

A Differential Scanning Calorimetry Study of Plasma Irradiation Grafting of Nascent Polyethylene Reactor Powder

JUN TIAN, XIAO LIN, JIPING XU, and BAOTONG HUANG*

Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, People's Republic of China

SYNOPSIS

The melting behavior of poly(methyl methacrylate)-grafted nascent polyethylene reactor powder by plasma irradiation was studied by differential scanning calorimetry (DSC). The grafting yield ranged from 11 to 190%. Grafting was found to lower both melting point and heat of fusion during the first run of DSC determination. The heat of fusion was used to calculate the apparent grafting yield of the samples. There was little strain induced by plasma-irradiated grafting on the surface of the polyethylene crystals. A method to determine the covalent grafting yield in the graft copolymer systems was developed. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

The grafting of a polymer has a pronounced effect on its physical and mechanical properties.¹ Although this technique is widely used in modifying polymer properties, there are relatively few studies dealing with the effect of side chains on the melting behavior of grafted polymers. Recently, we became interested in the structure of nascent polyethylene, prepared by the zirconocene/methylaluminoxane (MAO) catalyst system, in connection with its mode of formation.^{2,3} This article is concerned with the melting behavior of poly(methyl methacrylate) (PMMA)-grafted nascent polyethylene reactor powder,^{2,3} where grafting is initiated by plasma irradiation.⁴⁻⁷ The objective is to quantitatively isolate the effect of covalent grafting on the melting of polyethylene; a little microdispersed PMMA homopolymer (< 1%) is also present.^{5,6} Melting point and heat of fusion were determined by differential scanning calorimetry (DSC) and are discussed in reference to previously studied copolymer systems.

It is well known that plasma irradiation effec-

tively creates a large amount of stable free radicals on polymer surfaces without damaging bulk properties. This confirms that Flory's equation for the melting-point depression of random copolymers^{8,9} can in some cases be used to describe the variation in crystallinity of graft copolymers.¹⁰ In the present work, melting point and heat of fusion data for grafted polyethylene powders were determined. Data were compared to Flory's theoretical treatment of random copolymers and the influence of the degree of branching and the length of the branches was examined. The results were comparable to those obtained in other systems.^{10,11}

EXPERIMENTAL

Materials

Nascent polyethylene powder synthesized with a biscyclopentadienylzirconium dichloride (Cp_2ZrCl_2)/methylaluminoxane (MAO) homogeneous catalyst system¹² at room temperature in our laboratory was screened with a 200 mesh sieve for grafting use. Analytical-grade methyl methacrylate (MMA), a product of Beijing Chemical Factory, was first washed with an aqueous solution of sodium hydroxide and then with water, dried with calcium chloride, and

* To whom correspondence should be addressed.

distilled under reduced pressure over CaH_2 . Reagent-grade ethanol, a product of Beijing Chemical Factory, was used without further purification.

Preparation and Plasma Irradiation of Samples

Nascent polyethylene reactor powder was accurately weighed (1.0 g) and placed in an ampule (40 mm i.d., 100 mm long) with a capillary tube (2 mm i.d.) at the ampule end, which was then filled with argon gas and sealed (1.33 Pa). The plasma state of argon was sustained at the upper part of the ampule by rotating the sample, while discharging an inductive coupling at 13.56 MHz frequency from an RF (13.56 MHz) generator (Model JP300), between external plate electrodes (150×100 mm) with the supplied power (100 W), for a prescribed period of time. MMA (10 mL) was injected into the ampule under vacuum. Oxygen dissolved in the monomer had been removed by freeze-thawing. Grafting was carried out at 30°C in a water bath for a given time. The grafted products were washed with ethanol to remove the excess monomer and then dried under vacuum to constant weight at 30°C . The yield of the MMA homopolymer by Soxhlet extraction (acetone as the solvent) was so little that the total increase in weight could be assumed to be resulting from the grafting.^{5,6} The grafting yield was the percentage increase in weight of the original polyethylene.

