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# Thermal Degradation of HDPE in a Batch Pressure Reactor: Reaction Time and Mechanical Stirring Effect

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The effect of reaction time and mechanical stirring on thermal degradation of high density polyethylene (HDPE) was studied at 350°C under nitrogen atmosphere in a batch pressure reactor. Changes in molecular weight (MW), molecular weight distribution (MWD), and crystalline behaviors of the degraded products were investigated by gel chromatography (GPC) and differential scanning calorimetry (DSC). It was found that MWD curves all shifted toward lower molecular weight with increasing reaction time, with both the extent of the movement and its  $\overline{Mw}$  showing a rapid initial drop and then leveling off. In a short period of reaction time, the MW, MWD and crystalline behaviors of the degraded products were affected notably by the mechanical stirring. The  $\overline{Mw}$  of the degraded products without stirring was lower than that of products with stirring in the same time, which should be related to the large difference of temperature distributions in the reactor. When the reaction time reached 4 h, the  $\overline{Mw}$  of the degraded products had dropped to about  $5 \times 10^3$  g/mol from about  $3 \times 10^5$  g/mol for the original  $\overline{Mw}$ , and the product did not show the melting and crystallization behaviors of high density polyethylene again.

**Keywords:** Thermal degradation, HDPE, mechanical stirring, degradation time, pressure reactor

## 1 Introduction

Over the last few decades, polyethylene has been one of the most widely applied polymer materials; however, the main drawback to the growth of this polymer industry is the increase of the plastic waste generated; Therefore, recycling of polyethylene has become of significant importance. Among the different recycling techniques, thermal degradation of polyethylene has always been an important area of research (1–7). Recently, in order to obtain petrochemical products such as fuel oil and gas, extensive studies of the thermolysis of polyethylene at high temperatures (400–800°C) have been conducted (8–14). At relatively lower temperature, for example, below 400°C, the degradation reactions of polyethylene are moderate, and the products are mainly waxy products, which can be further processed into numerous derivatives and additives.

The mechanisms of thermal degradation of polyethylene have been generally considered as typical random scission type reactions (15), and obvious thermal degradation of

normal polyethylene cannot be observed until the temperatures reaches 300°C.

Oakes and Richards (16) studied the thermolysis of low density polyethylene (LDPE) under vacuum at temperatures between 295°C and 360°C, and found that the MW of the residue dropped sharply in the initial stage and then leveled off when plotted against time. Quackenbos (17) treated HDPE in nitrogen and nitrogen containing 0.34% oxygen and followed the changes in intrinsic viscosity and carbonyl content at temperatures between 200°C and 400°C; his results showed that scission was quite slow at 300°C, but the process was sensitive to temperature and became very rapid near 400°C. Kuroki et al. (18) studied the thermolysis of linear high-density polyethylene (LHDPE) at temperatures between 350°C and 390°C under nitrogen containing 0.0007% oxygen by volume, and they indicated that both the molecular weight increase and the degradation reactions were considered to be dependent on the rate of diffusion, in relation to the viscosity of the media. Holmström and Sorvic (19) heated 0.25-mm-thick LDPE films placed on microscope cover glasses in a tubular oven under nitrogen atmosphere at temperatures between 284 and 355°C, and they found a MW increase reaction, as well as the MW decrease reaction. Guy and Fixari (20) reported the thermal degradation of HDPE in an inert and an H-donor solvent at 370°C and 390°C in a 300 cm<sup>3</sup> autoclave, and

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indicated that the diminution of medium viscosity by the solvent favoured products diffusion, thus lowering free radicals coupling reactions. However, we know of no reports on the bulk pyrolysis of HDPE in relatively large equipment below 400°C, especially systematic reports on the effect of factors such as reaction time and mechanical stirring, on the structure and properties of the degraded products. Furthermore, if molecular weight, molecular weight distribution and distribution characteristic (such as the peak position) of HDPE can be regulated properly through thermal degradation, it would permit producing polyethylene of desired molecular weight and MWD, which would be beneficial to study the relationships between MWD and properties of polyethylene (such as bimodal polyethylene) systematically.

