Grafting of Maleic Anhydride onto Polypropylene: Synthesis and Characterization

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SYNOPSIS

Isotactic polypropylene was grafted with maleic anhydride using benzoyl peroxide as an initiator and toluene as a solvent. Effects of various parameters such as monomer and initiator concentration, reaction time, and reaction temperature on percentage grafting were studied. Effect of various solvents on extent of grafting was also studied. The maximum extent of grafting achieved was 5.3%. The graft copolymers were characterized by i.r., thermal, viscometric, and contact angle studies. Improved thermal stability and decreased intrinsic viscosity and critical surface tension were observed for graft copolymers. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Isotactic polypropylene (IPP) has become the largest and fastest growing plastic because of its versatility, wide applicability, and low cost.[1] However, it has limitations such as lack of reactive sites, poor hydrophilicity, difficulty to dye, low melting and sticking temperatures, and sensitivity to photooxidation. Chemical modification of IPP through grafting offers an effective means for introducing some desirable properties into the polymer without adversely affecting the nature of polymer backbone.

Grafting of vinyl monomers onto IPP was carried out by several workers using various methods and was reviewed by Singh.[2] Very few methods are available for solution grafting of vinyl monomers onto IPP. A mixture of alkyl acrylates was used by Canterino[3] for grafting onto IPP using benzoyl peroxide initiator. Grafting of acrylic acid and methacrylic acid onto IPP in o-dichlorobenzene was carried out by Pegoraro et al.[4,5] and Masahiko and Iwata[6] using benzoyl, dicumyl, and t-butyl peroxide initiators. They[4,5] observed highest grafting efficiency, lower melting temperatures, and heats of fusion and molecular weights for the synthesized graft copolymers. IPP was grafted with acrylamide, eth-

ylene glycol methacrylate, and membranes of these graft copolymers were prepared by solvent evaporation technique.[7] Ide and Hasegawa[8] and Park and Shin[9] synthesized IPP-g-maleic anhydride using benzoyl peroxide in xylene. Kiyotada[10] and Klosiewicz[11] modified IPP by grafting bycyclo (2,2,1) hept-5-ene 2,3-dicarboxylic acid anhydride and butyl methacrylate in o-chlorobenzene using t-butyl peroxide as an initiator. Kiyotada[10] has reported 3% grafting but good adhesion property for graft copolymers. Masahiko[12] synthesized 10.5 : 89.5 N-butyl maleimid propylene graft copolymer using chlorobenzene as a solvent and dicumyl peroxide initiator at 125°C.

Though maleic anhydride (MAH) is very reactive, its use for grafting onto IPP has hardly been explored. In this article, the synthesis and characterization of IPP-g-MAH is discussed. The effects of various factors such as monomer concentration initiator concentration, reaction time, and reaction temperature on the percent grafting of maleic anhydride onto IPP are studied.

EXPERIMENTAL

Materials

Isotactic polypropylene used in this work was Koylene (M 0030) from Indian Petrochemicals Corporation Ltd., Vadodara, India with melt flow index

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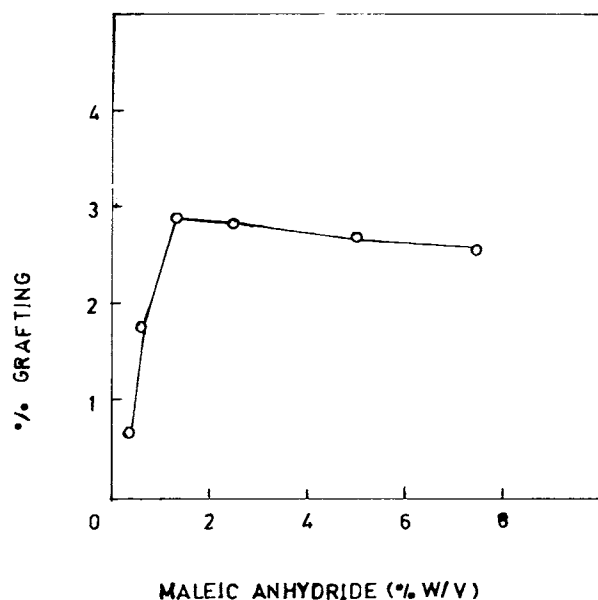
Figure 1 Effect of monomer concentration on percent grafting.

