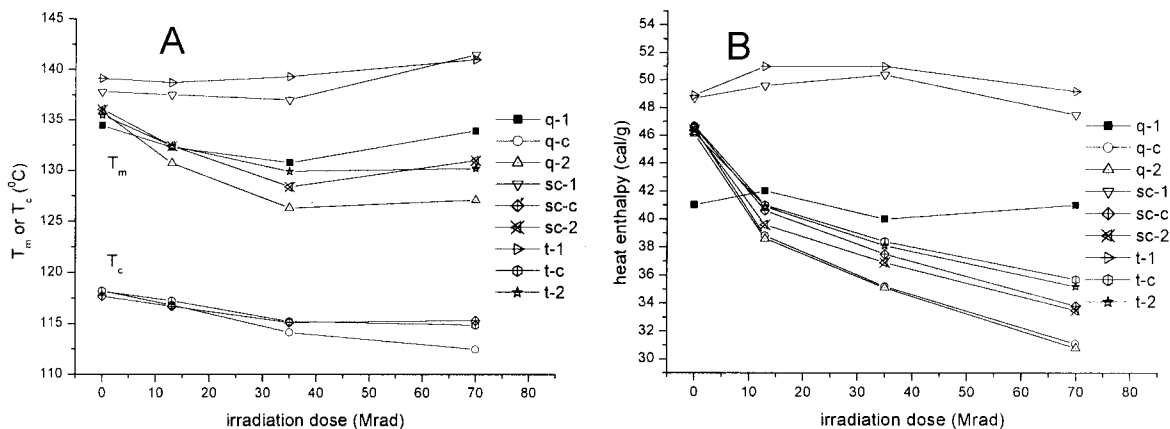
Figure 2 Variation of (A) T_m/T_c and (B) ΔH of HDPE with irradiation dose. -1, -c, and -2 represent the first heating, cooling, and second heating scans, respectively.
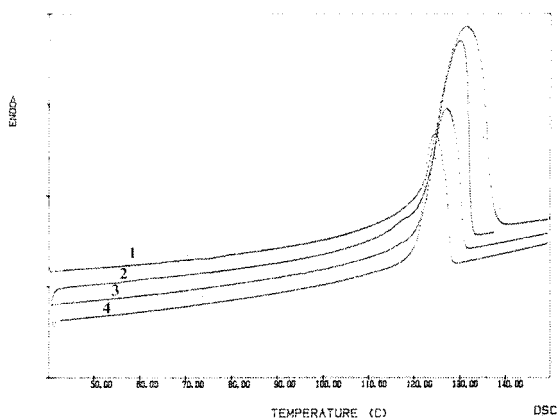
Figure 3 Heating curves of HDPE-t-70 with different scanning rates: (1) 20°C/min; (2) 10°C/min; (3) 5°C/min; (4) 2°C/min.

of the quenched ones (denoted as q- in the figures) with the same irradiation dosage, which is related to the more perfect crystallization after the annealing process. For the quenched samples, the T_m of the first heating scans decreased at first and then increased with increasing irradiation dosages, and ΔH was maintained almost at the same level [as seen in Figs. 1(A) and 2]. The T_m of the slowly cooled and the thermally segregated samples in the first heating scan show almost no decrease but an increasing tendency with increasing dosage. Their ΔH's increased a little at first, then decreased slightly with increasing dosage. The T_c of the three different thermally treated samples all decreased monotonously in the cooling scan (Fig. 3) and the crystallization peak broadened with an increasing dosage [Fig. 1(D)]. In the second heating scan, the T_m of the three samples all decreased first and then increased somewhat with an increasing dosage (Fig. 3), and their ΔH's all decreased throughout.

The decrease of the T_m in the first heating scan can be attributed to the breakage of the longer crystalline segments caused by the chain-scission reaction in the crystalline region according to Flory's theory. This is supported by the lower and broader crystallization peaks in the DSC cooling scan [Fig. 1(D)]. The increasing of the T_m should be the result of melting kinetics due to the constrained effect resulting from the increasing amount of crosslinking networks at the crystal surface. Especially at a higher irradiation dose, the T_m of the slowly cooled and the thermally segregated samples increased so much that their end melting temperatures in the DSC curves exceeded the highest theoretical value of T_m^0 for linear PE (146°C in theory). When the scanning rate was decreased, the obtained T_m decreased at the same time (Fig. 3), which proved the assumption of melting kinetics due to the constrained environment caused by irradiation. The changing tendency of T_m indicates that the chain-scission reaction at a low dose is more obvious in a homogeneous quenched sample compared with the

more perfectly crystallized ones, and only a higher dose can result in the prominent constrained effect due to the formed network. Both the chain scission and the crosslinking reaction result in the decrease of T_c, that is, shorter crystalline chain segments due to a thermodynamic reason and more crosslinking points for crystallization kinetics.

