The Study of Melt Grafting Mechanism of Acrylic Acid and Butyl Acrylate onto Low Density Polyethylene and Its Application as Internal Plasticizer

Shenglong Ding, Mingzhu Liu, Haibin Fang

Department of Chemistry and State Key Laboratory of Applied Organic Chemistry, Lanzhou University, Lanzhou 730000, People's Republic of China

ABSTRACT: Melt grafting of acrylic acid (AA) and butyl acrylate (BA) (equal molar ratios) onto low-density polyethylene (LDPE) was carried out in Haake internal mixter by free radical grafting copolymerization. The graft degree of AA and BA in the grafted LDPE (LDPE-*g*-(AA+BA)) was determined by FTIR. The influences of initiator on the graft degree of AA and BA, melt flow rate (MFR), and gel content were investigated, and the optimum conditions were obtained. The successive self-nucleation/annealing (SSA) thermal fraction method was used to characterize the molecular structure and polydispersity of LDPE-*g*-(AA+BA) with various graft degrees. The effects of thermal fraction parameters on fraction of LDPE-*g*-(AA+BA) were investigated. On the basis of the results of SSA, the grafting reaction mechanism of AA and BA onto LDPE was proposed, i.e., grafting reaction preferentially occurred on the tertiary carbons of LDPE. The grafted LDPE possessed suitable reactivity and rheological property. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 108: 423–430, 2008

Key words: low density polyethylene; acrylic acid; butyl acrylate; melt grafting; rheological property

INTRODUCTION

Low-density polyethylene (LDPE) is one of the most widely used thermoplastics owing to its low cost, and excellent mechanical, electrical and optical properties. However, because of its lower reactivity, the potential applications of LDPE are greatly limited. Different chemical modifications via post reactions have been explored to improve its performances,[1–6] among which the reactive extrusion process has been widely employed because of its high efficiency and economic advantages.[7–10] It has been found that reactive extrusion process could improve the reactivity of LDPE, but decrease its flow behavior.[11]

Some small molecular materials, such as unsaturated fatty acid,[12] stearic acid, and phthalate ester[13] have been employed as plasticizers to improve the flow properties of the modified LDPE during the extrusion process, since both reactivity and flow property were very important for the application of LDPE. However, most of the blended plasticizers could migrate from the products during the processing, and then the properties of the blend materials tend to become inferior again. Moreover, the widely used plasticizers, such as dibutyl phthalate, triphenyl phosphate, and dioctyl phthalate, are not environment-friendly, so it is necessary to develop new less toxic and environment-friendly plasticizers and materials. Unfortunately, few studies addressed this problem in literatures.

To improve the reactivity and rheological properties, using the copolymers of acrylate and butyl acrylate as plasticizer has been found to be an effective method.[14,15] Although, grafting either AA or BA onto polyethylene has been well documented,[16–20] to the best of our knowledge, the grafting of both AA and BA simultaneously onto LDPE has not been investigated. In addition, little work has been done to investigate the grafting site of the functional monomers onto LDPE.

Meanwhile, self-nucleation and annealing (SSA) could be understood as the accumulation of SSA steps. This technique could be used to investigate the mechanism of graft copolymerization.[21] The most common instrument in SSA technique is differential scanning calorimeter (DSC). Different from the previous work, gas chromatography (GC) was adopted in SSA in this work.

In this work, equal-molar feed composition of AA and BA was employed to modify LDPE in the presence of dicumyl peroxide (DCP) in the molten state. The optimum amount of DCP was determined by the values of the melt flow rate (MFR) and gel content. The resulted polymers were characterized by

FTIR and successive SSA technique. It is expected that the modified polymer could act as both compatilizer and plasticizer for the LDPE and other polar polymers, such as nylon, polybutylene terephthalate, and polyethylene terephthalate.

EXPERIMENTAL

Materials

The materials employed in this work were LDPE, supplied by Lanzhou petro-chemical Co. (China), has a melt index of 2 g/10 min. Reagent-grade acrylic acid (AA) and butyl acrylate (BA), with a purity of 99%, were purchased from Tianjin Institute of Chemical Reagents (China). (DCP), purchased from Shanghai reagent Co. (China), was purified by recrystallization from ethanol before use, and its half-time at the melt grafting temperature (175°C) was about 1.45 min. Oleic acid (OA) was supplied by Xi'an Chemical Agent Factory (Xi'an, China) and it was of analytical purity. The LDPE modified using AA and BA was designated as $LDPE_n$-g-(AA+BA) and footnote n indicated the code of samples.