10 g/10 min at 230°C and a 2.16-kg load. Maleic anhydride (Fluka) was used as received without purification. Benzoyl peroxide (Fluka) was purified by dissolving it in chloroform and reprecipitating with methanol. AR grade toluene and acetone were used as received without further purification.

Grafting Procedure

The graft copolymerization was carried out in four neck round-bottom flasks equipped with overhead stirrer, condensor, thermometer, and a nitrogen gas inlet. The temperature was maintained with accuracy of ±0.5°C by using a contact thermometer in an oil bath. A known amount of isotactic polypropylene (2.5% w/v) was dissolved in toluene at 110°C. Nitrogen gas was purged throughout the reaction to remove dissolved oxygen. To this homogenized solution, we added benzoyl peroxide (0.15% w/v) in toluene followed by maleic anhydride solution (1.25% w/v) in toluene, and the reaction was continued for 6 h. The reaction mixture was then poured into 1.5 L of acetone under vigorous stirring. The precipitated graft copolymer was isolated and washed several times with acetone, and then Soxhlet extracted with acetone for 16 h to remove traces of maleic anhydride and toluene. Finally, products were dried under reduced pressure at 80°C to constant weight.

To see any degradation of IPP taking place due to benzoyl peroxide, a blank experiment was carried out under identical condition without addition of monomer.

The percent grafting (G) was determined gravimetrically by using the following relation.

$$\% \text{ Grafting (G)} = \frac{W_1 - W_0}{W_0} \times 100$$

where W_0 = the weight of original IPP and W_1 = the weight of grafted IPP after complete removal of unreacted MAH.

The rate of grafting was calculated following the method reported by Vijaykumar.[13]

R_g (mol L^{-1} s^{-1})

$$= \frac{\text{Wt of grafted maleic anhydride} \times 1{,}000}{\text{Mol wt of monomer}}$$
$$\times \text{ time of polymerization (s)}$$
$$\times \text{ vol of reaction mixture (mL)}$$

Characterization

The graft copolymers were compression molded into thin films on Metro Compression molding machine (India) at 190°C under 100 kg/cm² pressure. I.R. spectra of these films were recorded onto a Shimadzu I.R. 408 Spectrophotometer.

Contact angle measurements were made by using compression-molded films of graft copolymers, and contact-θ-meter developed at the University of Leeds, Leeds, England (U.K.). From these results, critical surface tension (γ_c) values of graft copolymers were calculated by plotting surface tension against cos θ.

Differential scanning calorimetric studies were conducted using a DuPont-2000 thermal analyzer. The analysis was carried out at a constant heating

Table I Effect of Monomer Concentration[a]

MAH (% w/v)	Rg × 10⁷ mol L^{-1} s^{-1}	Critical Surface Tension (γ_c)	Intrinsic Viscosity dL/g
0.38	0.80	30.00	1.25
0.63	2.13	29.10	1.20
1.25	3.42	24.00	1.01
2.50	3.30	24.70	0.95
5.00	3.17	25.40	0.92
7.50	3.07	26.10	0.86

