

Solid-Phase Grafting of Glycidyl Methacrylate onto Polypropylene

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Received 10 September 1996; accepted 12 February 1997

ABSTRACT: Free-radical grafting of glycidyl methacrylate (GMA) onto polypropylene (PP) powder was studied in a batch mixer. The reaction temperature was below the melting point of PP so that PP was modified in the solid phase. The graft yield of GMA obtained under various experimental conditions allowed for a good appreciation of the effects of chemical parameters (the concentration of monomer, initiator, and interfacial agent) and those of processing parameters (reaction time and temperature). Toluene was used as an interfacial agent to etch the surface of PP powder to provide more sites for reaction. Quantitative determination of the graft level was performed by wet chemical methods. The results showed that the solid-phase grafting could take place over a temperature range of 100–140°C in the initiation of benzoyl peroxide (BPO). The ultimate GMA grafting level achieved was higher than that obtained in the melt state with dicumyl peroxide (DCPO) as a radical initiator. The grafting of GMA affected the crystalline morphology of PP and speeded up the crystallization process. The energy of activation and initial decomposition temperature of grafted samples were higher than those of ungrafted PP. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **65**: 1905–1912, 1997

INTRODUCTION

Because of its low cost, versatile properties, and growing commercial application, polypropylene (PP) has become the largest- and fastest-growing plastic. However, PP is limited in its application in several technologically important fields due to its low surface energy, lack of reactive sites, difficulty to dye, extremely poor hygroscopicity, low melting and sticking temperatures, low impact strength, sensitivity to photo- or thermal oxidation, and poor compatibility with synthetic polar polymers. Graft copolymerization onto PP with a variety of vinyl monomers offers an effective approach to introduce some desirable properties into the polymer and thus expands the

available market for polymer application without adversely affecting the architecture of the PP backbone.¹

Efforts to modify PP with the combinations of peroxides and vinyl monomers have been in progress since the 1960s. Most attention has been given to peroxide grafting of maleic anhydride (MAH), which has been found to be a successful compatibilizer in blend of PP and polyamides (PA). Grafting of vinyl monomers onto PP has been investigated by several investigators using various methods.^{2–5} Some of the key techniques were summarized by Rengarajan et al.⁶ The solid-phase graft copolymerization technique was advantageous over other processes since it utilized small amounts of solvent. The reaction was performed at low temperatures, at atmospheric pressure, and with low residence times. It was found that reaction conversion in the solid phase can be increased up to 30% in

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the presence of a small amount of solvent, such as xylene.⁷ This novel process also utilized a conventional low-shear mixer which was modified to carry out the solid-phase graft copolymerization reaction.

Efforts to modify PP in the solid phase have been in progress since 1980s.^{8,9} In the present article, we turned our attention to grafting glycidyl methacrylate (GMA) onto PP. Although GMA is very reactive, its use for PP grafting in the solid phase has hardly been explored. During our work, the synthesis and characterization of the graft copolymer (PP-*g*-GMA) were carried out. The effects of various factors such as monomer, initiator, and interfacial agent concentration, reaction time, and reaction temperature on the graft level were studied.

EXPERIMENTAL

Materials

The isotactic polypropylene (IPP) used in this work was T300 supplied by Shanghai Petrochemicals Corp. and was ground cryogenically to a fine powder to pass through 40, 80, 120, and 160 mesh screens. This powdered PP was capable of absorbing a larger amount of liquid monomer than could the one in the normal pellets, therefore facilitating material feeding. Glycidyl methacrylate (GMA) was synthesized in our laboratory (purity: 97.5%). Benzoyl peroxide (BPO) was purified by dissolving it in chloroform and reprecipitating with methanol.

