# Study of Electron Beam Preirradiation-Induced Graft Copolymerization of Acrylic Acid onto Powdered Isotactic Polypropylene

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ABSTRACT: In order to obtain required polymer materials, acrylic acid was grafted onto powdered isotactic polypropylene by an electron beam preirradiation technique. All processes (including irradiation, storage of the samples, and grafting polymerization) were carried out in air. The effects of irradiation dose, storage time, reaction temperature, morh's salt, acid, and monomer concentration were investigated and discussed in detail. The results show that the grafting can be achieved well without purging oxygen, and morh's salt is indispensable for initiating grafting reaction and decreasing the homopolymerization. Optimal reaction conditions can be generalized for large-scale production of the desired polymer materials. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 1357–1362, 1999

**Key words:** graft; electron beam preirradiation; powdered isotactic polypropylene; acrylic acid

## INTRODUCTION

The irradiation-induced grafting copolymerization is a well-known method to produce a special polymer or to modify the chemical and physical properties of polymer materials, and it did provide some valuable and interesting materials, such as ion-exchange fiber,<sup>1</sup> protein collection membrane,<sup>2</sup> and blend compatibilizer.<sup>3</sup> Compared with other grafting methods, the irradiation induced one has a superior advantage in that it is suitable for an arbitrary kind of chemically or physically stable polymer substrate and a large range of monomers. It is also a "pure" or "clear" method because no chemical initiator is needed. In recent years, attention was paid to the modification of polypropylene (PP) because of its wide industrial applications, cheapness, low density, and excellent mechanical properties. P. Citovicky<sup>4</sup> investigated the mechanism of graft styrene (ST) and methyl methacrylate (MAA) onto PP. They<sup>5-7</sup> also attempted to explain the "real" initiating center of this kind of reaction. Romero and Domard<sup>8</sup> studied the accurate grafting site by infrared (IR) spectra and demonstrated the effect of additive on grafting. Lu Yun<sup>1</sup> grafted MAA, acrylic acid (AA), and diglycol acrylate onto PP fiber. Eman<sup>9</sup> studied the effect of solvent on grafting yield, and Mehta<sup>10</sup> suggested that water was the best solvent to get the maximum grafting yield when grafting AA and acrylamide (AAm) onto PP.

Because oxygen is a well-known polymerization inhibitor, these kinds of experiments were always achieved without the presence of oxygen. But the purge of oxygen imparts an inconvenient process and some uncertain effects on grafting

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and limits the application in large scale reaction. In this study, we graft AA onto powdered IPP by the electron beam (EB) preirradiation technique; all processes were carried out without the purge of oxygen. The reaction conditions, such as the irradiation dose, temperature, monomer, and morh's salt concentration, were investigated and discussed in detail.

# **EXPERIMENT**

## **Materials**

Unstabilized powdered isotactic polypropylene, with a particle size less than 0.5 mm, was given by the Institute of Chemistry of Chinese Academic of Science as a gift. Analytical-grade acrylic acid was supplied by Qiuxian Chemical Co. (Zhe Jiang Province) and was used without further purification. It is not necessary to purge the inhibitor because of the addition of morh's salt in the following experiment. Other chemical reagents used were all analytical grade.

## Irradiation

The powdered IPP was placed in paper bags and irradiated under the electron beam of an electron linear accelerator (BF5 made in Beijing), which is operated at the beam energy of 4 MeV and with a current of  $2 \times 10^{6}$ A. The dose rate was approximately  $10^{2}$  Gy s<sup>-1</sup> (or Gy/s).

All irradiation was carried out at room temperature in air.

#### **Graft Polymerization**

A definite amount of acrylic AA, morh's salt, and distilled water were introduced into the reaction flask, and the total volume of liquid phase was maintained for 15 mL. Then a given amount of the irradiated PP sample was added into the flask. With a long water-cooled reflux condenser, the flask was immersed in a water bath, which was maintained at a constant temperature. After the desired reaction period, the sample was filtered and immersed in diluted HCl solution overnight and then extracted with distilled water in a Soxhlet extractor for 7 h. After removing the homopolymer, the grafted sample was oven-dried at  $60^{\circ}$ C to a constant weight. The grafting yield (*G*) was calculated by the following equation:

$$G = (W_g - W_0)/W_0 \times 100\%$$



**Figure 1** Effect of dose on the grafting yield reaction temperature (60°C), time (2 h), monomer concentration (33 wt %), and morh's salt concentration (0.08 wt %).

where  $W_g$  and  $W_0$  represent the weight of the grafted and the initial IPP sample, respectively.

## Fourier Transform Infrared Spectroscopy

The infrared measurements were taken by the KBr pellet technique. Spectra were obtained in the wave number region of 4000-400 cm<sup>-1</sup> using a Nicolet Magna-FTIR 750 spectrometer.

