# Grafting onto Isotactic Polypropylene. III. Gamma Rays Induced Graft Copolymerization of Water Soluble Vinyl Monomers*

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## Synopsis

Graft copolymerization of water soluble vinyl monomers such as acrylic acid and acrylamide onto isotactic polypropylene by the pre-irradiation method has been studied. Grafting was carried out in a water and water-methanol solvent system. The percentage of grafting has been determined as a function of (i), total dose (ii) concentration of monomers, (iii) reaction time, and (iv) the composition and amount of water-methanol solvent system. Water was found to be the best solvent for affording maximum grafting. The grafted samples were characterized by spectroscopic and thermogravimetric methods. Acrylic acid was found to be more reactive than acrylamide towards graft copolymerization.

## INTRODUCTION

Isotactic polypropylene (IPP) has become the largest and fastest growing plastic because of its versatility, wide applicability and low cost. The inertness of polypropylene toward chemicals excludes its industrial applications such as dyeing of fibers, printing of films, paintability, adhesion, etc. In order to improve these and other properties of IPP, modification of isotactic polypropylene has been attempted by different groups of workers. Kirshenbaum and Stanley[1] grafted 4-vinyl pyridine onto IPP using boron in benzene. Umezawa and Hirota[2] grafted styrene maleic anhydride onto pre-irradiated polypropylene. Dyeing properties of grafted PP were enhanced and heat resistance was also improved. Mechanical, thermal, and dyeability properties of vinyl acetate grafted polypropylene were investigated by Torikai et al.[3] Kimura and Kitano[4] observed an increase in the grafting efficiency of styrene onto pre-irradiated PP by the addition of reducing agent. Solvent effects in the graft copolymerization of methylmethacrylate to PP film by mutual gamma radiation method were studied by Burchill et al.[5] A wide variety of vinyl monomers have been grafted onto PP by Jung Jui Wu et al.[6] using radiation method. Solvent effects on radiation-induced graft copolymerization of acrylonitrile onto polypropylene has been studied in our laboratory.[7,8] Water was found to be an excellent solvent. In this article we report on studies of radiation-induced grafting of water soluble monomers such as acrylic acid and acrylamide onto isotactic polypropylene.

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* Presented in part at the 1987 Spring Meeting of the American Chemical Society, held in Denver, Colorado.

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## EXPERIMENTAL

### Materials and Methods

Isotactic polypropylene (IPP) was received from the National Rayon Corporation, Bombay, in the fiber form. Acrylamide (AAm) (Burgyone Uribridges and Co.) was dried at 40°C prior to its use and freshly distilled acrylic acid (AAc) was used in all the experiments. Methanol was distilled before use.

Isotactic polypropylene was irradiated in air from a 2100 Ci Co$^{60}$ gamma radiation source at a constant dose rate of 0.27 MR/h. for different time periods. The thermogravimetric analysis (TGA) was carried at a heating rate of 10°C/min. The differential scanning calorimetry (DSC) analysis was carried on a Dupont 990 Thermal Analyzer with a 910 module at a heating rate of 20°C/min.

### Graft Copolymerization Method

Irradiated IPP (100 mg) was taken in a flask and to it was added a definite amount of different solvents ($H_2O$, $CH_3OH$ or $H_2O$–$CH_3OH$ mixture) and the monomer (AAc/AAm) immediately. The flask was placed in an oil bath maintained at 100°C. A long water cooled reflux condenser was attached to the flask and the graft copolymerization was allowed to continue for different time periods. After the completion of the reaction, the mixture was filtered and the residue washed thoroughly with excess of water and finally extracted with water to ensure complete removal of the homopolymer (PAAc/PAAm). The grafted IPP fiber was then dried in an oven at 50°C until constant weight was obtained.

Percentage of grafting was calculated from increase in the weight of original fiber in the following manner:

$$\% \text{ Grafting} = \frac{W_1 - W_o}{W_o} \times 100$$

where $W_o$ and $W_1$ are respectively the weights of original fiber and the grafted fiber after complete removal of the homopolymer.