[a] Polypropylene: 2.5% (w/v) solution in the toluene; benzoyl peroxide: 0.15% (w/v); reaction time: 6 h; reaction temperature: 100°C; reaction volume: 200 mL.
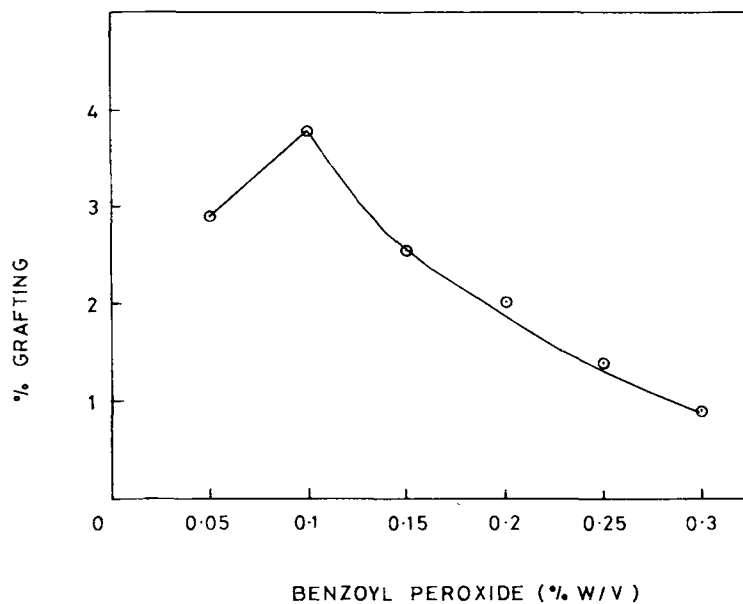
Figure 2   Effect of initiator concentration on percent grafting.

rate of 10°C/min in the temperature range of 25°–200°C under nitrogen atmosphere. The crystallinity of various samples was obtained by using the following expression.[14]

$$\% \text{ Crystallinity} = \frac{\Delta H_f^*}{\Delta H_f^o} \times 100$$

where ΔH_f^o is heat of fusion of 100% crystalline PP and ΔH_f^* is the heat of fusion of graft copolymer.

Thermogravimetric analysis (TGA) was carried out on a DuPont-990 thermal analyzer under nitrogen atmosphere. The samples were heated from 25° to 500°C with a uniform heating rate of 10°C/min.

The initial decomposition temperature (IDT) and the temperature at which a sample undergoes 50% decomposition (T_{50}) were calculated.

Viscosity measurements of Soxhlet-extracted graft copolymers were carried out in internal dilution ubbelhode viscometer at 135°C using 0.4% (w/v) solution in decaline.
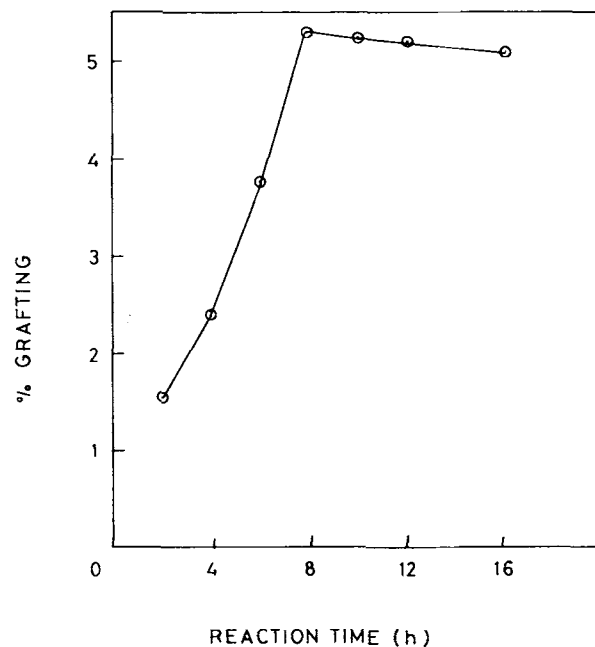
Table II   Effect of Initiator Concentrations[a]

BZ_2O_2 (% w/v)	$Rg \times 10^7$ mol L^{-1} s^{-1}	Critical Surface Tension (γc)	Intrinsic Viscosity dL/g
0.05	3.42	24.00	1.20
0.10	4.43	22.50	1.12
0.15	2.98	25.90	1.01
0.20	2.34	27.30	0.95
0.25	1.65	29.70	0.80
0.30	1.01	30.10	0.72

[a] Polypropylene: 2.5% (w/v) solution in the toluene; Maleic anhydride: 1.25% (w/v); reaction time: 6 h; reaction temperature: 100°C; reaction volume: 200 mL.

Figure 3   Effect of reaction time on percent grafting.