In this paper, the thermal degradation of HDPE was carried out at 350°C under a nitrogen atmosphere in a normal autoclave provided with a mechanical stirrer, and the changes of molecular weight, MWD and the melting and crystallization behaviors of the degraded products were studied.

## 2 Experimental

### 2.1 Materials

The HDPE(5000S) resin used in this work was obtained from Qilu Petrochemical, and the molecular weights were as follows:

$$\overline{Mw} = 2.99 \times 10^5; \quad \overline{Mn} = 6.01 \times 10^4$$

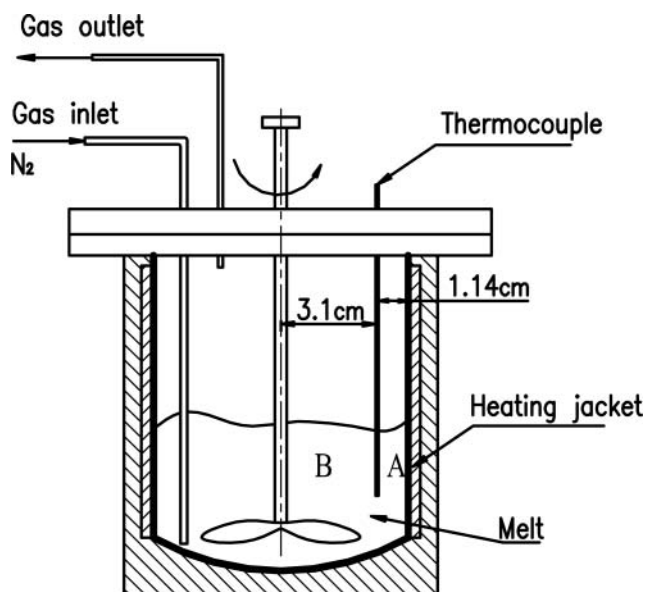


Fig. 1. Schematic diagram of the batch pressure reactor.

Table 1. Heating conditions of samples

Sample	$t$ (h)	$t_1, <300^\circ\text{C}$ (min)	$t_2, 300\sim 345^\circ\text{C}$ (min)	$t_3, 350 \pm 5^\circ\text{C}$ (min)	Stirring speed (r/min)
A1	2	80	20	20	60
A2	4	80	20	140	60
A3	6	80	20	260	60
B1	2	80	20	20	0
B2	4	80	20	140	0
B3	6	80	20	260	0

### 2.2 Thermal Degradation Procedure

The thermal degradation reactions were performed in a 1000 ml stainless steel autoclave (Fig. 1) with a mechanical stirrer and surrounded by a heating jacket for transferring heat to the reaction material. The reactor was operated in batch mode and was equipped with appropriate temperature and pressure controls. A thermocouple was in contact with the reaction material.

In a typical thermal degradation process, 300 g HDPE resin was charged into the reactor, then the resin was flushed with nitrogen without heating for 10 min to make sure an oxygen-free medium, and the pressure in the autoclave was maintained at 0.2 MPa. After that, the reaction temperature (the temperature in the reactor) was set at 350°C. In the degradation reaction with stirring, the mechanical stirrer did not start until the temperature reached 200°C, and the stirring intensity was maintained at 60 rpm; while in a degradation reaction without stirring, the temperature of the degradation reaction heated up to the set temperature directly. The processing parameters for each sample are shown in Table 1. At the end of a degradation reaction, the heating jacket was opened. When the temperature in the reactor cooled down to 160°C, gases were vented and the molten product was removed from the reactor, and cooled down to room temperature. The solid products were mainly waxy products.