Grafting Procedure

The solid-phase grafting of GMA onto powdered PP was conducted on a Haake Rheomix 600 internal mixer equipped with sigma blades, operating at 60 rpm. In a typical grafting process, the PP powder was moistened with a chosen amount of a liquid mixture of GMA, BPO, and toluene at room temperature for about 1 h in order that this mixture would be absorbed by the PP powder. The wet mixture was then fed into a preheated Haake mixer and allowed to react for 15 min. The modified PP samples were purified in this way: They were dissolved in refluxing toluene at a concentration of 4% (wt/vol) and then precipitated in three volumes of acetone at room temperature. The dissolving-precipitating procedure was conducted

three times to remove poly(glycidyl methacrylate) which might be formed during the free-radical grafting process. The purified graft copolymer was dried under a vacuum at 60°C. The quantification of the GMA grafted onto PP was performed by solving for the purified samples in a known volume of a boiling mixture of toluene and ethanolic-potasse where the ester groups of grafted GMA would hydrolyze. The excess of potasse was determined by neutralization with isopropanolic-chlorohydric acid. Differences between these two volumes are related to the amount of GMA grafted onto PP. The graft level (GL) was determined by using the following relation:

$$\text{GL}\% = \frac{N \cdot (V_0 - V) \times 142.15}{1000 \times W} \times 100$$

where N is the concentration of the isopropanolic-chlorohydric acid solution (mol/L); V_0 , the volume of the isopropanolic-chlorohydric acid for blank titration (mL); V , the volume of the isopropanolic-chlorohydric acid for sample titration (mL); W , the weight of the purified sample (g), and 142.15, the molecular weight of GMA.

Characterization

The samples for FTIR characterization were compression-molded into thin films between aluminum sheets on a laboratory press at 180°C under 100 kg/cm² pressure. FTIR spectra of these films were scanned on a Nicolet 5SXC spectrophotometer.

Wide-angle X-ray diffraction (WAXD) was carried out on a Rigaku D/max-rB diffractometer using Ni-filtered CuK α radiation. The crystallinity of samples crystallized at 110°C was determined by WAXD in terms of the peak separation method.

Thermogravimetric analysis (TGA) was conducted using a DuPont 1090B thermal analyzer under a nitrogen atmosphere. The purified samples were heated from 25 to 550°C with a uniform heating rate of 10°C/min. The energy of activation and initial decomposition temperature were calculated. Differential scanning calorimeter (DSC) testing was performed on DuPont 1090B and Mettler Toledo 821e thermal analyzers. The analysis of purified samples was conducted under a nitro-

gen atmosphere with a uniform heating or cooling rate of 10°C/min.

The crystallizing rate of the purified samples was measured on a JJY-1A crystallographic apparatus. The samples for testing were pressed at 230°C for 2 min to destroy residual nuclei and then placed into a crystallization oven set at 110°C. The crystallized samples were observed under a Leitz polarizing microscope (Ortho Ptom-Po1) equipped with a 35 mm camera. Visible observations were made using a magnitude of $\times 320$.

RESULTS AND DISCUSSION

To optimize the conditions for grafting, effects of various parameters such as monomer, initiator, and interfacial agent concentration, reaction time, and reaction temperature on the graft level were studied.

Homopolymerization of GMA

GMA is an active monomer which would homopolymerize through the vinyl group under the initiation of heat or free radicals. The influence of heat and initiator on temperature of polymerization is shown in Figures 1 and 2. Without the initiation of peroxide, GMA began to polymerize at 153.1°C, while the mixture of GMA and BPO in a 10 : 1 weight ratio showed the initial polymerization temperature at 92.4°C, which was far below that of a mixture of GMA and DCPO used in melt grafting.¹⁰ Therefore, the grafting temperature should

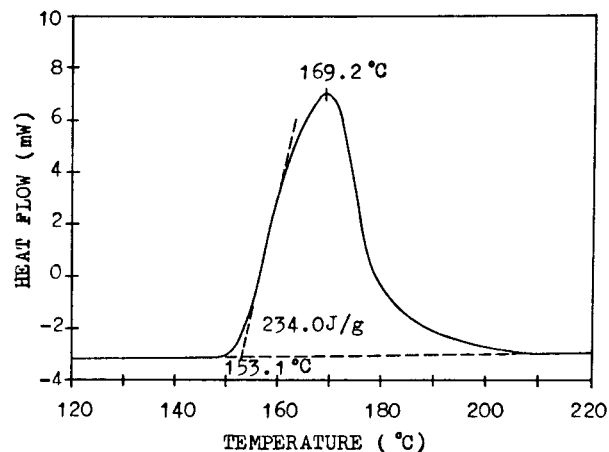


Figure 1 DSC curve of GMA; heating rate: 10°C/min.