The change of ΔH in the first heating scan is attributed mainly to the chain scissions, that is, the increasing and the decreasing of ΔH result from the reactions in the amorphous and crystalline phases, respectively. The crosslinking reactions in the amorphous region have little effect on ΔH when the dose is not very high. In the first heating scan, the slight change of ΔH indicates that the extent of chain reactions is not significant. The ΔH of the cooling and the second heating scans all decrease with an increasing irradiation dosage. This is caused by the hindrance of the crystallization process during the cooling from the melt due to the increasing amount of the branch points.

After irradiation, the gel content of the quenched HDPE is higher than that of the slowly cooled and the thermally segregated ones (Table II), which shows that the crosslinking reactions take place easily in the homogeneous samples containing more entanglements and crystal defects. The constrained effect on the increasing of T_m is not prominent for the loose network structure of the quenched sample despite its higher gel content compared with the others. As the irradiation dosage is increased, the gel content, that is, the crosslinking reaction, becomes more intense and the increasing tendency of T_m becomes more obvious.

Z–N LLDPE

The DSC curves of Ziegler–Natta-catalyzed LLDPE-1 with a certain thermal history and irradiation are shown in Figure 4. The variations of T_m, T_c, and ΔH are plotted in Figure 5. The variation of T_m and ΔH with an increasing irradiation dosage in the first heating scan is similar to that of HDPE for the same reason with a slight difference. There are several minor melting peaks in the heating scan of the thermally segregated