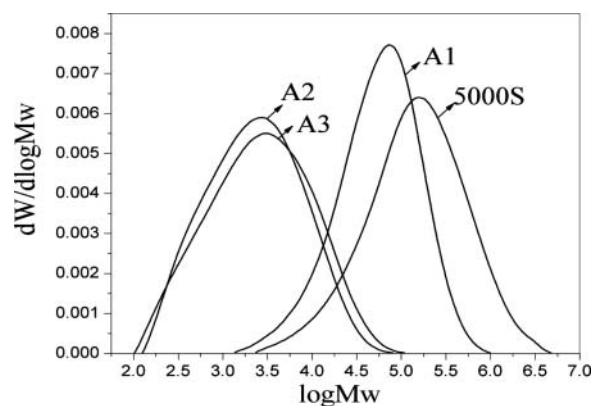


Fig. 2. GPC curves of HDPE thermolysis products with stirring at 350 ± 5°C.

**Table 2.** Data of GPC of HDPE thermolysis products with stirring at  $350 \pm 5^\circ\text{C}$ 

Sample	$M_p$	$M_w$	$M_n$	$M_w/M_n$	Half peak width ( $\Delta \lg M_w$ )
5000S	155200	299700	60100	4.96	1.26
A1	72700	89800	28800	3.12	1.02
A2	2750	4550	1140	4.01	1.52
A3	4360	8160	1610	5.07	1.60

## 2.3 Characterization

### 2.3.1. GPC

The number-average molecular weight ( $\overline{M}_n$ ), weight-average molecular weight ( $\overline{M}_w$ ) as well as polydispersity index ( $\overline{M}_w/\overline{M}_n$ ) of the degraded product were obtained by GPC (Model PL-GPC 220, UK). The instrument was operated at  $150^\circ\text{C}$  with 1,2,4-trichlorobenzene (TCB) as a solvent. Four columns with pore sizes of  $10^3$ ,  $10^4$ ,  $10^5$ ,  $10^6$  Å were calibrated using narrow molecular weight distribution polystyrene samples. The columns were calibrated at  $140^\circ\text{C}$  using 0.1 percent of polystyrene in TCB (21).

### 2.3.2. DSC

The melting and crystallization behavior of the degraded products were analyzed by a DSC Q20 apparatus produced by TA, America. Tests were carried out with 3–5 mg samples under dry nitrogen. All samples were first heated from  $40^\circ\text{C}$  to  $140^\circ\text{C}$  at a rate of  $200^\circ\text{C}/\text{min}$ , held for 3 min to remove the effect of the thermal history, then cooled at a rate of  $10^\circ\text{C}/\text{min}$  to  $40^\circ\text{C}$ . Then the samples were re-heated from 40 to  $140^\circ\text{C}$  at a rate of  $10^\circ\text{C}/\text{min}$ . The crystallization and melting curves were recorded. The degree of crystallinity of the samples was obtained from a comparison of the obtained enthalpies of fusion with that of 100% degree of crystalline of polyethylene ( $293\text{Jg}^{-1}$ ) (22).

## 3 Results and Discussion

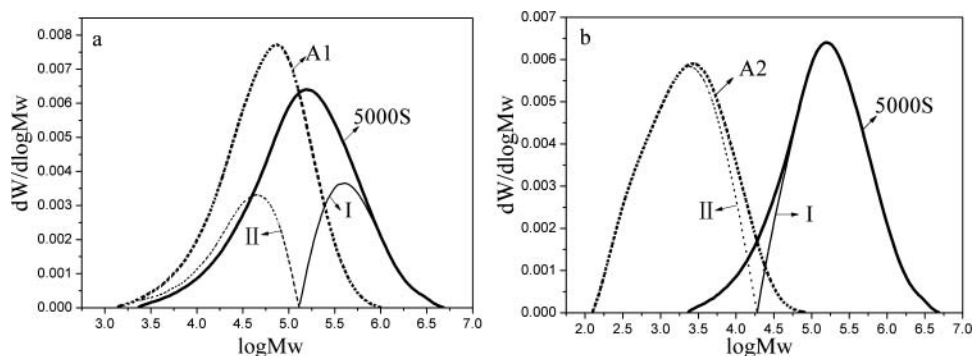
### 3.1 Effect of Reaction Time on Molecular Weight of the Degraded Product

The mechanisms of thermal degradation of polyethylene have generally been considered as typical random scission type reactions (15); the cracking of molecular chains certainly will lead to a decrease in the molecular weight and a change of MWD. At a given degradation temperature, the changes will be affected by the degradation reaction time. So the effect of degradation reaction time on the thermal degradation of HDPE resin, with and without stirring, was studied first.