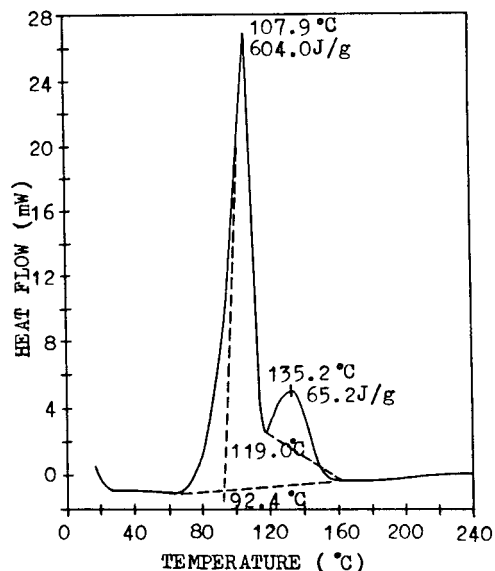


Figure 2 DSC curve of GMA and BPO mixture [GMA]/[BPO] = 10 : 1; heating rate: 10°C/min.

be kept low in order to reduce the homopolymerization of GMA.

Effect of Size of PP Powder

The interdependence of the graft level and the size of the PP powder is given in Figure 3. The solid-phase grafting reaction was conducted mainly on the surface of the PP powder. Therefore, the finer the powder, the higher the graft

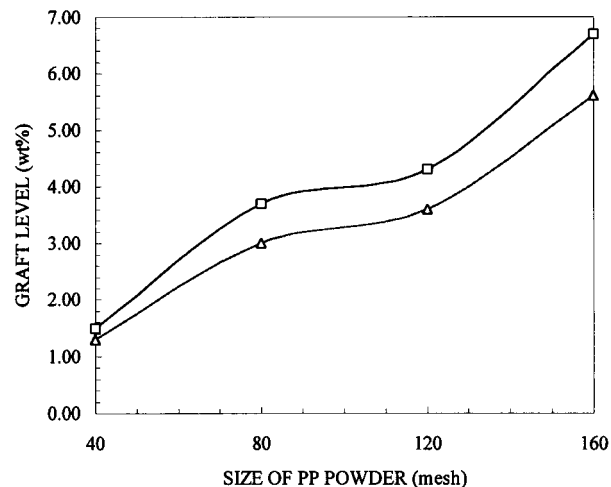


Figure 3 Influence of size of PP powder on graft level at various temperatures: (□) 120°C; (△) 130°C. [GMA] = 10.0 phr, [BPO] = 1.0 phr, [toluene] = 0 phr; t = 15 min; N = 60 rpm.

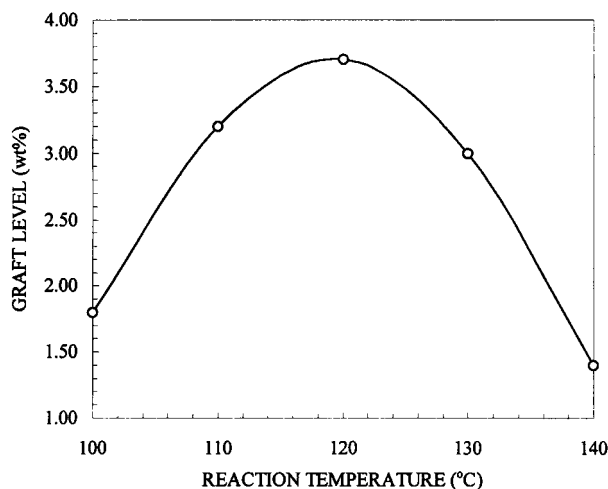


Figure 4 Effect of reaction temperature on graft level. [GMA] = 10.0 phr, [BPO] = 1.0 phr, [toluene] = 0 phr; t = 15 min; N = 60 rpm.

level. The graft level decreased at higher temperature due to enhancement of heat-initiated homopolymerization which consumed more monomer molecules. However, the size of the PP powder has little effect on the graft level in the melt grafting process.¹⁰ Because finer powder was difficult to acquire, 80-mesh PP powder was adopted in our further experiments.

