C H A P T E R - 2

SYNTHESIS AND CHARACTERISATION OF POLYPROPYLENE GRAFT COPOLYMERS

CHAPTER - 2

SYNTHESIS AND CHARACTERIZATION OF POLYPROPYLENE GRAFT COPOLYMERS

2.1 EXPERIMENTAL

Butyl acrylate (BA) and maleic anhydride (MAH) were graft copolymerised with polypropylene (PP) by free radical solution polymerisation technique using benzoyl peroxide as a free radical initiator and toluene as a solvent. All experiments were carried out in duplicate to ensure reproducibility. The work was developed in a logical progression.

2.1.1 Materials

Chemicals used during work were :

Acetone	: Ranbaxy, India.
Azo-bis-isobutyronitrile (AIBN)	: Fluka, Switzerland.
Benzoyl peroxide (Bz_2O_2)	: Fluka, Switzerland
Butyl acrylate (BA)	: BDH, India.
Dicumyl peroxide (DCP)	: Fluka, Switzerland
Maleic anhydride (MAH)	: Fluka, Switzerland.
Methanol	: Ranbaxy, India.
Polypropylene (PP)	: Indian Petrochemicals Co. Ltd. Vadodara, India.
Toluene	: Qualigen, India.
Xylene	: Ranbaxy, India.

Polypropylene(PP) used for the study has melt flow index 10 g/10 min and density 0.90 g/cm^3.

2.1.2 Purification of Chemicals

The inhibitor from butyl acrylate (BA) was removed by washing it with sodium hydroxide solution (5% w/v) and then with distilled water to remove the traces of alkali. It was finally dried over anhydrous calcium chloride and distilled under reduced pressure. The purity of monomer was ensured by gas chromatographic analysis.

Maleic anhydride (MAH) was purified by sublimation technique.

Benzoyl peroxide (Bz_2O_2) was purified by dissolving it in chloroform at room temperature and reprecipitating by addition of methanol. Solvents used were distilled prior to use. At all the stages attempts were made to ensure that all the glass wares were scrupulously clean and all transfer operations were performed with uniformity. The Samples given for the instrumental analysis were ensured to be in the most suitable forms.

2.2 SYNTHESIS OF GRAFT COPOLYMERS

2.2.1 Synthesis of polypropylene-g-butyl acrylate (PP-g-BA)

The grafting reaction was carried out in a four neck round bottom flask (r.b.f.) equipped with overhead stirrer, condensor, nitrogen gas inlet and thermometer. The temperature in r.b.f. was maintained with an accuracy of $\pm$ 0.5^{o}C by using contact thermometer in an oil bath. A known amount of PP was dissolved in toluene at 110^{o}C. Nitrogen gas

was purged through the solution for 30 min to remove dissolved oxygen and nitrogen atmosphere was maintained throughout the reaction. Benzoyl peroxide in toluene was added to the reaction mixture followed by butyl acrylate and the reaction was continued for 6 h. The homogeneous reaction mixture was poured into four fold excess of acetone under vigorous stirring. The mixture was kept undisturbed for 12 h for complete precipitation. The isolated precipitate was washed several times with small portions of acetone to remove unreacted butyl acrylate and polybutyl acrylate. Further, graft copolymer was Soxhlet extracted with acetone for 32 h to remove traces of homopolymer of butyl acrylate and finally dried under reduced pressure at $80^{o}C$ to constant weight.

To see any degradation of PP taking place due to addition of benzoyl peroxide, blank experiments were carried out under identical conditions without addition of monomer. The acetone extract was concentrated by evaporating the acetone. The homopolymer of butyl acrylate was recovered from concentrated acetone by using methanol as non solvent. Polybutyl acrylate was dried under reduced pressure for constant weight. For confirmation of the effectiveness of the product separation technique, the resultant graft copolymer was additionaly purified by dissolving it in hot toluene and then reprecipitating it with acetone. The results of the elemental analysis of both the products were similar indicating the negligible amount of impurity of unreacted monomer or homopolymer in the synthesised graft copolymer.

2.2.2 Synthesis of polypropylene-g-maleic anhydride (PP-g-MAH)

Same as given in section 2.2.1 but in place of butyl acrylate maleic anhydried was used. Recovery of homopolymer from acetone extract is undesirable in this process.

2.2.3 Synthesis of polypropylene-g-(Butyl acrylate - co-maleic anhydrid) [PP-g-(BA-co-MAH)]

The graft copolymer was synthesised using same experimental procedure as that for PP-g-BA copolymer (Section 2.2.1) and at the optimized conditions. But at the time of addition of monomer, instead of only butyl acrylate, mixture of butyl acrylate and maleic anhydride was added to the reaction mass.

The percentage of grafting(G), grafting efficiency (G.E.), rate of polymerisation (R_p), rate of grafting (R_g), and rate of homopolymerisation (R_h) were determined gravimetrically following the procedure given by Vijay Kumar et al. [1]

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

$$\% \text{Grafting efficiency (G.E.)} = \frac{W_1 - W_0}{(W_1 - W_0) + W_2} \times 100$$

Where,

W_0 is the weight of original PP,

W_1 is the weight of grafted PP after complete removal of homopolymer (poly butyl acrylate),

W_2 is the weight of homopolymer formed during reaction.

Rate of polymerisation (R_p) (mol l^{-1} sec^{-1})

$$= \frac{\text{Weight of grafted polymer} + \text{Weight of homopolymer}}{\text{mol.wt.of monomer} \times \text{time of the reaction (sec)} \times \text{volume of reaction mixture (ml)}} \times 1000$$

Rate of graft copolymerisation (R_g) (mol l^{-1} sec^{-1})

$$= \frac{\text{Weight of grafted polymer}}{\text{mol.wt.of monomer} \times \text{time of the reaction (sec)} \times \text{volume of reaction mixture (ml)}} \times 1000$$

Rate of homopolymerisation (R_h) (mol l^{-1} sec^{-1})

$$= \frac{\text{Weight of homopolymer}}{\text{mol.wt.of monomer} \times \text{time of the reaction (sec)} \times \text{volume of reaction mixture (ml)}} \times 1000$$

It is recognized that the percentage of grafting determined in this manner is an "apparent" value as the copolymer will contain ungrafted PP. Since, we are interested mainly in the applications of graft copolymers in the polymer blends, this point is recognised and is taken into account whenever necessary during the course of study. We also do recognise the source of heterogeneity in the product such as :

(a) heterogeneity in the polymer backbone,

(b) heterogeneity in the grafted branches.

However, this particular aspect we have not studied in the present work.

2.3 OPTIMISATION OF REACTION CONDITIONS

The reaction conditions for grafting of BA and MAH on to PP were optimised by varying monomer concentration, initiator concentration, reaction time and reaction temperature.

2.3.1 Type of Initiator

To study the effect of various initiators on percentage grafting; benzoyl peroxide, azo-bis-isobutyronitrile and dicumyl peroxide were used at different temperatures during grafting reactions. The initiator resulting into maximum percentage grafting was used in further studies.

2.3.2 Monomer concentration

To study the effect of monomer concentration on the grafting of BA and MAH onto PP, all other parameters except monomer concentration were kept constant. The reaction was carried out for six hours at 100^{o}C using 0.2 % (w/v) benzoyl peroxide and 5.0 g of PP. Total volume of the reaction mixture was maintained at 200 cm^{3}. BA concentration was varied from 1.25 % (w/v) to 10.0 % (w/v) and MAH concentration was varied from 0.38 % (w/v) to 7.5 % (w/v). Grafting reaction was carried out in toluene medium. Further treatment for the separation of graft and homopolymer was same as discussed in section 2.2.1. The optimised monomer concentration was used in further studies.

2.3.3 Initiator concentration

In order to study the effect of initiator concentration on grafting of BA and MAH onto PP, the reaction was carried out using 5.0 g of PP and 5.0 % (w/v) BA and 1.25 % (w/v) MAH in toluene having total volume 200 cm^3 for 6 h reaction period. Reaction temperature was kept at 100^{o}C. The initiator concentration was varied from 0.05 % (w/v) to 0.30 % (w/v). Isolation, purification and drying of graft copolymer and homopolymer was done in the same way as discussed in section 2.2.1.

2.3.4 Reaction time

To study the influence of reaction time on the grafting reaction, the grafting was carried out as mentioned in section 2.3.3 using 0.2 % (w/v) and 0.1 % (w/v) benzoyl peroxide for grafting of BA and MAH onto PP respectively. The reaction time was varied from 2 h to 16 h. The method of precipitation of graft copolymer and separation and isolation of homopolymer from graft copolymer was similar to the one discussed in section 2.2.1.

2.3.5 Reaction temperature

The effect of temperature on the grafting of BA and MAH onto PP was studied following the procedure described in section 2.3.3 by using 0.2 % (w/v) and 0.1 % (w/v) benzoyl peroxide respectively but varying the reaction tempertaure from 80^{o}C to 110^{o}C. Precipitation, separation and drying of graft

copolymer and homopolymer was carried out as discussed in section 2.2.1.

2.3.6 Reaction medium

To study the effect of reaction medium on grafting of BA and MAH onto PP, the grafting reaction was carried out at optimized conditions using different solvents such as xylene, decaline, dichlorobenzene. The reaction was also carried out in nitrogen and air atmosphere.

2.4 CHARACTERISATION OF GRAFT COPOLYMERS

The graft copolymers were characterised through spectral, thermal and viscosity studies. Surface characterisation of the graft copolymers was carried out through contact angle measurements.

2.4.1 I.R. analysis

I. R. spectroscopic information of the graft copolymers was obtained using Shimadzu IR-408 spectrophotometer. The graft copolymers were compression moulded into thin films on "Metro" (India) compression moulding machine at $190^{o}C$ under $100Kg/cm^{2}$ pressure. Care was taken to ensure uniformity in the thickness of the films.

