Grafting of 2-HEMA on IPP and *In Situ* Chlorinated PP through Solution Polymerization

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ABSTRACT: Grafting of 2-hydroxyethyl methacrylate (2-HEMA) on isotactic polypropylene (IPP) and *in situ* chlorinated polypropylene (CPP) by free radical process was carried out at 110°C using toluene as solvent. Various conditions for grafting were optimized. The maximum percent of grafting of 2-HEMA achieved on IPP was 3.6%, whereas that on *in situ* CPP was 8.7%. The products were characterized by Fourier transform infrared spectroscopy and thermal and contact angle measurements. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 69: 2107–2113, 1998

Key words: polypropylene; grafting; hydroxyethyl methacrylate; chlorinated polypropylene

INTRODUCTION

Due to the low cost, versatile properties, and rapidly growing applications of olefinic polymers in household and industrial uses, research activities have concentrated around these polymeric materials. However, lack of chemical functionalities, difficulty of dyeing, poor hygroscopicity, low impact strength, poor compatibility with other polymers, and poor adhesion to metal and glass have restricted the use of polypropylene (PP) and polyethylene. This can be overcome through functionalization of these polymers by hydrogen abstraction from tertiary carbon followed by ozonolysis,[1] hydroperoxidation,[2] chlorination,[3] and graft copolymerization.[1]

Grafting of various vinyl monomers on PP has been reviewed by Xu and Lin[4] and Singh.[5] Grafting up to 72% of vinylacetate on PP through the suspension polymerization process was reported by Schellenberg and coworkers.[6,7] Grafting of vinylchloride on PP through the vapor phase process was reported by Toyo Soda Mfg Co.[8] A considerable amount of work has been done on the grafting of acrylates and methacrylates on PP.[9] Sathe and associates[10] reported 3.2% grafting of butylacrylate onto PP using benzoyl peroxide as initiator at 110°C through solution polymerization. Oomori and Iwater[11] also attempted to graft acrylic acid onto PP through solution polymerization using dicumylperoxide as initiator. At optimized conditions, the extent of grafting in chlorobenzene was reported to be 10.5%. Methacrylic acid was grafted on PP by Nemecek and colleagues[12] using benzoyl peroxide as initiator. Natta and coworkers[13] achieved grafting of methyl methacrylate on PP using a hydroperoxidic derivative of PP.

Various techniques were used for the grafting of maleic anhydride onto PP,[14–16] however most of these works are in patented form. Sathe and associates [17] have reported 5.2% grafting of maleic anhydride onto PP using benzoylperoxide as an initiator. Glycidyl methacrylate was grafted

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through the melt process by Sun and colleagues.[18] Grafting of hydroxy ethyl acrylate on PP through solution polymerization was reported by Denko Showa.[19] However, there are no reports on solution grafting of 2-hydroxyethyl methacrylate (2-HEMA) onto PP. Shukla and Athalye[20] and Fang and Shi[21] have reported grafting of 2-HEMA on PP; however, the products are crosslinked and hence experience difficulties in processing. Moreover, radiation grafting only alters the surface properties. Hence we are reporting the solution grafting of 2-HEMA onto isotactic PP (IPP), and *in situ* chlorinated PP (CPP).

EXPERIMENTAL

Materials

IPP was of M0030 grade and 10 g/10 min MFI (230°C and 2 kg load) was supplied by Indian Petrochemical Corporation Ltd., Vadodara, India. 2-HEMA (Fluka, Buchs, Switzerland) was used after purification by vacuum distillation. 2,2′-Azobis isobutyronitrile (AIBN) was received from Trizma Chemicals (Vadodara, India) and was used after recrystallization in methanol. Benzoyl peroxide (BPO) was received from Fluka and was used after recrystallization in chloroform. Dicumyl peroxide (DCPO) from National Chemicals (Vadodara, India) was used after recrystallization in toluene.

Chlorine gas was generated in our laboratory by the reaction of potassium permanganate and concentrated hydrochloric acid. The gas was dried over concentrated sulfuric acid, over silica gel, and finally over anhydrous calcium chloride.

Xylene, toluene, decalin, and chlorobenzene were received from Qualigen (Bombay, India) and were dried over sodium metal in a vertical distillation column. Methanol received from Qualigen was used with no further purification.

