

Morphology, Structure, and Rheological Property of Linear Low-Density Polyethylene Grafted with Acrylic Acid

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ABSTRACT: The chain structure, spherulite morphology, and rheological property of LLDPE-*g*-AA were studied by using electrospray mass spectroscopy, ^{13}C -NMR, and rheometer. Experimental evidence proved that AA monomers grafted onto the LLDPE backbone formed multiunit AA branch chains. It was found that AA branch chains could hinder movement of the LLDPE main chain during crystallization. Spherulites of LLDPE became more anomalous because of the presence of AA branch chains. Rheological behavior showed that AA branch chains could act as an inner plasticizer at the temperature range of 170–200°C, which made LLDPE-*g*-AA easy to further process. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 80: 2538–2544, 2001

Key words: LLDPE-*g*-AA; morphology; structure; rheological property

INTRODUCTION

The functionalization of polyolefins through a grafting reaction is becoming an important industrial process. The monomers grafted onto polyolefins usually are unsaturated functional monomers, such as maleic anhydride (MAH),^{1–4} glycidyl methacrylate (GMA),^{5–7} acrylic acid (AA)^{8,9} and its derivatives, and so forth. The properties and applications of these grafting functionalized polyolefins are very much dependent on the nature and degree of grafting (DG) of the monomers used.

Grafting of polyethylene (PE) with acrylic acid is an important method used for the modification of PE. The functionalized PE-*g*-AA can be applied as a compatibilizer of PE blended with polyamide, polyester, or other polar polymers to prepare poly-

meric alloys or as an interfacial adhesion with metal, ceramic, glass, and so forth.^{10,11} The chain structure of PE-*g*-AA was suggested in earlier literature,⁹ and it was also generally accepted that AA grafted onto linear low-density polyethylene (LLDPE) was a multiunit. However, knowledge of the details of PE-*g*-AA chain structure is still limited. To date, direct experimental proof has not been definitively presented, and the effect of the degree of grafting of AA on the morphology and the rheological behavior of grafted PE has seldom been reported.

The present study reports (1) the characterization of AA branch-chain structure grafted onto LLDPE carried out by using electrospray mass spectroscopy and ^{13}C -NMR; (2) the effect of the degree of grafting of AA on spherulite morphology and rheological property of LLDPE-*g*-AA.

EXPERIMENTAL

Materials

LLDPE (DFDA7042) was provided by Daqing Petrochemical Co. (China), with melt flow rate (MFR)

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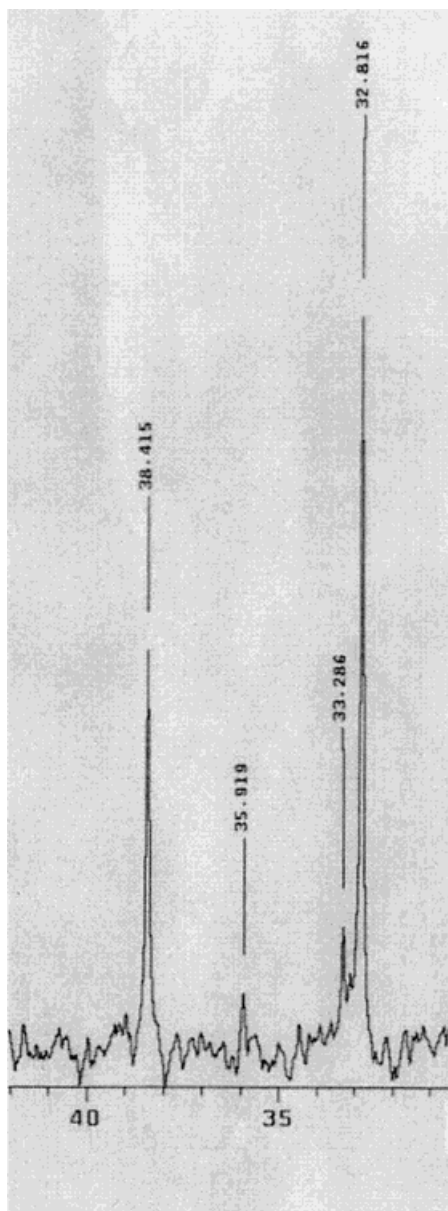


Figure 1 ^{13}C -NMR spectrum of LLDPE-g-AA.

of 5.1 g/10 min (190°C, 5 kg). Acrylic acid (AA), supplied by Tianjin Chemical Agent Factory (China), was reagent grade. Xylene and acetone were all reagent grade and used as received.