### Evidence of Grafting

The infrared spectra of IPP fiber and IPP-g-PAAm fiber were compared. IPP-g-PAAm showed a sharp peak at 1670 cm$^{-1}$ which was attributed to $\diagdown$C=O group of grafted PAAm. No such peak is observed in the IR spectrum of IPP suggesting that AAm is grafted onto the IPP fiber.

## RESULTS AND DISCUSSION

Irradiation of polypropylene fiber in the presence of air forms polypropylene hydroperoxides owing to the presence of tertiary hydrogen atoms. The macrohydroperoxides decompose upon heating to generate macro-free-radicals on backbone polymer where grafting of appropriate monomer can take place.

## Effect of Total Dose and Solvent

Percentage grafting of acrylic acid (AAc) and acrylamide (AAm) onto pre-irradiated IPP was studied in water, methanol, and water–methanol mixture. Under optimum conditions AAc produced a maximum percentage of grafting (649%) using 10 mL water at 7.7 MR, whereas acrylamide (AAm) in water under optimum conditions produced maximum grafting of 176% at 7.7 MR. In pure methanol, under optimum conditions, AAc produced maximum grafting of 195% and AAm gave maximum grafting of 12%. This is explained by the fact that acrylic acid is more soluble in both water and methanol than acrylamide. Enhancement of grafting of both the monomers in water is due to the fact that the macro-backbone radical (IPP-Ȯ) may undergo swelling in water which facilitates accessibility of the monomer to the active sites. Water has a zero chain transfer constant and consequently various chain transfer reactions are minimal. Decrease of grafting of both the monomers in methanol is due to the fact that some wastage reactions involving chain transfer with methanol occur. The effect of composition of water and methanol system on percentage grafting of both AAc and AAm is described as follows: Figures 1 and 2 illustrate the effect of different compositions of water and methanol mixture on percentage grafting of AAc and AAm as a function of total dose. In the presence of 10 mL of 3 : 7 $H_2O$–$CH_3OH$ mixture, AAc produces maximum grafting of 402% at the optimum dose of 7.7 MR whereas AAm produces a maximum grafting of 30% at a total dose of 14.7 MR. In 10 mL of 1 : 1 $H_2O$–$CH_3OH$ system, AAc gave maximum grafting of 360% at a total dose of 10.13 MR and AAm gave 40% grafting at an optimum total dose of 7.7 MR. It is apparent that there exists a critical composition of $H_2O$–$CH_3OH$ mixture, at which AAc and AAm afford maximum grafting and this corresponds to 3 : 7 $H_2O$–$CH_3OH$ system for AAc and 1 : 1 $H_2O$–$CH_3OH$ system for AAm.

## Effect of Monomer Concentration

Effect of monomer concentration on percentage grafting of AAc and AAm using 10 mL of 1 : 1 $H_2O$–$CH_3OH$ solvent mixture is described in Figures 3 and 4. It is observed that there exists a critical monomer concentration at which the percentage of grafting is maximum and this corresponds to [AAc] = 0.073 mol and [AAm] = 0.021 mol. Further increase in monomer concentration decreases grafting due to preferential formation of homopolymer.

