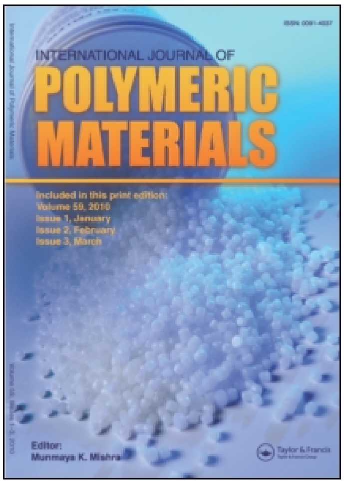

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Isothermal Crystallization and Crystallization Morphology of Non-cross-linking Linear Low-density Polyethylene-grafted-acrylic acid

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Non-cross-linking linear low-density polyethylene-grafted-acrylic acid (LLDPE-g-AA) was prepared by melting reactive extrusion in our laboratory. The thermal behavior of LLDPE-g-AA was investigated by using differential scanning calorimetry (DSC). Compared with neat linear low-density polyethylene (LLDPE), melting temperature (*Tm*) of LLDPE-g-AA increased a little, the crystallization temperature (*Tc*) increased about 4°C, and the melting enthalpy (ΔHm) decreased with increase of acrylic acid content. Isothermal crystallization kinetics of LLDPE and LLDPE-g-AA samples was carried out using DSC. The overall crystallization rate of LLDPE was smaller than that of grafted samples. It showed that the grafted acrylic acid monomer onto LLDPE acted as a nucleating agent. Morphologies of LLDPE-g-AA and LLDPE were examined using SEM. Spherocrystal diameters of LLDPE-g-AA samples were lower than that of LLDPE.

Keywords: LLDPE-g-AA; Non-cross-linking; Thermal behavior; Crystallization kinetics; Morphology

INTRODUCTION

As is widely practiced in plastic processing, grafted polyolefins with polar groups alter the properties of the polymer, their crystallization

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characterization, and morphology. The temperature dependence of the effect of a nucleating agent on crystallization becomes important since it help to determine the processing conditions and controls the properties of fabricated articles. The nucleation effect is estimated by means of a crystallization kinetics analysis, which may be isothermal or non-isothermal. The Avrami equation has been commonly employed to study the isothermal crystallization kinetics of modified polyethylenes [1–9].

Crystallization can be studied by several methods which follow changes in properties sensitive to the degree of crystallinity, *e.g.*, specific volume, crystallization enthalpy, birefringence. In this paper, calorimetry was used to investigate the isothermal crystallization of linear low-density polyethylene grafted acrylic acid. The method has been widely used [4–11]. The results are usually evaluated by the Avrami equation [12]: The Avrami equation is usually valid for a limited range of the process, the deviation from linearity being obvious with increasing conversion. With increasing crystallization temperature, the range of linearity becomes narrower as demonstrated by Phillips and Kao [7] for polyethylene.

When the isothermal crystallization is investigated by DSC, the relative amount of crystalline content $X(t)$ developed in time t corresponds to the following equation [12]:

$$X(t) = \left[\int_0^t (d\Delta H/dt)dt\right] \Big/ \left[\int_0^\infty (d\Delta H/dt)dt\right] \tag{1}$$

The integrals are expressed as the areas under the DSC curve, *i.e.*,

$$X(t) = A_t/A \tag{2}$$

A_t corresponding to the heat generated during crystallization time t and A is related to the overall crystallization heat. The crystallization half-time ($t_{1/2}$), which is easy to determine, is proportional to the Avrami rate constant according to simple relation [12]:

$$K = \ln 2/t_{1/2}^n \tag{3}$$

The aim of this work is to study the influence of the grafting on thermal properties of LLDPE-g-AA. The isothermal crystallization thermagrams of both a pure LLDPE and LLDPE-g-AA measured by differential scanning calorimetry (DSC) were analyzed based on the Avrami equation. The crystallization kinetics was investigated.

EXPERIMENTAL

Materials

The linear low-density polyethylene was purchased from China Petrol Daqing Petrochemical Co., its trade name is DFDA 7042, and the Melting Flow Rate (MFR) is 2.3 g/10 min (190°C, 2.16 Kg). LLDPE-g-AA was prepared by melting reaction extrusion, the degree of grafting and MFR are listed in Table I.