samples due to the multiple crystallization pretreatment, indicating that some shorter crystallizable segments are present besides the longer ones in the polymer. The obvious increase of T_m with the irradiation dosage in the first heating scan for the slowly cooled and the thermally segregated samples takes place in a lower dose range than that of HDPE with the same pretreatment. This can be attributed to the presence of more amorphous fractions in LLDPE, which results in more crosslinking points and more perfect networks. The crystalline segments constrained in a perfect network are difficult to relax to reach the melting state. The smaller crystallite dimension caused by the more branched chains may also
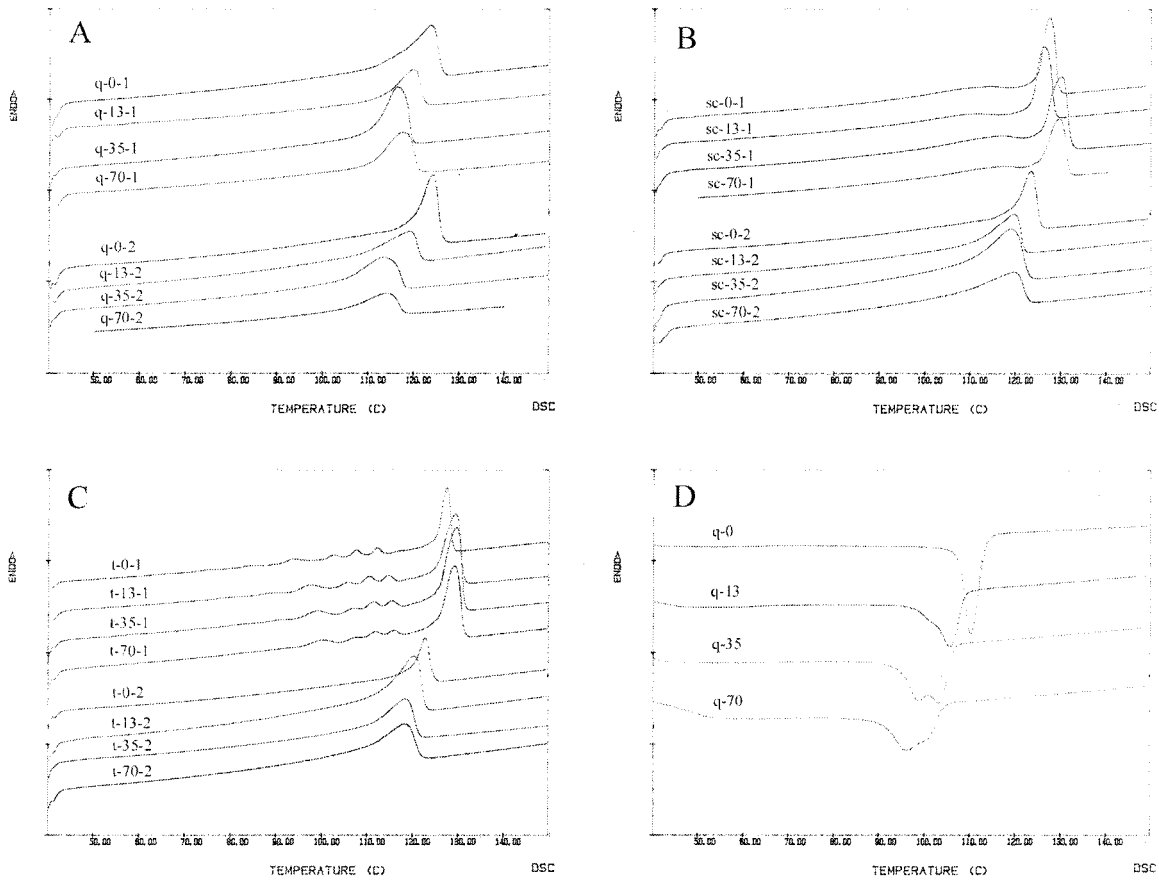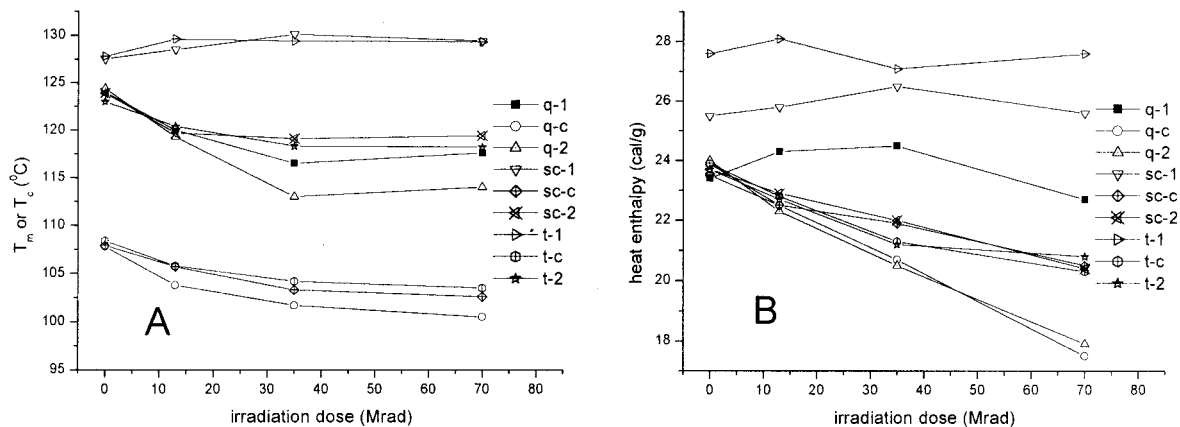
Figure 4 DSC curves of LLDPE-1 treated with different thermal history and irradiation dose. The meanings of the symbols are the same as in Figure 1.

favor limiting the motion of crystalline segments after the amorphous region is crosslinked at the surface of the crystallites.

The lower T_c and T_m of the quenched sample in the cooling and the second heating scan indicates that its crystallizability decreases more obviously than that of the slowly cooled and the thermally segregated ones after irradiation. This agrees with the results of the variation of ΔH with an increasing irradiation dosage.

In the cooling scan of the quenched sample [Fig. 4(D)], T_c decreases with an increasing dosage and a new lower crystallization peak appears. The higher the irradiation dose, the more obvious is the lower temperature part of the crystallization peak, implying that a portion of the longer crystalline segments is broken by the irradiation to form the shorter ones.