## Effect of Reaction Time

Figures 5 and 6 describe the effect of reaction time on percentage of grafting of AAc and AAm in 1 : 1 $H_2O$–$CH_3OH$ system. It is observed from these figures that grafting increases with increasing time of reaction and then decreases. The maximum percentage of grafting of AAm and AAc (62 and 402%) under optimum conditions was obtained within 240 and 180 min respectively. The decrease in grafting percentage with further increase in time may be due to the fact that the grafted polymeric chains mutually annihilate themselves leading to decrease in percentage of grafting.
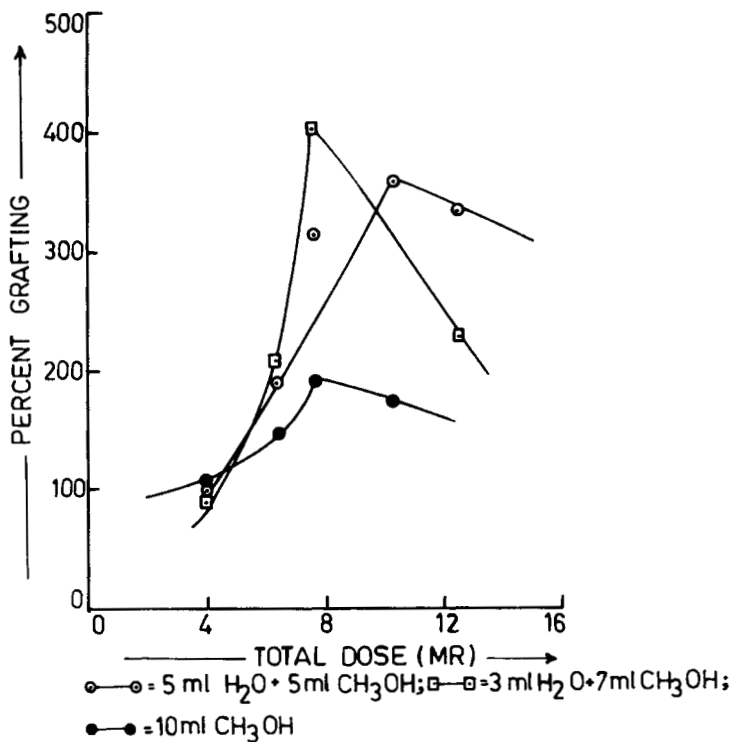
Fig. 1.   Effect of total dose on percentage of grafting of AAc in the presence of solvents.
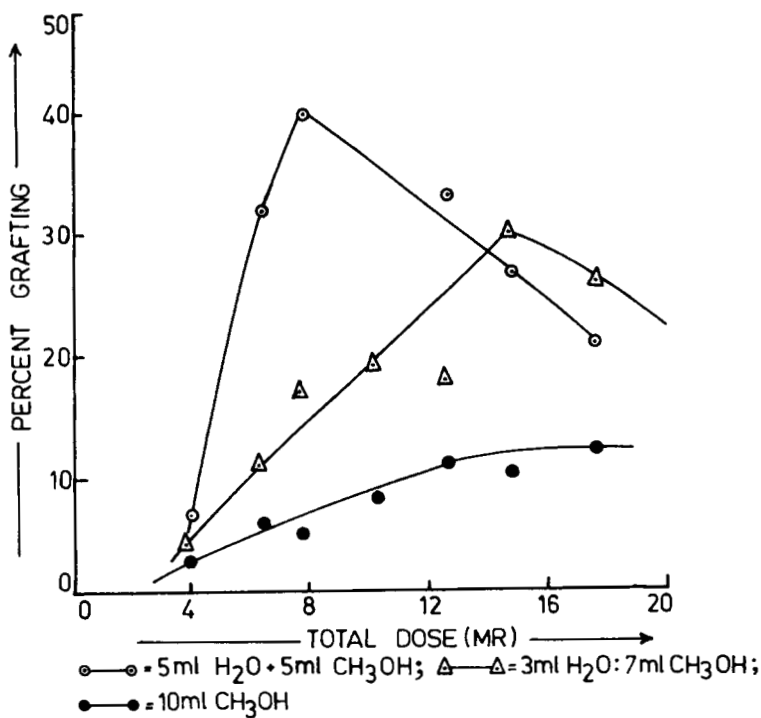