Thermal Behavior

Thermal properties were measured from differential scanning calorimetry (DSC, Perkin–Elmer 7). Samples were first heated to 180°C at 10°C/min and kept for 5 min, then were cooled to room temperature. The crystallization temperature (*Tc*) was recorded. Crystalline melting temperature (*Tm*) and melting enthalpy (ΔHm) were measured during the second heating cycle.

Isothermal crystallization was carried out on the same equipment with about 5 mg sample. The sample was always heated to 180°C and kept 5 min before cooling it to predetermined crystallization temperature. The cooling rate to the predetermined crystallization temperature was faster than 100°C/min and the crystallization temperature was controlled with an accuracy of ±0.05°C. The corresponding exotherms were scanned as a function of time until the crystallization was completed. All samples were extracted in actone in order to remove the non-grafting acrylic acid monomer; the neat LLDPE was also subject to the same procedure.

TABLE I Melting Flow Rate (MFR) of LLDPE-g-AA with different degree of grafting

Code	*LLDPE content* (*wt%*)	*AA content* (*wt%*)	*Degree of grafting* (*wt%*)	*MFR* (*g/10 min*)
A	100	0	0	2.30
B	100	4	1.99	1.82
C	100	6	3.21	1.88
D	100	8	5.67	1.93

RESULTS AND DISCUSSION

Thermal Parameters

The melting temperature (*Tm*), crystallization temperature (*Tc*) and melting enthalpy (ΔHm) of LLDPE-g-AA are listed in Table II. It can be noted that the ΔHm values of LLDPE-g-AA decreased with an increasing degree of grafting. For example, the ΔHm values of LLDPE-g-AA with degree of grafting 5.38 wt% were 10.8 J/g lower than that of LLDPE-g-AA with degree of grafting 1.99 wt%. For LLDPE-g-AA, the *Tc* increased about 3–4°C and the *Tm* increased a little. These results could be explained from monomer grafted on LLDPE molecular chains. The grafted acrylic acid monomer acted as a nucleating agent; this improved the crystallization capability of LLDPE might crystallize at higher temperature. In Table II, it can be seen that the *Tm* is much smaller than the change in *Tc*, leading to a reduced degree of supercooling (*Tm* – *Tc*). Because of grafting acrylic acid molecular on LLDPE molecular chains, the perfection of LLDPE molecular chains regularity were destroyed, which would lead to a reduction in total crystallinity.

Determination of Isothermal Crystallization Kinetic Parameters

The samples Avrami equation for isothermal crystallization is represented by Eq. (4).

$$1 - X(t) = \exp(-Kt^n) \tag{4}$$

where $X(t)$ is the relative crystallinity, K is the rate constant, and n is the Avrami exponent. K and n were determined by the conventional

TABLE II Melting temperature (*Tm*), crystallization temperature (*Tc*), melting enthalpy (ΔHm), and *Tm* – *Tc* of LLDPE and LLDPE-g-AA with different AA content

Code	*Degree of grafting* (*wt%*)	*Tm* (°*C*)	*Tc* (°*C*)	ΔHm (*J/g*)	*Tm* – *Tc* (°*C*)
A	0	122.9	108.4	89.9	14.5
B	1.99	123.9	111.3	85.3	12.6
C	3.21	123.6	111.8	82.6	11.8
D	5.38	123.7	112.1	74.5	11.6

Avrami plot method. The Avrami plots with the isothermal DSC data obtained at various crystallization temperatures for LLDPE and LLDPE-g-AA are shown in Figures 1–4. It is easily seen in the Avrami plots that the Avrami equation describes the isothermal crystallization fairly well in the early stage. Due to the curvature at the later stage of crystallization, only the linear portion stage was used for

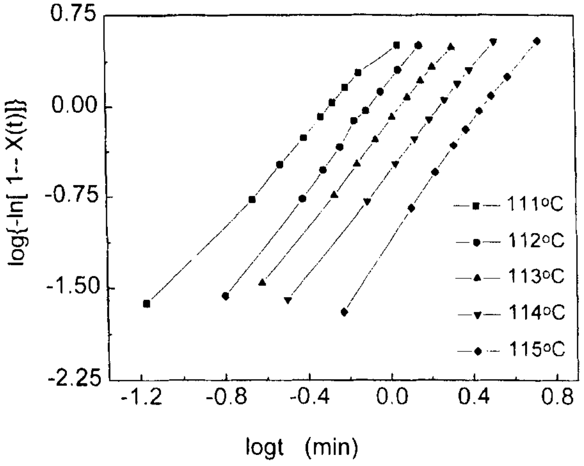

FIGURE 1 The Avrami plot of neat LLDPE.