Purification of LLDPE-g-AA

About 2 g of gross LLDPE-g-AA product prepared in this laboratory was dissolved in 100 mL boiling xylene and precipitated in 100 mL acetone to remove unreacted monomer and AA homopolymer formed during extrusion. The precipitated LLDPE-g-AA was filtered, washed, and then dried in a vacuum oven at 60°C for 48 h.

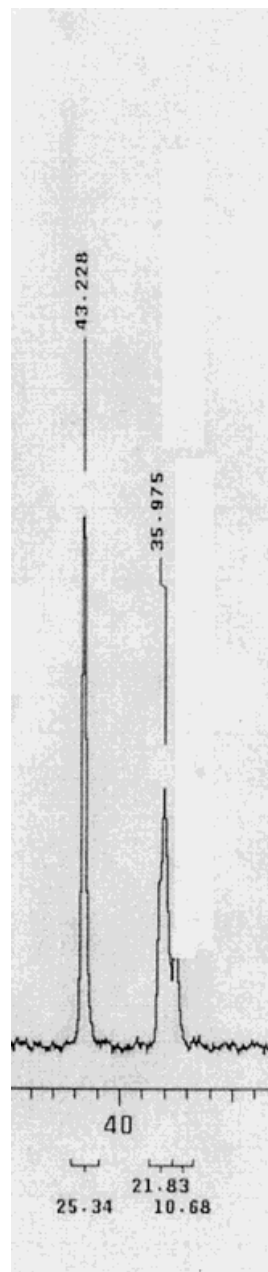
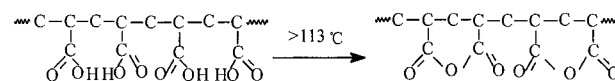


Figure 2 ^{13}C -NMR spectrum of poly(acrylic acid) (PAA).

Determination of Degree of Grafting of LLDPE-g-AA

The DG was defined as the weight percentage of AA grafted onto LLDPE. About 0.5 g of the puri-



Scheme 1

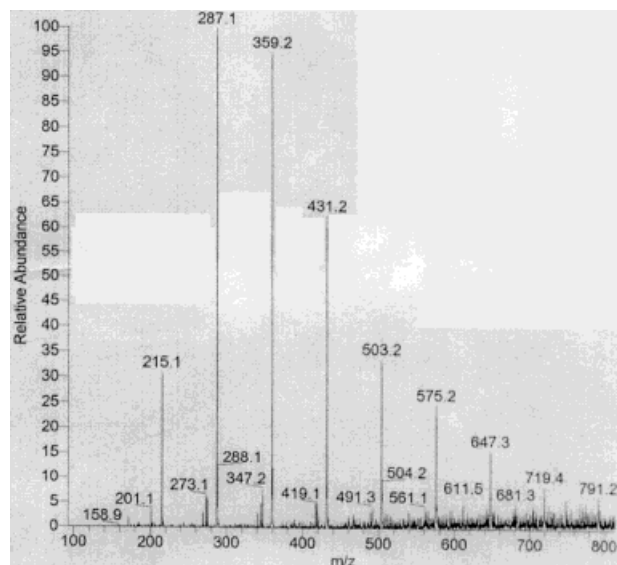


Figure 3 Mass spectrum of extraction filtrate containing AA oligomers in gross LLDPE-*g*-AA product.

fied LLDPE-*g*-AA sample was dissolved in 50 mL hot xylene, then titrated with 0.05N KOH in methanol using phenolphthalein as an indicator.

The equation to calculate the degree of grafting of AA can be expressed as

$$\text{DG (wt \%)} = \frac{V \times N \times M}{W} \times 100$$

where V is the volume of KOH/MeOH solution used for titration of grafted LLDPE, N is the molar concentration of KOH/MeOH solution, M is the molecular weight of AA, and W is the weight of grafted LLDPE.