Thermal Measurements

Melting point and heat of fusion were determined for each copolymer sample of ca. 10 mg in the cell

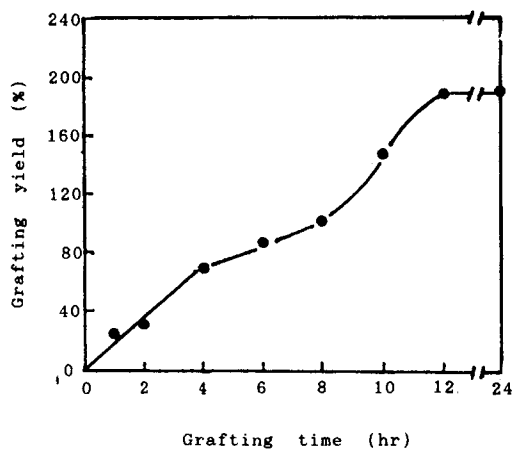


Figure 1 Relationship between grafting yield and grafting time. Plasma power: 100 W; plasma treatment duration: 5 min; grafting temperature: 30°C .

of a Perkin-Elmer DSC-7C thermal analyzer. The temperature was raised at $15^\circ\text{C}/\text{min}$ from 50 to 180°C . The thermogram peak was taken as the melting point and the heat of fusion was calculated from the area under the thermogram. It should be emphasized that, due to rapid heating, the melting points were not the equilibrium melting points of the samples. However, since only relative changes in melting points and heats of fusion were desired, this variation was relatively unimportant.

Wide-angle X-ray diffraction (WAXD) experiments were performed on a Philip PW 1700 automated powder diffractometer: $\text{CuK}\alpha$ radiation, voltage 40 kV, current 30 mA. Scans in the reflection mode were performed through a 2θ range of 5 – 40° .

RESULTS AND DISCUSSION

Plasma irradiation grafting polymerization consists of two successive processes, i.e., plasma surface activation of the substrate and graft polymerization of the vinyl monomers. The grafting is naturally dependent on the reaction factors inherent in the process.^{13–15} In the plasma irradiation pretreatment, plasma power and plasma duration affect the concentration of radicals on the polymer surface. Several factors connected to postpolymerization, such as reaction time and grafting temperature, have significant influence on the grafting yield.^{5,6} Figure 1 shows a typical curve plotting the degree of grafting vs. reaction time for nascent polyethylene powder at 30°C , where the plasma power was 100 W, and plasma treatment duration, 5 min.

The grafting yield increased with reaction time. At the initial stage of graft copolymerization, the grafting yield increased linearly with reaction time. During this period, the viscosity of the reaction system was very low due to the low conversion of the MMA monomer ($< 10\%$),^{5,6} and diffusion of MMA did not affect the grafting process. After a period of 4 h, apparently, the viscosity of the reaction system increased, and the grafting process was then controlled by the diffusion of MMA monomer, leading to a decrease in the rate of grafting. The grafting yield again increased from a reaction time of 8 h (102% grafting) to 12 h (190% grafting). Autoacceleration occurred just as in the case of homopolymerization of MMA. This phenomenon was best explained by the incursion of a Trommsdorff-type effect.¹⁶ After 12 h, the reaction system became gelatinous and the MMA monomer no longer diffused to the reactive sites.^{5,6}

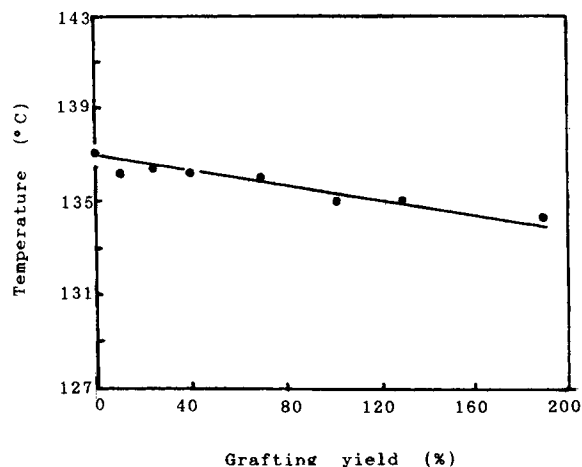


Figure 2 Melting point of PE-*g*-PMMA as a function of grafting yield.