#### 3.1.1. GPC Analysis of the Degraded Products Under Stirring

GPC results of the degraded products from HDPE resin under stirring are shown in Figure 2, and Table 2 gives related data ( $\overline{M}_p$  means molecular weight at the peak position). All the GPC curves of the HDPE resin and the degraded products conform to a unimodal normal distribution. Compared with the HDPE resin, the peak position of sample A1 shifted to lower molecular weight after degradation at  $350 \pm 15^\circ\text{C}$  for 20 min, and the  $\overline{M}_p$  decreased to about half that of the HDPE resin, but the mass fraction at the peak position increased from 0.636% to 0.772%; at the same time, the weight-average molecular weight ( $\overline{M}_w$ ) and number-average molecular weight ( $\overline{M}_n$ ) decreased rapidly to about only 1/3 and 1/2 that of the HDPE resin. These results may be due to the higher probability of the long molecular chains to break in a short time.

With proper treatment, the GPC curves can better reflect the change of molecular weight during degradation (the gaseous products are neglected). In Figure 3a, curve I is the difference between the GPC curves of HDPE resin and sample A1 when the abscissa was greater than the intersection point of the two curves, which can be considered as the part of the HDPE resin which underwent the degradation reaction; and curve II is the difference between the GPC curves of sample A1 and HDPE resin when the abscissa was smaller than the intersection point, which can be

**Fig. 3.** GPC curves of products before and after degradation with stirring.

regarded as the part from degradation of the HDPE resin. By calculation, the mass fraction of the part of the HDPE resin which degraded was about 33.84%, and its  $\overline{M}_p$ ,  $\overline{M}_w$  and  $\overline{M}_n$  were  $38.9 \times 10^4$ ,  $66.3 \times 10^4$ ,  $41.0 \times 10^4$ , respectively, which were 2.6, 2.2, 6.8 times that of the values of the whole HDPE resin; thus it reflects the relatively high cracking probability of molecules with higher molecular weight. The degraded products of this part contribute to the increased fraction of region III after thermal degradation, whose  $\overline{M}_p$ ,  $\overline{M}_w$  and  $\overline{M}_n$  were  $4.47 \times 10^4$ ,  $3.85 \times 10^4$  and  $1.77 \times 10^4$ , being only about 1/3, 1/8 and 1/4 of the corresponding values in the HDPE resin, respectively.

Also, from Figure 2 and Table 2, it can be seen that the peak width at half height of sample A1 was narrower and the polydispersity index dropped significantly relative to 5000S, indicating a more uniform length of the molecular chains. This may be because the long molecule chains have a greater chance to crack than short ones at the condition of the even temperature distribution under stirring, and moderate length molecular chains increased.

At  $350 \pm 5^\circ\text{C}$ , heating for 140 min resulted in a further decrease in molecular weight of the degradation product, A2. Its  $\overline{M}_p$ ,  $\overline{M}_w$  and  $\overline{M}_n$  all dropped to values below  $1 \times 10^4$ , which is far lower than the molecular weight of common polyethylene. Through further comparison as shown in Figure 3b, the  $\overline{M}_p$  of A2 obviously dropped, but the mass fraction at the peak position (0.53%) decreased only slightly. By calculation, the mass fraction of the part of the HDPE resin, which underwent degradation reaction was about 89.97%, and the  $\overline{M}_p$ ,  $\overline{M}_w$  and  $\overline{M}_n$  of this part before degradation were  $15.9 \times 10^4$ ,  $33.3 \times 10^4$  and  $11.6 \times 10^4$ , respectively; while after degradation, they became only  $0.24 \times 10^4$ ,  $0.31 \times 10^4$  and  $0.10 \times 10^4$ , respectively.