Table III   Effect of Reaction Time[a]

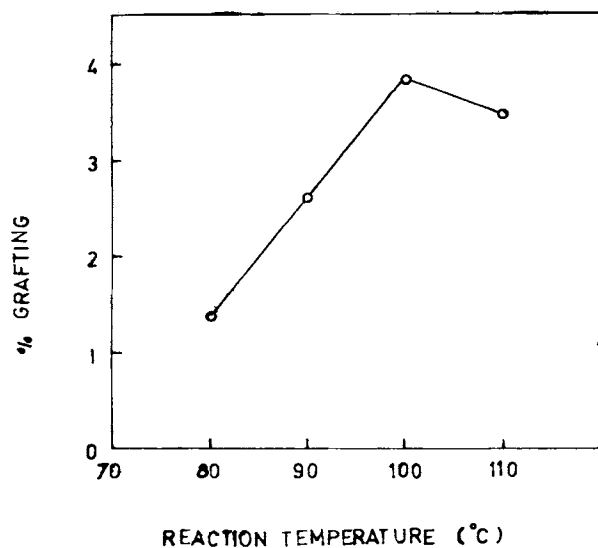| Reaction Time (h)	$Rg \times 10^7$ mol L^{-1} s^{-1}	Critical Surface Tension (γc)	Intrinsic Viscosity dL/g
2	5.66	27.50	1.25
4	4.23	26.30	1.19
6	4.43	22.50	1.10
8	4.71	20.10	0.96
10	3.68	21.60	0.80
12	3.07	22.30	0.71
16	3.01	23.00	—

[a] Polypropylene: 2.5% (w/v) solution in toluene; benzoyl peroxide: 0.1% (w/v); maleic anhydride: 1.25% (w/v); reaction temperature: 100°C; reaction volume: 200 mL.

Table IV   Effect of Reaction Temperature[a]

Reaction Temperature (°C)	$Rg \times 10^7$ mol L^{-1} s^{-1}	Critical Surface Tension (γc)	Intrinsic Viscosity dL/g
80	1.61	29.30	1.11
90	3.02	26.10	1.05
100	4.43	22.50	0.90
110	4.01	25.00	0.86

[a] Polypropylene: 2.5% (w/v) solution in toluene; maleic anhydride: 1.25% (w/v); benzoyl peroxide: 0.1% (w/v); reaction time: 8 h; reaction volume: 200 mL.

RESULTS AND DISCUSSION

In order to optimize the conditions for grafting of maleic anhydride onto polypropylene, we note that the concentration of monomer and initiator as well as reaction time and temperature were varied.

Effect of Monomer Concentration

The effect of monomer concentration on percent grafting (G) is illustrated in Figure 1. The percent grafting increases initially with an increase in monomer concentration up to 1.25 (% w/v) and then remains constant. This may be because initially the number of monomer molecules diffusing through the reaction medium and reaching the free radical sites on the polypropylene backbone govern the grafting extent, whereas at higher concentrations of monomer, the percent grafting remains almost constant as the number of free radical sites available on the polypropylene backbone becomes a limiting factor. This is also supported by the results obtained for the rate of grafting (R_g) (Table I).

Effect of Initiator Concentration

Figure 2 shows the effect of initiator concentration on percent grafting. The observed trend is typical for the graft copolymerization reaction occurring via chain transfer. The initial increase in the percent grafting is caused by an increase in concentration of radicals formed through the decomposition of initiator. Thus the higher the concentration of radicals, the higher the chain transfer to polymer backbone and the higher the percent grafting. Furthermore an increase in initiator concentration decreases the average molecular weight of the side chains because of mutual termination reactions. These two opposing tendencies result in the appearance of maxima. The effect of initiator concentration on R_g is also given in Table II.

Effect of Reaction Time

Figure 3 illustrates the effect of reaction time on the percent grafting of maleic anhydride onto polypropylene. It was observed that the percent grafting increases initially and then remains constant. With an increase in reaction time, the radicals will have more time for reaction, and, as a result, will increase in percent grafting. After some time all initiator is used up. As a result, no further change in grafting

REACTION TEMPERATURE (°C)

Figure 4   Effect of reaction temperature on percent grafting.