Synthesis

Solution Grafting of 2-HEMA on IPP

IPP (2% w/v) was dissolved in toluene at 110 ± 1°C in a five-neck reaction flask equipped with mechanical stirrer, air condenser, nitrogen inlet, dropping funnel, and thermo pocket. The initiator (BPO, 0.2% w/v) was dissolved in 5 mL of toluene and was added dropwise to the reaction mixture. This was followed by dropwise addition of 2-HEMA (2% w/v) in 5 mL toluene. The reaction was continued for 3 h at 110°C. After completion of the reaction, the reaction mixture was added slowly to the nonsolvent methanol. The precipitates were collected and Soxhlet-extracted to remove homopolymer. The final product was dried in a vacuum oven at 60;dgC and the percent of grafting was calculated by the following equation:

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

where W_0 is the initial weight of IPP and W_1 is the weight of grafted IPP after complete removal of homopolymer.

Grafting of 2-HEMA on In Situ PP

Another route for the grafting of 2-HEMA onto PP was followed by grafting 2-HEMA on *in situ* CPP. PP, 2% w/v, was dissolved in toluene at 110 ± 1°C in a five-neck reaction vessel under nitrogen atmosphere. To this, 0.2% w/v BPO in 5 mL toluene was added dropwise. The chlorine gas generated and purified as described earlier was passed along with nitrogen in the reaction mixture. To this, 2% w/v 2-HEMA was added and the reaction was continued for 5 h under a chlorine–nitrogen atmosphere. After completion of the reaction, the reaction mixture was added slowly to the nonsolvent methanol. The precipitates were collected and Soxhlet-extracted to remove homopolymer, then dried in a vacuum oven at 60°C. The percent of grafting was calculated as described earlier.

Characterization

The graft copolymers were characterized through Fourier transform infrared spectroscopy (FTIR), contact angle measurements, and thermogravimetric analysis (TGA). FTIR and contact angle measurements were carried out on the compression-molded films of graft copolymers prepared on a Metro compression-molding machine at 230°C using kg/cm^2 load. A Nicolet FTIR-269 spectrophotometer was used for recording IR spectra of these films. Contact θ angle measurements for the films were done on a contact θ meter developed at Leeds University (Leeds, U.K.), using various solvents with different surface tensions. Measurements were carried out at five different positions on a 1-cm^3 area and the mean of those values was recorded.

TGA of the graft copolymers was carried out on a Shimadzu DT30 thermal analyzer at 10°C/min heating rate in an air atmosphere.

Table I Effect of Initiator Type

Type	Percent of Grafting (wt %)	Activation Energy of Initiator (kJ mol^{-1})
AIBN	0.7	—
BPO	3.6	124
DCPO	2.2	159

Polymer/monomer ratio: 1 w/w; reaction time: 3 h; reaction temperature: 110 ± 1°C; reaction volume: 100 mL; solvent: toluene; initiator concentration: 0.2% w/v (BPO).

Differential scanning calorimetry (DSC) studies were conducted using a Perkin–Elmer DSC-7 thermal analyzer. The analysis was carried out at a constant heating rate of 10°C/min and also at a same cooling rate in the temperature range of 25 to 200°C under a nitrogen atmosphere. The percent of crystallinity of IPP, grafted PP, and *in situ* chlorinated graft copolymers was calculated from the DSC thermograms. The presence of chlorine and *in situ* CPP graft copolymers was detected qualitatively by Lasseign test.[22]