Preparation of graft copolymer

The grafting reaction was carried out in a Haake Rhemix 600P batch mixer equipped with roller blades and a mixing head, whose volumetric capacity is 69 cm^3. Vacuum dried LDPE was premixed with a desired amount of AA, BA, and DCP in a beaker, and then the mixture was fed into the mixer. The amounts of AA and BA were kept at AA/LDPE = 1.7 g/100 g and BA/LDPE = 3.1 g/100 g, respectively. The reaction temperature was set according to our previous work.[12] The mixing speed was set to 50 rpm to prevent excessively crosslinking at high shear rate, and the reaction time was set as 10 min. The torque and temperature of the system was monitored during the reaction. After the reaction, the samples were taken from the chamber and quenched in liquid nitrogen to stop further reaction. Then the crude samples were obtained for further characterization.

Purification of graft copolymer

About 3.0 g crude sample was dissolved in 150 mL boiling xylene, the solution was then dripped into 500 mL acetone. The precipitation was filtrated and washed with hot xylene until the weight of grafted LDPE was constant. Afterward, the filter cake was dried under vacuum at 50°C to give the purified sample.

Characterization of graft copolymer

The structure of purified LDPE-g-(AA+BA) was characterized by Fourier transform infrared (FTIR)

spectroscopy (Nicolet NEXUS 670 FTIR). The graft copolymers were pressed into thin films at 170°C for FTIR measurement. The resolution was 4 cm^{-1}, and the scan range was set between 4000 and 400 cm^{-1}.

Determination of graft degree of AA and BA

A deconvolution of the FTIR spectrum was performed by nonlinear fitting of the experiment points.[22,23] The Gaussian function approximation was exploited in curve-fitting process to obtain the peak positions and intensities, which would be used as diagnostic bands. The curve fitting was conducted until the root mean square of the error was smaller than 10^{-4}.

From the deconvoluted spectra, the relative graft degree of AA and BA, denoted as R_a and R_b, were calculated as the area ratios of the bands at 1710 cm^{-1} (AA) and 1738 cm^{-1} (BA) to that at 720 cm^{-1} respectively. The equations used for the calculation are as below

$$R_a = A_{1710}/A_{720} \qquad (1)$$

$$R_b = A_{1738}/A_{720} \qquad (2)$$

where A_{1710} is the peak area of absorbance at 1710 cm^{-1}, characteristic of the carbonyl groups from AA; A_{1738} is that of absorbance at 1738 cm^{-1}, characteristic of the carbonyl groups from BA; and the A_{720} is that of the absorbance at 720 cm^{-1}, characteristic of the methylene groups $((-CH_2-)_n, n > 4)$.

Gel content measurements

An unpurified sample (100–120 mg) was packed in a preweighed nickel net (120 mesh) and put in a Soxhlet extractor. The sample was extracted with xylene for 24 h, and then dried in a vacuum oven at 60°C until its weight remained constant. The gel content was calculated by the following equation:

$$\text{Gel content (\%)} = (W_s - W_n)/W_p \times 100\% \qquad (3)$$

where W_s, W_n, and W_p are the total weight of polymer and nickel net after being extraction, the weight of nickel net, and the weight of polymer, respectively.

Melt flow rate analysis

MFR measurements of the purified LDPE-g-(AA+BA) samples were carried out using XRZ-400 type MFR equipment at 190°C with a load of 2.16 kg according to the ASTM D1238-86T standard.
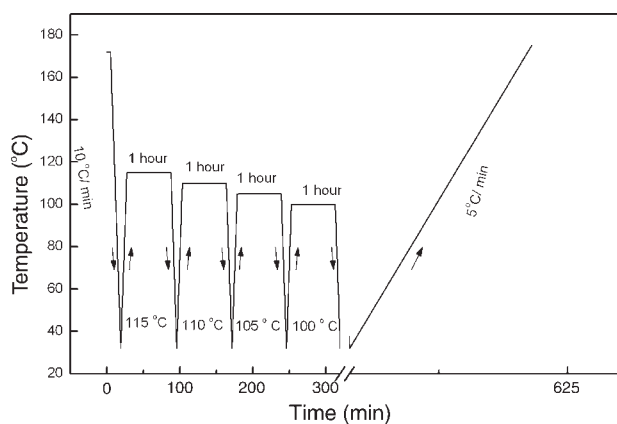
Figure 1 Schematic representation of successive self-nucleation/annealing (SSA) thermal treatment.

Figure 2 FTIR spectra of LDPE and LDPE-*g*-(AA+BA).