2.4.2 Contact angle measurements

Contact angle measurements were carried out using a contact- θ -meter developed at the university of Leeds. It is a versatile instrument which has been designed to allow

effective and reproducible measurements of the surface wetting characteristics of a variety of surfaces and as such it is of value to all concerned with assessment of planer solid surfaces. For measurement of contact angle, polymer films were prepared of uniform thickness by compression moulding. The polymer film was cut into the size of 40 mm x 75 mm and was placed on the upper surface of a plate. Then carefully a sessile droplet of liquid from a syringe was applied to the film. The droplet was then positioned so that its leading edge was in the centre of the area covered by viewing tube. When observed through the viewing tube, the reflection of the incident beam of light emitted from a narrow filament source, was seen as a bright star on the surface of the droplet. Then the viewing tube was moved keeping the image in the centre of the tube, until the reflection was just disappeared. The point at which the reflection just disappears was the contact angle (θ). The procedure was repeated for other areas of the film. Criticle wetting tension of the copolymer was determined by plotting $\cos\theta$ values against the surface tension of contacting liquids.

2.4.3 Viscometric study

The study of conformational changes occuring in dilute solutions has drawn the attention of researchers [2-5]. Hence viscosity measurements, a relatively simple technique, was used for the study of conformational changes [6,7].

Viscometric studies were carried out for Soxhlet extracted graft copolymers using an Ubbelohde viscometer at 135^{o}C using trichlorobenzene as solvent. The viscometer was fitted with a sintered glass filter in order to prevent any undissolved polymer or dust agglomerates from entering the capillary. The temperature in an oil bath was maintained with as accuracy of $\pm$ 0.05^{o}C. The initial concentration of the graft copolymeter was 0.4 % (w/v). Further dilutions were carried out insitu. The flow time for solvent (t_0) and for polymer solution (t) were measured accurately.

The ratio (t/t_0) was a measure of relative viscosity (η_r). The specific viscosity (η_{sp}) was calculated as ($\eta_r - 1$). The intrinsic viscosity was obtained from the combined plots of (η_{sp}/C) and ($\ln \eta_r/C$) versus concentration according to the relations,

$$\eta_{sp}/C = [\eta] + K[\eta]^2 C$$

$$\ln \eta_r/C = [\eta] - \beta[\eta]^2 C$$

where concentrations were expressed in g/dl. The intrinsic viscosity [η] was determined in each case from the best pair of the curves having the same intercepts and value of K and such that

$$K + \beta = 0.5$$

Using Mark-Houwink equation the molecular weights of graft copolymers were calculated as,

$$[\eta] = K\bar{M}^{\alpha}$$

Where, K and α are constants for a given polymer/solvent /temperature system and $[\eta]$ is intrinsic viscosity.

2.4.4 Thermal analysis

2.4.4.a Differential scanning calorimetry (DSC)

The DSC analysis was carried out using 7 mg. of the samples on a DuPont 2000 thermal analyser. The analysis was carried out at a constant heating rate of 10^{o}C/min in the temperature range of 25-200^{o}C under nitrogen atmosphere. The samples were kept for 2 min at the annealing temperature then they were cooled to room temperature at a cooling rate 10^{o}C/min. The next heating run was carried out at 10^{o}C/min. The $\triangle$H values of samples were used for further calculations. The percent crystallinity of various samples was obtained by using following expression [8].

$$\% \text{ Crytallinity} = \frac{\triangle Hf^{*}}{\triangle Hf^{o}} \times 100$$

Where, $\triangle Hf^{o}$ is the heat of fusion for 100 % crystalline polypropylene and $\triangle Hf^{*}$ heat of fusion for the graft copolymer.

2.4.4.b Thermogravimetric analysis (TGA)

This technique involves measurement of the extent and rate of change of the mass of a sample continuously either as a function of increasing temperature (dynamic study) or preheated temperature over a period of time (isothermal

study) in a controlled atmosphere. The thermogravimetric analysis of all the graft copolymers was carried out on the DuPont 990 thermal analyzer. The samples were weiged into platinum sample pans and heated in the range 25^{o}C to 500^{o}C at the heating rate of 10^{o}C/min. All the measurements were made under nitrogen atmosphere. The initial decomposition temperature (IDT) and temperature at which sample undergoes 50% decomposition (T_{50}) were calculated from the thermograms.

2.5 RESULTS AND DISCUSSION

2.5.1 Optimisation of reaction conditions

2.5.1.a Types of initiators

To study the effect of different initiators on the percentage grafting, reaction was carried out under nitrogen atmosphere for PP-g-BA and PP-g-MAH using various initiators such as benzoyl peroxide, dicumyl peroxide and azo-bis-isobutyronitrile at different temperatures keeping the other parameters constant as mentioned in section 2.3.2. The results obtained are given in Table 2.1 and 2.2. It was observed that with benzoyl peroxide the grafting was higher than other initiators for both the systems. Hence benzoyl peroxide was used in the further studies.

2.5.1.b Monomer concentration

The effect of monomer (BA) concentration on percentage of grafting and grafting efficiency is shown in Fig. 2.1.a. It was observed that percentage grafting increases initially

Table 2.1

Effect of type of initiator on grafting of BA onto PP.

PP	:	2.5 % (w/v)
BA	:	5.0 % (w/v)
Time	:	6 h
Total volume	:	200 cm^3 Toluene

Initiator	% G at 100^oC	% G at 110^oC
Azo-bis-isobutyronitrile (0.2 % w/v)	0.35	0.77
Benzoyl peroxide (0.2 % w/v)	2.85	1.47
Dicumyl peroxide (0.2 % w/v)	0.58	0.92

Table 2.2

Effect of type of initiator on grafting of MAH onto PP.

PP	:	2.5 % (w/v)
MAH	:	1.25 % (w/v)
Time	:	6 h
Total volume	:	200 cm^3 Toluene

Initiator	% G at 100^oC	% G at 110^oC
Azo-bis-isobutyronitrile (0.15 % w/v)	1.35	1.20
Benzoyl peroxide (0.15 % w/v)	3.42	3.08
Dicumyl peroxide (0.15 % w/v)	3.15	2.91

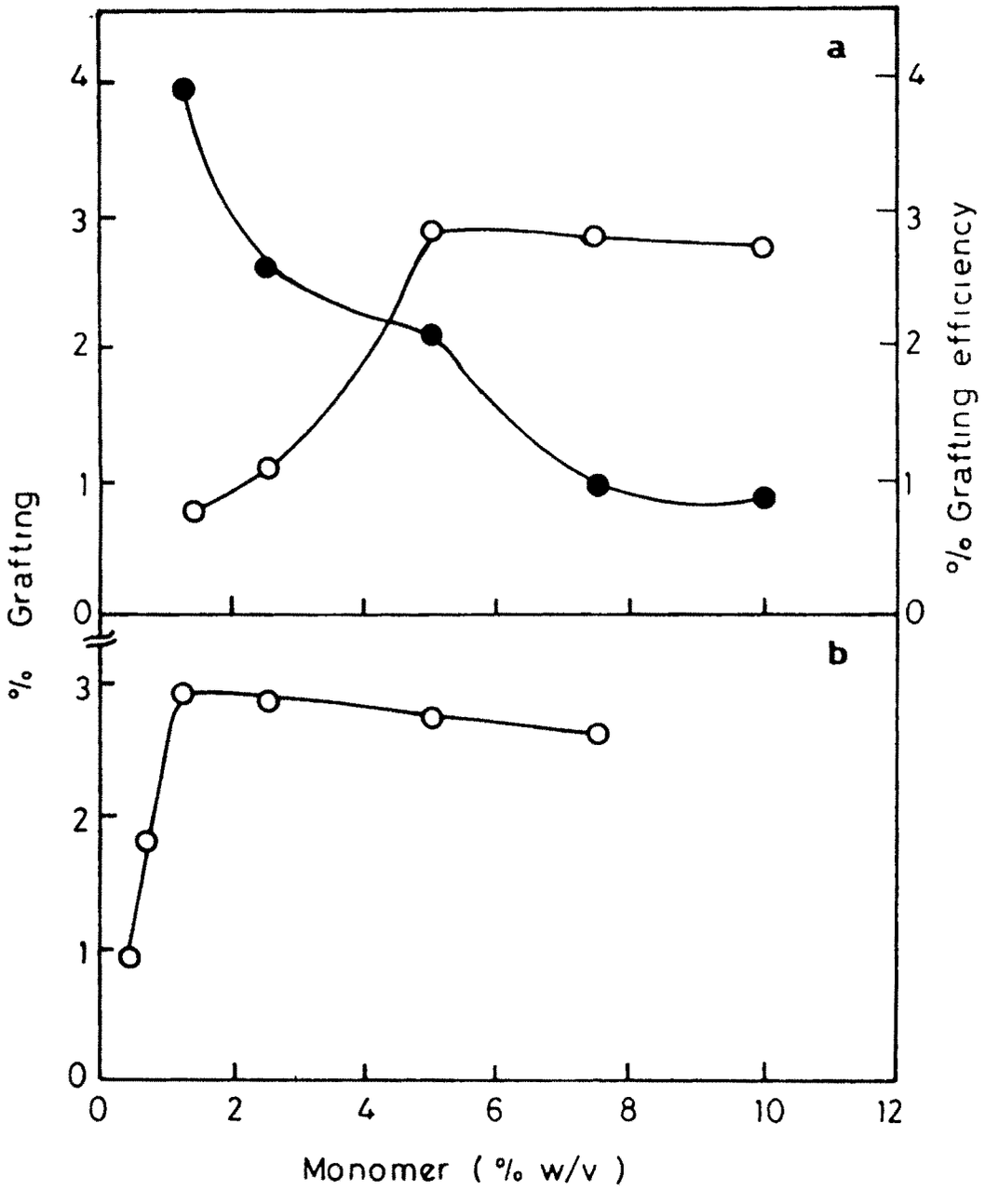


Fig. 2.1 Effect of monomer concentration

a. for PP-g-BA : ○, % grafting ; ●, % grafting efficiency. 100°C, temperature ; 6h, reaction time; 0.2% (w/v), Bz_2O_2.

b. for PP-g-MAH : ○, % grafting. 100°C, temperature; 6h, reaction time ; 0.15% (w/v), Bz_2O_2.

with increase in monomer concentration and then remains constant. Similar trend was observed by Mukherjee and Gupta [9] for radiation induced grafting of methacrylic acid onto PP fiber. This may be because at lower concentration most of the monomer molecules diffusing through the reaction medium reach the free radical sites on the polypropylene backbone, whereas at higher concentration of monomer the percent grafting remains almost constant, as the number of free radical sites available on PP bakbone becomes a limiting factor. But the free radicals in the solution initiate homopolymerisation to greater extent with increased monomer concentration. Hence, the grafting efficiency goes on decreasing as the monomer concentration increases. This is indicated by steady growth in the rate of homopolymerisation (Table 2.3).