Effect of Reaction Temperature

The effect of reaction temperature on the graft level is shown in Figure 4. With increasing tem-

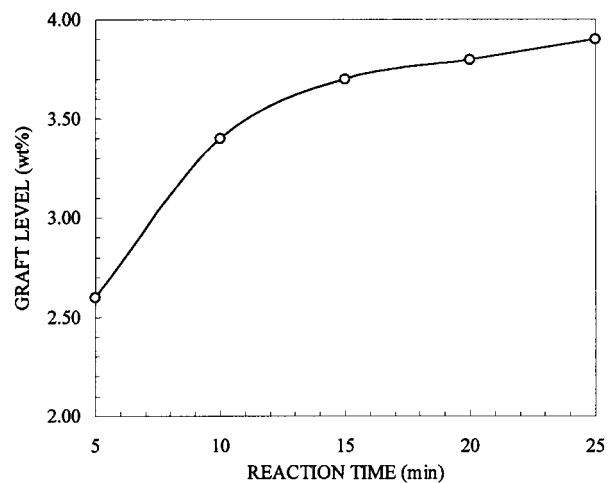


Figure 5 Effect of reaction time on graft level. [GMA] = 10.0 phr, [BPO] = 1.0 phr, [toluene] = 0 phr; T = 120°C; N = 60 rpm.

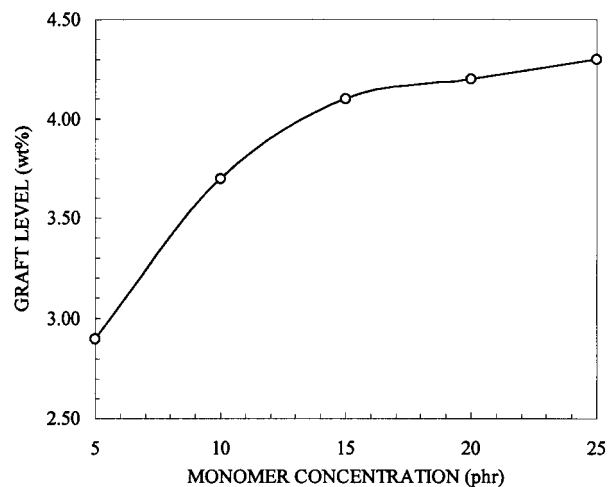


Figure 6 Effect of monomer concentration on graft level. [BPO] = 1.0 phr, [toluene] = 0 phr; T = 120°C; t = 15 min; N = 60 rpm.

perature, the graft level increases initially due to an increased decomposition rate of the initiator. Therefore, the amount of free radicals as well as their mobility also increases, which results in a higher level of grafting. However, further increase in reaction temperature leads to mutual termination of various free radicals and serious homopolymerization initiated by heat. These factors result in the optimum temperature for solid-phase grafting of GMA. Therefore, the reaction temperature was set at 120°C in our further studies. Basically, the results obtained are similar to those obtained in the molten state with DCPO as a radical initiator.¹⁰

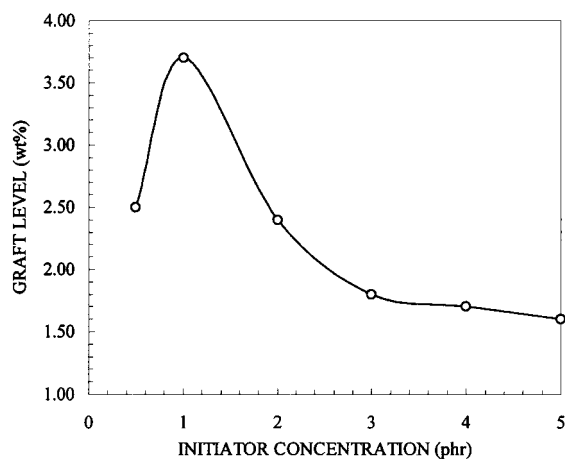


Figure 7 Effect of initiator concentration on graft level. [GMA] = 10.0 phr, [toluene] = 0 phr; T = 120°C; t = 15 min; N = 60 rpm.