Thermal fractionation method

About 0.01 g sample was thermally fractionated using a Finngan GC 2000 under the protection of nitrogen gas. The process was conducted as following: the sample was placed in the oven of GC and purged by N_2 for 2 min. The oven was heated rapidly to 172°C and kept for 10 min to eliminate the thermal history, then cooled at a rate of 10°C/min. After the temperature was lowered to 30°C, the sample was reheated to the first predetermined annealing temperature (T_s) and kept for 60 min. The annealing steps were repeated at different temperatures, which were 115, 110, 105, 100, 95, 90, 85, and 80°C, and denoted as T_{s1}, T_{s2}, $T_{s3}\cdots T_{s8}$, respectively.
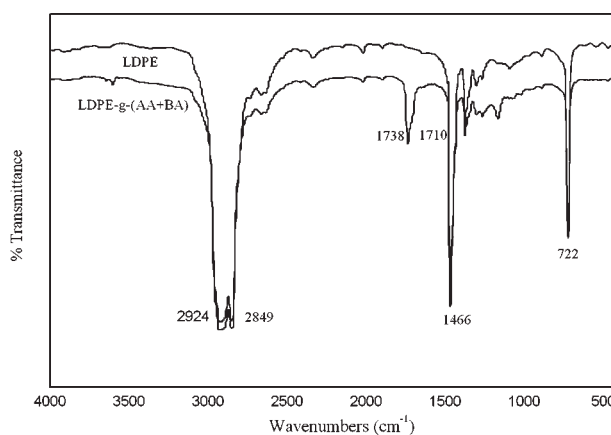
Thermal analysis

After the thermal conditioning, the melting behavior was recorded at a rate of 5°C/min under nitrogen atmosphere with a Perkin–Elmer DSC-SAPPHIRE DSC, which was calibrated using indium as standard. Corresponding to T_{si}, the melting temperature T_{mi} was obtained. The above procedure was shown in Figure 1.

RESULTS AND DISCUSSION

Structure of graft copolymer

The FTIR spectra of the control LDPE and purified LDPE-*g*-(AA+BA) are shown in Figure 2. For LDPE-*g*-(AA+BA), new overlapped absorption bands at 1710 and 1738 cm^{-1} were observed, which could be assigned to the absorption of carbonyl groups of AA and butyl acrylate, respectively.[16] The absorption bands at 722, 1466, 2849, and 2924 cm^{-1} are assigned to the characterization absorption of LDPE skeleton.[12] The appearance of new peaks confirms that
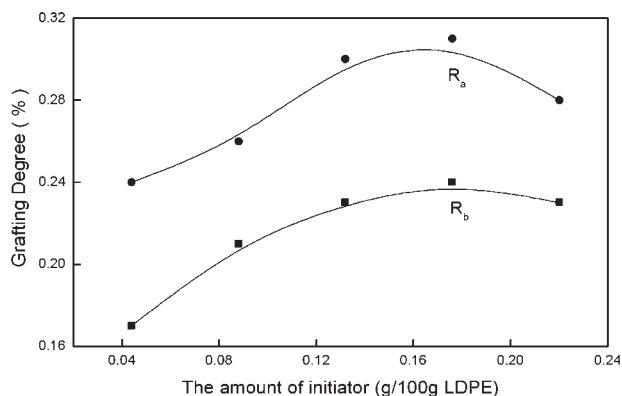
AA and BA have been successfully grafted onto the LDPE backbone.