Table V   Effect of Solvent on Percent Grafting[a]

	Dipole Moment	% G
o-Xylene	2.57	1.92
o-Dichlorobenzene	2.26	2.24
Toluene	0.42	5.20
Decalin	0.00	5.00

[a] Polypropylene: 2.5% (w/v) solution in toluene; maleic anhydride: 1.25% (w/v); benzoyl peroxide: 0.1% (w/v); reaction time: 8 h; reaction temperature: 100°C.

percentage was observed with an increase in reaction time. The effect of reaction time on R_g is given in Table III.

Effect of Temperature

The effect of temperature on the percent grafting is shown in Figure 4. With increasing temperature, percent grafting increases due to increased decomposition of initiator. Therefore, the number of free radicals as well as their mobility also increases resulting in a higher percent of grafting. Higher mobility also results in mutual termination of free radicals resulting in decreased availability of the free radicals for polymerization, hence, the observed na-

ture of the reaction. The Rg calculated is in agreement with this and is presented in Table IV.

Effect of medium (solvent) on % grafting was studied by synthesizing the graft copolymers in o-dichlorobenzene, o-xylene, toluene, and decalin. It was observed from the results (Table V) that the maximum percent of grafting was achieved in nonpolar solvents, whereas as the polarity increased % grafting extent continues to decreased.

Characterization

The i.r. spectra of polypropylene and grafted polypropylene (3.7% grafting) are given in Figures 5 and 6. The i.r. spectra of graft copolymers showed bands at 1860, 1790, and 1720 cm^{-1}, characteristics of cyclic anhydride groups. Also in grafted samples, the intensity of the few characteristic bands of polypropylene diminish and broadening of some other peaks takes place, showing that MAH has been introduced as a graft into polypropylene.