Fig. 2.   Effect of total dose on percentage of grafting of AAm in the presence of solvents.
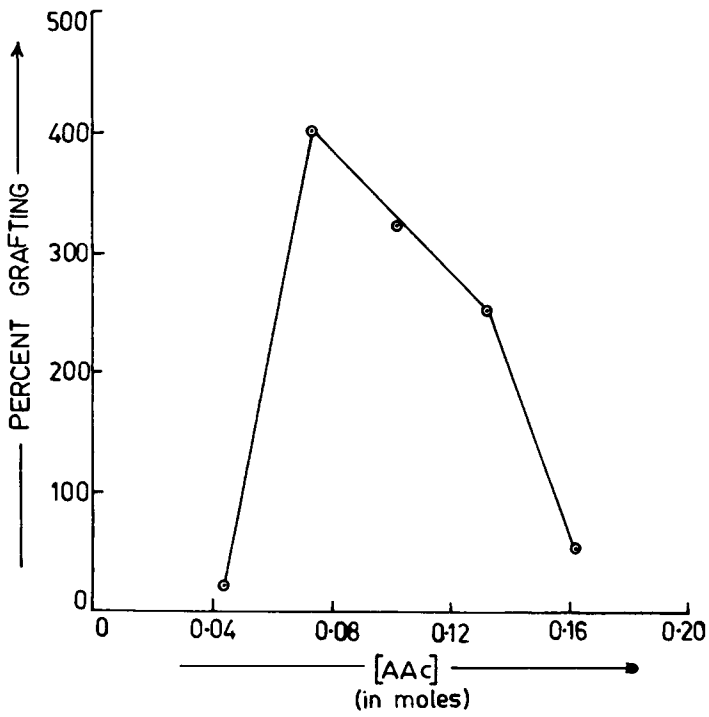
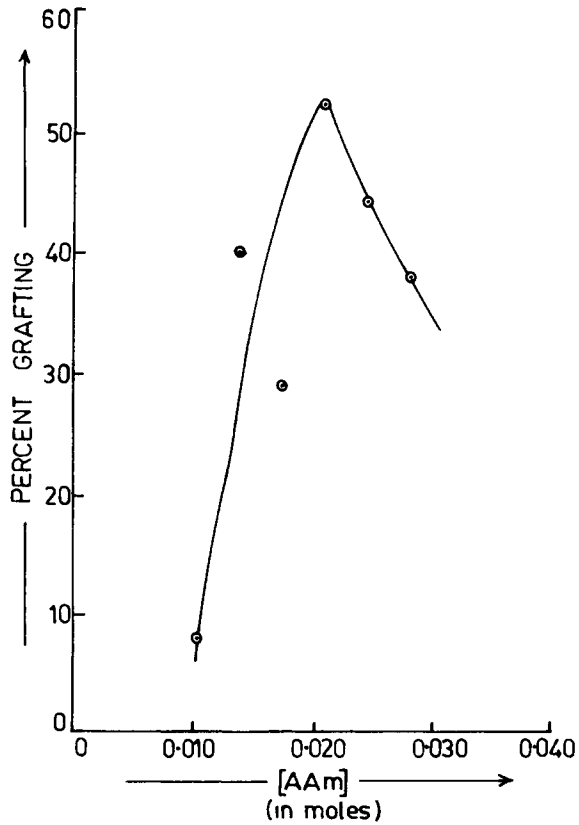Fig. 3. Effect of concentration of acrylic acid on percentage of grafting in the presence of solvents.