Graft degree of AA and BA

When AA and BA are grafted onto LDPE, the carbonyl peaks should present in the region of 1710–1750 cm^{-1}. However, because the two carbonyl peaks are strongly overlapped, it was difficult to determine the relative graft degree of AA and BA directly. A deconvolution to the FTIR spectra was performed to determine the R_a and R_b,[22,23] and the results are shown in Figure 3. It could be found from Figure 3 that R_a is larger than R_b, which indicates that the graft degree of AA is higher than that of BA. This could be attributed to the reactivity difference between the AA and BA moities.[24] For AA, the group bonded to the carboxyl group is hydrogen, the hyperconjugation produced by hydrogen is small, and the polarity of vinyl group is high, which would lead to the higher reactivity of AA. For BA, as the group bonded to the carboxyl group is a butyl
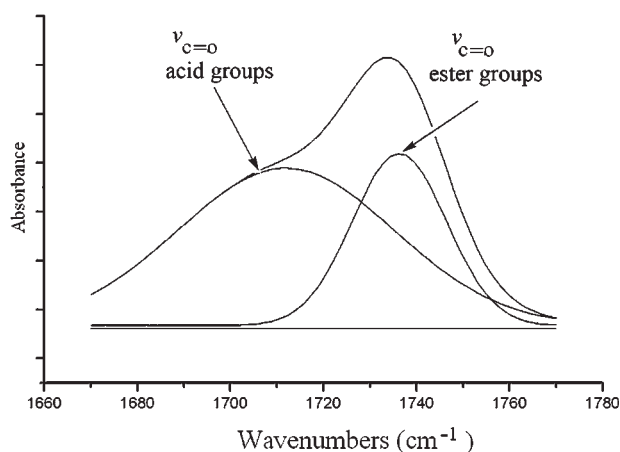
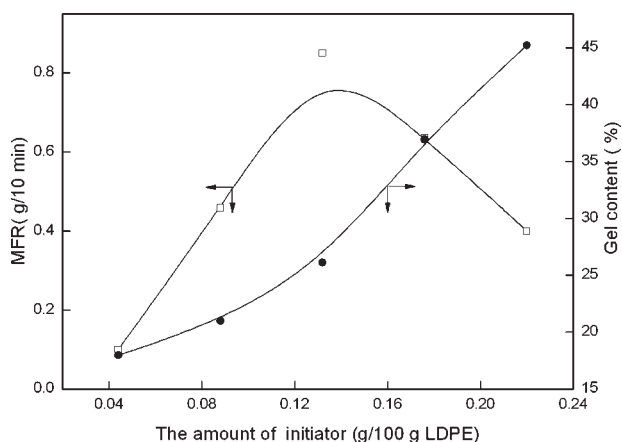**Figure 3** Spectrum of LDPE-*g*-(AA+BA) and its Gaussian curve-fitting ranging from 1660 to 1780 cm^{-1}.

Figure 4 Effect of amount of the initiator on R_a and R_b.

Figure 6 Effect of t_{sp} on polydispersity of grafted LDPE (heating rate = 7°C/min, (a) t_{sp} = 30 min; (b) t_{sp} = 60 min).
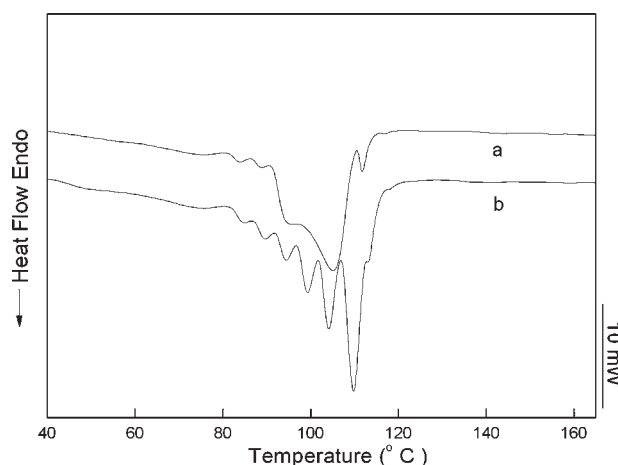
group, the hyperconjugation produced by butyl is large and the polarity of vinyl group is low. This would lead to the lower reactivity of BA. As a result, when AA and BA with equal molarities were introduced, the graft degree of AA would be higher than that of BA naturally.

The influence of DCP on graft degree

Figure 4 shows the influence of DCP on graft degree of AA and BA. It displays that the graft degrees of AA and BA increase with the increase of DCP untill it reaches a maximum at DCP/LDPE = 0.175 g/100 g; after which, the graft degrees of AA and BA decrease with the increase of DCP. This phenomenon is attributed to the reaction mechanism. In the reaction, the DCP firstly decomposed and produced primary radicals. These primary radicals would further react with the hydrogen on the LDPE chain and produce second radicals. The second radicals would favor the grafting reaction. With the increase of DCP, the amount of primary and secondary radical increase, and graft degrees of AA and BA also increase.[25] However, excessive amount of DCP

would lead to the polymerization of AA and BA, and decrease the graft degrees of AA and BA. So the graft degrees decrease with the increase of DCP after DCP/LDPE = 0.175 g/100 g.