In case of maleic anhydride similar results were obtained for the effect of monomer (MAH) concentration on percentage grafting (Fig. 2.1.b). The percent grafting increases initially with increase in monomer (MAH) concentration and remains almost constant thereafter. This is also supported by the results obtained for the rate of grafting (Table 2.4).

2.5.1.c Initiator concentration

Fig. 2.2.a shows the effect of initiator concentration on the grafting reaction of BA onto PP. The observed trend is typical characteristic of grafting reactions occuring via chain transfer. The initial increase in percentage grafting

Table 2.3

Effect of monomer concentration on the grafting of BA onto PP.

PP	:	2.5 % (w/v)
Benzoyl peroxide	:	0.2 % (w/v)
Temperature	:	$100^{o}C$
Reaction time	:	6 h
Total volume	:	200 cm^3 Toluene

BA (% w/v)	$Rpx10^6$ mol l^{-1} s^{-1}	$Rgx10^7$ mol l^{-1} s^{-1}	$Rhx10^6$ mol l^{-1} s^{-1}	Critical Surface tension ($\sqrt{c}$)	Intrinsic Viscosity (dl/g)	$\bar{M}vx10^{-4}$
1.25	1.93	0.75	1.86	31.00	1.27	18.34
2.50	5.55	0.96	5.45	30.50	1.22	17.35
5.00	11.18	2.44	10.96	29.00	0.80	9.69
7.50	14.08	2.29	13.85	29.70	0.90	11.41
10.00	22.48	2.17	22.22	30.00	1.00	13.19

Table 2.4

Effect of monomer concentration on the grafting of MAH onto PP.

PP	:	2.5 % (w/v)
Benzoyl peroxide	:	0.15 % (w/v)
Temperature	:	$100^{o}C$
Reaction time	:	6 h
Total volume	:	200 cm^3 Toluene

MAH (% w/v)	Rgx10^7 mol l^{-1} s^{-1}	Critical Surface tension (γc)	Intrinsic Viscosity (dl/g)	$\bar{M}vx10^{-4}$
0.38	0.80	30.00	1.25	17.94
0.63	2.13	29.10	1.20	16.96
1.25	3.42	24.00	1.01	13.37
2.50	3.30	24.70	0.95	12.29
5.00	3.30	25.40	0.82	9.70
7.50	3.17	26.10	0.72	—

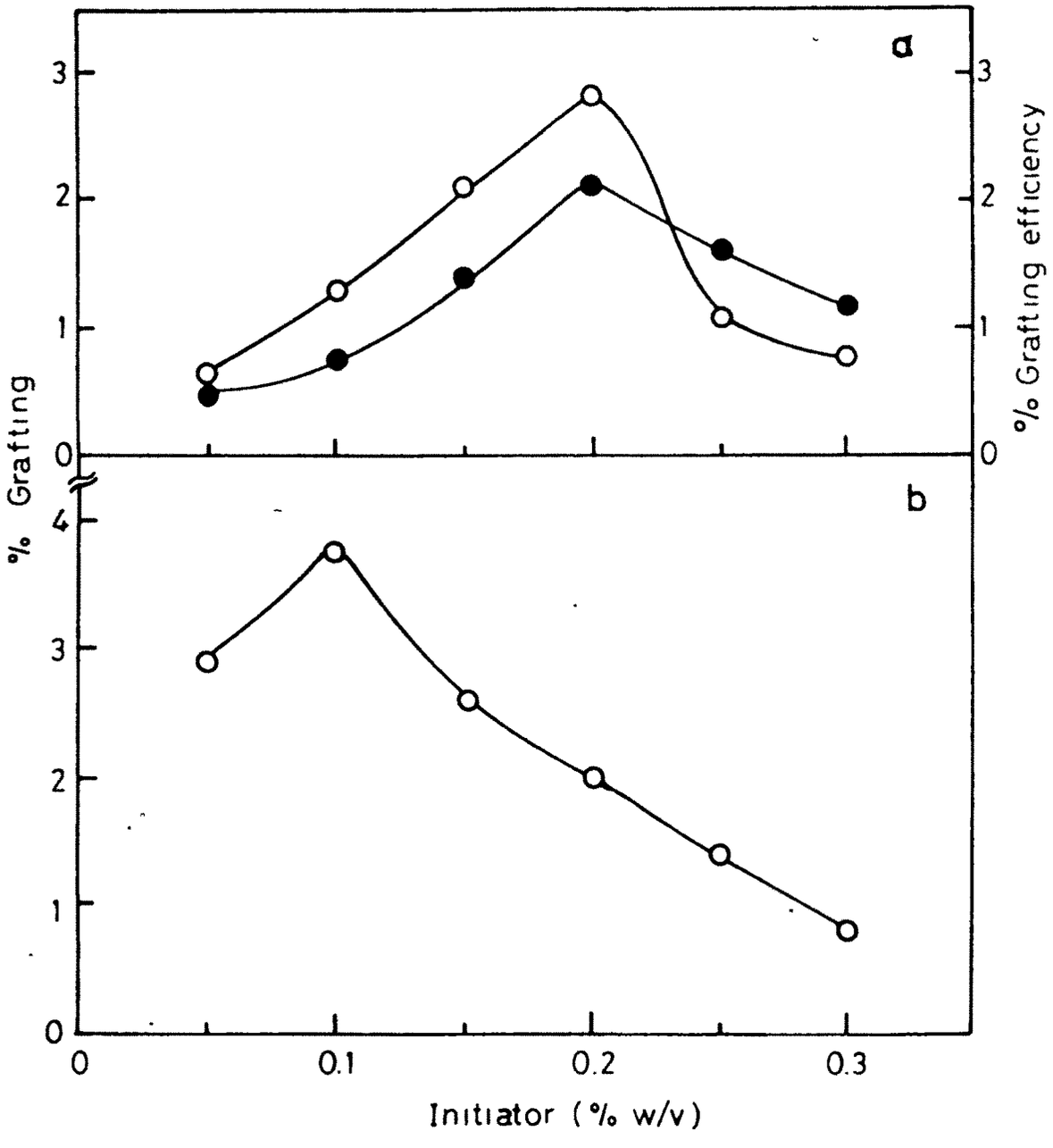


Fig. 2.2 Effect of initiator concentration

a) for PP-g-BA : ○, % grafting; ●, % grafting efficiency. 100°C, temperature ; 6h, reaction time ; 5.0 % (w/v), BA.

b) for PP-g-MAH : ○, % grafting. 100°C, temperature; 6h, reaction time ;1.25 % (w/v), MAH .

and grafting efficiency is caused by an increase in the concentration of free radicals formed through the decomposition of initiator. Thus, higher the concentration of radicals higher the chain transfer to polymer and higher the percentage grafting and grafting efficiency. But further increase in initiator concentration decreases the molecular weight of side chains due to increased consumption of monomer in the process of homopolymerisation and mutual termination reaction. These two opposite tendencies result in the appearance of maxima. Effect of initiator concentration on R_p, R_g and R_h is given in Table 2.5. It is observed that R_p, R_g and R_h initially increase and then decrease with increasing initiator concentration.

Fig. 2.2.b shows effect of initiator concentration on percentage grafting of maleic anhydride onto PP. Here also maxima is appeared as in case of PP-g-BA. Effect of initiator concentration on rate of grafting (R_g) is given in Table 2.6.

2.5.1.d Reaction time

The effect of reaction time on percentage grafting and grafting efficiency of BA onto PP is shown in Fig. 2.3.a. With increase in time both percentage grafting and grafting efficiency initially increase and then decrease. Because with increase in reaction time, number of radicals taking part in the reaction increases resulting into increase in percentage grafting and grafting efficiency. Further increase in time causes mutual annihilation of grafted polymeric chains

Table 2.5

Effect of initiator concentration on the grafting of BA onto PP.

PP	:	2.5 % (w/v)
Butyl acrylate	:	5.0 % (w/v)
Reaction time	:	6 h
Temperature	:	$100^{o}C$
Total volume	:	200 cm^3 Toluene

Bz_2O_2 (% w/v)	$Rpx10^{6}$ mol l^{-1} s^{-1}	$Rgx10^{7}$ mol l^{-1} s^{-1}	$Rhx10^{6}$ mol l^{-1} s^{-1}	Critical Surface tension (γ_c)	Intrinsic Viscosity (dl/g)	$\bar{M}vx10^{-4}$
0.05	0.47	0.54	9.40	32.70	1.18	16.57
0.10	11.07	1.15	10.96	31.60	1.05	14.11
0.15	11.63	1.83	11.62	31.30	0.95	12.29
0.20	12.16	2.44	11.79	29.00	0.80	9.70
0.25	11.44	1.37	11.28	32.00	0.72	8.38
0.30	5.48	0.68	5.33	32.80	0.63	6.97

Table 2.6

Effect of initiator concentration on the grafting of MAH onto PP.