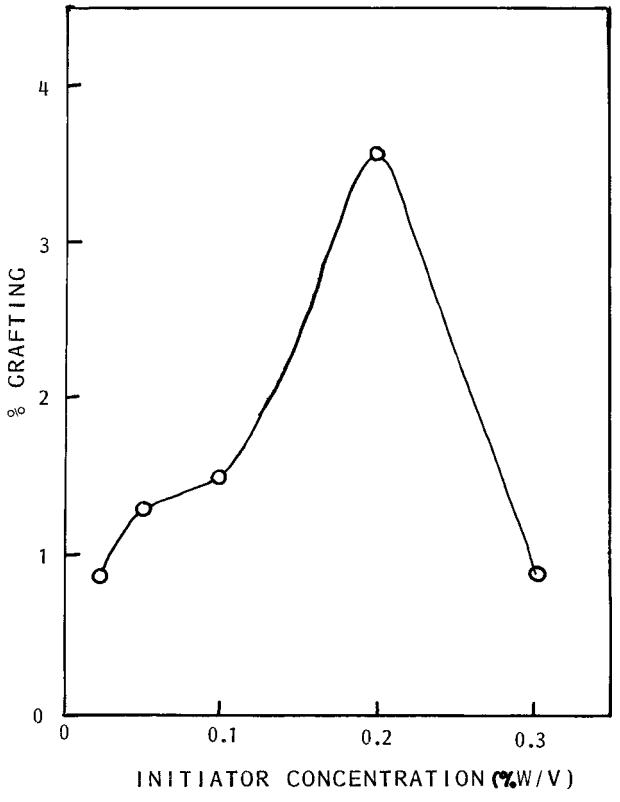

Figure 1 Effect of initiator concentration on the percentage grafting of 2-HEMA on IPP. Polymer/monomer ratio: 1 w/w; reaction temperature: 110 ± 1°C; reaction volume: 100 cm^3; reaction medium: toluene; reaction time: 3 h.

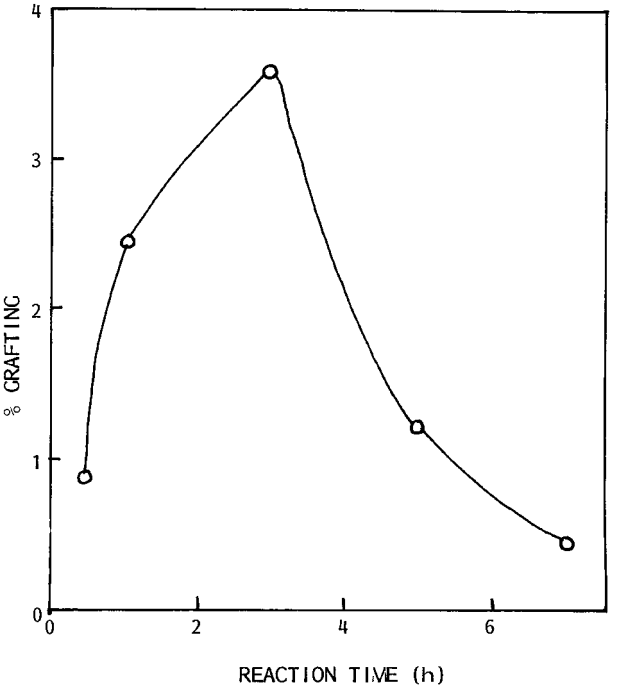

Figure 2 Effect of reaction time on the percentage grafting of 2-HEMA on PP-backbone. Polymer/monomer ratio: 1 w/w; reaction temperature: 110 ± 1°C; reaction volume: 100 cm^3; reaction medium: toluene; initiator concentration: 0.2% w/v (BPO).

RESULTS AND DISCUSSION

Effect of Initiator Type

The grafting of 2-HEMA onto IPP was carried out by using various initiators such as AIBN, DCPO, and BPO. The results are given in Table I. The lower percentage of grafting achieved with AIBN

Table II Effect of Reaction Temperature

Reaction Temperature (°C)	Percent of Grafting (wt %)	Critical Surface Tension, γc (dyne/cm^2)
90	0.4	27.5
100	0.7	24.9
110	3.6	24.0

Polymer/monomer ratio: 1 w/w; reaction times: 3 h; reaction volume: 100 mL; solvent: toluene; initiator concentration: 0.2% w/v (BPO).