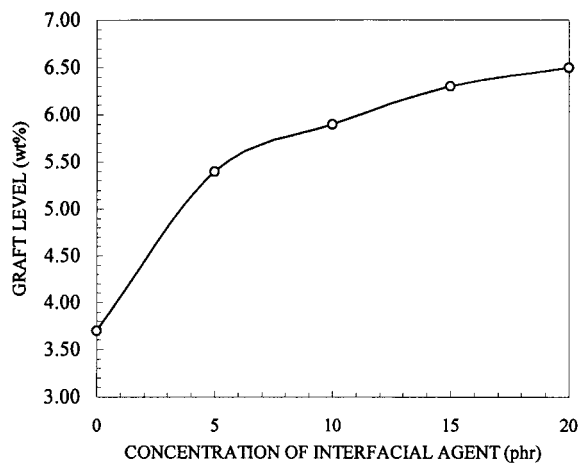


Figure 8 Effect of interfacial agent concentration on graft level. [GMA] = 10.0 phr, [BPO] = 1.0 phr; $T = 120^{\circ}\text{C}$; $t = 15$ min; $N = 60$ rpm.

Effect of Reaction Time

The half-lifetime of BPO is about 4 min at 120°C . Therefore, most of the initiator decomposes in about 15 min. This primarily determines the reaction time. Figure 5 illustrates the effect of reaction time on the graft level. From the figure, it is evident that the graft level increases initially and reaches a plateau in 10 min. With an increase in reaction time, the free radicals will have more time for reaction and therefore result in a higher level of grafting. After some time, all the initiator and monomer are used up. Thus, no further change in the graft level was observed with increasing reaction time. The results are in agreement with the findings obtained in the melt grafting of GMA.¹⁰

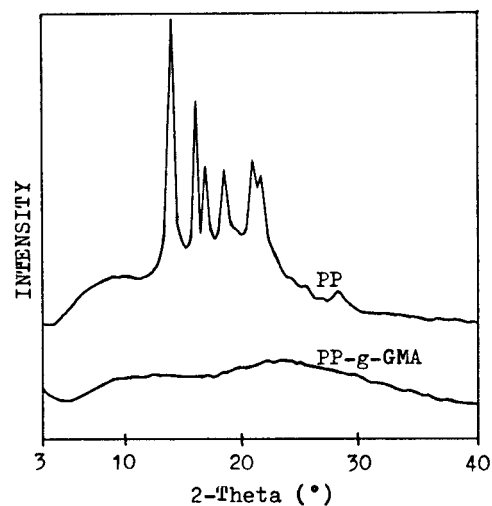
Effect of Monomer Concentration

The effect of monomer concentration on the graft level is shown in Figure 6. It is evident that the

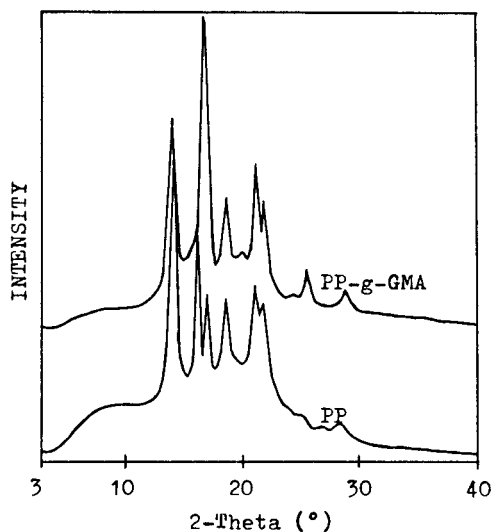
Table I TG Analysis of Various PP

Graft Level (wt %)	Energy of Activation (kJ/mol)	Initial Decomposition Temperature ($^{\circ}\text{C}$)
0	96.4	364.8
1.5	103.5	373.7
3.7	116.9	380.9
5.6	131.4	389.4

Heating rate: $10^{\circ}\text{C}/\text{min}$.



crystallized at 25°C



crystallized at 110°C

Figure 9 WAXD curves of PP and grafted PP.

graft level increases initially with an increase in monomer concentration up to 10 phr and then increases slowly. This may be because, initially, the number of monomer molecules reaching the free-radical sites on the polymer backbone govern the grafting extent. However, at higher monomer concentration, the number of free-radical sites available on the PP backbone becomes a limiting factor and homopolymerization of the monomer becomes great. The result also agrees with what

Table II Crystallization Behavior of PP

Graft Level (wt %)	Crystallization Half-Life ^a $t_{1/2}$ (s)	Degree of Crystallinity ^b X_c (%)	Crystallization Temperature ^c T_c (°C)	Heat of Crystallization ^c ΔH_c (J/g)
0	53.5	43.0	113.41	85.98
1.5	20.4	57.1	116.88	93.30
2.5	21.8	—	117.59	90.50
3.3	18.4	55.7	117.72	87.97
3.7	19.4	54.5	117.98	87.73
4.7	22.2	—	118.26	85.97
5.6	23.6	48.9	118.63	84.55

^a Crystallized at 110°C.