PP	:	2.5 % (w/v)
MAH concentration	:	1.25 % (w/v)
Temperature	:	$100^{o}C$
Reaction time	:	6 h
Total volume	:	200 cm^3 Toluene

Bz_2O_2 (% w/v)	$Rgx10^7$ mol l^{-1} s^{-1}	Critical Surface tension (γ_c)	Intrinsic Viscosity (dl/g)	$\bar{M}vx10^{-4}$
0.05	3.42	24.00	1.20	16.96
0.10	4.43	22.50	1.12	15.20
0.15	2.98	25.40	1.01	13.37
0.20	2.24	27.30	0.95	12.30
0.25	1.65	29.70	0.80	9.70
0.30	1.01	30.10	0.71	8.89

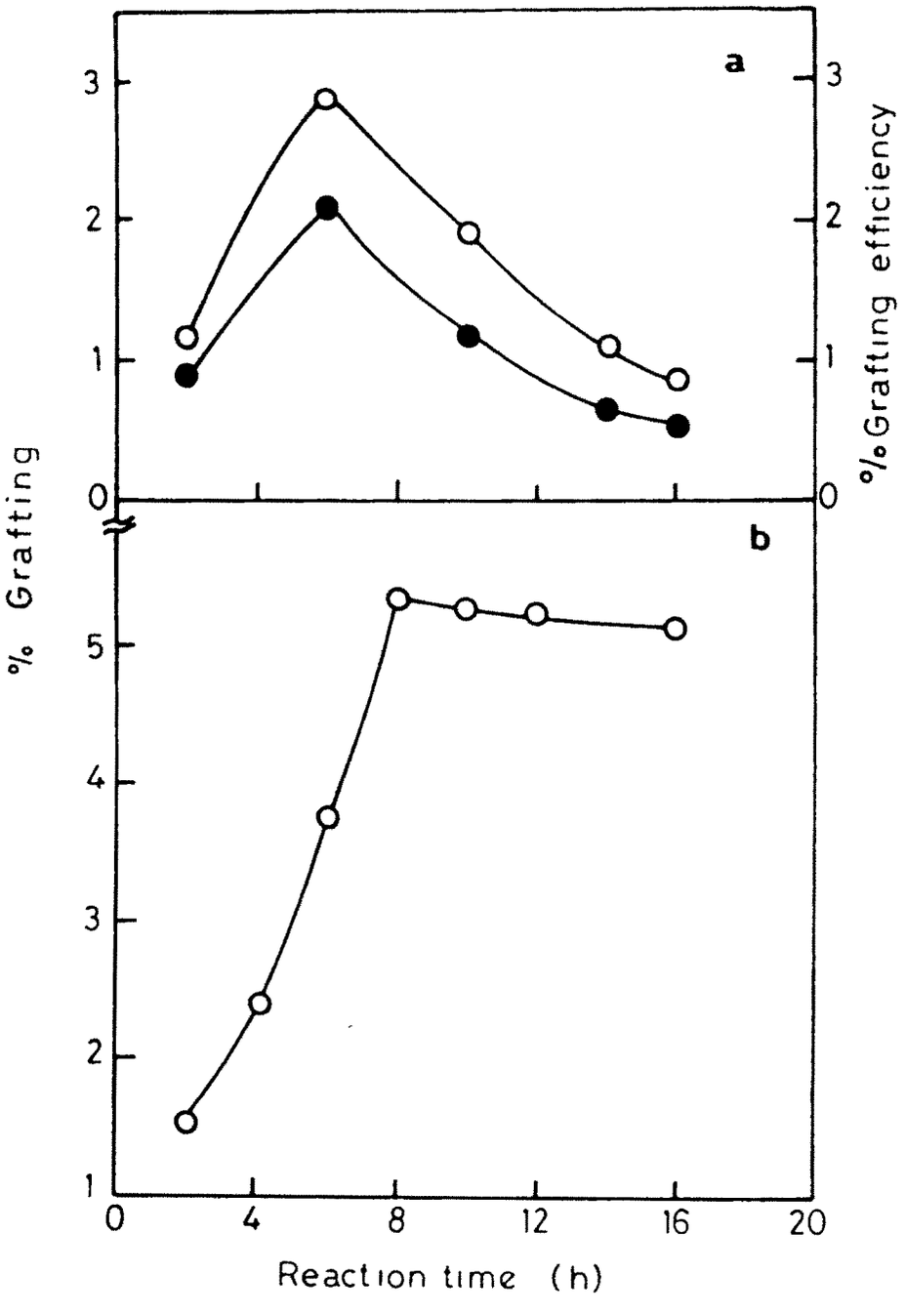


Fig. 2.3 Effect of reaction time

a) for PP-g-BA : ○, % grafting ; ●, % grafting efficiency. 100°C, temperatue ; 5.0% (w/v), BA; 0.2% (w/v), Bz_2O_2.

b) for PP-g-MAH ; ○, % grafting. 100°C, temperature ; 1.25% (w/v), MAH ; 0.1% (w/v), Bz_2O_2

leading to decrease in percentage grafting. Similar observation was made by Mehta et al. [10]. The rate of polymerisation decreases with increasing reaction time. This effect can be attributed to the fact that the relative increment in the total yield is comparatively less when compared to that of time, and in the expression for R_p, the numerator becomes almost constant and when the time for the reaction is raised, the denominator becomes larger thus reducing R_p accordingly. since R_g and R_h are related to R_p, the relative decrease of R_g and R_h with time can be understood (Table 2.7).

The effect of reaction time on the percentage grafting of MAH onto PP is also shown in Fig. 2.3.b. It is observed from the results that unlike BA the percentage grafting increases initially but then remains constant. Because mutual termination of grafted polymeric chains is difficult due to bulky cyclic anhydride groups and also the increased time causes depletion of initiator and monomer, resulting into almost constant percentage grafting at higher reaction times. The results for effect of time on rate of grafting (R_g) are given in Table 2.8.

2.5.1.e Reaction temperature

The effect of temperature on percentage grafting and grafting efficiency of BA onto PP is shown in Fig. 2.4.a. On increasing the temperature both percentage grafting and grafting efficiency pass through maxima. The increase in

Table 2.7

Effect of reaction time on the grafting of BA onto PP.

PP	:	2.5 % (w/v)
Benzoyl peroxide	:	0.2 % (w/v)
BA concentration	:	5.0 % (w/v)
Temperature	:	$100^{o}C$
Total volume	:	200 cm^3 Toluene

Reaction time (h)	$Rpx10^6$ mol l^{-1} s^{-1}	$Rgx10^7$ mol l^{-1} s^{-1}	$Rhx10^6$ mol l^{-1} s^{-1}	Critical Surface tension (γ_c)	Intrinsic Viscosity (dl/g)	$\bar{M}vx10^{-4}$
2	31.12	0.37	30.82	31.20	1.10	15.04
6	11.20	2.44	10.95	29.00	0.08	19.70
10	8.34	0.98	8.20	31.60	0.59	6.37
14	6.43	0.42	6.38	32.30	0.45	4.38
16	4.60	0.27	4.56	33.40	--	--

Table 2.8

Effect of reaction time on the grafting of MAH onto PP.

PP	:	2.5 % (w/v)
Benzoyl peroxide	:	0.1 % (w/v)
MAH concentration	:	1.25 % (w/v)
Temperature	:	$100^{o}C$
Total volume	:	200 cm^3 Toluene

Reaction time (h)	$Rgx10^7$ mol l^{-1} s^{-1}	Critical Surface tension (γc)	Intrinsic Viscosity (dl/g)	$\bar{M}vx10^{-4}$
2	5.66	27.50	1.25	17.94
4	4.23	26.30	1.19	16.78
6	4.43	22.50	1.10	15.04
8	4.71	20.10	0.96	12.47
10	3.68	21.60	0.80	9.70
12	3.07	22.30	0.71	8.22
16	3.01	23.00	--	--