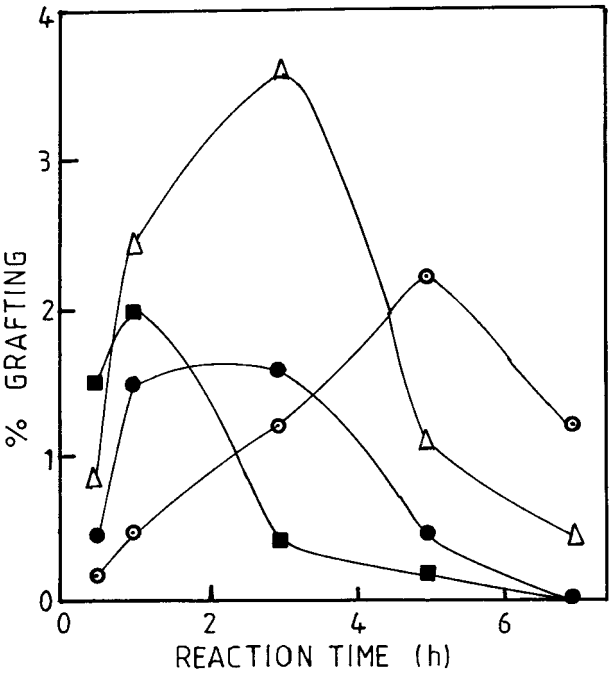

Figure 3 Effect of monomer-to-polymer ration on percentage grafting of 2-HEMA on IPP-backbone. Reaction temperature: 110 ± 1°C; reaction volume: 100 cm^3; reaction time: 3 h; reaction medium: toluene; initiator concentration: 0.2% w/v (BPO). Monomer: polymer ratio: (⊙——⊙) 1 : 2; (△——△) 1 : 1; (●——●) 1.5 : 1; (□——□) 2 : 1.

may be due to the steric hindrance generated at the free radicals causing decreased ability to abstract hydrogen atom from the tertiary carbon of PP. The activation energy for decomposition of DCPO at 110°C is much higher than that for BPO (159 kJ/mol for DCPO and 124 kJ/mol for BPO). Hence, at 110°C the extent of BPO decomposition is higher than DCPO. As a result, a higher percentage of grafting is obtained with BPO than with DCPO. Hence, further work was carried out using BPO as initiator.

Table III Effect of Reaction Medium

Reaction Medium	Dipole Moment	Percent of Grafting	
		N_2	Air
Toluene	0.42	3.6	2.1
Xylene	2.57	0.8	n.d
Decalin	0.00	2.2	n.d
Chlorobenzene	1.72	0.6	n.d

Polymer/monomer ratio: 1 w/w; reaction time: 3 h; reaction temperature: 110 ± 1°C; reaction volume: 100 mL; initiator concentration: 0.2% w/v (BPO). n.d.: not done.

Effect of Initiator Concentration

The results obtained in the study of effect of initiator concentration on percent of grafting of PP are given in Figure 1. It was observed that with increasing concentration of BPO, the percent of grafting initially increases and then passes through the maxima. Similar results were obtained by Nagata.[23] This is a typical behavior observed in grafting processes occurring via chain transfer mechanism. Initially, the percent of grafting increases due to increased availability of free radicals for grafting of monomers, but when the concentration of initiator exceeds a certain limit, increased free radical concentration in the solution increases homopolymerization and hence decreases the percent of grafting.

Effect of Reaction Time

Figure 2 illustrates the results obtained in the study of the effect of reaction time on the percent

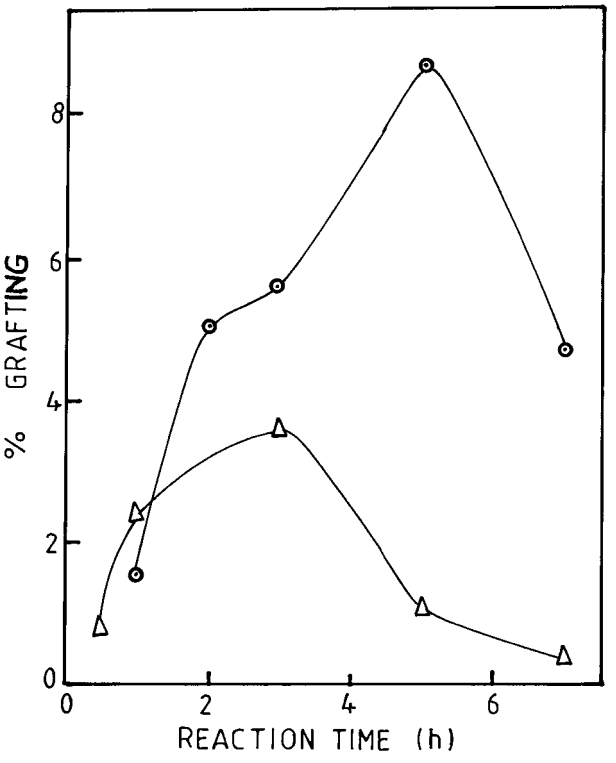

Figure 4 Effect of reaction time on percent of grafting of 2-HEMA on IPP and CPP. Polymer : monomer ratio: 1 w/w; reaction temperature: 110 ± 1°C; reaction volume: 100 cm^3; reaction medium: toluene; initiator concentration: 0.2% w/v (BPO). (△——△) IPP; (⊙——⊙) CPP.