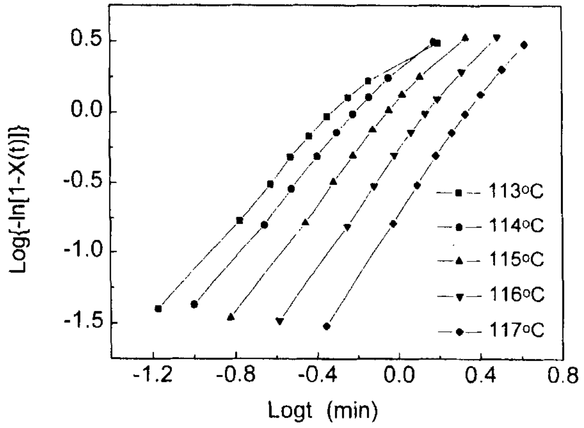

FIGURE 2 The Avrami plot of LLDPE-g-AA with degree of grafting of 1.99 wt%.

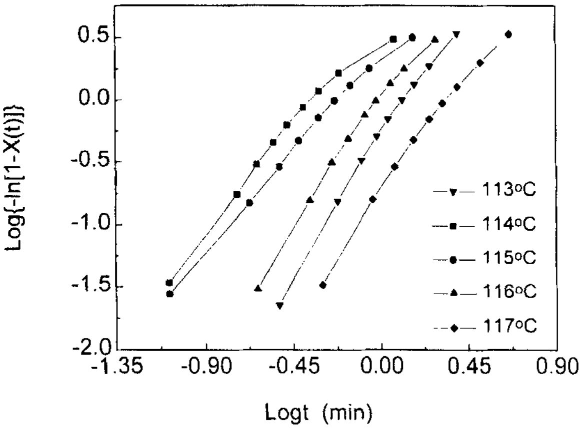

FIGURE 3 The Avrami plot of LLDPE-g-AA with degree of grafting of 3.21 wt%.

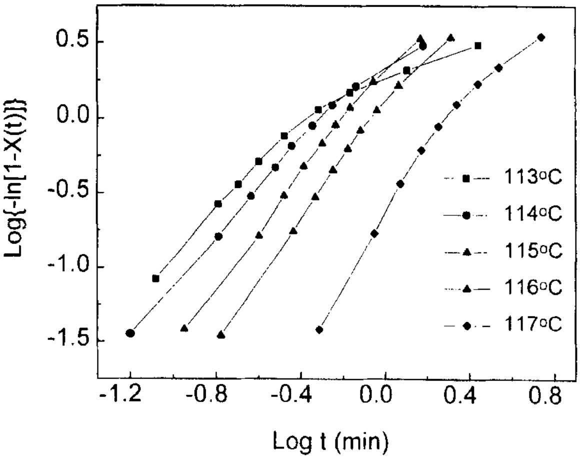

FIGURE 4 The Avrami plot of LLDPE-g-AA with degree of grafting of 5.38 wt%.

the samples studied. Some authors have attributed curvature to second crystallization leading to isothermal lamellar thickening and to nucleation and growth process occurring simultaneously [11], in addition to the growth site impingement, second crystallization, which was not taken into account by the Avrami equation either may by partly responsible for the observed deviations.

The kinetics parameters of LLDPE and LLDPE-g-AA determined by the plot $\log\{-\ln[1-X(t)]\}$ against $\log t$ were listed in Table III. We can see that the values of exponent n shown in Table III were not integral; it might be caused by such factors as mixed nucleation modes, second crystallization, or intermediate dimensionality of crystal growth [12]. Crystallization rates of polymers can be expressed in terms of the half-time $t_{1/2}$ obtained from the isothermal exotherm of the DSC results. The shorter the half-time $t_{1/2}$, the faster the crystallization rate, and *vice versa.* For the neat LLDPE and the LLDPE-g-AA, it was observed that the half-times $t_{1/2}$ of LLDPE higher than those of LLDPE-g-AA, and that the $t_{1/2}$ of LLDPE-g-AA decreased with degree of grafting. This indicated that the crystallization rates of LLDPE-g-AA were faster than that of LLDPE, and crystallization rates of LLDPE-g-AA increased with increase of degree of grafting.