Influence of DCP on gel content

The influence of DCP on the gelation is shown in Figure 5. It presents that the gel content increases continuously with the increase of DCP. The increase of DCP would lead to an increased crosslinking reaction when the amounts of monomers are fixed. Consequently, the gel content is increased. From the slope of the curve in Figure 5, it could be found the increasing trend of the gel contents is accelerated when the DCP/LDPE is above 0.135 g/100 g. This could be ascribed to the accelerated increase of crosslinking degree after the amount of DCP exceed the suitable amount.[26]

Figure 5 Effect of the initiator on MFR and gel content.
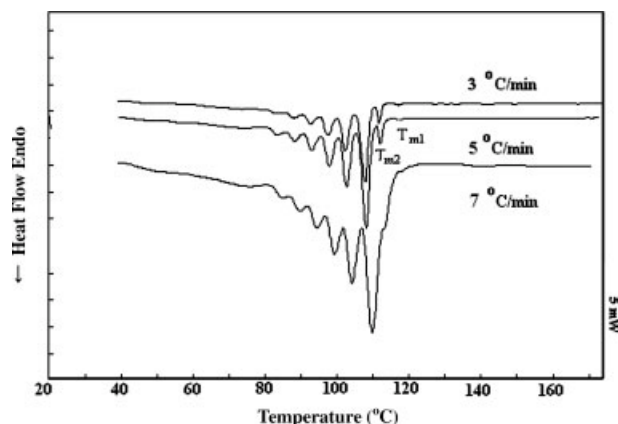
Figure 7 DSC heating scans at 3, 5, and 7°C/min after applying SSA to LDPE$_2$-g-(AA+BA).
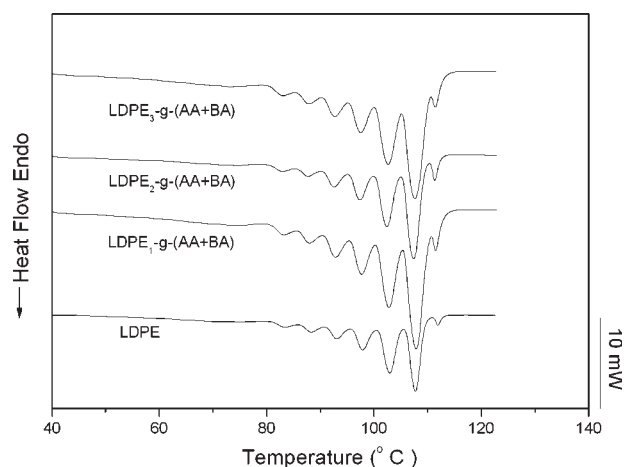
Figure 8 Final DSC heating scans at 5°C/min after applying SSA to LDPE and LDPE-g-(AA+BA) samples (LDPE$_1$-g-(AA+BA): DCP = 0.045 g/100 g LDPE; LDPE$_2$-g-(AA+BA): DCP = 0.090 g/100 g LDPE; LDPE$_3$-g-(AA+BA): DCP = 0.135 g/100 g LDPE).

Influence of DCP on MFR

Figure 5 also displays the influence of DCP on MFR. It could be found that the MFR shows a maximum as DCP/LDPE = 0.135 g/100 g. With the increase of DCP, both the chain initiation and termination increase, which would lead to the formation of many short grafted chains on LDPE. The grafted chain possesses the function of plasticizer and could increase the flow property of LDPE, hence, the MFR of grafted LDPE increases. However, excessive increase of DCP would lead to more second radicals of LDPE. The second radicals of LDPE could mainly react with each other and formed highly crosslinked product, which would naturally make MFR decrease markedly. From Figure 5, we found that DCP/LDPE = 0.135 g/100 g is an optimum quantity.

The mechanism of graft copolymerization

SSA technology was adopted to study the mechanism of graft polymerization in more details. Because both the fractionation conditions and graft degree could influence the fraction of grafted LDPE, it is necessary to optimize the major parameters of SSA before discussing the influence of graft degree on the polydispersity. These parameters include annealing temperature (T_s), temperature interval between $T_s(T_{sv})$, the permanence time at $T_s(t_{sp})$, and the heating rates (HR). In this work, T_s and T_{sv} were chosen according to literature,[27] while t_{sp} and HR was investigated.

Determination of SSA parameters

Figure 6 shows the effect of t_{sp} on polydispersity of grafted LDPE and presents the results of polydispersity at t_{sp}, 30 min (curve a) and 60 min (curve b). It could be seen that polydispersity of grafted LDPE is better at t_{sp} = 60 min than that of t_{sp} = 30 min. It was reported that t_{sp} was only a few minutes for linear LDPE,[28] but it was not enough for nonlinear LDPE to anneal even in half an hour (as shown in the curve a of Fig. 6). It could be seen from curve b of Figure 6 that the polydispersity of grafted LDPE is perfect at t_{sp} = 60 min. Therefore, t_{sp} = 60 min was adopted as the temperature permanence time in our experiment.