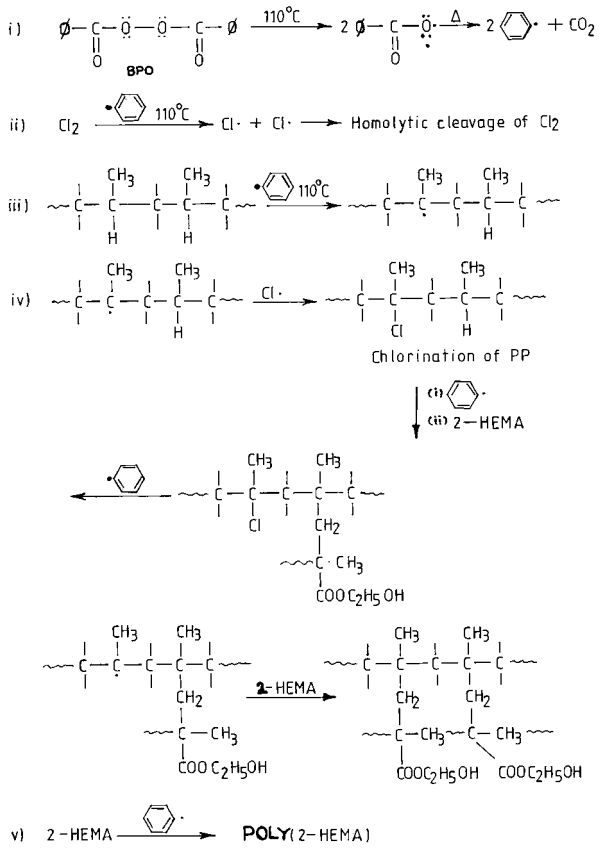

Figure 5 Plausible mechanism for the grafting of 2-HEMA on CPP.

of grafting. It was observed that grafting increases initially with time, up to 3 h; but further increases in reaction time might cause the β-chain scissioning of side chains from the PP backbone, resulting in a decreased percentage of grafting. Similar results were obtained by Sathe and colleagues.[17]

Effect of Temperature

Grafting of PP with 2-HEMA was carried out at 90, 100, and 110°C for 3 h using 0.2% (w/v) BPO and a 1 : 1 (w/w) PP : 2-HEMA ratio. It was observed that as the temperature increases, the percent of grafting increases (Table II). This can be attributed to the increased number of free radicals generated and to the increased mobility of the free radicals at higher temperatures. An increased rate of grafting was also observed with increasing temperature.

Effect of Monomer Concentration

Figure 3 shows the effect of monomer concentration on the percent of grafting of 2-HEMA on PP. It was observed that as the monomer concentration increases, the percent of grafting initially increases and then decreases. At lower concentrations of the monomer, most of the monomer is quantitatively utilized by the available free radical sites on the PP backbone, and the extent of homopolymerization is much smaller. At higher concentrations of monomer, free radicals generated in the solution come into contact with the monomer more easily. As a result, homopolymerization increases and the grafting percentage decreases. As the monomer : polymer ratio continues to increase, the time required to attain maximum grafting percentage decreases. However, maximum grafting percentage was observed when the monomer : polymer rat was 1 : 1. Grafting reaction was also carried out in various solvents. From the results given in Table III, it is observed that maximum grafting is achieved in