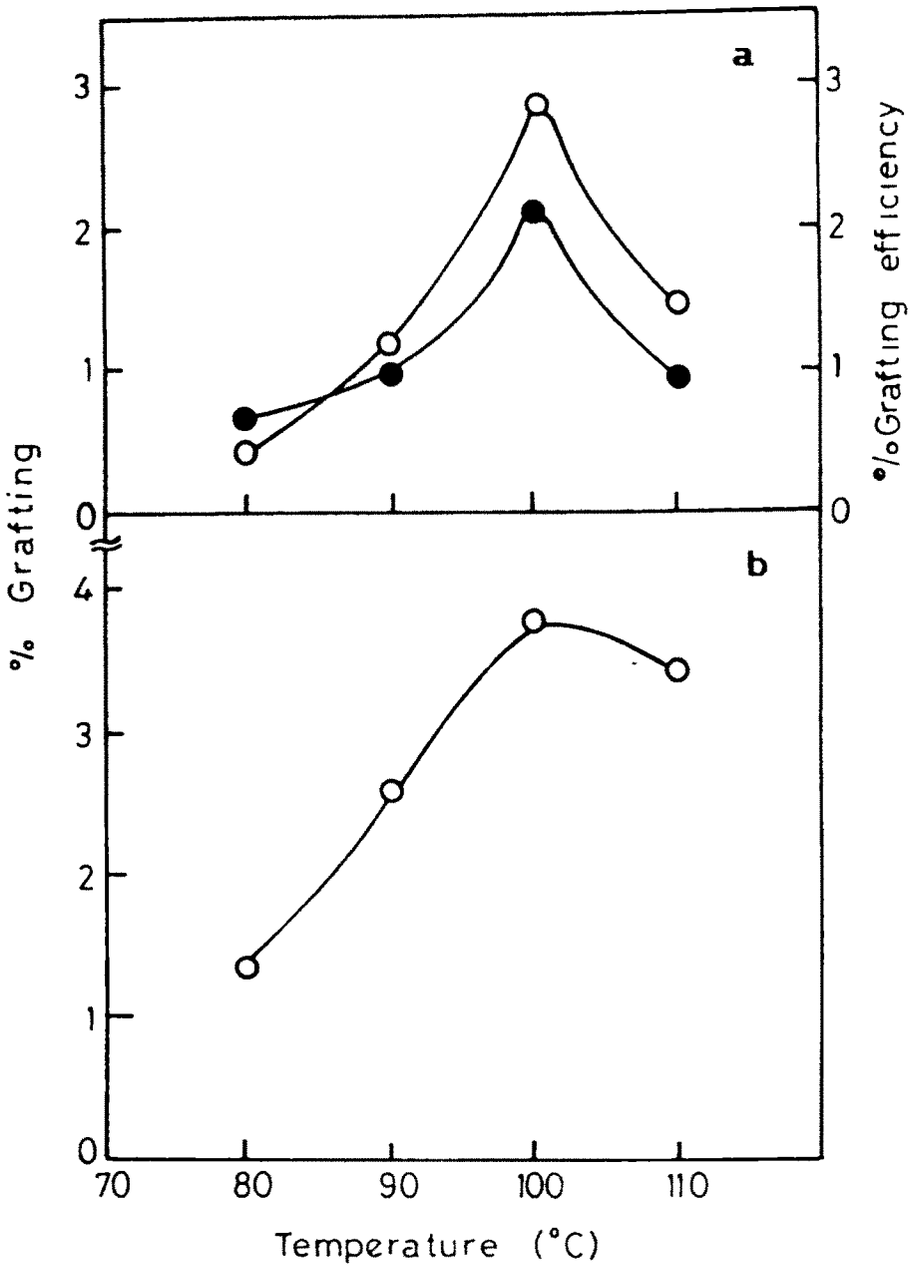


Fig. 2.4 Effect of temperature

a. for PP-g-BA : ○, % grafting ; ●, % grafting efficiency. 6h, reaction time ; 5.0% (w/v), BA ; 0.2% (w/v), Bz_2O_2.

b) for PP-g-MAH : ○, % grafting. 8h, reaction time ; 1.25% (w/v), MAH ; 0.1% (w/v), Bz_2O_2.

temperature is expected to increase the rate of grafting as well as homopolymerisation. Hence, initially both percentage grafting and grafting efficiency increase with the temperature. The grafting does not depend only on the number of active sites available on the polymer backbone but it also depends upon the molecular weight of side chains formed during the grafting process. Increase in temperature increases the mobility of free radicals resulting into their mutual termination and decreasing the availability of the free radicals for polymerisation. This results into decrease in R_p, R_g and R_h (Table 2.9). Similar trend was observed also in the study of the effect of temperature on the percentage grafting of MAH onto PP (Fig. 2.4.b). The values for R_g are given in Table 2.10.

2.5.1.f Reaction atmosphere

To study the effect of atmosphere on the percentage grafting, reaction was carried out under air and nitrogen atmosphere, at optimized conditions. Grafting of BA onto PP was carried out at 100°C, using 0.2 % (w/v) Bz_2O_2 and 5.0 % (w/v) BA for 6 h. The observed percentage grafting was 1.24 and 2.85 respectively in air and nitrogen atmosphere. For PP-g-MAH system, reaction was carried out at 100°C for 8 h using 1.25 % (w/v) MAH and 0.1 % (w/v) Bz_2O_2. The percentage grafting was observed to be 2.28 and 5.36 respectively in air and nitrogen atmosphere. Thus, it can be concluded that percentage grafting decreases in the presence of oxygen. This can be explained from the reaction.

Table 2.9

Effect of temperature on the grafting of BA onto PP.

PP	:	2.5 % (w/v)
Benzoyl peroxide	:	0.2 % (w/v)
BA concentration	:	5.0 % (w/v)
Reaction time	:	6 h
Total volume	:	200 cm^3 Toluene

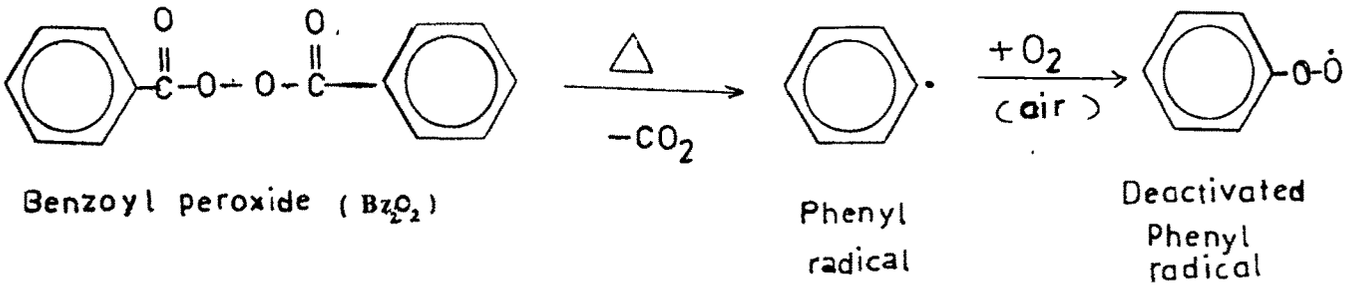
Temperature (^oC)	$Rpx10^6$ mol l^{-1} s^{-1}	$Rgx10^7$ mol l^{-1} s^{-1}	$Rhx10^6$ mol l^{-1} s^{-1}	Critical Surface tension (γ_c)	Intrinsic Viscosity (dl/g)	$\bar{M}vx10^{-4}$
80	6.10	0.37	6.00	33.10	1.11	15.23
90	9.93	1.04	9.82	31.30	1.05	14.11
100	11.20	2.44	10.92	29.10	0.80	19.70
110	10.96	1.26	10.72	30.40	0.93	11.93

Table 2.10

Effect of temperature on the grafting of MAH onto PP.

PP	:	2.5 % (w/v)
Benzoyl peroxide	:	0.1 % (w/v)
MAH concentration	:	1.25 % (w/v)
Reaction time	:	8 h
Total volume	:	200 cm^3 Toluene

Temperature (^oC)	Rgx10^7 mol l^{-1} s^{-1}	Critical Surface tension (γc)	Intrinsic Viscosity (dl/g)	$\bar{M}v$x10^{-4}
80	1.61	27.30	1.11	15.24
90	3.02	26.10	1.05	14.11
100	4.43	22.50	0.90	11.41
110	4.01	25.00	0.86	10.71



The deactivation of free radicals takes place in the presence of oxygen and hence the decreased percentage of grafting.

2.5.1.g Reaction medium

The effect of solvent on percentage grafting was studied by synthesing the graft copolymer in o-di-chlorobenzene, xylene, toluene and decalin at the optimized conditions for PP-g-MAH system. It was observed from the results shown in Table 2.11 that maximum percent grafting was achieved in non polar solvents.

2.5.2 Evidence of grafting

PP-g-BA and PP-g-MAH copolymers are white in colour with solubility behaviour almost similar to that of PP.

2.5.2.a I.R. analysis

Figs. 2.5.a, 2.5.b and 2.5.c give the comparision of I.R. spectra of PP, PP-g-BA and PP-g-MAH respectively. In Fig. 2.5.b a new peak is seen for the PP-g-BA at 1740 cm^{-1} due to the presence of ester group (- $\overset{|}{C}$ = O) of butyl acrylate. In

Table 2.11

Effect of Medium on the grafting of MAH onto PP.

PP	:	2.5 % (w/v)
Benzoyl peroxide	:	0.1 % (w/v)
MAH	:	1.25 % (w/v)
Temperature	:	$100^{o}C$
Reaction time	:	8 h
Total volume	:	200 cm^3

Solvents	Dipole moment	% G
Xylene	2.57	1.92
O-Dichloro benzene	2.25	2.24
Toluene	0.42	5.20
Decaline	0.00	5.00

