Radiation-Induced Graft Copolymerization of Methacrylic Acid onto Polypropylene Fibers. IV. Thermal Behavior

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Synopsis

Thermal behavior of polypropylene-*g*-poly(methacrylic acid) fibers prepared by graft copolymerization of methacrylic acid onto polypropylene fibers, using simultaneous-irradiation technique, was evaluated by thermogravimetric analysis, differential scanning calorimetry, and limiting oxygen index measurements. In general, the thermal properties of polypropylene fiber were markedly improved by the grafting of methacrylic acid. The inherent crystallinity of polypropylene, as deduced from DSC, did not show any change in the grafted fibers, suggesting that the grafting occurs in the amorphous region, without disrupting the crystalline part of the polymer. The LOI of grafted fibers showed an increase over the original fiber.

INTRODUCTION

Graft copolymerization of vinyl monomers onto polypropylene by irradiation technique has evoked considerable interest[1-4] because it offers a versatile technique to impart desirable properties to the polymer, without much affecting its original properties.[5]

Lodesova et al.[6] have shown that the thermal decomposition temperature of polypropylene fibers grafted with acrylonitrile and glycol methacrylate is increased and reaches in the range of 298–423°C. Sundardi[4] has shown that the grafting of vinylpyrrolidone, acrylonitrile, acrylamide, and acrylic acid results in an improvement in the melting behavior of polypropylene fiber. Recently, in another study,[7] it has been reported that the thermal stability of polypropylene fiber depends largely on the nature of monomer used for grafting. The grafting of vinyl monomers containing phosphorous has also been observed to introduce good flame proofing into polypropylene.[8,9]

The present investigation aims at studying the effect of methacrylic acid grafting on thermal properties of polypropylene fiber.

EXPERIMENTAL

Various polypropylene-*g*-poly(methacrylic acid) (PP-*g*-PMAA) samples with different percent graft were obtained by graft copolymerization of methacrylic acid onto polypropylene fibers by simultaneous irradiation technique using a γ-ray source, as reported previously.[10,11] Thermal behavior of samples was evaluated by thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), and limiting oxygen index (LOI) studies.

Thermogravimetric Analysis (TGA)

TGA studies were carried out on a Stanton Redcroft TG-750 thermobalance, under nitrogen atmosphere. The samples were made into powder form, and the heating was carried out at a uniform heating rate of 10°C/min, starting from room temperature to 700°C. Primary thermograms were obtained by plotting percent residual weight against temperature. Relative thermal stability of the samples was evaluated by the comparison of initial decomposition temperature (IDT), integral procedural decomposition temperature (IPDT), and the temperature at which sample undergoes 50% decomposition, t_{50}.

Differential Scanning Calorimetry (DSC)

DSC studies were carried out using a DuPont 990 Thermal Analyzer. The instrument was calibrated using indium as a reference material. The instrument was run at a constant heating rate of 10°C/min in the temperature range of 25–180°C, under nitrogen atmosphere. The heat of fusion (ΔH_f) and heat of crystallization (ΔH_c) were calculated from area under the thermogram curve and were related to the weight fraction of poly(methacrylic acid) (PMAA) in the grafted sample, as obtained by using the following equation[12]:

$$W_{\text{PMAA}} = \frac{G}{1 + G} \tag{1}$$

where W_{PMAA} is the weight fraction of poly(methacrylic acid) in the sample and G is the graft content. Crystallinity of various samples was obtained by using the following expression[13]:

$$\text{crystallinity (\%)} = \frac{\Delta H_f^*}{\Delta H_f^0} \times 100 \tag{2}$$

where ΔH_f^0 is the heat of fusion of 100% crystalline polypropylene and ΔH_f^* is the corrected heat of fusion of the grafted sample. The heat of fusion (ΔH_f^0) was taken 50 cal/g, as the reference value.[13] The heat of fusion (ΔH_f^*) and that of crystallization (ΔH_c^*) of the grafted sample, which are directly related to the area under the thermogram, have been obtained by correcting the area under the thermogram for the amount of backbone polymer, i.e., polypropylene in the sample:

$$\Delta H_f^* \text{ or } \Delta H_c^* = \frac{\text{area under the thermogram}}{1/(1+G)} \tag{3}$$

Infrared Spectroscopy

Infrared spectra were recorded on a Perkin-Elmer Model 580B Infrared Spectrophotometer in the range of 4000–400 cm^{-1}.