FTIR spectra were also used to determine the DG of LLDPE-*g*-AA. Purified LLDPE-*g*-AA samples with different DG were compressed into thin films with thickness of 0.1–0.2 mm at 180°C. Absorbance spectra of LLDPE and LLDPE-*g*-AA specimens were acquired by using an FTS-135 FTIR spectrometer at room temperature with a resolution of 4 cm⁻¹. The ratio of the height of the peak 1712 cm⁻¹ (corresponding to carbonyl groups of AA) and the height of the peak 1378 cm⁻¹ (corresponding to stretching of -CH₂ groups of LLDPE) was used to characterize their DG. A calibration equation was established between the DG value and the ratio of the heights of the two peaks.

¹³C-NMR Spectroscopy

About 200 mg of purified LLDPE-*g*-AA (DG = 7.6 wt %) and poly(acrylic acid) polymerized in this

laboratory were dissolved in 3 mL of deuterated chlorobenzene and heavy water, respectively, in 10-mm NMR tubes. ¹³C-NMR spectra were recorded with a Unity 400 NMR spectrometer at 90°C. The spectra were referenced relative to TMS using the solvent signal as an internal standard.

Test on Mass Spectroscopy

The testing sample was obtained from the clear filtrate that came from processing of purification of gross LLDPE-*g*-AA sample with a grafting degree of 5.8 wt %. The main content in the filtrate was homopolymer of AA, except for the solvents (mixture of xylene and acetone), which could be evaporated completely. The mass spectrum was acquired by using a Finnigan MAT LCQ electrospray mass spectrometer.

Morphology Observation

After melting, samples of LLDPE and LLDPE-*g*-AA with different DGs (2.0, 5.8, and 6.4 wt %) were crystallized at 96 ± 0.1°C in a constant-temperature oven for 12 h, and then immersed in chromic acid at 50°C for 45 min to etch out the amorphous phase. Their morphologies were examined with a scanning electron microscope (JEOL SEM, Model JAS-840; JEOL, Peabody, MA) employing the vacuum gold-coating technique.

Investigation of Rheological Property

Rheological properties of LLDPE and LLDPE-*g*-AA with different degrees of grafting were eval-

Table I Representative m/z of AA Oligomers and Their Relative Abundance

m/z	AA Oligomer	Relative Abundance
215.1	(AA) ₃	31
287.1	(AA) ₄ ^a	100
359.2	(AA) ₅	95
431.2	(AA) ₆	62
503.2	(AA) ₇	33
575.2	(AA) ₈	24
647.3	(AA) ₉	15
719.4	(AA) ₁₀	8

^a Tetraunit AA oligomer's relative abundance was defined as 100.