Fig. 4. Effect of concentration of acrylamide on percentage of grafting in the presence of solvents.
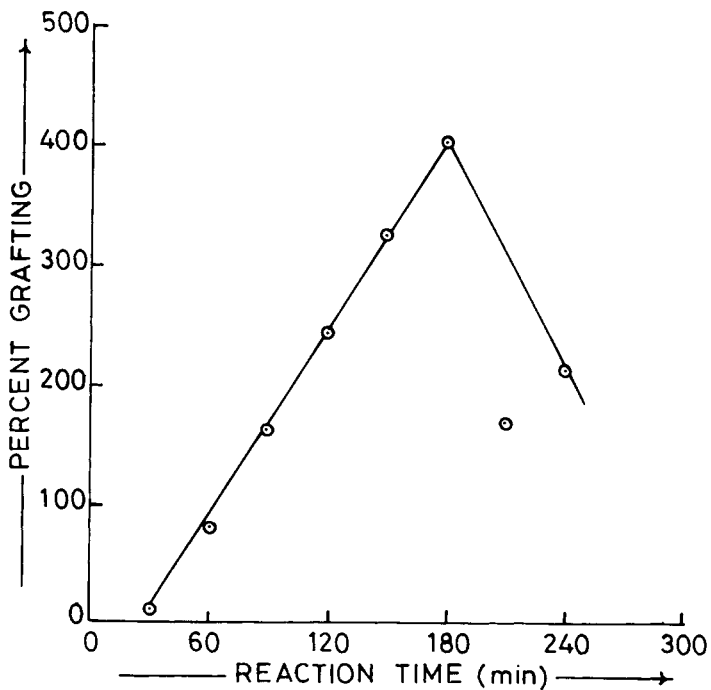
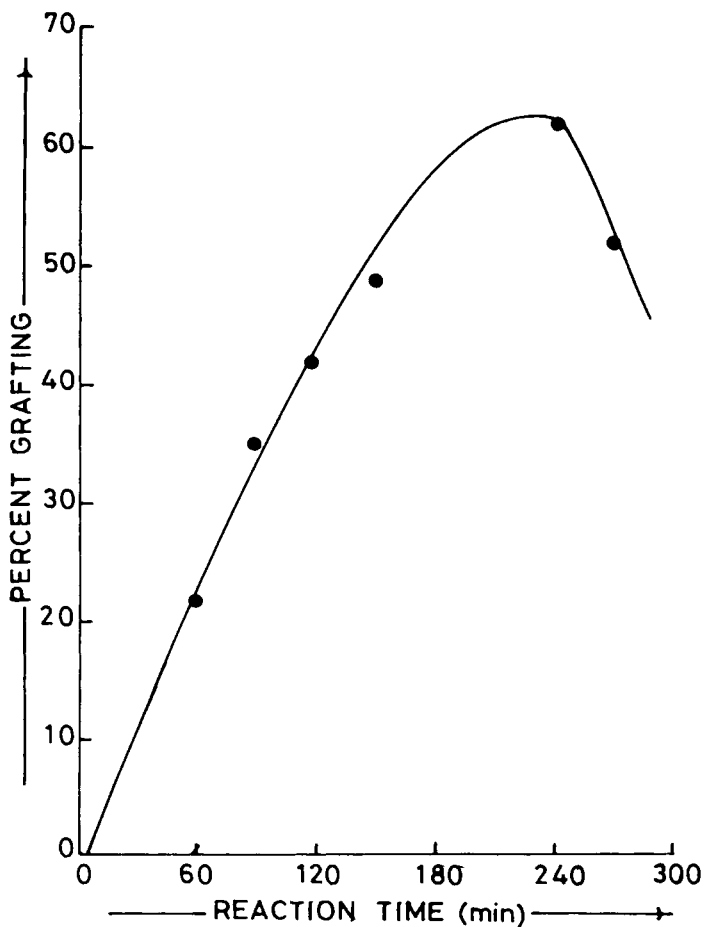Fig. 5.   Effect of reaction time on percent grafting of AAc.



Fig. 6.   Effect of reaction time on percent grafting of AAm.

## Thermal Characterization of IPP, IPP-g-PAAc and IPP-g-PAAm

The PAAm-grafted IPP fiber was characterized by thermogravimetric analysis and differential scanning colorimetry. The PAAc grafted IPP fiber was characterized by differential scanning colorimetry (DSC). The primary thermogram of IPP and IPP-g-PAAm and DSC curves of IPP-g-PAAm and IPP-g-PAAc are presented in Figures 7, 8, and 9.