Limiting Oxygen Index (LOI)

Oxygen index measurements of polypropylene samples were carried out using a Stanton Redcroft Flammability unit.

RESULTS AND DISCUSSION

Thermogravimetric Analysis (TGA)

Primary thermograms of ungrafted PP, irradiated PP, and PP-g-PMAA fibers have been presented in Figures 1 and 2. The results show that the thermogram of irradiated polypropylene is similar to that of the original fiber. This suggests that the irradiation of polypropylene with gamma rays under experimental dose does not bring about any detectable change in the fiber structure.

The thermograms of methacrylic-acid-grafted polypropylene samples show an increase in the IDT and IPDT values with the increase in the percent graft (Fig. 3). T_{50} values also increase with the increasing percent graft in the fiber (Fig. 4). These results show an improvement in the thermal stability of the graft copolymers over that of ungrafted polypropylene. An increase in the thermal decomposition of polypropylene by the grafting of acrylonitrile and glycol methacrylate has also been reported by Lodesova et al.[6]

This increase in thermal stability of polypropylene fiber may be attributed to two factors: one is the abstraction of "labile" hydrogen from the tertiary carbon atom, followed by the grafting of PMAA chain at the site generated, which produces an increased thermal stability into the polymer. The other factor is, essentially, the cyclization reaction involving PMAA moieties, taking place during the course of heating. The grafted PMAA chains undergo dehydration reaction, which results in the formation of six-membered polymethacrylic anhydride rings of increased thermal stability. The schematic representation of cyclization can be shown as follows:
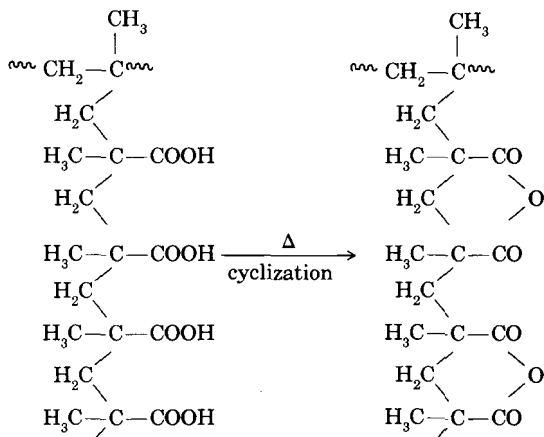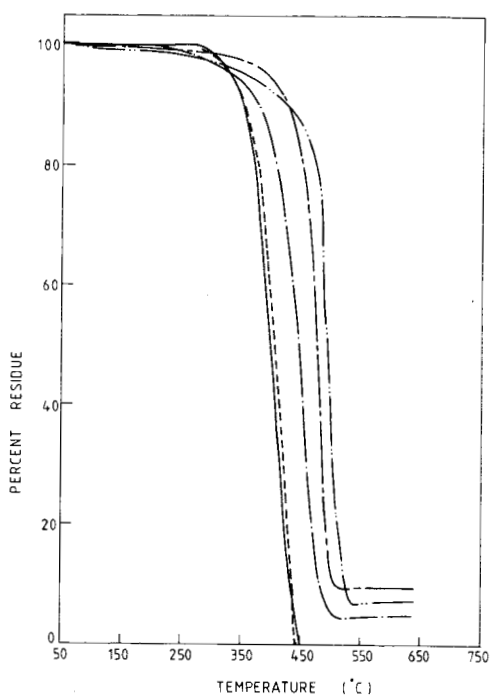
Fig. 1.   TGA thermograms of polypropylene and polypropylene-*g*-poly(methacrylic acid) fibers: (— · —) ungrafted PP fiber; (- - -) irradiated PP fiber and PP-*g*-PMAA fibers with (- · ·) 16% PMAA, (- ; -) 28% PMAA, and (- · · -) 40% PMAA.
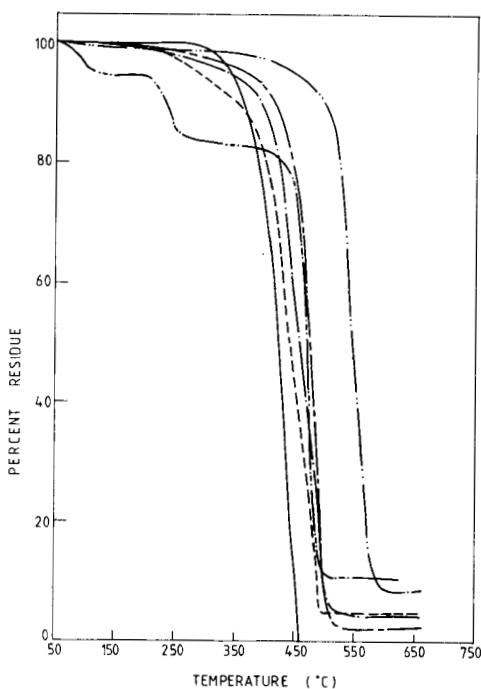