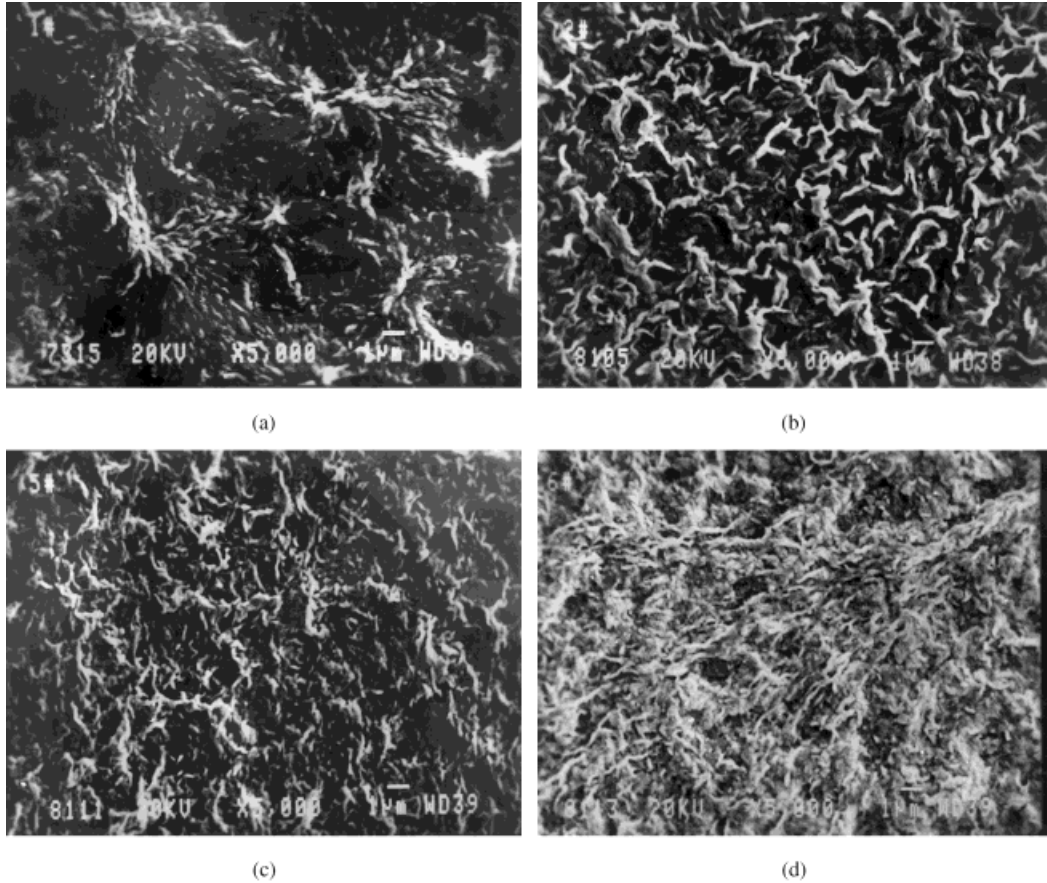


Figure 4 SEM micrographs of LLDPE (a) and LLDPE-g-AA with 2.0 wt % DG (b), 5.8 wt % DG (c), and 6.4 wt % DG (d).

uated by using a capillary rheometer (Model XYL-II; Jinlin University, China). The capillary used had a length-to-diameter ratio of 40 and diameter

of 1 mm. All samples were tested at 190°C, except where specially explained. The shear stress range was from 3×10^4 to 1.4×10^5 Pa.

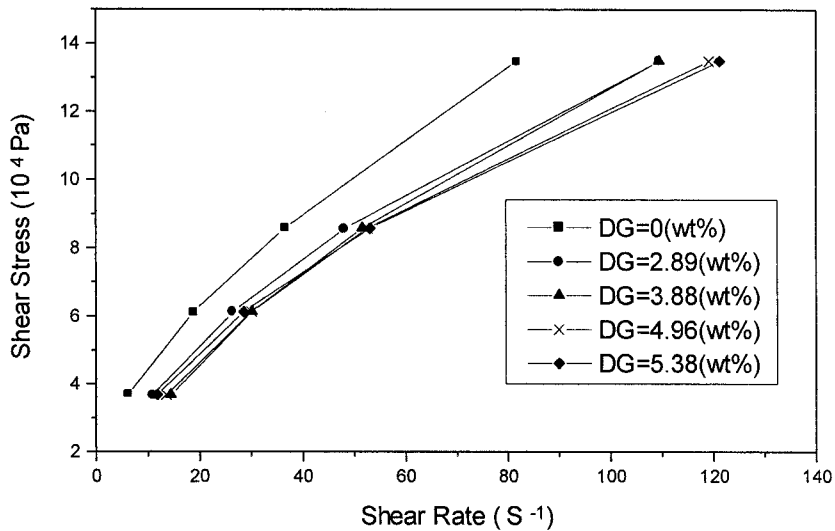


Figure 5 Plots of shear stress versus shear rate for LLDPE and LLDPE-g-AA with different DG values.