It is observed from Figure 7 that the inflextion between the region 150 and 200°C is absent in the primary thermogram of IPP and the appearance of a small inflextion between 150 and 200°C in the primary thermogram of IPP-g-PAAm is due to the presence of moisture in the graft. Two stages of decomposition are observed in the primary thermogram of both IPP and IPP-g-PAAm. The initial decomposition of IPP and IPP-g-PAAm begins at 290 and 360°C with the weight loss of 10 and 7.5%, respectively. With further rise in temper-
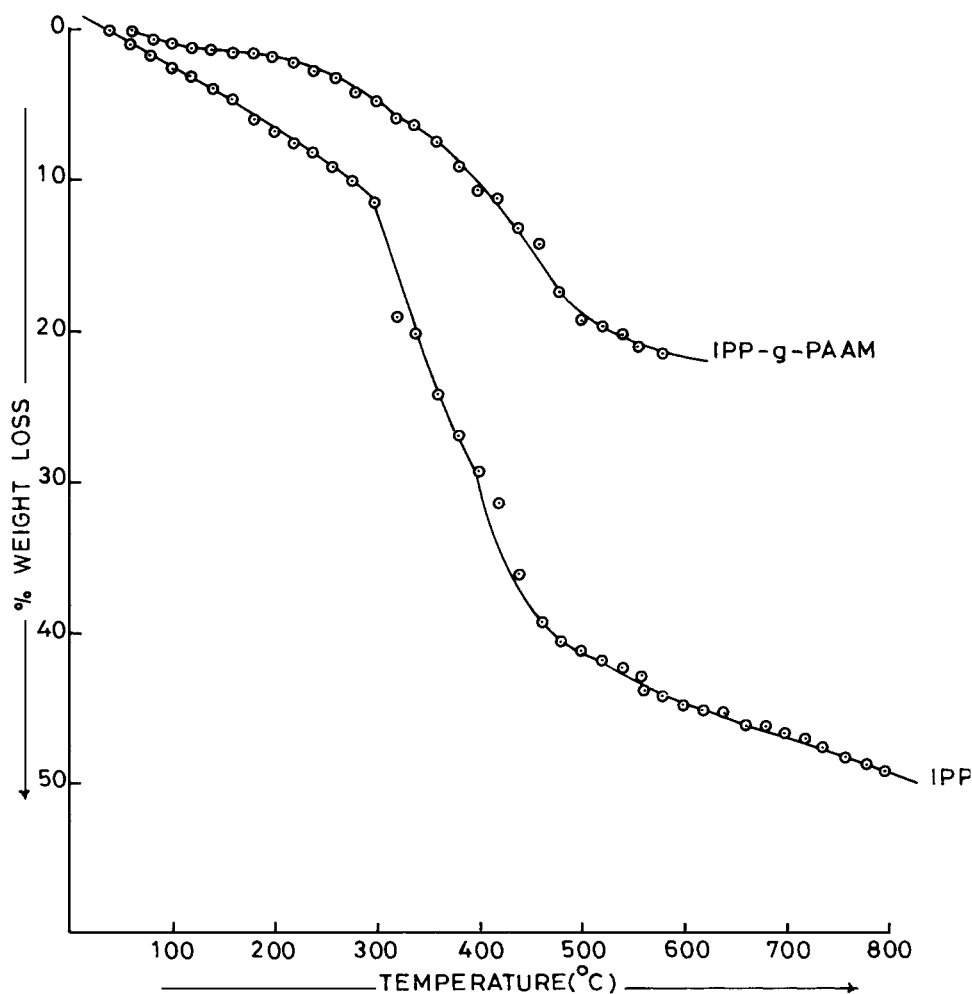


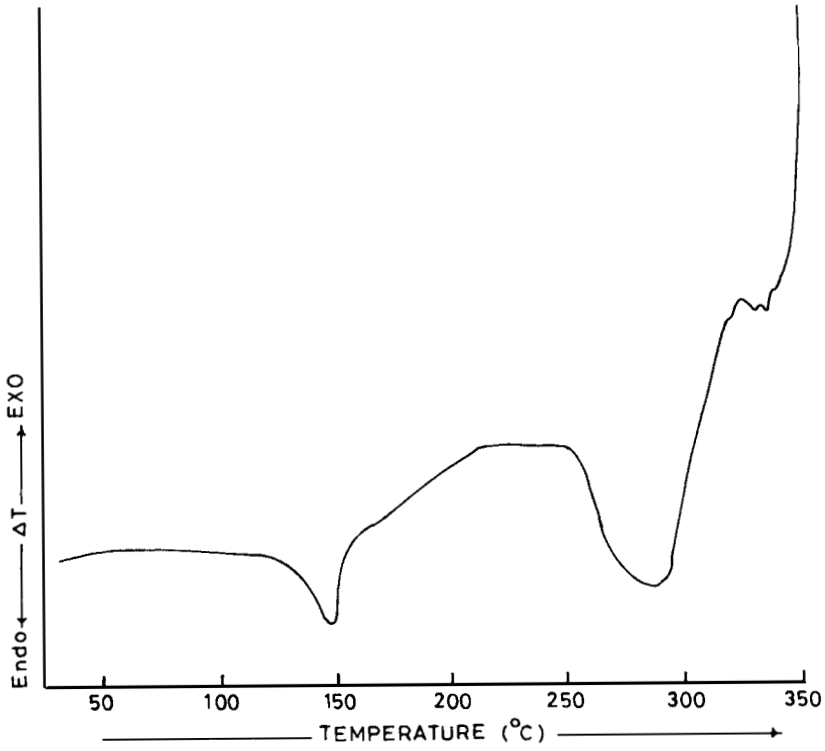Fig. 7. Primary thermogram of IPP and IPP-g-PAAm.