Fig. 2.   TGA thermograms of polypropylene-*g*-poly(methacrylic acid) fibers: (-) 5.5% PMAA; (- - -) 11.5% PMAA; (- - -) 21% PMAA; (- · · -) 35% PMAA; (- · · · -) 50% PMAA; (- · · · · -) PMAA homopolymer.
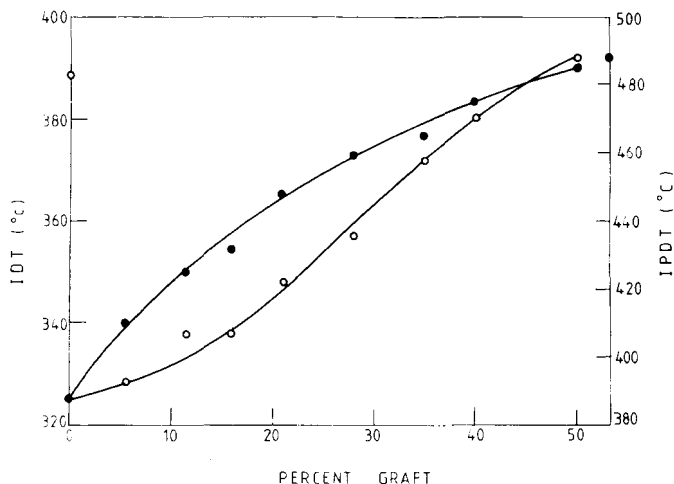
Fig. 3.   Variation of IDT and IPDT with percent graft in polypropylene-g-poly(methacrylic acid) fiber.