Figure 2 is a plot of melting points from DSC measurements as a function of grafting yield. Ungrafted nascent polyethylene showed no detectable change in melting point after plasma irradiation and no damage in crystallinity as shown by no substantial change in the crystal lattice constants (Table I), in good agreement with general characteristics of plasma treatment. As shown in Figure 2, grafting of PMMA caused only a slight depression in the melting temperature of the polyethylene.

The heats of fusion of the samples are plotted in Figure 3 as a function of grafting yield. Here, we do expect a decrease in heat of fusion with grafting due to an increase in amorphous content from the grafted PMMA. This is also found in WAXD patterns of polyethylene (PE)-*g*-PMMA copolymers with different grafting yields (See Fig. 4).

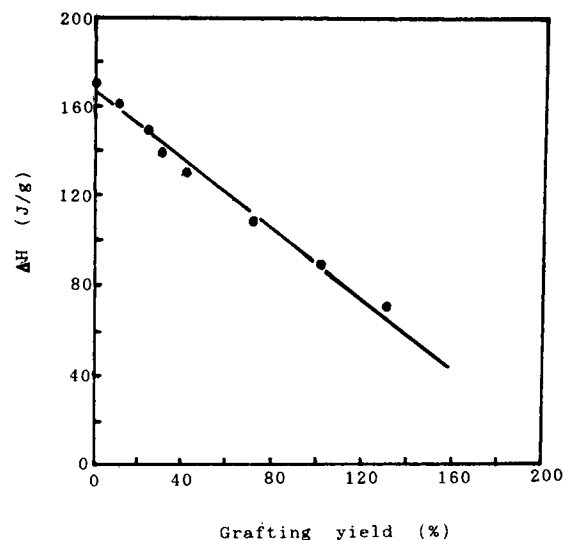


Figure 3 Heat of fusion of PE-*g*-PMMA as a function of grafting yield.

Table I Crystal Lattice Constants of Polyethylene in Nascent PE-*g*-PMMA Copolymers^a

Samples	Grafting Yield (%)	Crystal Lattice Constant		I_{200}/I_{100}
		a (Å)	b (Å)	
PE	—	7.470	4.985	23.8/100
PE ^a	—	7.445	4.985	22.3/100
LL-32	69	7.425	4.925	23.5/100
LL-22	130	7.425	4.955	23.4/100
LL-12	190	7.415	4.955	24.5/100

^a Nascent polyethylene reactor powder plasma-irradiated.

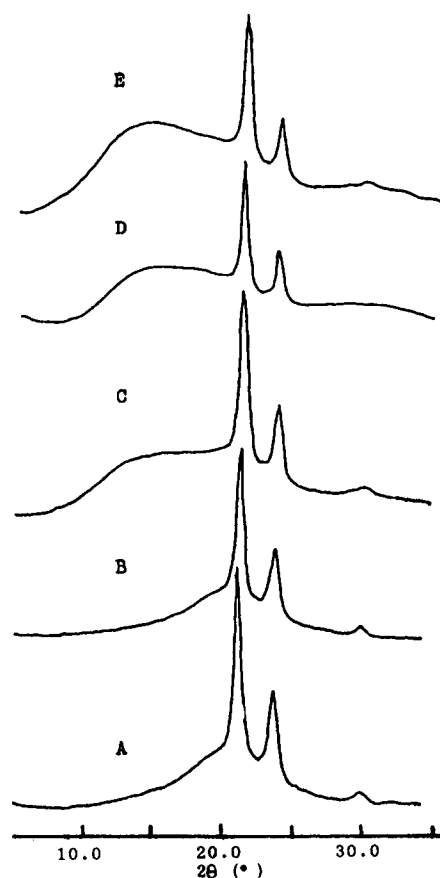


Figure 4 WAXD patterns of PE-*g*-PMMA of different grafting yields: (A) Nascent PE reactor powder; (B) plasma-irradiated PE; (C) PE-*g*-PMMA (69%); (D) PE-*g*-PMMA (130%); (E) PE-*g*-PMMA (190%).