In comparing Figure 5(B) and Figure 2(B), it can be seen that the variation of ΔH of LLDPE-1 with an

Figure 5 Variation of (A) T_m/T_c and (B) ΔH of LLDPE-1 with irradiation dose.
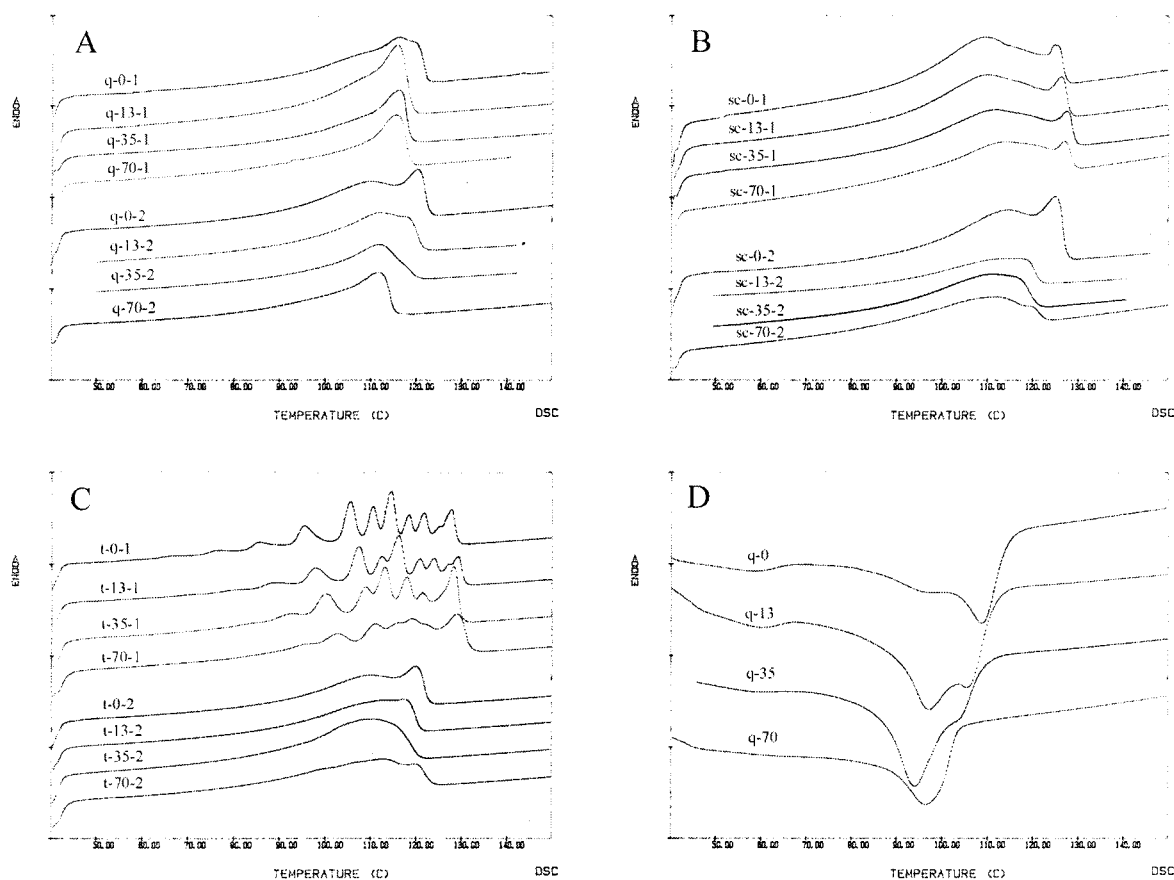
Figure 6 DSC curves of LLDPE-2 treated with different thermal history and irradiation dose. The meaning of the symbols are the same as in Figure 1.

increasing irradiation dosage is basically like that of HDPE because of the their similar chain structure, that is, both containing plenty of the longer crystallizable segments and fewer branched chains. The difference between the ΔH changes of the slowly cooled and the thermally segregated samples is more obvious than that for HDPE. The results above indicate that heat pretreatment before irradiation can affect the irradiation efficiency, which, in turn, will influence the thermal and mechanical properties of the materials obtained.

A higher irradiation dose will produce more gel. LLDPE-1 obeys the rule except that, at the end, the gel was degraded somewhat by the overirradiation (Table II). The thermal history of the sample has little effect on the gel content, while the results of T_m and ΔH are obviously different with various thermal treatments, which lead to the formation of different network structures. Although the gel content of the quenched sample is similar to that of the others when the dose is the same, its decreasing trend of T_m is different from the increasing of the others, indicating that the chain-scission reaction in the crystalline region of the quenched sample is prominent compared to the crosslinking reaction due to the larger number of defects therein.