The formation of six-membered anhydride structure during the course of heating was ascertained by the infrared spectroscopy. Polypropylene with 21% grafted PMAA content was heated in the thermobalance upto 200°C for 30 min. Both of the samples, i.e., before and after heating, produce similar spectra except few peaks (Fig. 5). The spectra of grafted polypropylene shows a peak at 1710 cm^{-1} characteristic of carbonyl group, which is essentially from the carboxyl groups of PMAA graft. Heating of the polymer results in two major changes from the original IR spectra: (a) appearance of twin peaks at 1720 and 1760 cm^{-1}, which may be attributed to the carbonyl group, and (b) occurrence of an intense peak at 1012 cm^{-1}, characteristic of anhydride (C—O—C) structure. These observations indicate that the anhydride structure is formed by the cyclization of two ad-
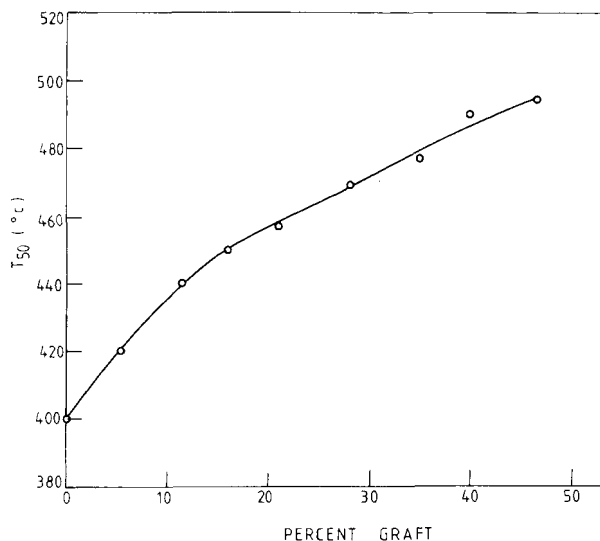

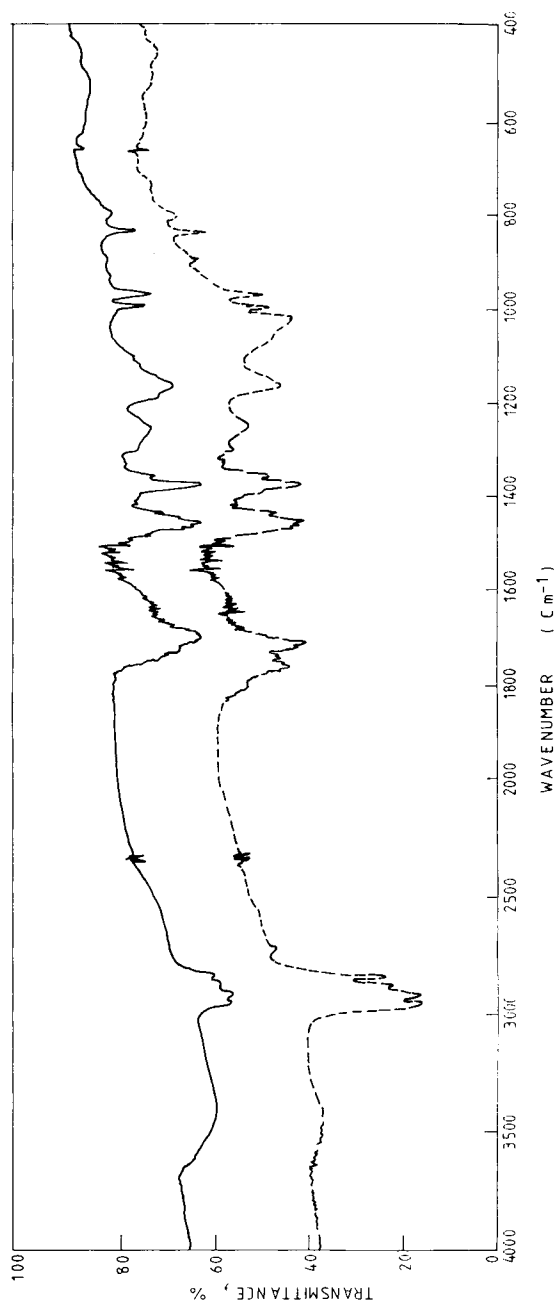Fig. 4.   Variation of T_{50} with percent graft in polypropylene-g-poly(methacrylic acid) fiber.