^b Obtained from WAXD.

^c Heating rate: 10°C/min.

was found for the melt grafting in an internal mixer.¹⁰

Effect of Initiator Concentration

The effect of initiator concentration on the graft level is illustrated in Figure 7. The initial increase in the graft level is caused by an increase in concentration of free radicals formed through the decomposition of the initiator. Therefore, the higher the concentration of radicals, the more radical sites on the PP backbone and the higher the graft level. Further increase in the initiator concentration results in serious homopolymerization of the monomer and decreases the average molecular weight of the incorporated GMA side chain because of the enhanced mutual termination reaction of radicals. These opposing tendencies result in the appearance of a maximum extent of grafting. This result is similar to those obtained in melt grafting carried out in an internal mixer, single-screw extruder, and counterrotating twin-screw extruder.¹⁰

Effect of Interfacial Agent Concentration

Toluene was used as interfacial agent for the current study. The effect of the interfacial agent concentration on the graft level is demonstrated in Figure 8. It is obvious that the graft level increases with increase in the interfacial agent concentration. The ability of the solvent to etch and swell the polymer surface at the reaction temperature provides a more surfacial area for the solid-phase grafting process. Additionally, increase in the concentration of the interfacial agent results

in decreased homopolymerization of GMA. The two factors are attributed to increase in the graft level. With the addition of a 5 phr interfacial agent, the graft level increases by 45%.

Characterization

The FTIR spectrum of the graft copolymer showed a band at 1730 cm^{-1} , corresponding to the ester group of grafted GMA. Additionally, the intensity of this characteristic band increased with increase in the graft level, showing that GMA had been introduced onto PP.

From Table I, it is evident that a considerable change in the thermal behavior of PP took place upon grafting. The energy of activation and initial decomposition temperature of grafted samples were higher than those of ungrafted PP, which was due to the abstraction or replacement of thermally sensitive tertiary hydrogen atoms on the PP backbone by graft chains.

The supermolecular structure and crystalline morphology of PP were also affected by grafting. The WAXD curves of PP and modified PP are shown in Figure 9. With the incorporation of GMA, the graft copolymer could not crystallize at room temperature, indicating a higher crystallization temperature for the grafted sample than for PP. The graft copolymer that crystallized at 110°C did not show a diffraction peak at the angle of 16°, which was characteristic of the β crystal form of PP, indicating the formation of a uniform α crystal form. The degree of crystallinity obtained from the WAXD curves is shown in Table II. The crystallinity of the grafted samples was higher than that of unmodified PP. However, with