When the heating time was extended to 260 min, the MWD of the degradation product A3 did not continue to shift toward lower molecular weight, and there was even a slight increasing trend of all molecular weight; its  $\overline{M}_p$ ,  $\overline{M}_w$  and  $\overline{M}_n$  were  $1.6 \times 10^3$ ,  $3.6 \times 10^3$  and  $0.47 \times 10^3$ ,

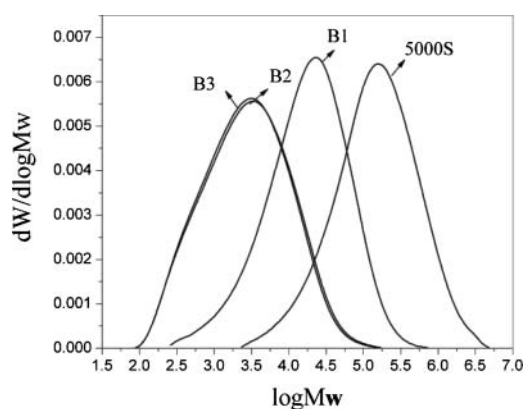


Fig. 4. GPC curves of HDPE thermolysis products without stirring at  $350 \pm 5^\circ\text{C}$ .

respectively, higher than that of A2, but on the whole, they still stayed at a much lower level compared with that of 5000S. This phenomenon was consistent with the results of Holmström and Sorvic (19) and Oakes and Richards (16). Through heating LDPE in a tubular oven at  $355^\circ\text{C}$ , Holmström and Sorvic found that  $\overline{M}_w$  dropped sharply in the initial stage and then leveled off when plotted against time, and sometimes  $\overline{M}_w$  increased slightly after the initial stage. It was proposed that the cracking reactions were accompanied by “molecular enlargement reactions” during thermal degradation of polyethylene at this temperature (19), and these reactions would reach a dynamic balance when the molecular weight dropped to some extent. It should also be noted that, from Table 2, compared with A1, both the polydispersity indices and half peak width of samples A2 and A3 increased. This may be caused by the fact that the collision opportunities of radicals increased with the decreasing melt viscosity, and the chain termination reactions became more complicated (18,19).

### 3.1.2. GPC Analysis of the Degraded Products Without Stirring

As mentioned above, mechanical stirring can increase the transfer efficiency of mass and heat, which can provide a more uniform temperature distribution for the polyethylene melt than without stirring. However, in the melt state, the mechanical stirring consumes much energy especially for a high viscosity melt and the effect of stirring on the degradation reaction is difficult to control. So, in this section, the thermal degradation of HDPE without stirring was also studied. The heating times and reaction temperatures were the same as used in section 3.1.1.

GPC results of the degraded products from HDPE resin without stirring are shown in Figure 4, and Table 3 gives related data. In this case, the GPC curves of degraded products without stirring also showed unimodal normal distributions; and the peak position of the GPC curves also shifted toward lower molecular weight initially and then showed no significant change with increasing reaction time. However, there were also some marked differences. After 20 min of heating at  $350 \pm 5^\circ\text{C}$ , the  $\overline{M}_p$  of degraded product B1 dropped to  $2.28 \times 10^4$ ; i.e., the decrement was much more than that of A1. On the other hand, the mass fraction at the peak position was only a little higher than that of HDPE resin; and its  $\overline{M}_w$  and  $\overline{M}_n$  were only 1/2 and 1/4

Table 3. Data of GPC of HDPE thermolysis products without stirring at  $350 \pm 5^\circ\text{C}$

Sample	$M_p$	$M_w$	$M_n$	$M_w/M_n$	Half peak width ( $\Delta \lg M_w$ )
5000S	155152	299666	60103	4.98587	1.258
B1	22839	34336	6840	5.01988	1.236
B2	3362	6302	1207	5.22121	1.533
B3	3230	5896	1187	4.96714	1.533