Fig. 5. Infrared spectra of polypropylene-*g*-poly(methacrylic acid) fiber (21% PMAA) (-) before and (- -) after heating at 200°C for 30 min.

jacent carboxyl groups (as indicated in the scheme). Using mass spectrometric technique, Bresler et al.[14] showed that the partial dehydration of poly(methacrylic acid) results in an increase in the thermal stability of polymer due to the formation of poly(methacrylic anhydride) rings. This view point is further strengthened by a study on homopoly(methacrylic acid) prepared by gamma radiation. The homopolymer was heated at 200°C for 30 min. The partial conversion of acid groups into the anhydride can be recognized by the disappearance of broad hydroxyl peak at 3600–2500 cm^{-1}, appearance of twin carbonyl peaks at 1760 and 1805 cm^{-1}, and an intense anhydride peak at 1020 cm^{-1} (Fig. 6). The results are in good agreement with those of Grant and Grassie,[15] who showed that the degradation product of PMAA at 200°C consists, predominently of linked six-membered anhydride rings with occasional crosslinks. The results have been summarized in Table I. A close relationship exists between the thermogram of PMAA and the above results. A two-step thermal decomposition has been observed from the primary thermogram of PMAA (Fig. 2). First decomposition occurs at 197°C followed by another decomposition at 415°C. It appears that the decomposition at 197°C is due to the dehydration reaction between adjacent monomer units. As a result, the macromolecular chain becomes more stable due to the presence of anhydride rings[14] and undergo further decomposition only above 415°C.

Differential Scanning Calorimetry (DSC)

The variation of heat of fusion (ΔH_f) with the PMAA content in polypropylene fiber has been presented in Figure 7. The dotted circle in the figure indicates the heat of fusion of irradiated polypropylene.

It may be seen from the figure that original polypropylene and irradiated but ungrafted polypropylene do not show any change in the heat of fusion. These results further strengthen the contention that the irradiation dose, used in the present study, is insufficient to cause any detectable radiation damage to polypropylene fiber. Further, the heat of fusion decreases linearly with the increase in the weight fraction of PMAA in the copolymer sample. All the points lie on a straight line, so that the heat of fusion of the grafted samples is related to that of ungrafted sample by the relationship:

$$H_f = \frac{24.2}{1+G}$$

where G is the graft content. As the heat of fusion is directly related to the amount of crystalline polypropylene in the sample, these results do not register any change in the heat of fusion of backbone polymer and an apparent decrease in heat of fusion is essentially due to the decrease in the weight fraction of crystalline polypropylene in the copolymer.

The PMAA is incorporated into the polypropylene matrix as an amorphous component.[16] Hence, the area under the thermogram has been corrected for the amount of PP in the grafted sample, according to eq. (3). This corrected area represents the heat of fusion or that of crystallization contributed by the backbone polymer in the grafted sample. The heat of fusion
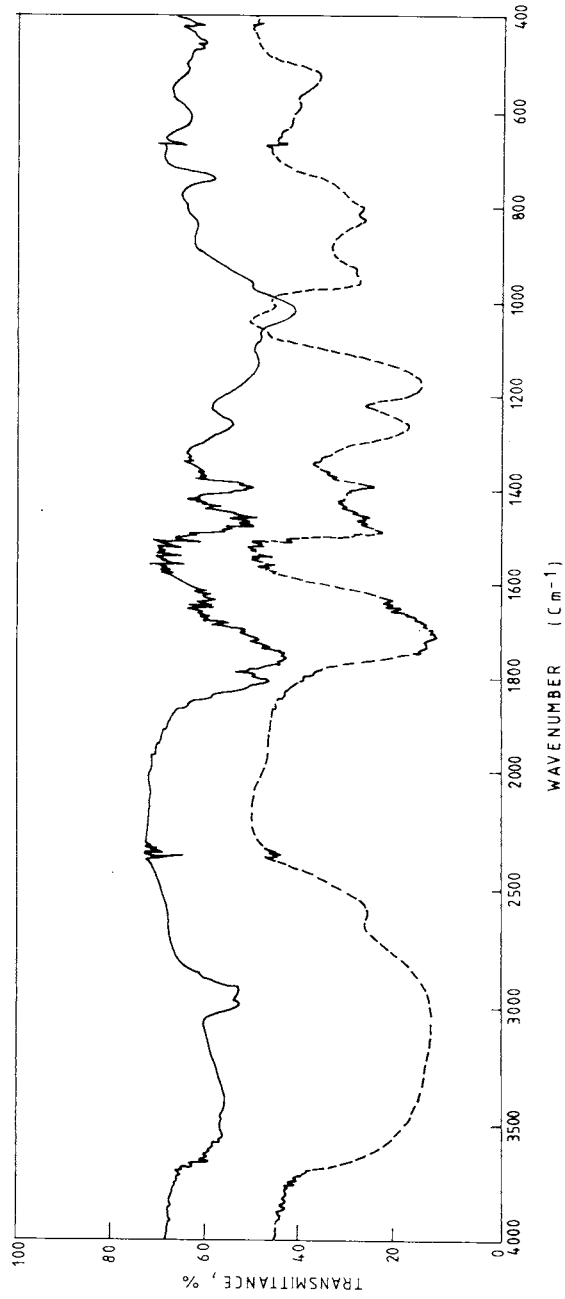
Fig. 6. Infrared spectra of poly(methacrylic acid) (- -) before and (—) after heating at 200°C for 30 min.