The contact angles (θ) of graft copolymer films were measured for different solvents of variable surface tensions. From the results obtained, the critical surface tension (γ_c) values of grafted samples were calculated by extrapolating the surface tension against cos θ plot to cos $\theta = 1$. It was observed that the surface polarity of graft copolymer is augmented with an increase in percent grafting.
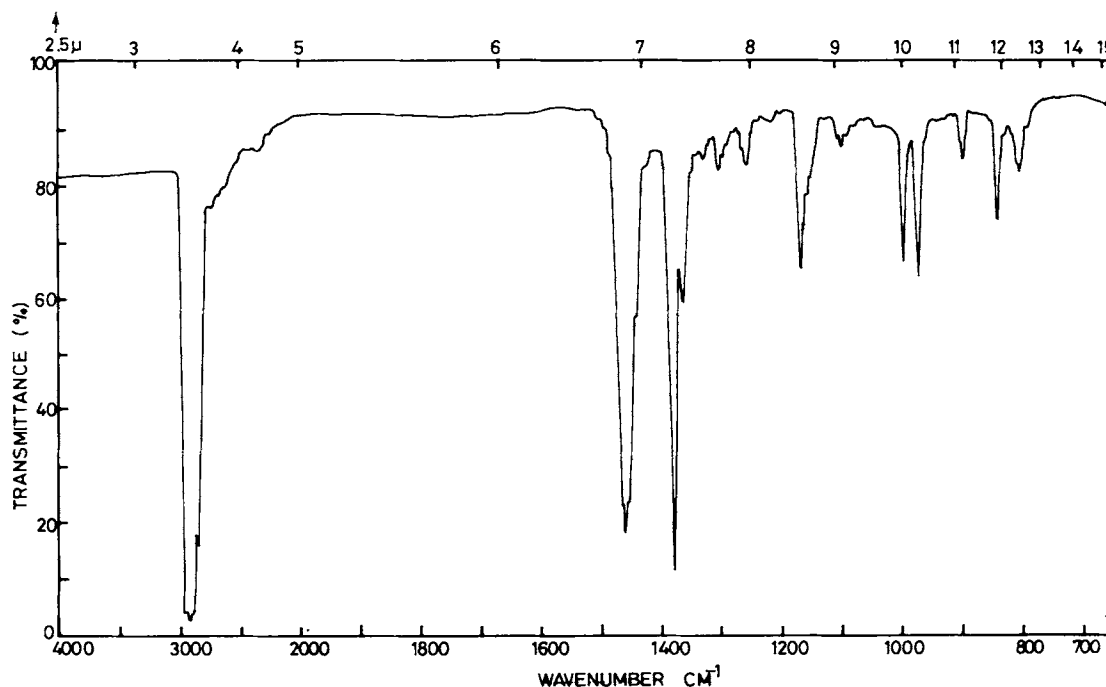
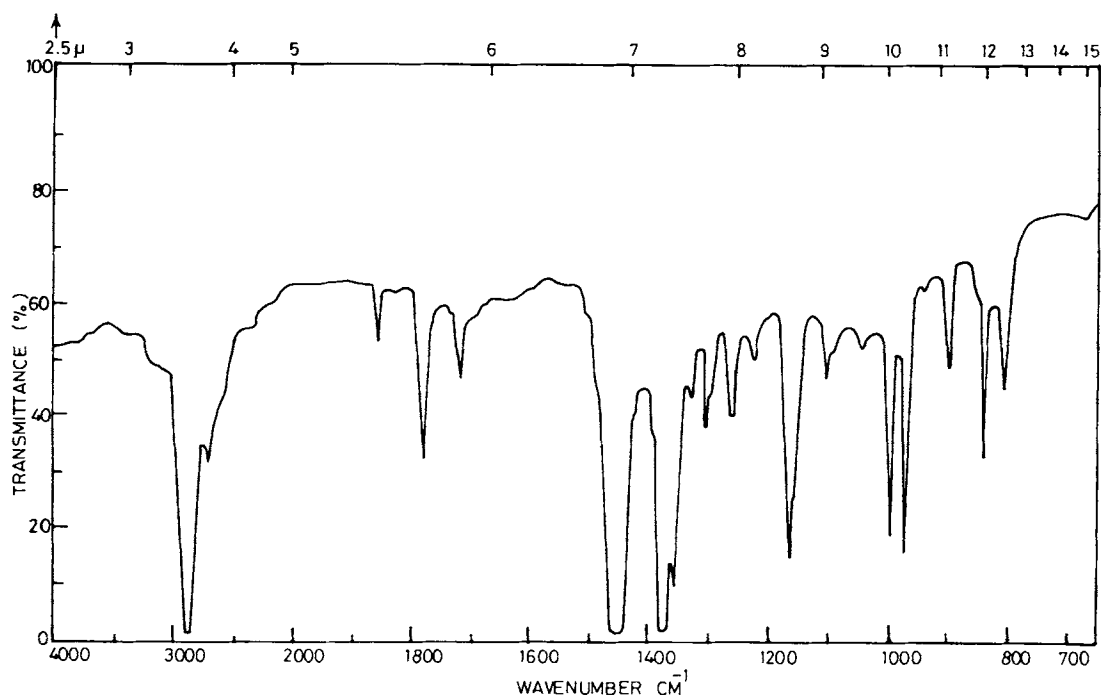**Figure 5**   I.R. Spectra of isotactic polypropylene.
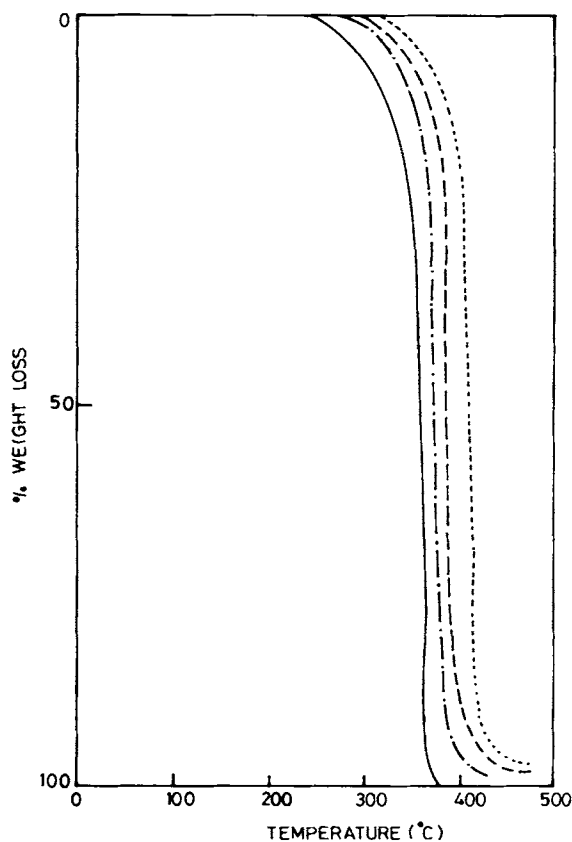
Figure 6 I.R. Spectra of IPP-g-MAH.