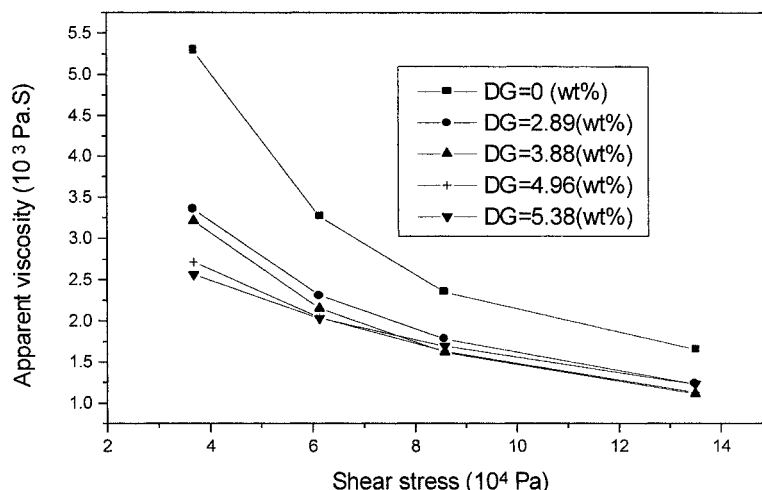


Figure 6 Apparent viscosity of LLDPE and LLDPE-*g*-AA with different DG as function of shear rates.

RESULTS AND DISCUSSION

Figures 1 and 2 are ^{13}C -NMR spectra of LLDPE-*g*-AA (DG = 7.6 wt %) and poly(acrylic acid) (PAA). From Figure 1, we detect two small signals ($\delta_1 = 35.9$ ppm, $\delta_2 = 33.3$ ppm), which are attributed to the methylene and methine carbon of AA grafted onto the LLDPE chain. The signal of a single AA unit grafted onto the LLDPE chain does not appear in Figure 1. These features suggest that AA monomers, grafted onto LLDPE, should be present as short chains with several AA units. This conclusion was confirmed by mass spectroscopy. However, these two signals did not match

with the corresponding carbon signals of PAA (43.228 and 35.975 ppm, respectively), as shown in Figure 2, which could be tentatively explained as follows: because the temperature of reactive extrusion is about 200°C, the multi-AA units grafted onto LLDPE chains could be easily converted to anhydride, as shown in **Scheme 1**,^{12,13} and the two small signals in Figure 1 should be associated with the methylene and methine carbon of AA anhydride.

The mass spectrum of the extracted filtrate of LLDPE-*g*-AA (DG = 5.8) with acetone is shown in Figure 3. The assignments of m/z peaks, corresponding to AA oligomers, and their relative

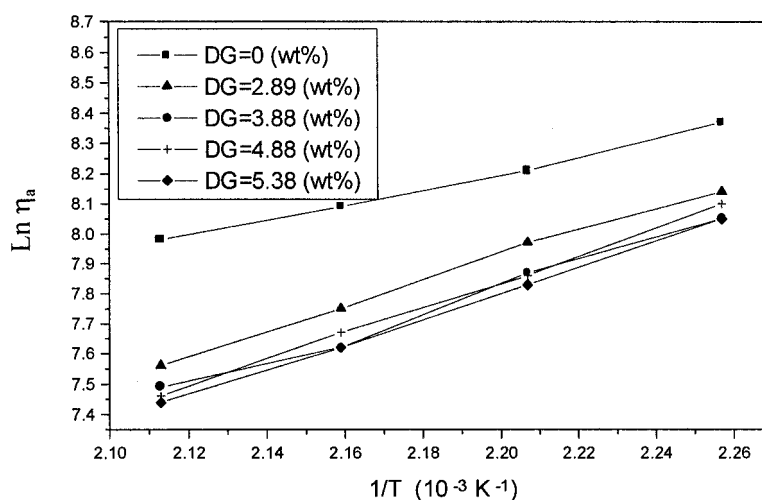


Figure 7 Plots of $\ln \eta_a$ versus $1/T$ for LLDPE and LLDPE-*g*-AA with different DG.

abundance are presented in Table I. In Figure 3, we did not find unreacted AA monomer whose m/z peak would be 71: all AA monomers formed multiunit AA oligomers. Figure 3 also shows that the tetraunit oligomer had the greatest relative abundance, and the oligomers' relative abundance decreased with increasing AA unit number. These results confirmed that AA oligomers were formed during the reactive extrusion process. Although the AA oligomers were extracted from the gross product, it was proved unequivocally that AA monomers grafted onto the LLDPE chain were not a single unit, but formed multiunits.