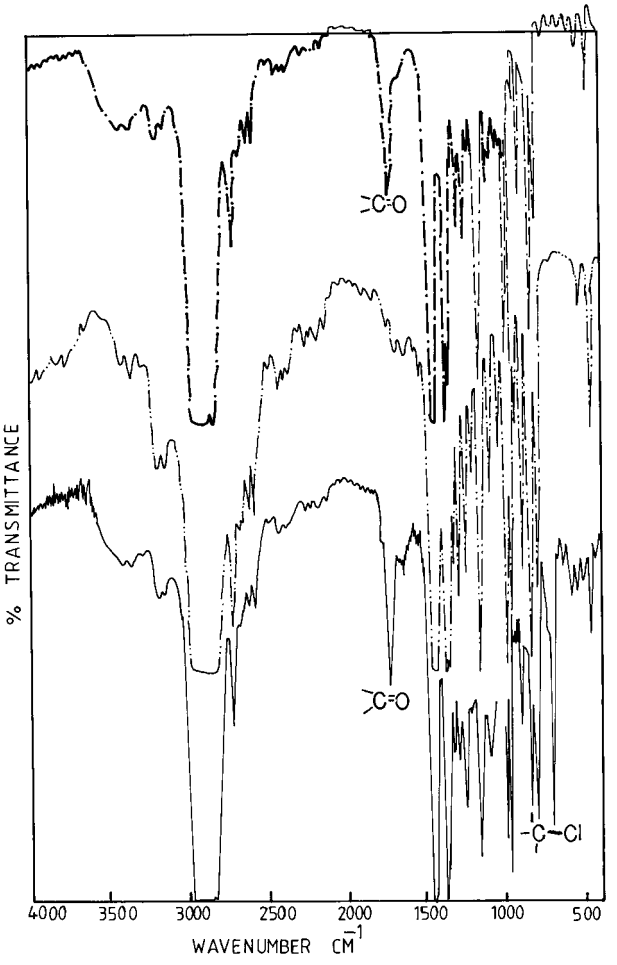

Figure 6 FTIR spectra of (——) *in situ* chlorinated PP-*g*-2-HEMA (8.4% grafting); (– · – · –) IPP-*g*-2-HEMA (3.4% grafting); (– · · – · · –) IPP.

toluene. However, except for decalin, the percent of grafting was observed to decrease with increasing polarity of the reaction medium. Similarly, when grafting was carried out in air and in a nitrogen atmosphere, the decreased percentage of grafting observed in air may be due to the deactivation of initiator[24] (Table III).

Effect of Grafting on *In Situ* Chlorinated IPP

CPP is expected to be more reactive. Hence, *in situ* chlorination was carried out as described earlier, which was followed by free radical graft copolymerization of 2-HEMA on CPP. From the results presented in Figure 4 for the grafting of PP with 2-HEMA in the presence and absence of chlorine, it is observed that extent to grafting increases with increased chlorination time. As shown in Figure 5, the percent of grafting is a result of two graft copolymerization processes directed by BPO and chlorine itself. As a result, a maxima is observed.

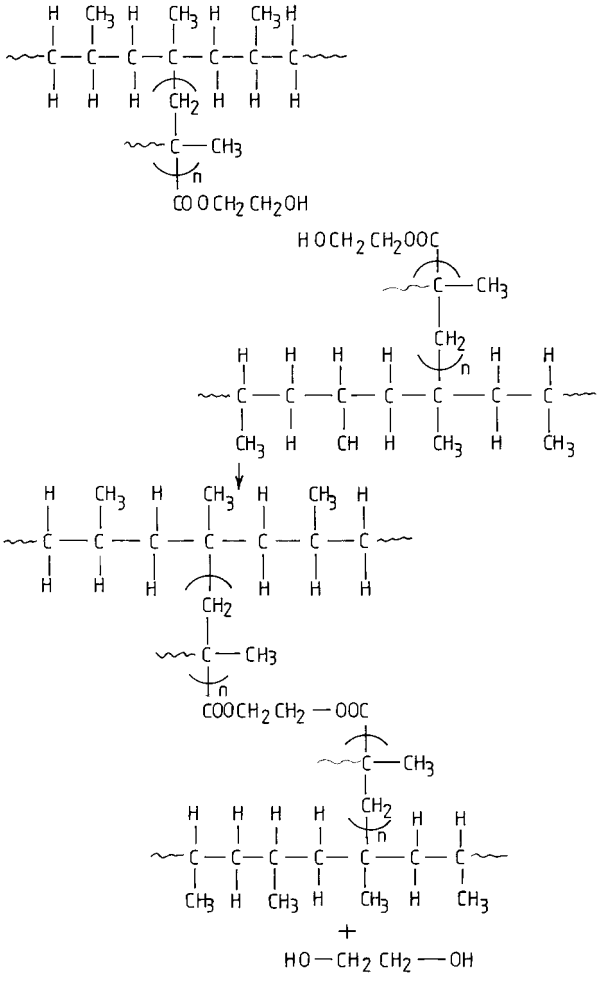

Figure 7 Intermolecular dimerization in IPP-*g*-2-HEMA.