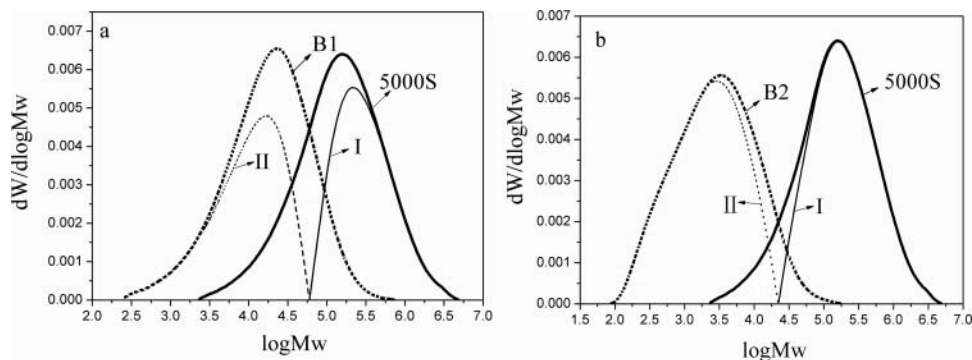


Fig. 5. GPC curves of products before and after degradation without stirring.

of A1, respectively. Through further comparison, shown in Figure 5a, about 60.27% of 5000S (its  $\overline{M}_p$ ,  $\overline{M}_w$  and  $\overline{M}_n$  were  $21.88 \times 10^4$ ,  $45.37 \times 10^4$  and  $22.94 \times 10^4$ , respectively) was degraded in forming B1; (its  $\overline{M}_p$ ,  $\overline{M}_w$  and  $\overline{M}_n$  were  $1.66 \times 10^4$ ,  $1.41 \times 10^4$  and  $0.46 \times 10^4$ , respectively). It was thus clear that the thermal degradation reaction without stirring was more vigorous compared with thermolysis with stirring in the same short time (20 min); this result can be attributed to the structure of the reactor and the heating method.

The internal structure of the reactor is given in Figure 1; the heat inside the reactor is provided by an electric jacket outside the reactor. So the heat transfer without stirring results in a decrease in the melt temperature from the wall to the center of the reactor, especially for a high viscosity polymer melt (with quite low thermal conductivity and low mobility) during the initial stage of degradation. In Figure 1, the temperatures in area A (between thermocouple and the wall of the reactor) were all higher than the set temperature ( $350 \pm 5^\circ\text{C}$ ); while temperatures in area B (between thermocouple and the central axis) were all lower than the setting temperature. According to the structure of the reactor, there was about 49% of the melt, in volume, at high temperatures; that is, nearly half of the melt experienced thermal degradation at temperatures higher than the set temperature.

In contrast, the mechanical stirring can increase the transfer efficiency of mass and heat, which results in relatively uniform temperature distribution in the reactor. Since the rate of degradation is sensitive to temperature, the molecules of the polymer melt near the wall for the B samples will undergo more rapid degradation reactions at higher temperature, causing the increased degradation extent of B1. Besides, unlike A1, the polydispersity index and half-peak width of B1 shown in Tab.3 were all similar to that of the HDPE resin, which showed all molecular chains underwent similar cracking conditions for the uneven temperature distribution in the reactor. Compared with A1, the GPC curve of B1 may be considered as the result of a simple translation of the GPC curve for HDPE resin, but both of the two methods can provide processes to produce polyethylenes with certain MW and MWD.