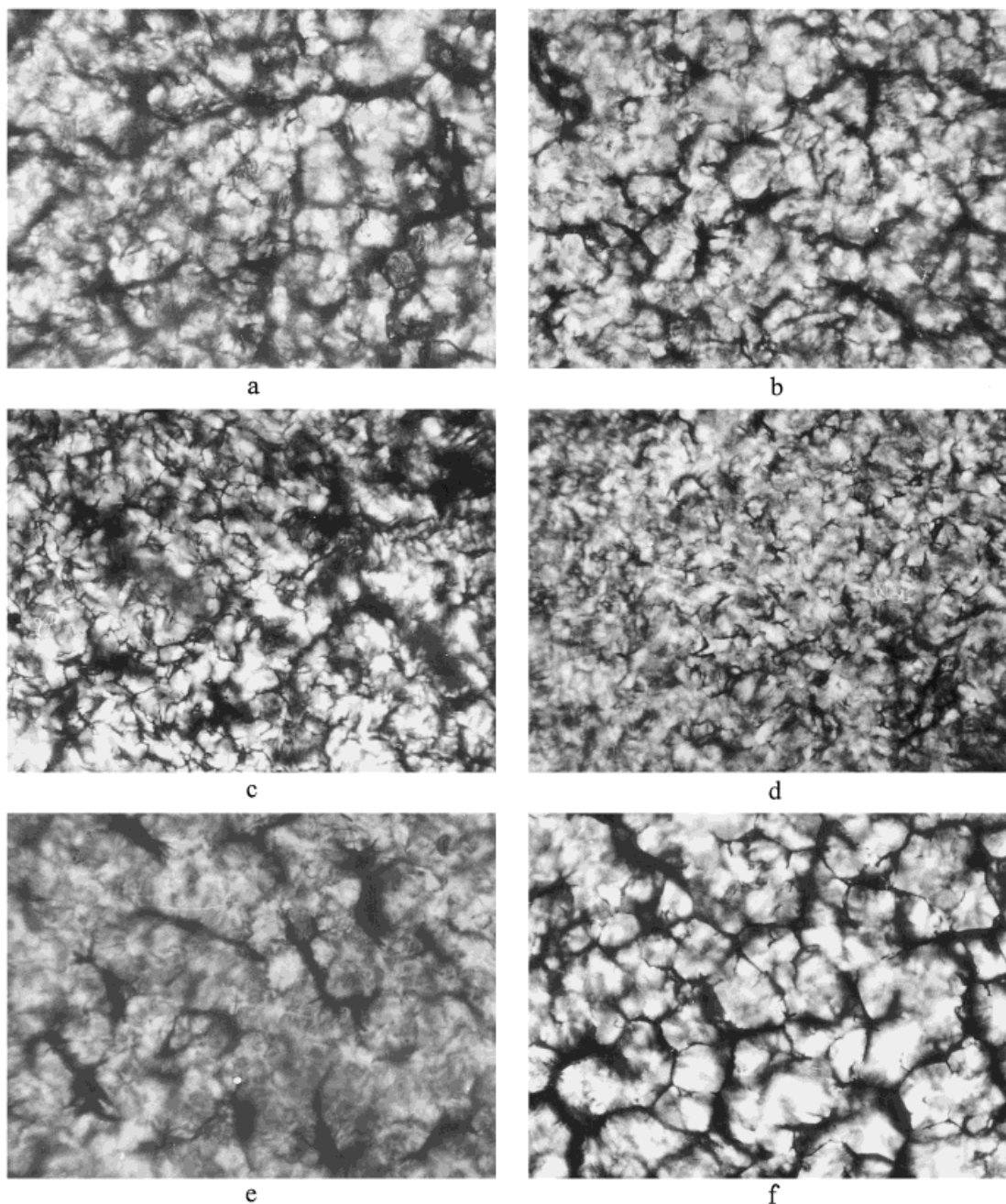


Figure 10 Optical micrographs of grafted PP crystallized at 110°C under crossed polarizers: (a) GL = 1.5 wt %; (b) GL = 2.5 wt %; (c) GL = 3.3 wt %; (d) GL = 3.7 wt %; (e) GL = 4.7 wt %; (f) GL = 5.6 wt %.

increase in the graft level, the degree of crystallinity decreased.

The crystallization half-life of the grafted samples is also given in Table II. As the crystallization half-life indicates the crystallizing rate of the samples, it decreases initially and then increases with an increase in graft level. At a

low level of grafting, large amounts of short graft chains acting as the nuclei agent speed up the crystallization process and therefore decrease the size of the crystal. However, at a high level of grafting, long graft chains hinder the crystallization, resulting in a big crystal particle. This phenomenon was confirmed by the ob-

servation of the optical microscopy under cross polarizers, which is shown in Figure 10. The crystallizing behavior obtained from DSC is also listed in Table II. The crystallization temperature of the grafted samples increased with increase in the graft level, which supports the argument obtained from WAXD. However, the heat of crystallization decreased with increase in the graft level.

CONCLUSION

This article concerned the performance of an internal mixer as a chemical reactor for the free-radical grafting of GMA onto PP in the solid phase. The effects of chemical and processing parameters were discussed. The results showed that solid-phase grafting could take place over a temperature range of 100–140°C in the initiation of BPO. The grafting of GMA affected the crystalline morphology of PP and speeded up the crystallization process. The energy of activation and initial decomposition temperature of the grafted samples were higher than those of ungrafted PP. Despite

the very big differences between the solid- and molten-state processes, the same level of grafting was achieved.

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