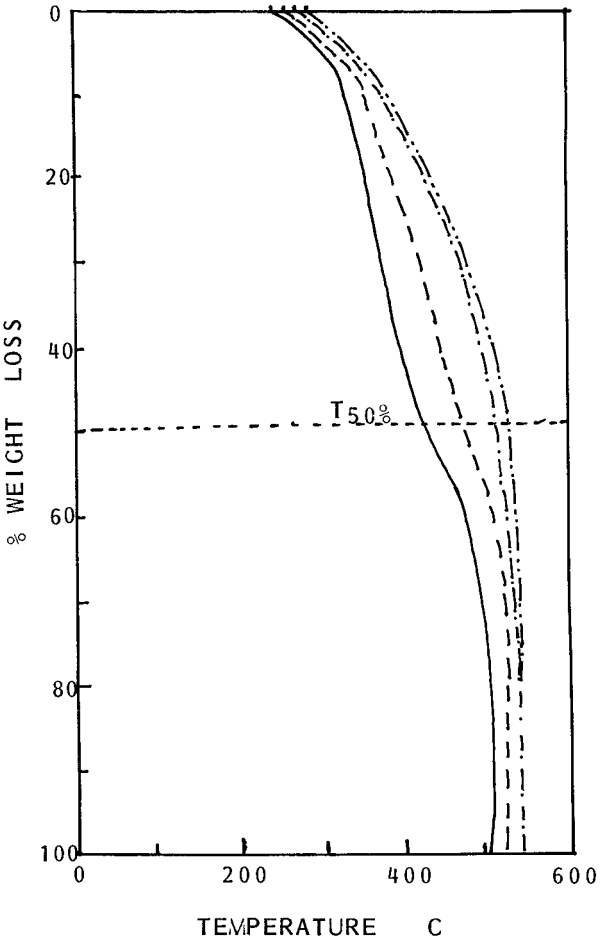

Figure 8 TGA curves.(– · · – · · –) *in situ* chlorinated PP-*g*-2-HEMA (8.4% grafting); (– · – · – · –) IPP-*g*-2-HEMA (3.4% grafting); (----------) IPP-*g*-2-HEMA (2.4% grafting); (——) IPP.

The higher percentage of grafting of 2-HEMA on CPP can be explained by the difference in the grafting mechanism. Due to chlorination, the crystallinity of IPP is decreased. In addition, CPP being more reactive and free radicals being generated by the removal of chlorine from CPP by BPO, as well as by hydrogen abstraction, greater numbers of free radicals are generated, leading to a higher percentage of grafting.

Characterization

Grafting of 2-HEMA onto IPP was confirmed through FTIR analysis. The IR spectra (Figure 6) of PP-*g*-2-HEMA and CPP-*g*-2-HEMA show stretching bands at 1725 cm^{-1} and bending bands

Table IV Thermal Analysis

Grafting (%)	T_m (°C)	ΔH_f (cal/g)	Crystallinity (%)	IDT	$T_{50\%}$
IPP	168.71	—	—	230	425
2.4 (on IPP)	166.89	20.37	40.75	240	475
8.6 (on *in situ* CPP)	126.78	11.25	28.00	250	515

at 708 cm^{-1} for $\upsilon_{c=0}$ and υ_{c-cl} groups, respectively. However, the characteristic band for the —OH stretching of PP-*g*-2-HEMA was not observed at 3500 cm^{-1} due to the intermolecular dimerization of grafted 2-HEMA onto PP backbone. Figure 7 shows the plausible reaction mechanisms of dimerization.

The TGA curves of IPP, PP-*g*-HEMA, and CPP-*g*-HEMA are given in Figure 8. From these thermograms, it was observed that an increase in the percent of grafting increases the thermal stability of the PP. The T_{50} values of graft copolymers were observed to be somewhat higher than those for the virgin PP.

The contact angles (θ) for the graft copolymer films were measured for different solvents of variable surface tensions. The critical surface tension (γ_c) values of the grafted polymers were calculated by extrapolating the plot of surface tension versus cos θ to cos θ = 1. It was observed that γ_c decreases with increasing percentages of grafting. All grafted samples showed 22–27 dynes/cm^2 critical surface tension values, whereas IPP showed 29 dynes/cm^2. This indicates that grafting has imparted surface polarity to the samples prepared in our laboratory.

The heats of fusion obtained from DSC heating curves (ΔH_f^*) of grafted samples are given in Table IV. (We have taken the samples of graft copolymer with 2.5% of grafting on IPP and 8.6% of grafting on in situ CPP.) The percentage of crystallinity was calculated on the assumption that the heat of fusion (ΔH_f°) of 100% crystalline IPP is 50 cal/g. As the heat of fusion is directly proportional to the amount of crystallinity in the samples, it decreases linearly with an increase in grafting percentage.[17]

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