The molecular weight of the degraded product B2 decreased further with increased reaction time; as shown in Figure 5b, about 86.97% of the mass of the HDPE resin degraded. There was only a limited difference between samples B2 and A2 at this point. This may be because the mobility of the molecular chains increased after a significant decrease of the melt viscosity in the initial stage of degradation (23, 24), and then the melt temperature became more uniform with increased heating time. Thus, the effect of mechanical stirring (its presence or not, and the stirring

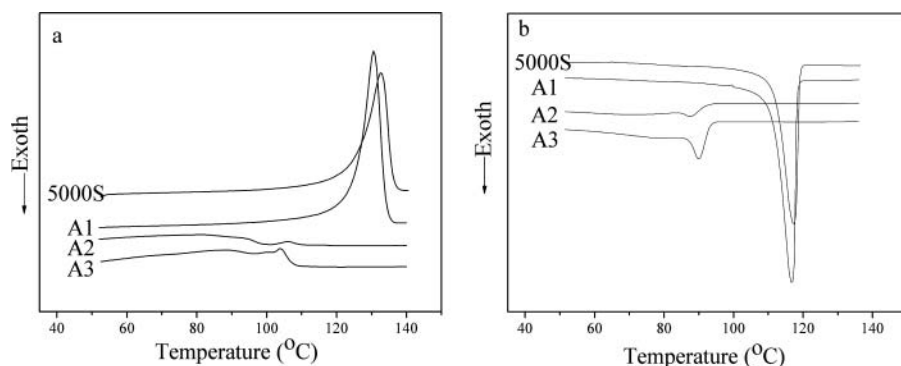


Fig. 6. DSC curves of HDPE thermolysis products with stirring at  $350 \pm 5^\circ\text{C}$  (a: heating scan; b: cooling scan).

**Table 4.** Data of DSC of HDPE thermolysis products with stirring at  $350 \pm 5^\circ\text{C}$ 

Sample	$T_m$ ( $^\circ\text{C}$ )	$\Delta H_m$ (J/g)	$X_c$ (%)	Half peak width ( $^\circ\text{C}$ )	$T_c$ $T_c$	Half peak width ( $^\circ\text{C}$ )
5000S	132.72	177.9	61.34	6.44	117.30	4.37
A1	130.61	189.3	65.26	5.26	116.79	4.15
A2	106.44	2.149	—	—	87.80	—
A3	104.04	5.913	—	—	90.02	—

intensity) on thermal degradation is closely related to reaction time. The shorter the reaction time, the larger the influence.

When the reaction time was further extended to 260 min, the molecular weight of B3 did not continue to decrease, which can also be attributed to the cracking reactions and molecular enlargement reactions reaching a dynamic balance. The polydispersity index of B2 and B3 in Table 3 were similar to that of the HDPE resin, while their half-peak width appeared to slightly increase, which may also be related to the long reaction time and the complicated chain termination reactions.

### 3.2 Effect of Degradation Reaction Time on the Crystallization and Melting Behaviors of the Degraded Products

As a typical crystalline polymer, the melting and crystallization behaviors of HDPE are associated with its molecular weight and molecular weight distribution. So the change of molecular weight and molecular weight distribution of degraded products can also be associated with its melting and crystallization behaviors.

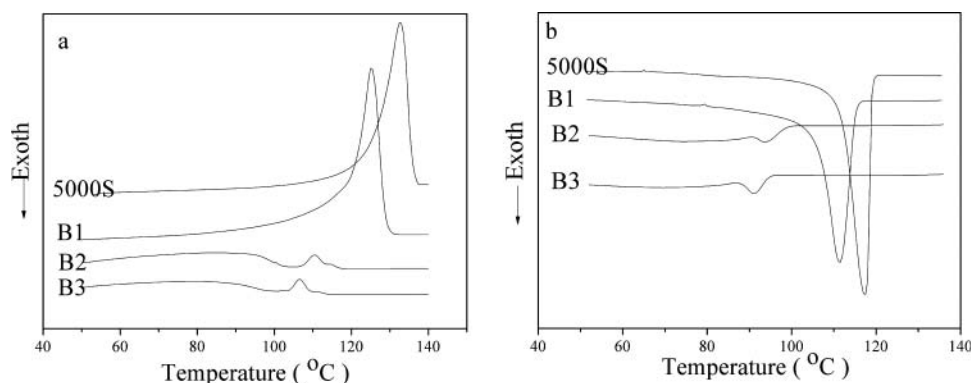
#### 3.2.1. DSC Analysis of Degraded Products with Stirring