TABLE I
Infrared Analysis of Degradation Product of Polymethyacrylic Acid

Peak	This work (cm^{-1})	Grant et al.[15] (cm^{-1})
OH peak	3600–2500	3600–2500
Carbonyl peak	1805	1795
	1760	1750
C-O-C peak	1020	1022

of ungrafted polypropylene was found to be 24.2 cal/g, while, in the case of grafted samples, it was found to be in the range of 23.6–24.2 cal/g, depending upon the graft level. This shows that the heat of fusion of the backbone polymer remains essentially unchanged by the grafting of PMAA which is incorporated only in the noncrystalline region.[17,18] This is in agreement with the results of X-ray investigations[16] that the grafted PMAA chains are amorphous in nature.

A relative change in the heat of crystallization of backbone polymer ($\Delta H_c^*/\Delta H_{c_0}$, where ΔH_c^* and ΔH_{c_0} are heat of crystallization values of the grafted and original polypropylene fiber, respectively) against percent graft is presented in Figure 8. The results show that the heat of crystallization does not follow a linear relationship with PMAA content. Instead, it decreases initially and then remains almost unchanged with the further increase in the percent graft. It appears that the grafted PMAA branches fill in the amorphous regions of polypropylene and do not disrupt the crystallites (as the heat of fusion of backbone polymer in the grafts remains unchanged), but, once the grafted samples are melted, the amorphous PMAA chains have considerable mobility within the molten polypropylene matrix and can interfere with the growth of crystals.[19] It seems that the incorporation of 11.5% PMAA as the graft is sufficient to cause hindrance during
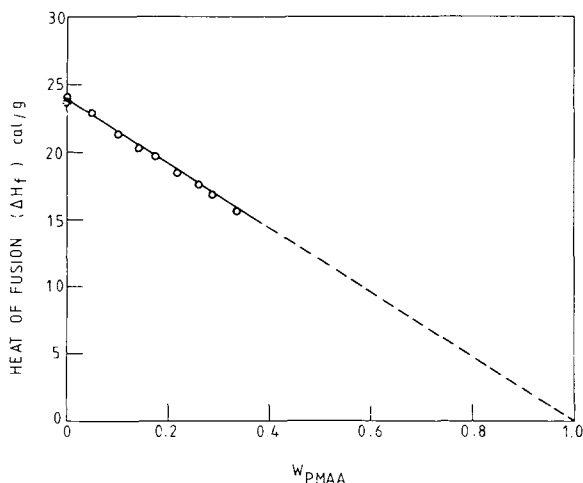