Metallocene LLDPE

The DSC results of metallocene-catalyzed LLDPE-2 with a certain thermal history and irradiation are plotted in Figure 6. The variations of T_m, T_c, and ΔH with respect to the irradiation dosage are plotted in Figure 7. The prominent appearance of a number of separate melting peaks in the first heating scan of the thermally segregated sample indicates that its crystallizable segments distribute extensively, which represents more homogeneous distribution of the branched chains in the polymer as compared with that in Z–N LLDPE-1. The T_m of the quenched sample decreases slowly all along with increasing irradiation in the first heating scan [Fig. 7(A)], while the T_m of the slowly cooled and the thermally segregated samples increase all along. The different result illuminates that the formation efficiency of the network of LLDPE-2 is higher than that of HDPE and LLDPE-1. The first heating scan of the thermally segregated sample can provide more information in detail. The increasing T_m of the lower melting temperature peaks is more obvious than that of the higher ones, which can be the result of the confined environment of the unmelted crystallites. The faintness, even the disappearance of some melting peaks with increasing dosage, may be the result of the break-
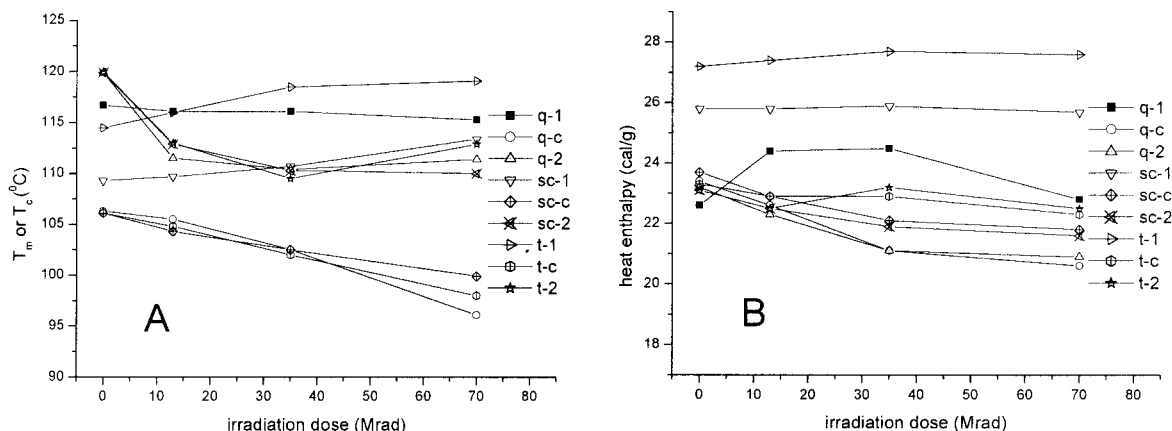
Figure 7 Variation of (A) T_m/T_c and (B) ΔH of LLDPE-2 with irradiation dose.

ing of the related crystalline segments and the melting kinetics, as can be proven by the transition of a higher crystallization peak to lower ones with increasing irradiation in the cooling scan [Fig. 6(D)]. In the second heating scan, the bimodel melting peak becomes a single one for the quenched sample and a wide one for the slowly cooled and the thermally segregated samples. It seems that the longer segments in the quenched sample are broken by the irradiation and rarely form a complete network structure. Admitting that the longer segments in the slowly cooled and the thermally segregated samples are also broken by the irradiation, their higher-temperature part of the melting peak in the second heating scan would be the result of slow melting kinetics. Surely, the crystalline region of the slowly cooled and the thermally segregated samples are more perfect than that of the quenched one and contains fewer defects, in which the amount of the reaction sites for chain scission is also relatively fewer.

The variation of ΔH with an increasing irradiation dosage [Fig. 7(B)] elucidates that ΔH stays at almost the same level in the first heating scan for the slowly cooled and the thermally segregated samples. It is the result of the balance between chain-scission reactions in the amorphous and crystalline regions. For the quenched one, the increasing of ΔH due to the chain scission in the amorphous region is obvious. ΔH decreases in the cooling scan and the second heating scan with increasing irradiation for the same reason as that of HDPE and LLDPE-1.