The DSC thermograms and related data for samples heated at  $350 \pm 5^\circ\text{C}$  with stirring are given in Figure 6 and Table 4. The melting temperature ( $T_m$ ) of A1 was a little lower than that of HDPE resin, but it was still above  $130^\circ\text{C}$ . The height of the melting peak of A1 increased while the

half peak width decreased, and its peak area (melting enthalpy  $\Delta H_m$ ) showed an obvious increase. These results showed that the crystal size and the regularity of molecular chains arrangement were more homogeneous, resulting in higher crystallinity. These results were also due to the priority cracking of longer molecular chains and resulting increase in medium-length molecular chains. The crystallization curve in Figure 6b showed that, compared with the pure resin, the crystallization temperature ( $T_c$ ) and the half peak width of A1 dropped a little, but its peak height and crystalline enthalpy increased obviously. These results were similar to those of melting curve, which could further suggest that the chemical structure of the molecular chains became similar after its MWD narrowed down, and thus facilitated the formation of uniform crystals. As the heating time extended further, the melting and crystallization peaks of A2 and A3 were hard to be observed, and their  $T_m$ s and  $T_c$ s were all lower by more than  $20^\circ\text{C}$ . This indicated that both products had lost the crystallization behavior of polyethylene.

#### 3.2.2. DSC Analysis of Degraded Products Without Stirring

Figure 7 and Table 5 give the DSC thermograms and related data for samples heated at  $350 \pm 5^\circ\text{C}$  without stirring, respectively. The variations of the  $T_m$ s and  $T_c$ s were similar to those in the case with stirring, that is, the  $T_m$ s and  $T_c$ s shifted toward lower temperature with increasing reaction time. However, there was also some differences. For samples prepared with relatively short reaction time, the decrease of the  $T_m$  and  $T_c$  of B1 was much more than that of A1, and the height of the melting and crystallization peaks did not increase but showed a slight decrease. This can be attributed to the lower molecular weight of the degraded product without stirring. But, for samples prepared with relatively longer reaction time, the  $T_m$ s and  $T_c$ s of B2 and B3 dropped to near those of A2 and A3 values, indicating that they also no longer possessed the crystallization behavior of polyethylene. Thus the effect of mechanical stirring on thermal degradation was obvious at the initial stage of the

**Fig. 7.** DSC curves of HDPE thermolysis products without stirring at  $350 \pm 5^\circ\text{C}$  (a: heating scan; b: cooling scan).

**Table 5.** Data of DSC of HDPE thermolysis products without stirring at  $350 \pm 5^\circ\text{C}$ 

Sample	$T_m$ ( $^\circ\text{C}$ )	$\Delta H_m$ (J/g)	$X_c$ (%)	Half peak width ( $^\circ\text{C}$ )	$T_c$ ( $^\circ\text{C}$ )	Half peak width ( $^\circ\text{C}$ )
5000S	132.72	177.9	61.34	6.44	117.30	4.37
B1	125.21	171.2	60.52	5.51	111.4	5.48
B2	110.57	6.942	—	—	94.01	—
B3	106.57	5.889	—	—	91.16	—

reaction, but the results were more similar for long time of reaction.

#### 4 Conclusions

The thermal degradation of HDPE resin was studied in an autoclave under nitrogen atmosphere at  $350 \pm 5^\circ\text{C}$ . The MWD of the degraded products all showed unimodal normal distributions and the MWD curves all shifted toward low molecular weight. The chain scission reactions and “molecular enlargement reactions” may reach a dynamic balance after a certain time, and the molecular weights and MWDs experienced little change with further increasing reaction time. The degradation product was mainly oligomers, and no longer showed the melting and crystallization properties of HDPE resin. Reaction time and mechanical stirring, which were closely related, showed significant effects on the thermal degradation of HDPE resin.

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