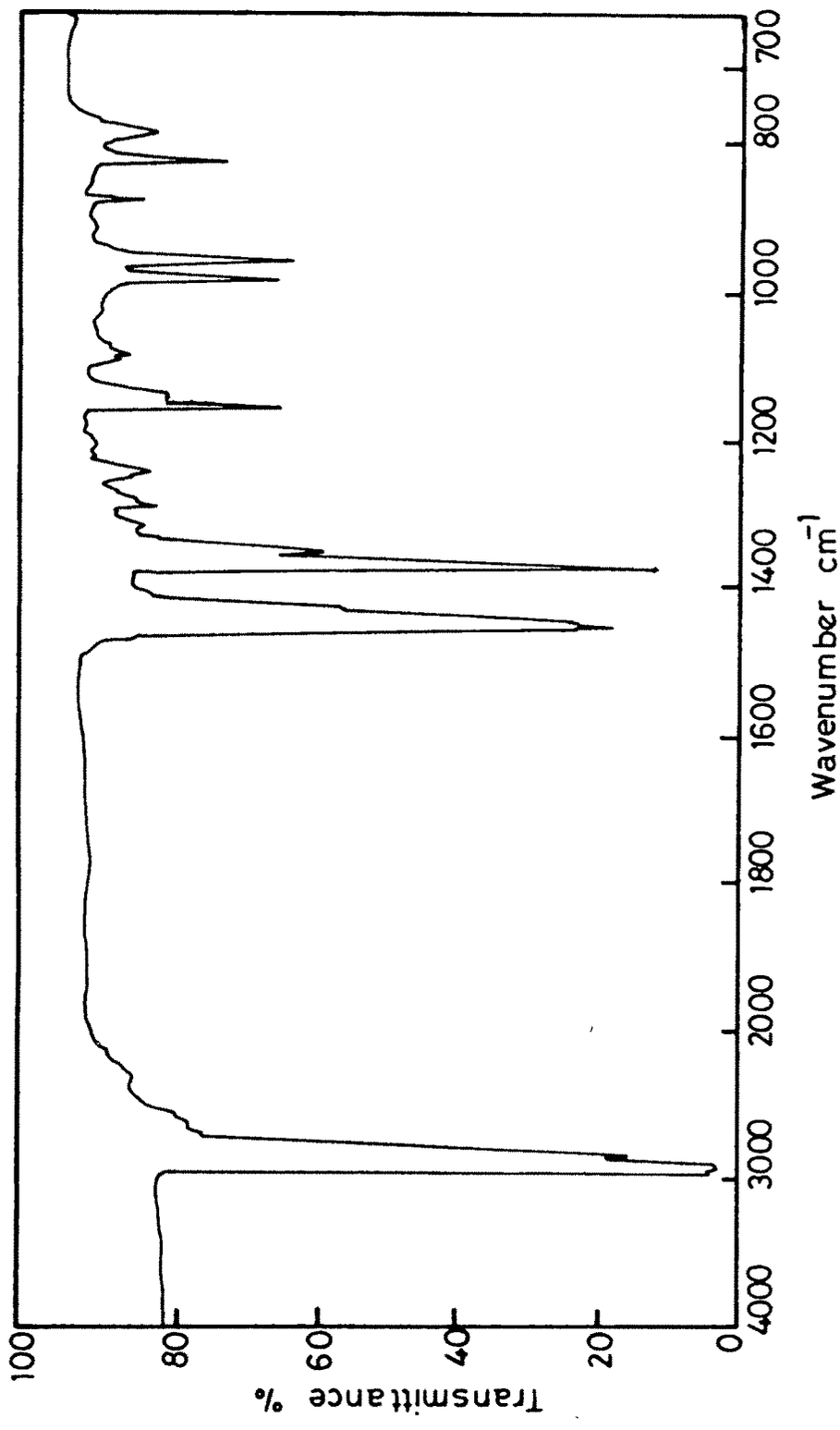


Fig. 2.5.a IR spectra of polypropylene

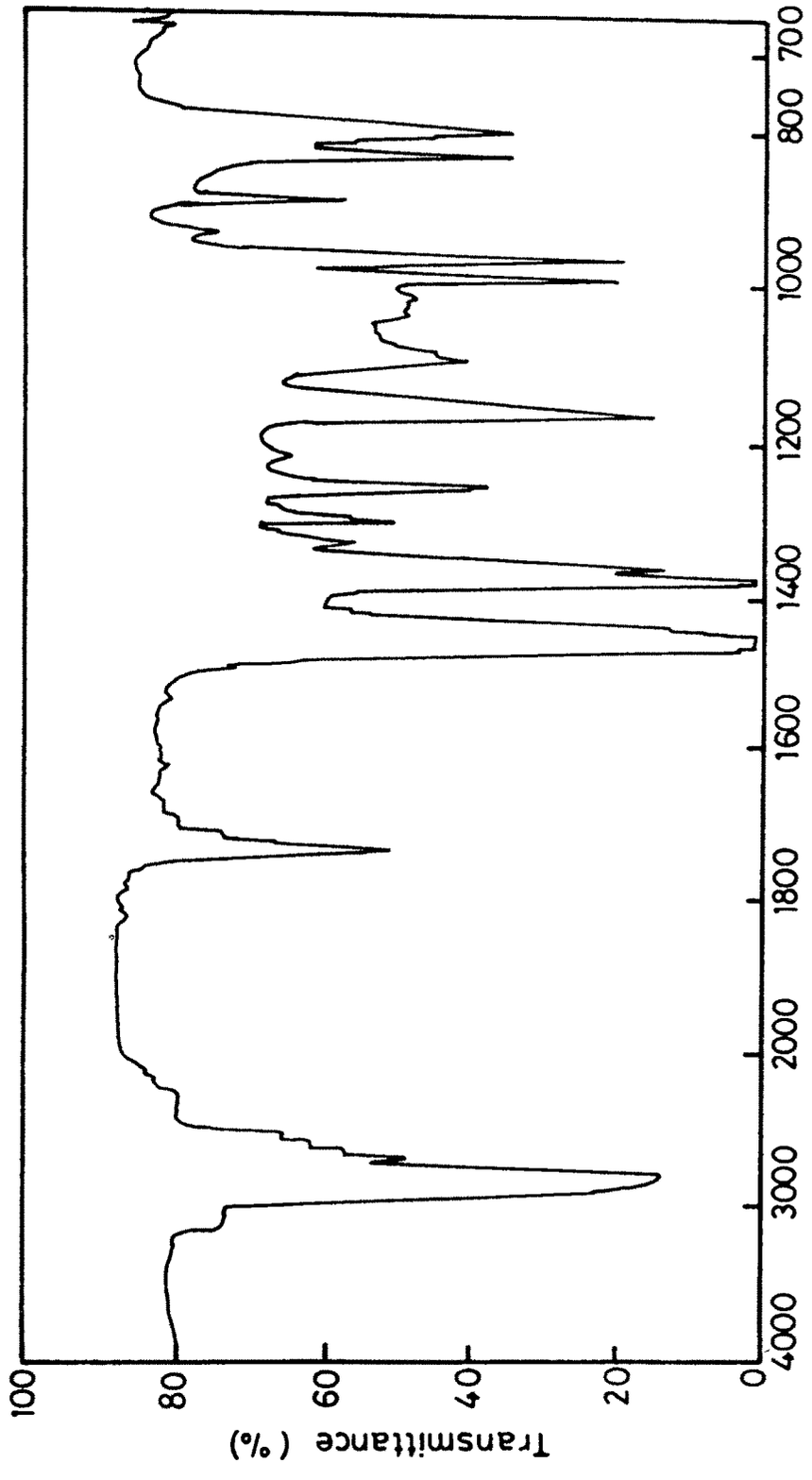


Fig.2.5.b IR spectra of PP-g-BA (D.C. = 2.85%)

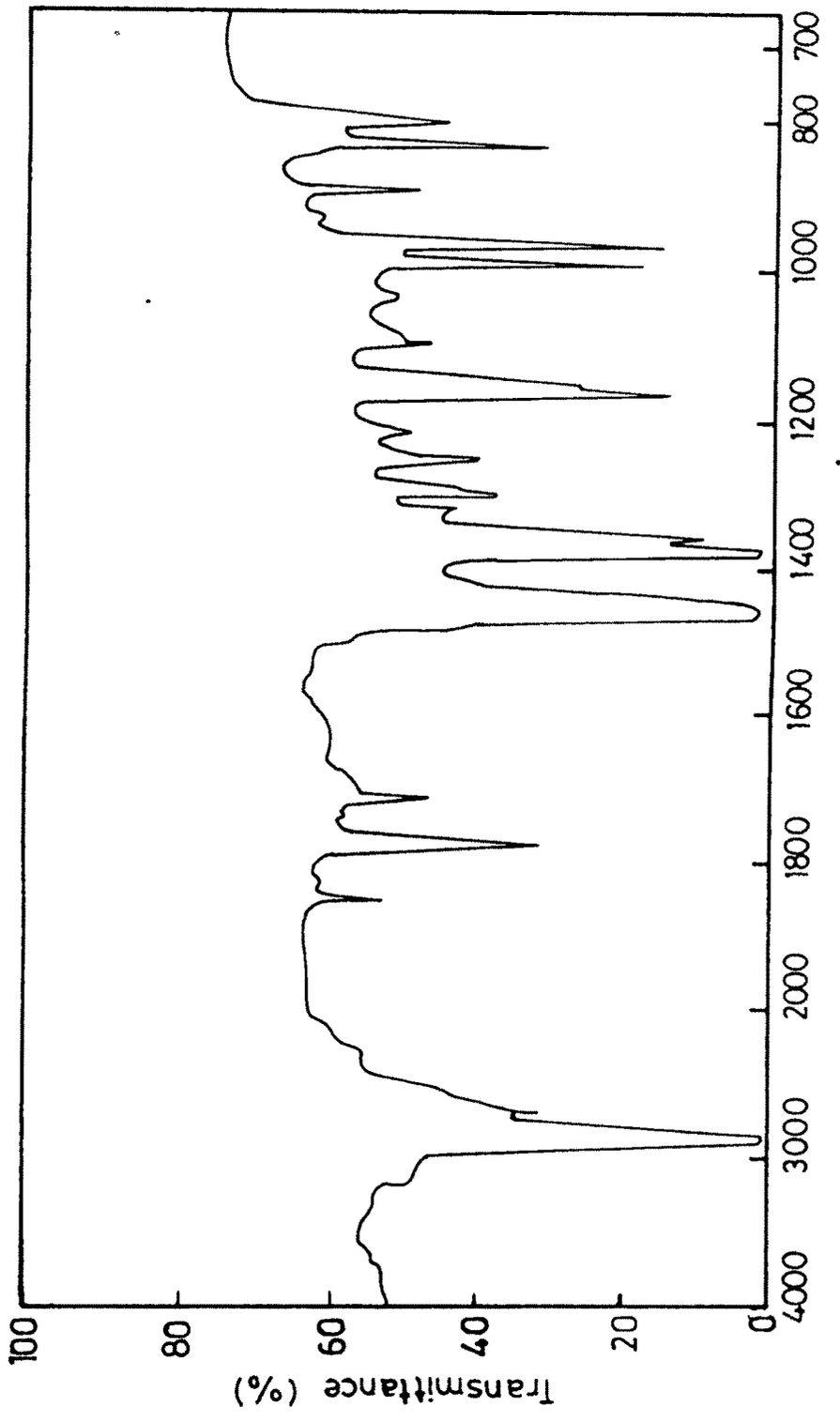


Fig. 2.5.c IR spectra of PP-g-MAH (D.C. = 3.4%)

Fig. 2.5.c the I.R. spectra of PP-g-MAH copolymer shows bands at 1860 cm^{-1}, 1790 cm^{-1} and 1720 cm^{-1} which are characteristics of cyclic anhydride group, indicating the introduction of maleic anhydride in to the polypopylene. Further, the I.R. spectra of PP shows an intense band at 1170 cm^{-1} and a shoulder at 1152 cm^{-1}. The peak at 1170 cm^{-1} is related to crystalline nature of PP and the small shoulder peak is assigned to the amorphous nature of PP. With increase in BA and MAH content (essentially amorphous polymer) in the grafted samples, the peaks at 1152 cm^{-1} and 1170 cm^{-1} appear to merge together due to increase in the amorphous content in grafted PP. Similar observation was made by Mukherjee and Gupta [11] for grafting of methacrylic acid onto PP by radiation induced graft copomerisation.