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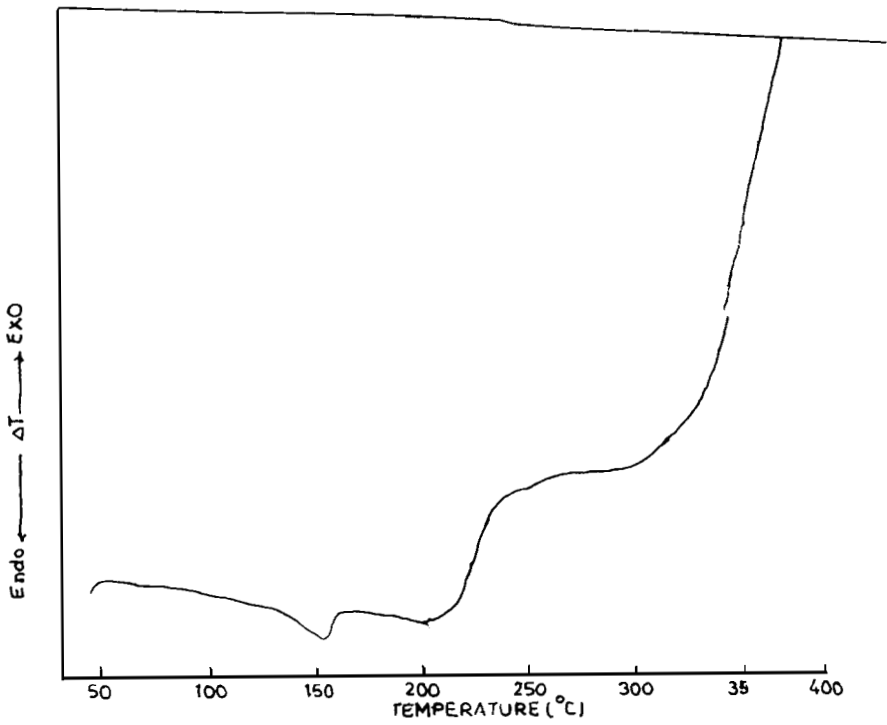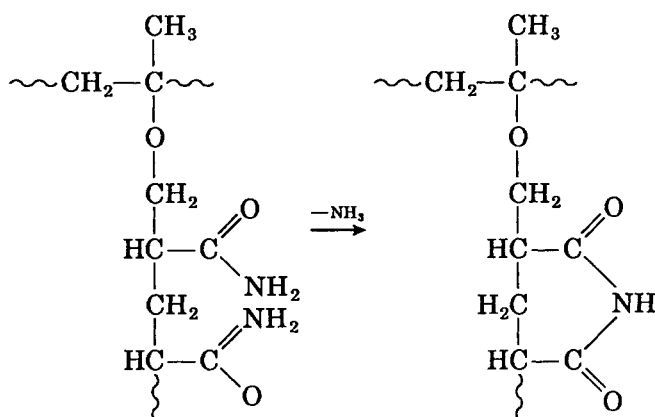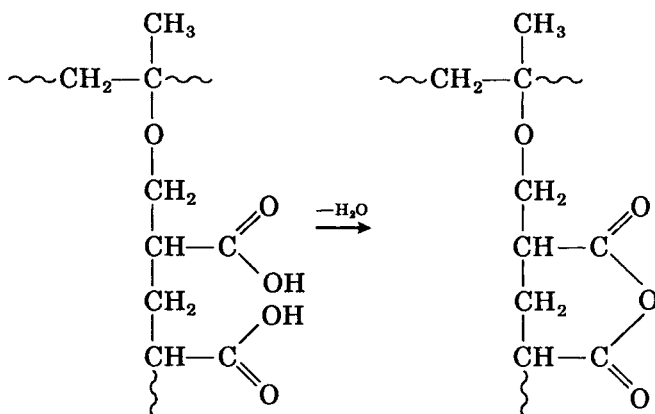Fig. 8.  DSC curve of IPP-g-PAAm.