According to Turndull–Fisher equation, the radial growth rate of polymer spherulites (G) is described as:

$$G = G_o \exp(-E^o/RT)\exp(-\Delta\phi^o/RT) \tag{5}$$

TABLE III The isothermal crystallization kinetics parameters of LLDPE and LLDPE-g-AA with different AA content at different crystallization temperature (*Tc*)

Sample	*Degree of grafting* (*wt%*)	*Tc* (°*C*)	*K* (*min*$^{-n}$)	*n*	$t_{1/2}$ (*min*)
LLDPE	0	111	3.04	1.82	0.44
		112	1.53	2.21	0.69
		113	1.38	2.15	0.72
		114	0.30	1.97	1.53
		115	0.07	2.43	2.49
LLDPE-g-AA	1.99	113	3.52	1.67	0.38
		114	2.42	1.76	0.49
		115	1.29	1.92	0.72
		116	0.53	2.07	1.14
		117	0.19	2.23	1.78
LLDPE-g-AA	3.21	113	6.36	2.11	0.35
		114	2.72	1.85	0.48
		115	0.97	2.20	0.85
		116	0.49	2.38	1.15
		117	0.21	2.05	1.79
LLDPE-g-AA	5.38	113	4.55	1.59	0.31
		114	3.39	1.66	0.38
		115	2.57	1.95	0.51
		116	1.46	2.10	0.47
		117	0.23	2.45	1.57

where E^o is the free energy of formation of a surface nucleus of critical size, $\Delta\phi^o$ is the diffusional activation energy of crystallizing segments across the phase boundary, R is the gas constant, and T is the crystallization temperature in K. Using WLF theory [15], E^o may be expressed as:

$$E^o = 4120Tc/(51.6 + Tc - Tg) \tag{6}$$

where T_c is the crystallization temperature and Tg is the glass transition temperature. In the present work, the Tg for neat LLDPE was almost equal to that of LLDPE-g-AA. Because the Tc values of LLDPE-g-AA were higher than that for LLDPE, we could conclude that the E^o-values of LLDPE-g-AA were higher than that of LLDPE.

The effect of $\Delta\phi^o$ on the radical growth rate could be analyzed as follows: $\Delta\phi^o$ was expressed by

$$\Delta\phi^o = 4b_o\sigma\sigma_e T^o m/\Delta Hm(T^o m - T_c) \tag{7}$$

where b_o is the monolayer thickness, σ is the lateral surface energy, σ_e is the fold surface energy, ΔHm is the heat of fusion, and $T^o m$ is the equilibrium melting temperature. From Table II, we knew that the Hm for LLDPE-g-AA were lower than that for LLDPE, and the equilibrium melting temperatures of LLDPE and LLDPE-g-AA were almost identical. We could also conclude that the $\Delta\phi^o$ values of LLDPE-g-AA were higher than that of LLDPE.

Because the E^o and $\Delta\phi^o$ of LLDPE-g-AA samples were higher than that of LLDPE, when the growth rate was determined by Eq. (4), we knew the G values of the LLDPE-g-AA were lower than that for LLDPE. But in previous studies, we knew the crystallization rates of LLDPE-g-AA were higher than that of LLDPE. We could conclude that AA in LLDPE-g-AA acts as a nucleating agent; and its presence lead to an increase of crystallization rate.

SEM of LLDPE and LLDPE-g-AA Isothermal Crystallization Samples

The SEM pictures of LLDPE and LLDPE-g-AA isothermal crystallization samples are shown in Figure 5. All samples were etched with