# DISCUSSION

#### **Preirradiation Dose**

When polyolefine was irradiated with an electron beam or  $\gamma$ -ray, alkyl ("trapped") radical P<sup>•</sup> and peroxy-radical (peroxide POOP and hydroperoxide POOH group) will be generated.

$$P^{\bullet} \sim -> P^{\bullet}$$

$$P^{\bullet} \sim -> POO^{\bullet}$$

$$POO^{\bullet} + PH \sim -> POOH + P^{\bullet}$$

$$POO^{\bullet} + POO^{\bullet} \sim -> POOP + O_{2}^{\bullet}$$

They are generally assumed to be the initial centers for grafting, although the detailed mechanism of initiation is not yet fully clear. Figure 1 shows the effect of the irradiation dose on the grafting yield. Within the investigated dose range (50-400 KGy), the grafting yield increases



**Figure 2** Effect of storage time on grafting irradiation dose 200 KGy. Other reaction condition is the same as in Figure 1.

with the increment of irradiation dose and has a tendency to level off at higher dose. This is consistent with the variation of the radical numbers observed by Louis et al.<sup>11</sup> The level-off tendency may be due to the recombination of the radical, which limits the increment of the radical number at a high dose. No higher dose was investigated because the IPP sample turns yellow and gives off a disagreeable smell when the dose is 400 KGy.

# **Storage Time**

As a two-step process, one of the advantages of the preirradiation technique is that the irradiation polymer substrate can be stored in a suitable environment for further use without losing the initiating center. Figure 2 shows the effect of storage time on the grafting yield. In our study, the irradiated IPP was sealed in a ground glass, stoppered bottle in the dark at  $-15^{\circ}$ C.

From the figure, no obvious change of grafting yield was observed even after 40 days storage. It appears that the initiating center is "very stable" and this phenomenon suggests that the initiating center may mainly be the peroxide and hydroperoxide group because alkyl radical (P<sup>•</sup>) decayed fast in air.<sup>12</sup> In fact, according to Louis et al.,<sup>11</sup> for PP irradiated in air, the alkyl radical can not exist long because it rapidly react with oxygen to produce peroxy-radical which will soon evolve into peroxide or hydroperoxide group. Especially in our study, the powdered sample has large surface and P<sup>•</sup> contact with oxygen fully. It is interesting to note that Gupta and Chapiro<sup>13</sup> got a similar conclusion when discussing the grafting of PE film with different experiment fact and explanation.

# Morh's Salt

Morh's salt is one of the most important factors to control the grafting. As an inhibitor, it can effectively stop the polymerization of acrylic acid by consuming the active radical. Thus, not only the formation of homopolymer, but also the production of grafting polymer, will be suppressed. The more important effect of morh's salt is that the reducible Fe<sup>2+</sup> takes part in the decomposition of the peroxide and hydroperoxide group. In our grafting system, P<sup>•</sup> does not exist, and the thermal stability of the peroxide and hydroperoxide group is so high that no obvious polymerization reaction occurs, even when heated to 60°C in the absence of  $Fe^{2+}$  (a higher temperature only results in the formation of a large amount of homopolymer). With  $Fe^{2+}$ , the initiating reaction is dominated by the following redox process:

POOH + 
$$Fe^{2+} \rightarrow PO^{\bullet} + Fe^{3+} + OH^{-}$$
  
POOP +  $Fe^{2+} \rightarrow PO^{\bullet} + Fe^{3+} + PO^{-}$ 

Figure 3 clearly demonstrates the effect of morh's salt on the grafting yield; low concentration salt initiates the grafting reaction, and a higher concentration brings a negative effect. Although grafting yield obtains the highest value when the morh's salt concentration is around 0.008 wt %, a



**Figure 3** The effect of morh's salt on grafting reaction temperature (60°C), time (2 h), monomer concentration (33 wt %), and morh's salt concentration (0.08%).



**Figure 4** Effect of temperature on the grafting yield temperature is indicated in the figure. The other reaction condition is the same as in Figure 2 (40°C; morh's salt concentration is 0.3 wt %).

large amount of homopolymer is also produced, which makes the purifying process very difficult. For the convenience of operations, the subsequent experiments were performed with 0.08 wt % morh's salt.

## Temperature

Temperature has primary importance on controlling polymerization. Figure 4 shows the effect of temperature on grafting yield. The initial grafting rate increases more rapidly, and the reaction stops earlier at a higher reaction temperature. Above 60°C, the grafting yield exhibits a maximum value after 2 h of reaction. Not in agreement with other similar studies,<sup>14,15</sup> the figure shows that the final grafting yield also increases with temperature.

This can be more clearly seen from Figure 5. It must be pointed out that the morh's salt concentration is 0.8 wt % at  $40^{\circ}$ C. No weightable grafted polymer was produced when the morh's salt concentration was lower than 0.1 wt %.