2.5.3 Contact angle measurement

One way of characterising polymer surface is to measure the contact angle (θ) made by a drop of liquid on the surface at the point where the two phases meet. The surface tension of solid surface and that of a liquid determines whether the liquid will wet the surface when applied to it. Perfect wetting occures when $\cos\theta = 1$, i.e. when $\theta = 0$. The contact angle θ for graft copolymer films was measured for the different solvents of variable surface tensions. From the contact angle θ, the plots of $\cos\theta$ versus surface tension of the contacting liquid was plotted. From these graphs the critical surface tension (γ_c) for grafted samples were calculated by extrapolating the line to $\cos\theta = 1$. It was

observed from the results given in Tables 2.3 to 2.10, for PP-g-BA and PP-g-MAH, that the critical surface tension values decrease with increase in percentage grafting. This shows that the surface polarity of graft copolymer increases with increase in percentage grafting.

2.5.4 Viscosity Studies

From the viscosity measurements of the Soxhlet extracted graft copolymers in trichloro benzene, the intrinsic viscosities of the copolymers and homopolymers were calculated and are given in Table 2.3 to 2.10.

From the intrinsic viscosity data it is observed that the intrinsic viscosity of the graft copolymer is less than that of the polypropylene. This may be due to, PP under going degradation as a result of the disproportionation of PP radicals generated by hydrogen abstraction. The degradation is greater in the presence of monomer and initiator than in the presence of the initiator alone. PP degradation in the presence of monomer and initiator is due predominantly to interactions with species arising from the monomer-initiator interaction [12].

Viscosity molecular weights of the graft copolymers were calculated using K and α values from literature. The K and α values taken were 1.90×10^{-4} and 0.725 respectively for PP in trichlero benzene at $135^{o}C$ [13]. The results are given in Tables 2.3 to 2.10. It is observed that $\bar{M}v$ decreases as the percentage grafting increases.

2.5.5 Thermal Analysis

2.5.5.a Differential scanning calorimetry (DSC)

The DSC cooling curves of PP, PP-g-BA and PP-g-MAH are given in Fig. 2.6.a and 2.6.b. From the curves it is observed that the exotherms were obtained for PP at 113^{o}C. The exotherms for PP-g-BA and PP-g-MAH were observed at 118^{o}C and 121.5^{o}C respectively. This suggests the shift of crystallisation temperature (Tc) to higher side for graft copolymer. The observed increase in crystallisation temperature can be attributed to the BA and MAH acting as nucleating agents. Rybnikar et al. [14,15] also found nucleation effect due to incorporation of carbonyl group in PP.

The heats of fusion ($\triangle Hf^{*}$), from DSC melting curves, of PP-g-BA and PP-g-MAH copolymers are given in Table 2.12 and 2.13 respectively. The percentage crystallinity was calculated on the assumption that heat of fusion ($\triangle Hf^{o}$) of 100% crytalline PP is 50 cal/g [16]. As the heat of fusion is directly proportional to the amount of crystalline PP in the sample, it decreases linearly with increase in grafting percent. An apperent decrease in heat of fusion was due to the decrease in weight fraction of crystalline PP in copolymer due to the incorporation of amorphous polybutyl acrylate and maleic anhydride in PP. Similar trend was observed by Mukherjee [16], and Agrawal and Harrison [17] for PP-g-MAH and PE-g-AA.

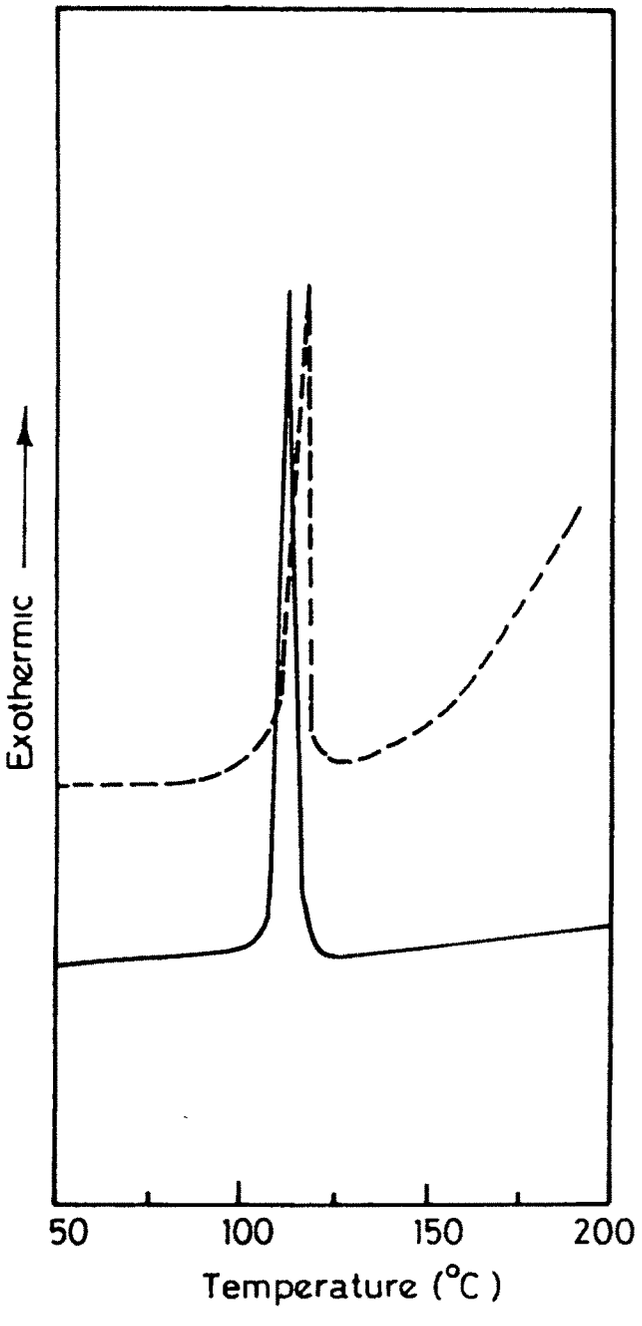


Fig. 2.6.a DSC cooling curves for
——, PP ; ------,
PP-g-BA (D.G. = 2.85%).

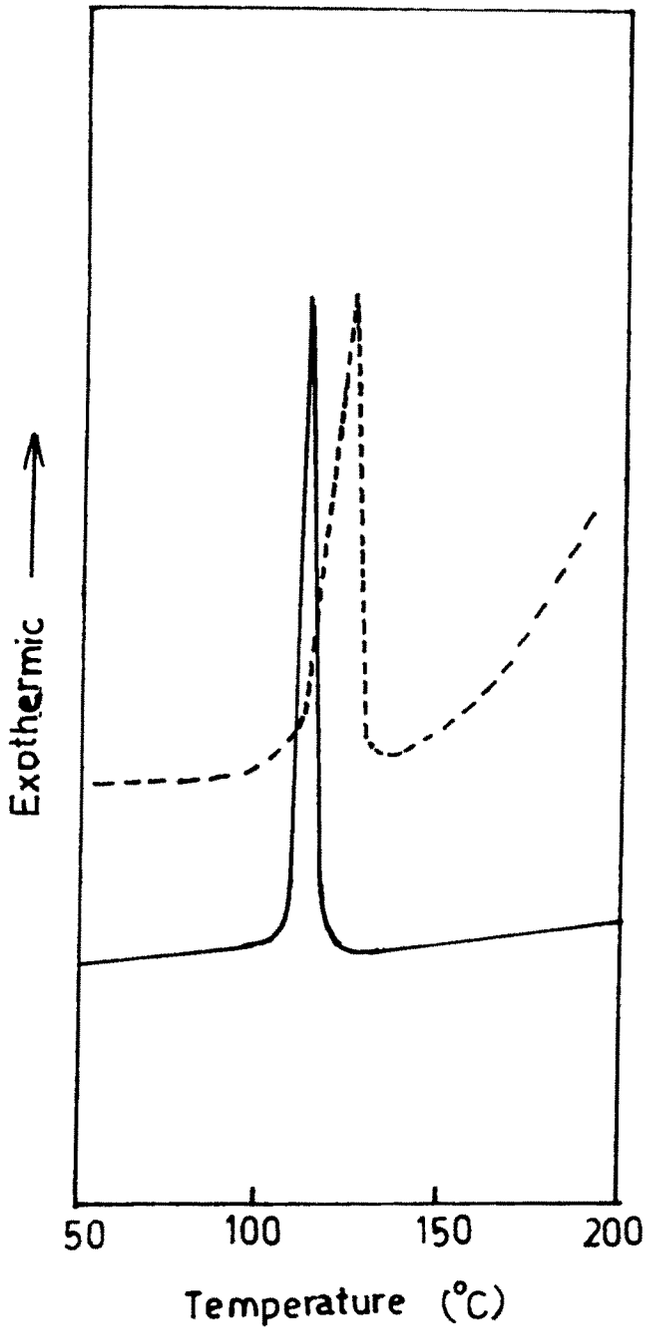


Fig. 2.6b DSC cooling curves for

———, PP ; ---------,

PP-g-MAH (D.C. = 5.36%).

Table 2.12

Thermal analysis of PP-g-BA.

Percentage grafting (% G)	Melting temperature Tm (^{o}C)	Heat of fusion $\triangle Hf^{*}$ (cal/g)	% Crystallinity	IDT (^{o}C)	T_{50} (^{o}C)
PP	165.12	--	--	235	355
0.63	161.65	20.73	41.46	-	-
1.10	161.66	20.16	40.32	-	-
1.64	162.21	19.94	39.94	245	360
2.13	162.75	19.83	39.64	260	365
2.85	163.07	19.06	38.13	272	372

Table 2.13

Thermal analysis of PP-g-MAH.