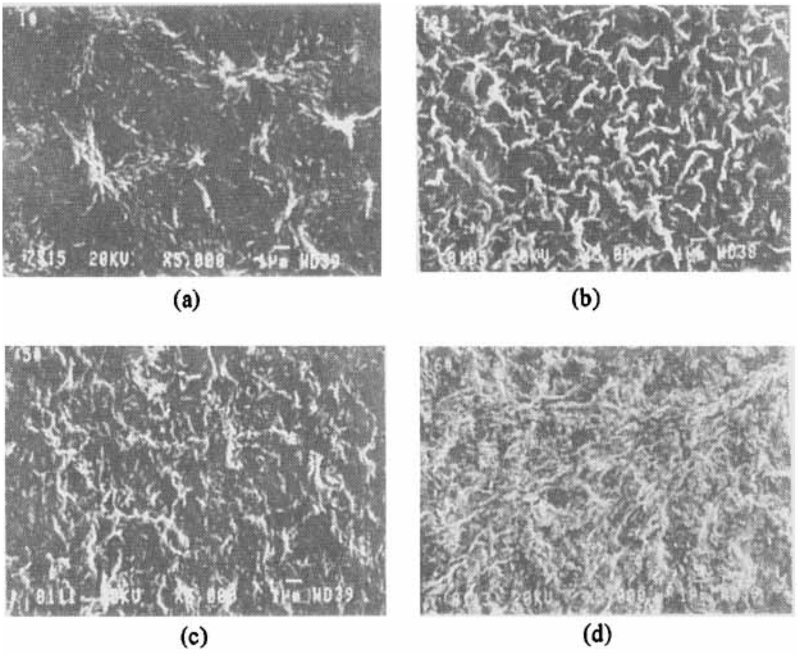
(a) (b) (c) (d)

FIGURE 5 The SEM pictures of LLDPE and LLDPE-g-AA with different degree of grafting. (a) LLDPE; (b) LLDPE-g-AA with degree of grafting of 1.99 wt%; (c) LLDPE-g-AA with degree of grafting of 3.21 wt%; (d) LLDPE-g-AA with degree of grafting of 5.38 wt%.

chromic acid. It was observed that spherocrystal sizes of LLDPE-g-AA were smaller than that of LLDPE, and spherocrystal size of LLDPE-g-AA increased with increasing of degree of grafting of AA. This result further confirmed the above conclusion.

CONCLUSIONS

The grafting of LLDPE led to an increase of its crystallization temperature. It was attributed to the change of the structure of LLDPE molecular chains. The AA in LLDPE-g-AA acted as a nucleating agent for LLDPE. The isothermal crystallization kinetics showed that the crystallization rates of LLDPE-g-AA were faster than that of LLDPE. The SEM of LLDPE and LLDPE-g-AA isothermal crystallization samples showed that spherocrystal sizes of LLDPE-g-AA were smaller than that of LLDPE, this further confirmed the previous conclusion.

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References

[1] Godovsky, Y. K. and Slonimsky, G. L. (1974). *J. Polym. Sci.*, **12**, 1053.
[2] Banks, W., Gordon, M., Roe, J. R. and Sharples, A. (1963). *Polymer*, **4**, 61.
[3] Kamal, M. R. and Chu, E. (1983). *Polym. Eng. Sci.*, **23**, 27.
[4] Yadav, Y. S., Jain, P. C. and Nanda, V. S. (1983). *Thermochim. Acta*, **71**, 313.
[5] Varga, J., Solti, A. and Menczel, J. (1978). *Periodica Polytechnica*, **22**, 297.
[6] Kao, Y. H. and Phillips, P. J. (1986). *Polymer*, **27**, 1669.
[7] Phillips, P. J. and Kao, Y. H. (1986). *Polymer*, **27**, 1679.
[8] Gohil, R. M. and Phillips, P. J. (1986). *Polymer*, **27**, 1687.
[9] Gohil, R. M. and Phillips, P. J. (1986). *Polymer*, **27**, 1696.
[10] Zerjal, B., Musil, V., Pregrad, B. and Malavasic, T. (1988). *Thermochim. Acta*, **134**, 139.
[11] Pedemonte, E., Turturro, A. and Semino, G. (1988). *Thermochim. Acta*, **137**, 115.
[12] Vilanova, P. C. and Ribas, S. M. (1985). *Polymer*, **26**, 423.
[13] Marker, L., Hay, P. M., Tilley, G. P., Early, R. M. and Sweeting, O. J. (1959). *J. Polym. Sci.*, **38**, 33.
[14] Griffith, J. H. and Ranby, B. G. (1959). *J. Polym. Sci.*, **38**, 107.
[15] Lauritzen, J. J. and Hoffman, J. D. (1959). *J. Chem. Phys.*, **31**, 1680.