Figure 7 TGA curves: Isotactic polypropylene (———).
IPP-g-MAH (– · – · – · –) 2.8% grafting; (– – – –) 3.75%
grafting; and (· · · · ·) 5.32% grafting.

The TGA curves of IPP and PP-g-MAH presented in Figure 7, show that considerable change in the thermal behavior of IPP has occurred upon grafting. The IDT and T_{50} of grafted IPP were considerably higher than those of ungrafted IPP (Table VI). The intrinsic viscosities of Soxhlet-extracted grafted copolymers given in Tables I–IV are lower in comparison with those of ungrafted IPP. This is assigned to main chain secession during grafting. Similar results were observed by Gaylord and Mishra[15] with PP-g-MAH.

The DSC cooling curves of IPP and IPP-g-MAH are given in Figure 8. The exotherms obtained for IPP and grafted IPP were at 113°C and 121.5°C, respectively, indicating a higher crystallization temperature (T_c) for grafted samples than for IPP. The observed increase in crystallization temperature

Table VI   Thermal Analysis

% G	T_m (°C)	ΔH_f^* (Cal/g)	% Crystallinity	IDT	T_{50}
PP	165.12	—	—	235	355
0.68	161.67	20.10	40.20	—	—
2.89	162.75	19.43	38.86	275	372
3.75	162.85	19.41	38.82	290	382
5.32	163.00	19.11	38.22	315	410
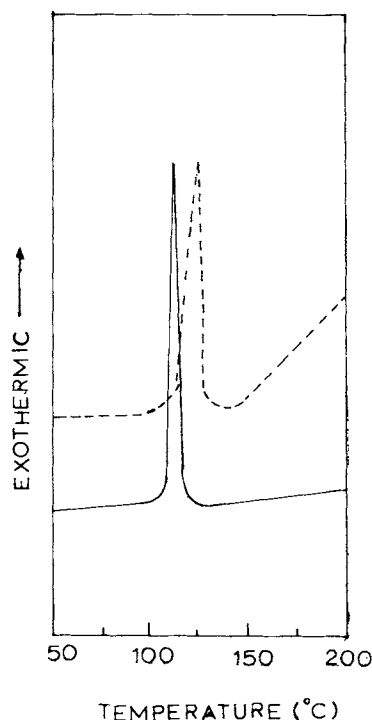
Figure 8 DSC colling curves. Isotactic polypropylene
(——). IPP-g-MAH (5.3%) (– – –).

can be attributed to the MAH acting as a nucleating agent. Rybnikar et al.[16] also found nucleation due to incorporation of carbonyl group in IPP.

The heats of fusion from heating curves (ΔH_f^*) of various grafted samples are given in Table VI. The percent crystallinity was calculated on the assumption that the heat of fusion (ΔH_f°) of 100% crystallins IPP is 50 cal/g.[14] As the heat of fusion is directly proportional to the amount of crystalline IPP in the sample, it decreases linearly with an increase in grafting percentage. An apparent decrease in heat of fusion was due to the decrease in weight

fraction of crystalline IPP in copolymer due to an incorporation of MAH. A similar trend was observed by Mukherjee[17] for pp-g-MAA.

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