The gel content increases with the irradiation dosage for LLDPE-2 with the same thermal history (Table II). Its gel content is lowest in the four quenched PE samples at a low irradiation dose (13 Mrad) while it is the highest at a high dose (70 Mrad), which illuminates its unique intrinsic morphological structure.
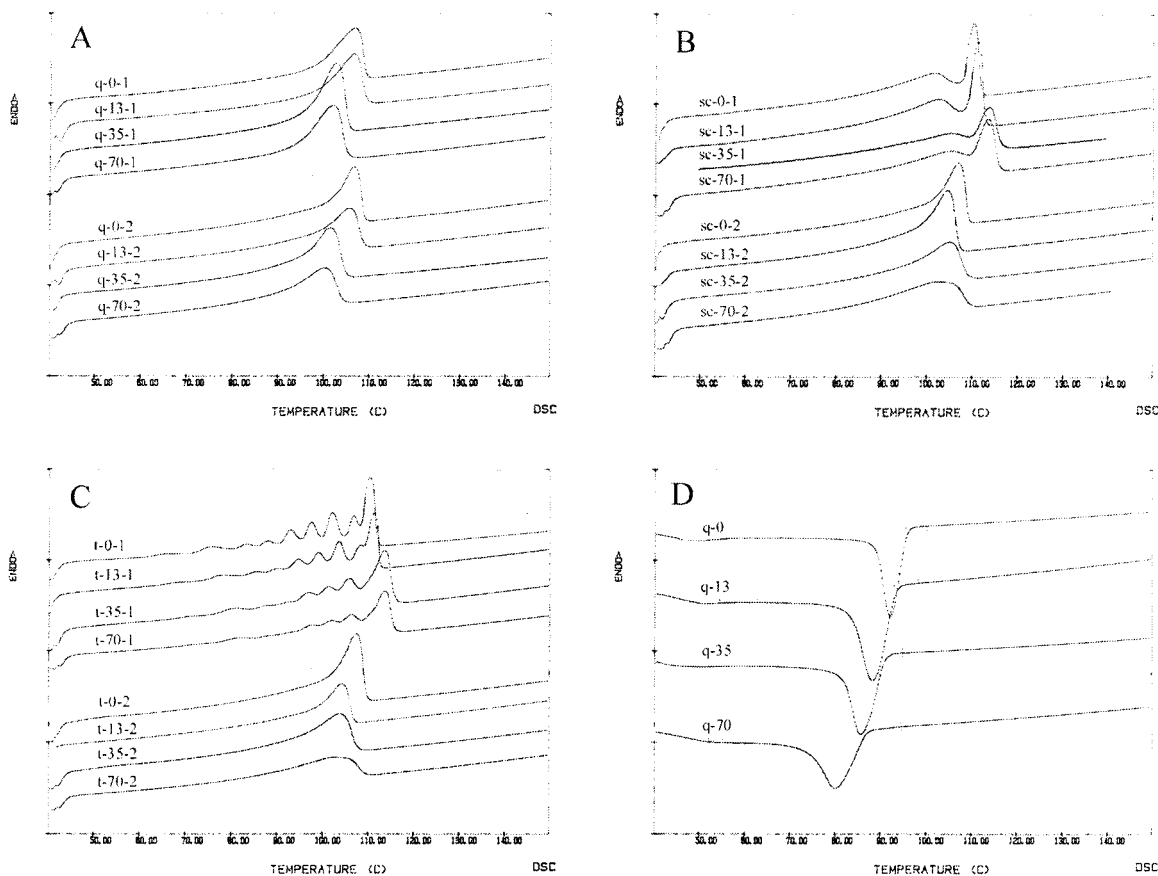
LDPE

The DSC results of LDPE with a certain thermal history and irradiation are shown in Figure 8. The vari-

ations of T_m, T_c, and ΔH with the irradiation dosage are plotted in Figure 9. Multiple melting peaks of the thermally segregated sample in the first heating scan [Fig. 8(C)] indicate that its crystalline segments are distributed in a wide range of length. The T_m of the quenched sample decreases with increasing dosage, and the T_m of the slowly cooled and the thermally segregated samples show the increasing trend [Fig. 9(A)]. These results are somewhat like that of LLDPE-2 for a similar reason—just the region and the extent of the T_m variation are different. T_c and T_m in the cooling scan and the second heating scan all decrease with increasing dosage for the same reason as that of the other three PE samples above. No new peak appears in the cooling scan, which represents that the chain-scission reaction is not prominent compared with that of the two LLDPE.[3]