It is generally assumed that the final grafting yield will decrease with the increment of temperature because higher temperature favors the chain termination by the interaction of two growing chain and decreases the number of the initial radical by accelerating the decay of the "trapped" radical. The unusual phenomenon in this grafting system can be explained reasonably by the following arguments. First, with the presence of morh's salt, the dominant chain termination reaction should be

$$\mathbf{P} - (M)_x^{\bullet} + \mathbf{F}\mathbf{e}^{2+} \rightarrow \mathbf{P} - (M)_x^{-} + \mathbf{F}\mathbf{e}^{3+}$$
$$\mathbf{P} - (M)_x^{\bullet} + \mathbf{F}\mathbf{e}^{3+} \rightarrow \mathbf{P} - (M)_x^{+} + \mathbf{F}\mathbf{e}^{2+}$$

and not the interaction of two grating chains. Second, as previous stated, the initial center is mainly the peroxide and hydroperoxide group and not the alkyl radical. So the high temperature will not decrease the grafting site. As a matter of fact, the higher temperature decreases the system viscosity, which favors the diffusion of the monomer to the grafting site, and high temperature accelerates the decomposition of the peroxide and hydroperoxide group, which initiates the grafting reaction. Meanwhile, a higher temperature effectively limits the inhibition effect of oxygen, the peroxy-radical generated by the reaction of oxygen, and the chain radical can be decomposed by  $\mathrm{Fe}^{2+}$  at a higher temperature. Thus, the grafting reaction will continue without losing the active site. From Figure 6, the apparent reaction activation energy of this reaction was calculated to be 137 KJ  $\cdot$  mol<sup>-1</sup>. The straight line indicates the uniform reaction in the investigated temperature range.16

## Acid

The effect of acid is one of the focuses in irradiation-induced grafting studies. In those "direct" radiation systems, it was suggested that the acid effect should not be due to the increment of  $H^+$ and the acid types have a significant influence on the grafting reaction. Dilli et al.<sup>17</sup> reported that a little sulfuric acid can increase the grafting yield



**Figure 5** Effect of temperature on the grafting yield. The reaction condition is the same as in Figure 2 (40°C; morh's salt concentration is 0.3 wt %).



**Figure 6** Arrhenius diagram for grafting of AA onto PP. The reaction condition is the same as in Figure 2.

sharply and minimize the molecular weight of the homopolymer. As for preirradiation system, it can be reasonably assumed that acid should enhance the grafting yield because the H<sup>+</sup> dissociated from it can accelerate the initiating reaction by consuming the OH<sup>-</sup> accumulated in the decomposition of hydroperoxide group. The acid effects are shown in Figure 7, and the situation is very complex. It appears that acids increase the grafting yield at a lower concentration and keep a higher value for  $H_2SO_4$ . A little decrement for  $HNO_3$  at a higher concentration is hard to explain, but the sharp decrement for HCl may be attributed to the reductive Cl<sup>-</sup>, which terminates the grafting chain by the following reaction at higher concentration:

$$\mathbf{P} - (M)_x^{\bullet} + \mathbf{Cl}^- \rightarrow \mathbf{P} - (M)_x^- + 1/2\mathbf{Cl}_2$$



**Figure 7** Effect of acid concentration on grafting. Acid types are indicated in the graph. Other reaction conditions are the same as in Figure 2.



**Figure 8** Effect of monomer concentration on grafting. The reaction condition is the same as in Figure 2.

(Detectable  $\text{Cl}_2$  was generated when the HCl concentration was higher than 0.4 mol/L). In other similar studies, Gupta and Chapiro<sup>12</sup> and Yong Chang Nho<sup>18</sup> studied the acid effect, and they also observed some unexpected decrement of the grafting yield when there is no morh's salt present or when the acid concentration or the monomer concentration is higher.

# **Monomer Concentration**

Figure 8 shows the effect of the monomer concentration on the grafting yield. From the figure, it can be seen that the grafting yield increases with the increment of the monomer concentration and reaches a maximum value around 55%. Beyond this critical concentration, the grafting yield decreases with the increment of monomer concentration. This decrement at a higher concentration is at least partly due to the formation of homopolymer, which enhances the viscous system to prevent the diffusion of the monomer to the grafting site and consumes the unreacted monomer available for grafting. In fact, when the monomer concentration is higher than 80%, the reaction liquid becomes a transparent gel with white powdered PP "floating" in it. No apparent grafting reaction occurs at all.

#### **FTIR Characterization**

Infrared spectra of irradiation PP and grafted PP are presented in Figure 9. After grafting, new bands appear at 1716 and  $1255 \text{ cm}^{-1}$ , corresponding to C=O and C-O stretching vibrations of the carboxyl group, respectively. The intensity of



**Figure 9** FTIR spectra of irradiated PP and grafted PP.

these new bands increases with the increment of the grafting yield.

# CONCLUSION

From the discussions above, we found that preirradiation grafting of acrylic acid onto powdered isotactic polypropylene can be achieved well without purging oxygen. Morh's salt is indispensable for this kind of reaction because, in addition to acting as a homopolymerization inhibitor, it initiates grafting by taking part in the decomposition of hydroperoxide and peroxide group. Acids increase the grafting yield at a lower concentration, but the situation is very complex. More detailed investigation is needed to get an accurate understanding of the acid effect.

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