Fig. 7.   Relation between heat of fusion and weight fraction of poly(methacrylic acid) in the grafted fiber.
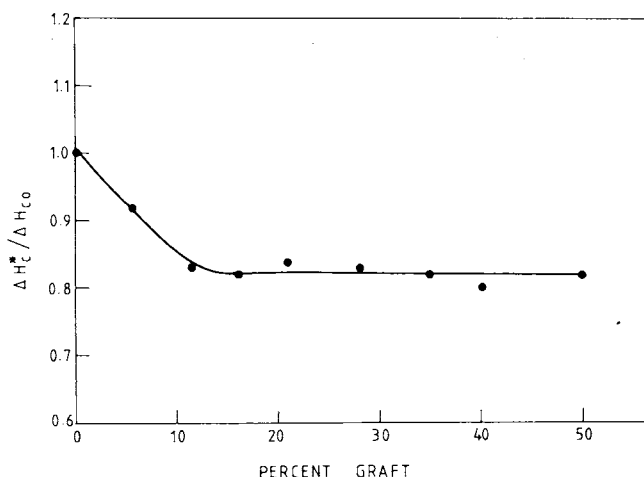
Fig. 8.   Relative change in the heat of crystallization with percent graft in polypropylene-*g*-poly(methacrylic acid) fiber.

crystallization of the grafted samples, and further grafting does not influence the crystallization anymore.

A linear relationship (followed by leveling off) between heat of fusion and heat of crystallization is shown in Figure 9. This can be attributed to the relative change in the heat of crystallization at low levels of grafting. In the present study, the heat of fusion values have been found not to coincide with that of crystallization for the identical sample and instead, it tends to have a lower value than that of crystallization. This may be ascribed to the previous history of the polymer. The polypropylene chips were melt-spun at 240°C, and the fibers were collected at room temperature, providing very less time for crystallization of the polymer. The effect was eliminated when samples were melted and, during crystallization, samples were cooled at a constant rate of 10°C/min, thus providing sufficient time for molecular
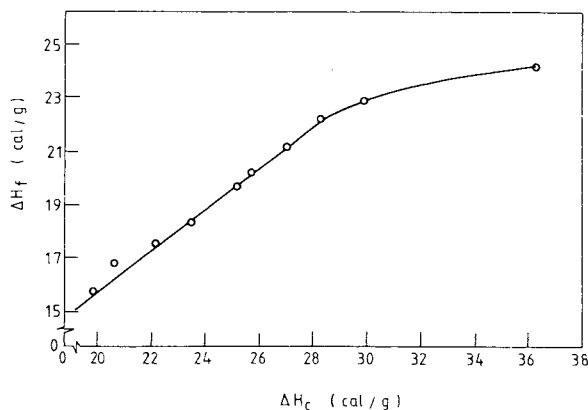

Fig. 9.   Relation between heat of fusion and heat of crystallization in the grafted fiber.

chains to crystallize and the result is reflected in the heat of crystallization which is higher than heat of fusion for the identical sample.

The melting behavior of the samples shows an increasing trend with the percent graft in the copolymers (Fig. 10). The results are in good agreement with the increasing thermal stability of the fibers. An improvement in the melting temperature of polypropylene fiber by the grafting of vinyl monomers has also been reported by Sundardi.[4]

The variation of crystallinity with the percent graft has been presented in Table II. It may be seen from the results that there is almost no change in the crystallinity of polypropylene fibers grafted with different amounts of PMAA. This indicates that the inherent crystallinity of the backbone polymer, i.e., polypropylene is not influenced by the graft copolymerization of methacrylic acid and the grafting takes place in the noncrystalline region of the fiber. Similar results have been obtained for polyethylene-g-styrene system.[12]

Limiting Oxygen Index (LOI)

The LOI values for PP-g-PMAA fibers have been presented in Figure 11. The LOI increases from 18.1 (for original polypropylene) to 19.6 for the sample with 50% graft content. From the results it appears that as long as the amount of PMAA in the copolymer is low, it does not exert any appreciable effect on the flammability characteristics of polypropylene. However, as the graft content increases and reaches 50%, there is a sharp increase in the LOI values.