All the ΔH of the LDPE samples with the different thermal histories decrease monotonously with the increasing irradiation dosage [Fig. 9(B)], which is different from the results of the other three PE samples. In the first heating scan, the decrease of ΔH with increasing dosage should be the result of a severe chain-scission reaction in the crystalline region due to the increasing defects. The ΔH's of the cooling scans and the second heating scans all decrease with increasing dosage for the same reason as that of the other three PE samples. There is no obvious difference in the ΔH values of the LDPE samples with different thermal histories, which also proves the homogeneous distribution of branch points in LDPE. The gel contents of the LDPE samples are larger than those of the other three PE samples when their thermal histories and irradiation doses are the same (Table II). It illuminates the unique structure of the homogeneous distribution of branch points in LDPE, which is favorable to both the chain scission and the crosslinking reaction.

CONCLUSIONS

1. For the same specimen, a larger irradiation dose results in the more severe breaking of crystalline

Figure 8 DSC curves of LDPE treated with different thermal history and irradiation dose. The meaning of the symbols are the same as in Figure 1.

segments, that is, the lower T_m. At the same time, the network structure based on the crosslinking reactions limits the melting of crystalline segments, resulting in the higher T_m. The overall change would lie on the cooperative effects of the two factors. The variation of ΔH depends on the species and thermal history that they have undergone.

2. For the same specimen with a different thermal history, the T_m of the slowly cooled and the thermally segregated samples in the first heating scan change little with increasing dosage, and the T_m of the quenched samples show a decreasing trend. The ΔH's of the slowly cooled and the thermally segregated samples are higher than those of the quenched ones.
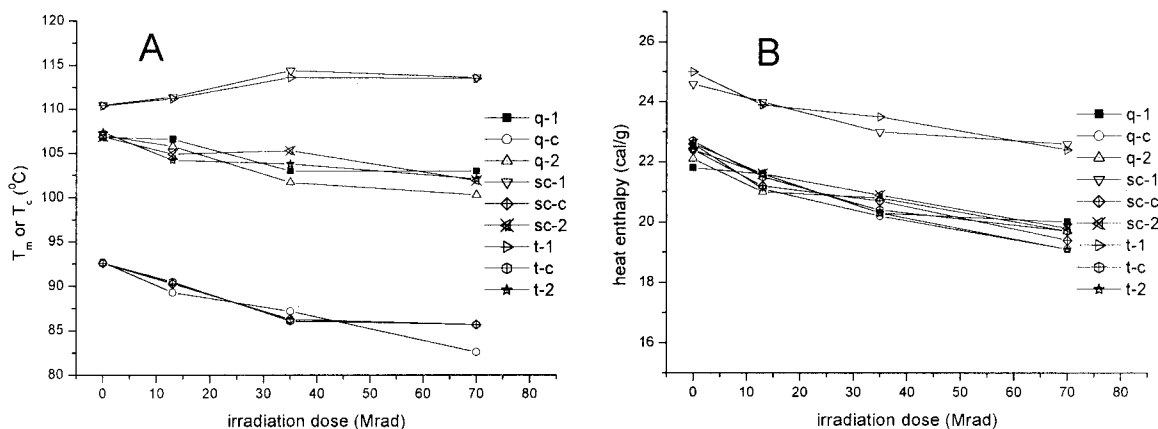
Figure 9 Variation of (A) T_m/T_c and (B) ΔH of LDPE with irradiation dose.

3. With the same thermal history, the T_m changes of HDPE are similar to those of LLDPE-1, and the T_m changes of LLDPE-2 are similar to those of LDPE in the first heating scan. The results indicate that there are some similarities in their chain structures. The difference between LLDPE-1 and LLDPE-2 are reflected their different segment structure, that is, the different distribution of side chains in the backbone. The changes of the ΔH values for the three PE polymers, that is, HDPE, Z–N LLDPE, and m-LLDPE, are similar to each other and that for LDPE is unique. It illuminates the difference between the intrinsic structures of LLDPE-2 and LDPE.

In a word, the mechanisms of irradiation reactions are different for different types of ethylene polymers with different thermal histories. They supply some helpful revelation in the application of irradiated ethylene polymers.

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