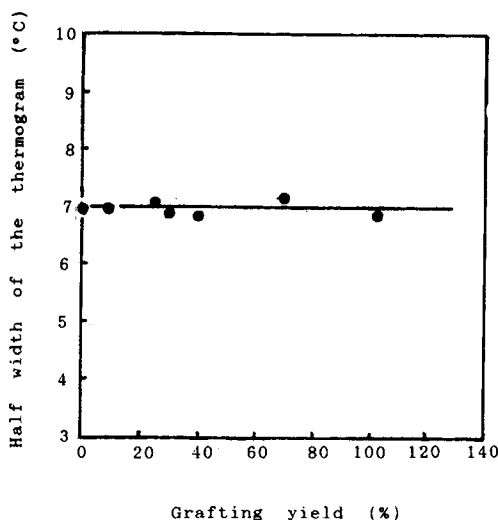


Figure 5 Half-width of normalized DSC thermograms of PE-*g*-PMMA as a function of grafting yield.

One interesting observation on these thermograms is that, although they vary in area according to the PMMA content, their shape seems to be unchanged. Taking it for granted that the shape of a thermogram is a rough measure of the crystal-size distribution,¹⁷ we can therefore suggest that plasma-irradiation-induced grafting occurs randomly on the material surface, keeping the crystal size intact. The widths at half of the peak heights of the normalized thermograms were constant over the entire grafting range (see Fig. 5), supporting their observed similarity in shape. This observation was further supported by the almost unchanged crystal lattice constants of the nascent polyethylene before and after graft polymerization (see Table I).

The heat of fusion of the polymer samples, ΔH , was calculated directly from the thermogram area A :

$$\Delta H \text{ (J/g)} = (A/m)K, \quad (1)$$

where m is the mass of the sample, and K , a calibration constant of the instrument. Noting that the total mass of a grafted sample is the sum of the mass of polyethylene (PE), m_{PE} , and the mass of PMMA, m_{PMMA} , the heat of fusion of the ungrafted polyethylene to that of the grafted samples can be compared as follows:

$$\Delta H_{\text{PE}}/\Delta H_{\text{sample}} = 1 + m_{\text{PMMA}}/m_{\text{PE}} \quad (2)$$

If the grafting yield in the sample, G_a , is defined as

$$G_a(\%) = (m_{\text{PMMA}}/m_{\text{PE}}) \times 100 \quad (3)$$

the grafting yield from the thermograms of the sample and of pure polyethylene can be calculated by combining eqs. (1)–(3) to get

$$G_a(\%) = \{[(A/m)_{\text{PE}}/(A/m)_{\text{sample}}] - 1\} \times 100 \quad (4)$$

In arriving at eq. (4), we made the critical assumption that the PMMA chains grafted to the surface of the polyethylene did not affect the heat of fusion of these crystalline parts. Only by making this assumption is it possible to calculate the percent grafting yield from the decrease in the thermogram area of the grafted samples. This decrease in area is solely due to the increased amorphous content of the grafted sample due to the incorporation of PMMA.

Figure 6 shows the apparent grafting yield calculated by eq. (4) using the thermogram data vs. the apparent grafting values calculated directly from the weights before and after grafting. It is apparent from Figure 6 that the grafting of PMMA had no effect on the heat of fusion of the polyethylene crystals during the DSC determination and, hence, we had a 1 : 1 correspondence, within experimental error,

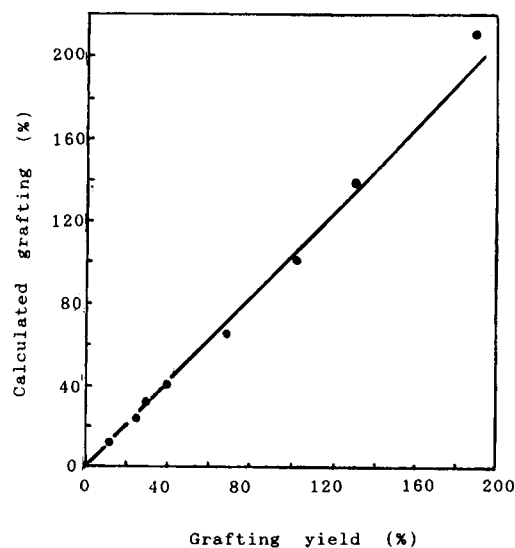


Figure 6 Grafting yield calculated by eq. (4) using heat of fusion of PE-*g*-PMMA (DSC) as a function of grafting yield.