Figure 7 shows the influence of HR on the polydispersity of grafted LDPE. It could be found that when the HR was 7°C/min, the peaks of T_{m1} and T_{m2} disappeared when compared with those of 3°C/min and 5°C/min. As HR was low, the performance time between temperature intervals was long, the melting of a fraction was adequate, and the polydispersity of grafted LDPE was clear. In this study, it was found that a HR of 5°C/min produced adequate

TABLE I
Melting Peaks Temperature for all Melting Endotherms Obtained After the SSA Treatment (Fig. 8) as a Function of Self-Seeding Temperature (T_s)

T_s (°C)	T_m (°C)			
			Sample code	
	LDPE	LDPE$_1$-g-(AA+BA)	LDPE$_2$-g-(AA+BA)	LDPE$_3$-g-(AA+BA)
115	–	–	–	–
110	111.3	111.1	111.3	111.2
105	106.6	106.4	106.2	106.3
100	101.8	101.4	101.0	100.5
95	96.6	95.8	95.1	94.5
90	91.8	89.9	89.0	88.4
85	86.7	86.0	85.4	85.0
80	82	81.9	81.4	81.0

TABLE II
Partial Areas Obtained After Integration of Each DSC Scan in Figure 8 (i.e. After SSA) as a Function of Self-Seeding Temperature (T_s)

	Partial area (%)			
	Sample code			
T_s (°C)	LDPE	LDPE$_1$-g-(AA+BA)	LDPE$_2$-g-(AA+BA)	LDPE$_3$-g-(AA+BA)
115	0	0	0	0
110	1.76	1.70	1.73	1.32
105	20.35	20.50	20.23	17.10
100	15.45	15.20	15.02	12.30
95	7.48	5.63	4.84	2.28
90	3.93	3.00	2.82	2.65
85	2.27	1.54	1.47	1.13
80	1.60	0.90	0.85	0.83

separation of the melting peaks, while slower heating rates did not provide any significant improvement in the resolution of the peaks.

The influence of graft degree on the T_m of grafted LDPE

Figure 8 shows the influence of graft degree on the polydispersity of LDPE. It could be found that the shape of curves in Figure 8 were almost similar for the four samples. This indicated that there was not an obvious variety in the polydispersity before and after the grafting reaction.

Table I shows the T_m of all fractions per sample at different T_s obtained from Figure 8. It could be seen from Table I that the T_{m4}, T_{m5}, T_{m6}, T_{m7}, T_{m8} of LDPE-g-(AA+BA) tend to decrease and the T_{m2}, T_{m3} of that are almost steady with the increase of graft degree. The decrease of the T_{m4}, T_{m5}, T_{m6}, T_{m7}, T_{m8} was attributed to that the grafted (BA + AA) on polyethylene chain would induce "structure defect" and make the chain segment incorporate into the crystal lattice difficult, which would further lead to the decrease of the crystallinity of the grafted LDPE.[21] As a result, the mean lamella thickness of crystal lattice became thinner and T_m is reduced. The constant T_{m2} and T_{m3} are due to the unchanged ethylene sequence in LDPE backbone (see below).

The mechanism of graft copolymerization

The DSC curves in Figure 8 could be integrated and the partial areas corresponding to each peak can be considered to be proportional to a normalized weight fraction of certain comonomer content.[21] The change of partial areas indicated the variety of fraction with certain methylene sequence length. Table II presented the values of partial areas (in percentage terms) for each endotherm of each DSC heating curve in Figure 8. From Table II, a decrease in the partial areas of the fractions at T_s = 95, 90, 85, 80°C was observed as compared with the control one. But

for the T_s of 110, 105, 100°C, partial areas tended to remain constant as graft degree increased.

It is well known that the fraction with more branches possessed lower melting temperature, and *vice versa*. The decrease of T_m means the increase of branch contents. In Table II, a slight depression of the T_{m5}, T_{m6}, T_{m7}, and T_{m8} of LDPE-g-(AA+BA) with respect to the control LDPE in Table I could be seen, which confirms that the grafting reaction occurred onto the fraction with low T_m. That is to say, the grafting reaction mainly occurred onto the fraction with more branches, i.e., onto the tertiary carbons within the main chain for the samples, even though the monomer grafting onto the secondary carbons or allylic terminal radical is not ruled out. This conclusion is in good agreement with the results reported in the literature.[29]