Morphologies of LLDPE and LLDPE-*g*-AA are shown in Figure 4. With increasing DG of AA, not only was there a corresponding decrease both in the size and the perfection of spherulites but spherulites also became more anomalous. These features indicate that AA branch chains imparted some hindrance to the movement of LLDPE chains during the crystallization process. In the meantime, AA branch chains might also play the role of a nucleating agent, which made the spherulites become smaller.

Rheological behaviors of LLDPE and LLDPE-*g*-AA with different DG at 190°C are shown in Figures 5 and 6. Both LLDPE and LLDPE-*g*-AA were pseudoplastic fluid. Their apparent viscosity (η_a) decreased with increasing shear stress. It was determined that the apparent viscosity of LLDPE was higher than that of grafted LLDPE in the shear stress range of 3×10^4 to 1.4×10^5 Pa; however, when the DG increased from 2.9 to 5.4 wt %, their apparent viscosity did not obviously change.

The apparent viscosities of LLDPE and LLDPE-*g*-AA at different temperatures are shown in Figure 7. The viscosity of LLDPE was higher than that of LLDPE-*g*-AA in the temperature range of 170–200°C. However, when the temperature was lower than this range, LLDPE-*g*-AA had a higher apparent viscosity. This feature can be attributed to the difference of the slopes of the two flow curves. According to the relationship $\eta_a = Ae^{E_a/RT}$, we obtained the flow activation energy (E_a) of LLDPE and LLDPE-*g*-AA (see Fig. 8). The flow activation energy of LLDPE-*g*-AA is higher than that of LLDPE, so the apparent viscosity of LLDPE-*g*-AA was more sensitive to the change of temperature.

According to the above-noted rheological behavior, the following assumption is tentatively

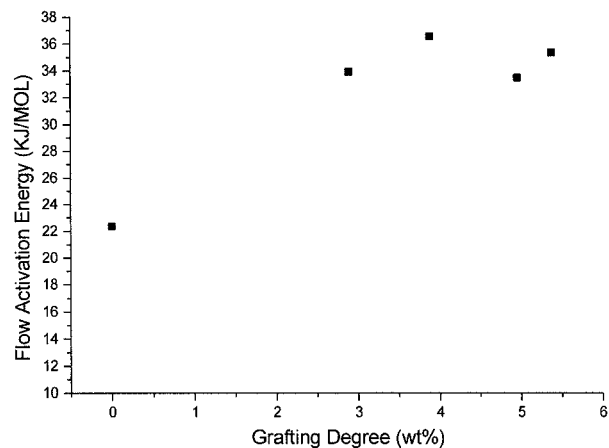


Figure 8 Melt activation energy of LLDPE and LLDPE-*g*-AA with different DG.

proposed: AA branch chains could act as an inner plasticizer at high temperature; therefore, the processing behavior of LLDPE could be improved dramatically by grafting AA.

CONCLUSIONS

1. Experimental results obtained by using electrospray mass spectrum and ^{13}C -NMR spectra provided evidence that AA monomers grafted onto LLDPE main chains formed branches with several AA units. Because of the high temperature during reactive extrusion, the neighboring AA units of branches could dehydrate and convert to anhydride.
2. AA branches grafted onto the LLDPE backbone could hinder the orderly movement of main chains of LLDPE and might act as a nucleating agent during crystallization of LLDPE. Therefore, the morphology of the functionalized LLDPE with AA became more anomalous and their spherulites became smaller than those of the plain LLDPE.
3. AA branches of LDPE-*g*-AA acted as an inner plasticizer during processing of LLDPE-*g*-AA at the shear stress range of 3×10^4 to 1.4×10^5 Pa and the temperature range of 170–200°C. So, LLDPE-*g*-AA has a lower melt apparent viscosity than that of LLDPE and LLDPE-*g*-AA is easier to further process than is the plain LLDPE.

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