between the apparent grafting yield calculated from eq. (4) and the actual increase in powder weight. This indicated that covalent grafting had induced little strain on the surface of the polyethylene crystals.^{10,18-20}

An attempt was made in this investigation to test the possibility of relating the melting-point depression of this copolymer to its crystallinity using a Flory-type equation.⁹ It is understood that the present copolymer is far from the ideal one described by Flory in his derivation of this thermodynamic equation. However, a comparison with the ideal case will contribute to a better understanding of the present system. If we consider the relative crystallinity (X) of the nascent polyethylene reactor powder before grafting to be $X = 1$, the polyethylene melting point T_0 , the copolymer melting point T , and the relative crystallinity of the copolymer X can be related by the following relationship of Flory:

$$(1/T) - (1/T_0) = -(R/\Delta H_u)\ln X \quad (5)$$

where R is the gas constant, and H_u , the enthalpy of fusion per mol of crystalline units. X , the ratio of the mol fraction of crystalline units in the copolymer to that of the polyethylene, can be expressed in terms of the heat of fusion data as follows:

$$1/X = 1 + [(M_{PE}/M_{PMMA})(m_{PMMA}/m_{PE})] \quad (6)$$

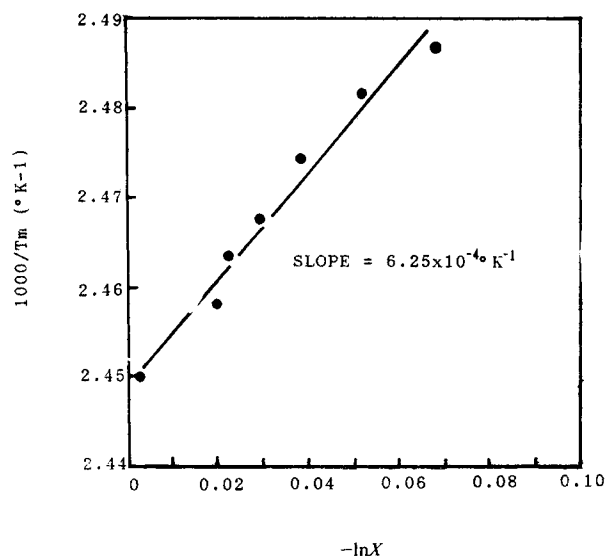


Figure 7 $1/T_m$ vs. $-\ln X$ calculated by eq. (7) using heat of fusion of PE-*g*-PMMA from DSC.

where M_{PE} is the molecular weight of the polyethylene repeating unit, 14, and M_{PMMA} is the molecular weight of PMMA repeating unit, 100. Substituting eq. (2) for the mass ratio (m_{PMMA}/m_{PE}) in eq. (6), we can get X in terms of the heats of fusion:

$$1/X = 1 + (M_{PE}/M_{PMMA})[(\Delta H_{PE}/\Delta H_{\text{sample}}) - 1]$$

$$1/X = 0.86 + 0.14/\Delta HR \quad (7)$$

where $\Delta HR = \Delta H_{PE}/\Delta H_{\text{sample}}$. Figure 7 shows a plot of $-\ln X$ [or $\ln(1/X)$] calculated from eq. (7) vs. $1/T$; the slope of this curve, however, is much lower than the value of $R/\Delta H_u$ predicted by Flory. In other words, the experimental results indicate that the change in the crystallinity of the copolymer is exaggerated. In reality, the PMMA chains exhibit a much lower level of interference with the crystallization and melting of the polyethylene crystals than predicted from eq. (5). This deviation from ideality can be accounted for by assuming that the covalently grafted polymer is composed of long chains and a few grafted sites that do not markedly interfere with the crystallization and melting of the polyethylene.

CONCLUSION

Results indicate that thermal measurements by DSC can be correlated to the covalent grafting yield in copolymer samples. This technique, fast and relatively simple, requires only a small sample weight (5–10 mg) and is also relatively insensitive to measurement errors since only relative changes, rather than absolute values, are utilized. Therefore, this method is quite convenient to determine the covalent grafting yield in the graft copolymer systems.

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