On the other hand, for the LDPE used in this work, there are great amounts of branching chain within its backbone. The higher the branch contents, the more amount of tertiary carbons. Much greater numbers of tertiary carbons could enhance the probability of grafting reaction between the monomers and tertiary carbons. Besides, according to literature,[30] the radical reactivity for peroxide-initiated grafting would be tertiary carbons > secondary
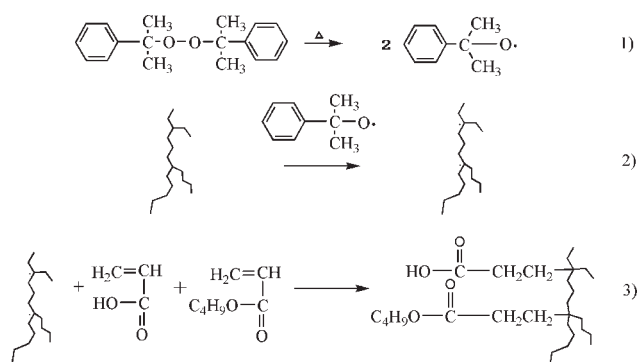

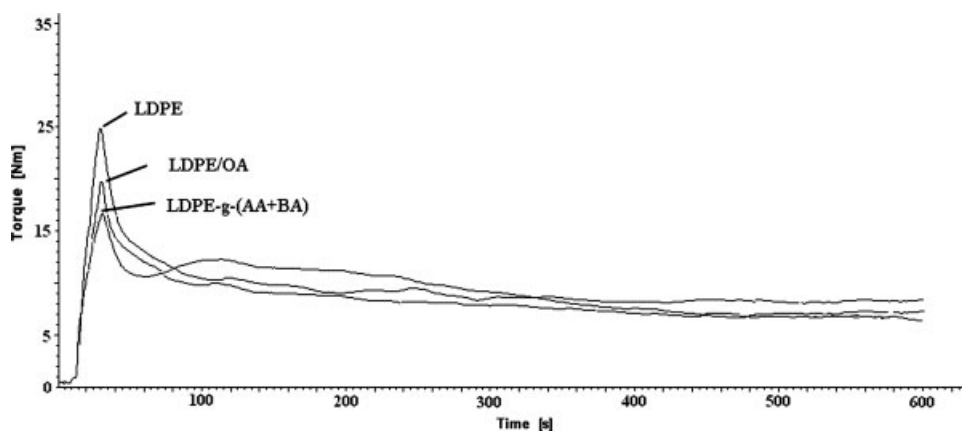**Figure 9** The scheme of the reaction for branch formation.

Figure 10 Plots of the torque as a function of time in different systems.

ones > primary ones at high temperature. Above two reasons supported the enough sites and probability for the reaction mainly occurred onto the tertiary carbons. Figure 9 shows the modified mechanism of grafting reaction of AA and BA onto LDPE according to the literature.[31]

The behavior of torque of grafted LDPE

Plots of the torque as a function of time in different systems, LDPE/AA/BA/DCP (100.0/1.70/3.10/0.135), LDPE/OA(100/0.2), and control LDPE were shown in Figure 10. From Figure 10 we could see that the viscosity of three systems was almost constant in less than 20 s, and subsequently, the viscosity increased dramatically and reached a maximum in less than 40 s, which was called melting peaks of the mixture system. As shown in Figure 10, the viscosity decreased with prolonged time and stabilized after 3 min for LDPE and LDPE/OA. This behavior arose from the consecutively increasing temperature due to the heat generated by friction and shear. Apparently, the OA could act as an internal plasticizer for LDPE, since its equilibrium torque was lower than that of control LDPE after addition of the OA to the system. But it was not perfect internal plastisizer, for there was no covalent bond between them, so it easily migrated from the products during employment.

But for the LDPE/(AA+BA)/DCP system, a new and smooth torque peak appeared in Figure 10. Such an increase in torque indicated that the grafting reaction of (AA+BA) onto the LDPE backbone occurred. The reason was that the branched macromolecules were produced during the grafting reaction and they had a higher melt viscosity than that of linear macromolecules. Moreover, it is very interesting to note that the difference of end-torque values between the LDPE and LDPE/(AA+BA) system was about 2 Nm. This was mainly because the BA grafted onto the polymer acted as a plasticizer for its soft side

chain[15]. So the modified LDPE was a suitable compatilizer and internal plasticizers.

CONCLUSIONS

The AA and BA have been successfully grafted onto LDPE in the presence of DCP in the molten state. The optimum amount of the initiator was about DCP/LDPE = 0.135 g/100 g for both higher reactivity and rheological properties. MFR confirmed that the AA and BA grafted onto the LDPE acted as an internal plasticizer and improved its flow properties.