Percentage grafting (% G)	Melting temperature Tm (^{o}C)	Heat of fusion $\triangle Hf^{*}$ (cal/g)	% Crystallinity	IDT (^{o}C)	T_{50} (^{o}C)
PP	165.12	--	--	235	355
0.68	161.67	20.10	40.20	-	-
2.89	162.75	19.43	38.86	275	375
3.75	162.85	19.41	38.82	290	382
5.32	163.00	19.51	38.22	315	410

2.5.5.b Thermogravimetric analysis (TGA)

TGA curves of PP-g-BA and PP-g-MAH with different percentage grafting along with PP are shown in Fig. 2.7.a and 2.7.b respectively. From the thermograms it is observed that increase in initial decomposition temperature (IDT) and temperature for 50% decomposition (T_{50}) takes place with increase in grafting. From thermograms it is also observed that amount of residue left increases with increase in percent grafting. This can also support the observed increase in thermal stability corresponding to increased polarity of the graft copolymers. The IDT and T_{50} are given in Table 2.12 and 2.13 for PP-g-BA and PP-g-MAH respectively.

We have also synthesised PP-g-(BA-co-MAH) at the optimised conditions. The observed percentage grafting was 4.8. The amount of MAH incorporated in the copolymer was calculated from unreacted MAH left in to acetone extract. The acetone extract was concentrated and kept over night for the hydrolysis of maleic anhydride. The hydrolysed extract was titrated with standard NaOH solution to determine the amount of unreacted MAH in terms of maleic acid. The amount of grafted MAH was calculated by substracting this value from the initial amount of MAH taken. From the calculation it was observed that PP-g-(BA-co-MAH) contains 2.1% of MAH.

The resultant graft copolymers i.e. PP-g-BA, PP-g-MAH and PP-g-(BA-co-MAH) have been used as compatibilisers for PP/NY-6 blends. The synthesis and characterisation of the blends is discussed in the following chapters.

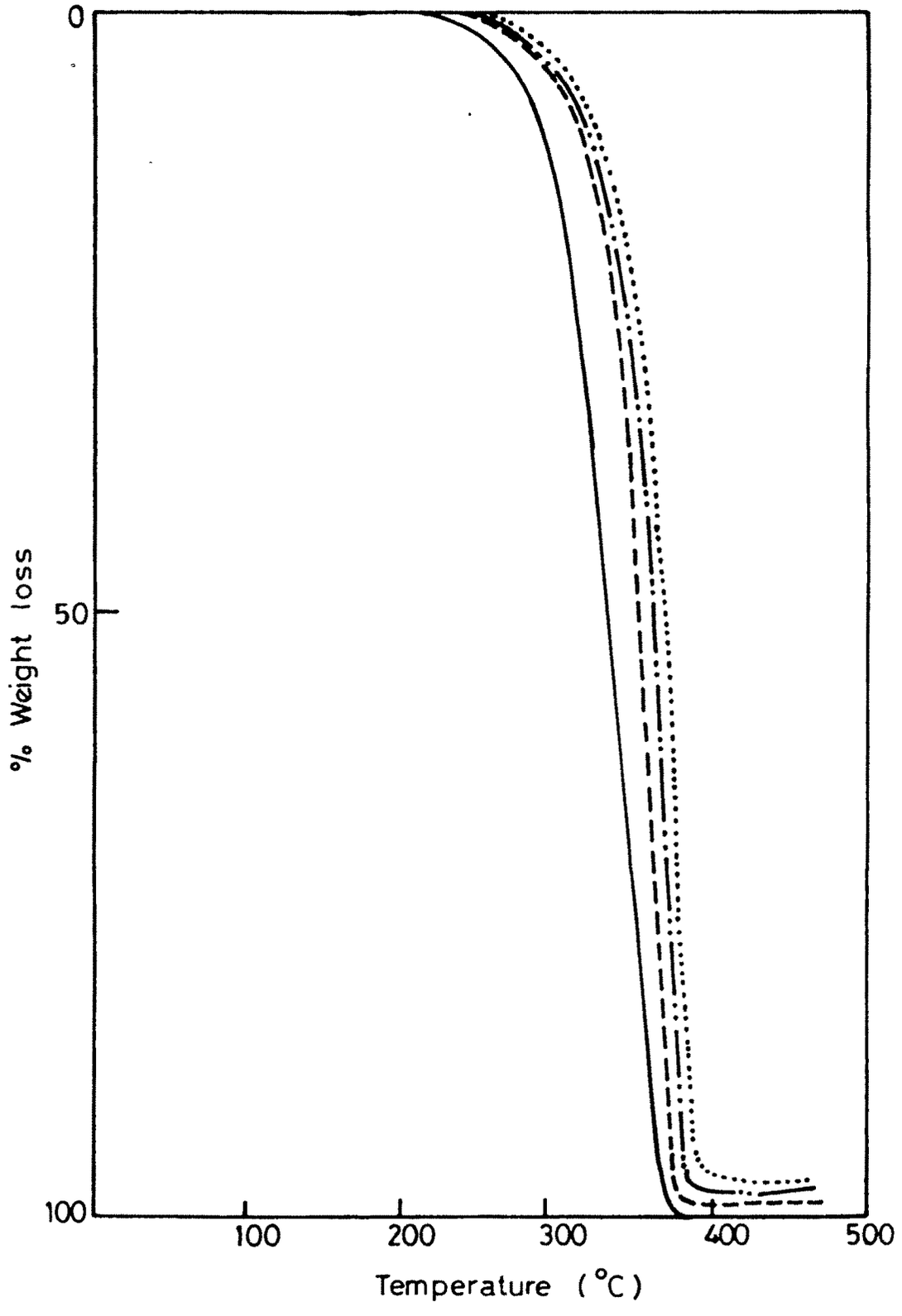


Fig. 2.7.a TGA curves for
———, PP ; ---------, PP-g-BA (D.G. = 1.64%) ;
—.—.—, PP-g-BA (D.G. = 2.13%) ; .....
PP-g-BA (D.G. = 2.85%).

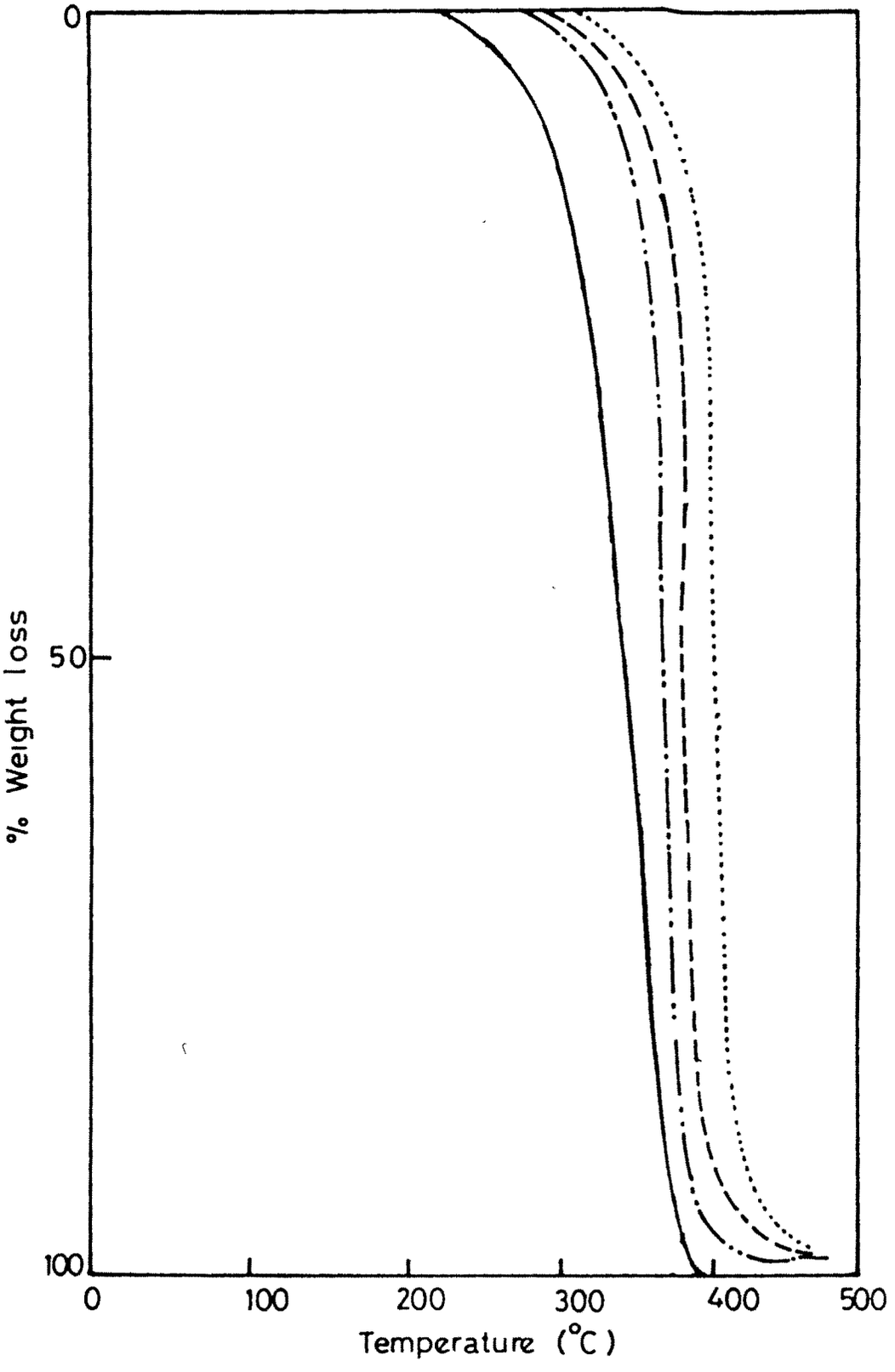


Fig. 2.7.b TGA curves for
——, PP ;——·· ——·——, PP-g-MAH (D.G. = 2.3%)
---------, PP-g-MAH (D.G. = 3.75%) ; ·····
PP-g-MAH (D.G. = 5.32%).

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