Fig. 9.  DSC curve of IPP-g-PAAc.

ature IPP decomposes with continuous weight loss and the final decomposition begins at 470°C and continues up to 800°C with 50% weight loss. In case of IPP-g-PAAm, further rise in temperature causes decomposition of the grafted fiber with slight weight loss and final decomposition begins at 535°C and the residue left at 575°C is 77.5% indicating that poly(acrylamide) grafted IPP possesses superior thermal properties over IPP.

In the DSC curve for IPP-g-PAAm (Fig. 8) two prominent endothermic peaks appear between 150 and 160°C and at 285°C. The former peak is due to the loss of moisture from the graft and the peak appearing at 285°C is explained by the fact that upon heating deamination reaction between two adjacent pendant amide groups of IPP-g-PAAm occurs to give the imide in the following manner

$$
\begin{array}{ccc}
& \text{CH}_3 & \text{CH}_3 \\
& | & | \\
\sim\!\text{CH}_2\!-\!\text{C}\!\sim & & \sim\!\text{CH}_2\!-\!\text{C}\!\sim \\
& | & | \\
& \text{O} & \text{O} \\
& | & | \\
& \text{CH}_2 & \text{CH}_2 \\
\text{HC}\!-\!\text{C}\!\!=\!\!\text{O} & \xrightarrow{-\text{NH}_3} & \text{HC}\!-\!\text{C}\!\!=\!\!\text{O} \\
| \quad \backslash\text{NH}_2 & & \text{H}_2\text{C} \quad \backslash\text{NH} \\
\text{CH}_2 \quad /\text{NH}_2 & & | \quad / \\
\text{HC}\!-\!\text{C}\!\!=\!\!\text{O} & & \text{HC}\!-\!\text{C}\!\!=\!\!\text{O}
\end{array}
$$

The DSC curve for IPP-g-PAAc (Fig. 9) shows two endothermic peaks occurring between 150 and 200°C and another at 210°C. The first peak is due to the loss of moisture and the peak at 210°C may be due to a dehydration reaction occurring between the pendant carboxylic groups of IPP-g-PAAc as shown

$$
\begin{array}{ccc}
& \text{CH}_3 & \text{CH}_3 \\
& | & | \\
\sim\!\text{CH}_2\!-\!\text{C}\!\sim & & \sim\!\text{CH}_2\!-\!\text{C}\!\sim \\
& | & | \\
& \text{O} & \text{O} \\
& | & | \\
& \text{CH}_2 & \text{CH}_2 \\
\text{CH}\!-\!\text{C}\!\!=\!\!\text{O} & \xrightarrow{-\text{H}_2\text{O}} & \text{CH}\!-\!\text{C}\!\!=\!\!\text{O} \\
| \quad \backslash\text{OH} & & | \quad \backslash \\
\text{CH}_2 \quad /\text{OH} & & \text{CH}_2 \quad /\text{O} \\
\text{CH}\!-\!\text{C}\!\!=\!\!\text{O} & & \text{CH}\!-\!\text{C}\!\!=\!\!\text{O}
\end{array}
$$

In the DSC curve of IPP-g-PAAc another endothermic peak appears at 300°C which may be due to the decarboxylation reaction.

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