When the other conditions are equal, the permanence time $t_{sp} = 60$ min and the heating rates, HR = 5°C/min was obtained for adequate separation of fraction. After grafting, the melting temperature of LDPE-g-(AA+BA) tended to decrease. Results of SSA proved that the preferred sites for grafting were the tertiary carbons within the LDPE chains. A graft mechanism of AA and BA onto LDPE was proposed.

This modified LDPE was a sutiable compatilizer and internal plasticizer for its low torque value. Grafting modification of polyolefin with multi-monomer may be an effective approach to enhance its properties.

References

1. Novák, I.; Pollák, V.; Chodák, I. Plasma Process Polym 2006, 3, 355.
2. Gilliam, M. A.; Yu, Q. S. J Appl Polym Sci 2006, 99, 2528.
3. Ma, D. L.; Akpalu, Y. A.; Li, Y.; Siegel, R. W.; Schadler, L. S. J Polym Sci Part B: Polym Phys 2005, 43, 488.
4. Masashi, K.; Hisaya, S. Macromol Chem Phys 2005, 206, 456.
5. Yang, P.; Deng, J. Y.; Yang, W. T. Macromol Chem Phys 2004, 205, 1096.

6. Felipe, W. F.; Fernanda, C. S.; Raquel, S. M.; Sônia, M. B. N. Eur Polym J 2004, 40, 1119.
7. Zhang, X.; Simon, L. C. Macromol Mater Eng 2005, 290, 573.
8. Liao, H. T.; Wu, C. S. J Polym Sci Part B: Polym Phys 2004, 42, 4272.
9. Cazacu, G.; Mihaies, M.; Pascu, M. C.; Profire, L.; Kowarskik, A. L.; Vasile, C. Macromol Mater Eng 2004, 289, 880.
10. Tan, L.; Deng, J. P.; Yang, W. T. Polym Adv Technol 2004, 15, 523.
11. Bhattacharya, A.; Misra, B. N. Prog Polym Sci 2004, 29, 767.
12. Liu, M. Z.; Liu, Z. M.; Ding, S. L.; Li, S. Q.; Zhang, L. J. J Appl Polym Sci 2003, 90, 3299.
13. Teil, M. J.; Blanchard, M.; Chevreuil, M. Sci Total Environ 2006, 354, 212.
14. Sombatsompop, N.; Phromchirasuk, C. J Appl Polym Sci 2004, 92, 782.
15. He, M. J.; Chen, W. X.; Dong, X. X. Polymer Physics; Fudan University Press: Shanghai, 1990.
16. Ghosh, P.; Chattopadhyay, B.; Sen, A. K. Polymer 1998, 39, 193.
17. Oromehie, A. R.; Hashemi, S. A.; Meldrum, I. G.; Waters, D. N. Polym Int 1997, 42, 117.
18. Ghosh, P.; Dev, D. Eur Polym J 1998, 34, 1539.
19. Huang, H. L.; Yao, Z. H.; Yang, J. H.; Wang, Y.; Shi, D. A.; Yin, J. H. J Appl Polym Sci 2001, 80, 2538.
20. Yao, Z. H.; Gao, Y.; Yin, J. H. J Appl Polym Sci 2002, 86, 2626.
21. Marquez, L.; River, I.; Müller, A. J Macromol Chem Phys 1999, 200, 330.
22. Dongye, G. Z.; Zhou, Q.; Sun, S. Q. Comput Appl Chem 1999, 16, 379.
23. Coiai, S.; Passaglia, E.; Aglietto, M.; Ciardelli, F. Macromolecules 2004, 37, 8414.
24. Chen, Z. Q.; Cheng, S. J.; Zhou, D. F. J East Chin Univ Sci Technol (Natural Science Edition) 2006, 32, 422.
25. Yilser, G.; Sinan, E.; Zakir, M. O. R.; Erhan, P. J Appl Polym Sci 2003, 92, 3675.
26. Liu, N. C.; Yao, G. P.; Huang, H. Polymer 2000, 41, 4537.
27. Xie, Y. C.; Zhang, Q.; Fan, X. D. J Appl Polym Sci 2003, 89, 2686.
28. Müller, A. J.; Arnal, M. L. Prog Polym Sci 2005, 30, 559.
29. Gaylord, N. G.; Mehta, R.; Mohan, D. R.; Kumar, V. J Appl Polym Sci 1941 1992, 44.
30. Keating, M.; Lee, I.-H.; Wong, C. S. Thermochim Acta 1996, 284, 47.
31. Wei, Q.; Chionna, D.; Galoppini, E.; Pracella, M. Macromol Chem Phys 2003, 204, 1123.