TGA studies have shown that the PP-g-PMAA fibers, when heated at 200°C, undergo dehydration reaction to eliminate water molecules from the grafted PMAA chains, resulting in the formation of more stable anhydride rings in the molecule. Hence, this endothermic release of water during ignition may provide a cooling effect on the surface of polymer, and the result is reflected in an increase in LOI of polypropylene fibers. A similar
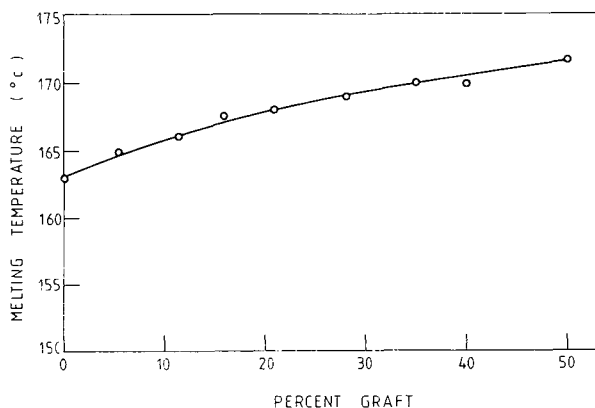

Fig. 10. Variation of melting temperature with percent graft in polypropylene-g-poly(methacrylic acid) fiber.

TABLE II
Crystallinity of Polypropylene-g-Poly(methacrylic Acid) Fibers

Percent graft	Percent crystallinity
Ungrafted PP	48.40
[PP]$_I^a$	48.02
5.5	48.36
11.5	47.36
16.0	46.98
21.0	47.70
28.0	47.06
35.0	47.40
40.0	47.18
50.0	47.20

ᵃ Irradiated PP fiber

effect of water release during the polymer combustion in increasing LOI has been shown in several systems.[20,21]

CONCLUSIONS

The graft copolymerization of methacrylic acid onto polypropylene fibers does not influence the heat of fusion and crystallinity of polypropylene in the grafted samples, indicating that the grafting takes place only in the amorphous portion without influencing the crystalline nature of the polymer. The overall thermal stability of polypropylene fiber is increased markedly, by the grafting of methacrylic acid.

LOI values also show an increasing behavior with the increase in graft content in copolymer samples.

It has been proposed that the major contribution to the increase in thermal stability of polypropylene fiber by the grafting of MAA is via a dehydration reaction eliminating water molecules involving carboxyl groups
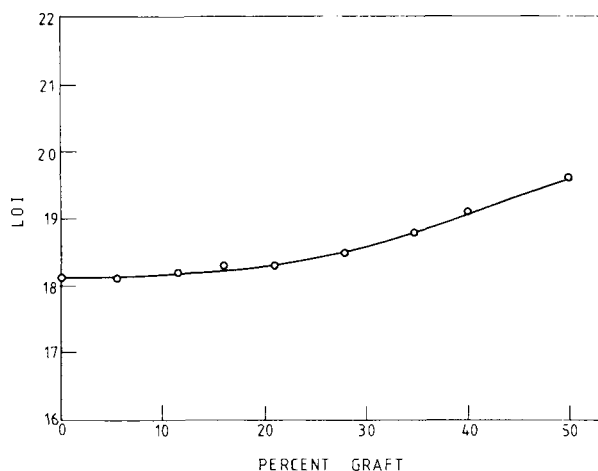

Fig. 11.   Variation of LOI with percent graft in polypropylene-g-poly(methacrylic acid) fiber.

of PMAA grafts which provides a cooling effect to the ignited polymer, thereby increasing LOI. This elimination of water molecules is followed by the formation of more stable polymethacrylic anhydride rings in the macromolecular structure.

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