

# Polyacrylic Acid Grafting Onto Isotactic Polypropylene Fiber: Methods, Characterization, and Properties

S. D. Bhattacharya,<sup>1</sup> M. S. Inamdar<sup>2</sup>

<sup>1</sup>Department of Textile Chemistry, Faculty of Technology and Engineering, The M. S. University of Baroda, Vadodara, 390001, India

<sup>2</sup>Faculty of Textile Processing, Sarvajanic College of Engineering and Technology, Surat, 395001, India

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**ABSTRACT:** The graft copolymerization of acrylic acid onto isotactic polypropylene has been investigated. The grafting was carried out using benzoyl peroxide initiator. Grafting is essentially a surface phenomenon and takes place, mostly, in amorphous region of the fiber. Emphasis, therefore, was placed on various pretreatment techniques for swelling of the fiber, viz, pretreatment with toluene and 1,1'2,2'tetrachloroethane, ultrasound, and photoirradiation. Process parameters, characterization study such as IR spectroscopy, TGA, and DTA, and properties such as tensile properties, melting temperature, dyeability towards basic dyes, and ion exchange properties were investigated. Benzene was found to be the most suitable solvent for initiator as

against the acetone. Tenacity was found to be increased with increase in graft yield and reached to maximum at about 5% graft add-on, and then decreased with further increase in graft add-on. Proportionally, a converse effect was reported in the study of elongation to break. Thermal stability of polypropylene was found to be improved because of grafting. The grafted polypropylene also showed satisfactory dyeability toward basic dyes and also exhibits very good ion exchange properties.

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**Key words:** graft polymerization; polypropylene; polyacrylic acid; methods; chemical; ultrasound; photoirradiation; properties; thermal; tensile; ion exchange; dyeing

## INTRODUCTION

Grafting is a novel technique of imparting several desired properties such as hydrophilicity, dyeability, high wicking speed, soil repellency, antistatic properties, thermal stability, etc to hydrophobic and undyeable polypropylene fibers. It is, indeed, a process of copolymerization producing a polymer that consists of a backbone polymer with large number of small branches of other polymer. For this, various monomers containing anionic, cationic or ester groups can be used to graft onto polypropylene fiber to impart dyeability towards cationic, acid, or disperse dyes.<sup>1–4</sup>

The creation of active sites followed by grafting onto polypropylene can be done mainly by two methods, like *Chemical methods*<sup>5,6</sup> where active sites onto polypropylene can be created by oxidizing it to hydroperoxide, using initiators, at several points along the chain and then allowing to decompose into active sites. Various initiators used are; benzoyl peroxide, hydrogen peroxide, 2,2'-bisazo isobutyronitrile etc. and *Irradiation methods*<sup>5,7,8</sup> where ionizing radiations like  $\gamma$ -rays or high energy electrons interact with polypropylene to produce radical sites. These active sites

permit the attachment of monomer molecules that may grow into short chains.

A great deal of research work has been carried out for the grafting of polypropylene by various methods. Grafting of I.P.P. in solution (homogeneous system) was successfully carried out by Pregararo et al.<sup>9</sup> and Sathe et al.<sup>10</sup> using solvents of different polarity such as *o*-dichlorobenzene and toluene. They reported maximum graft in nonpolar solvent i.e., toluene. Mukharjee<sup>4,11,12</sup> and Mehta<sup>13</sup> employed the irradiation techniques using  $\gamma$ -rays for grafting of I.P.P. with methacrylic acid. They reported increased graft yield and dyeability towards cationic and disperse dyes and improved thermal stability. They reported that *n*-pentanol as a medium gave higher graft yield. Electron beam irradiation technique was employed by Gawish et al.<sup>14</sup> for grafting of I.P.P. with acrylic acid. They were able to obtain up to about 82% graft add-on and moisture regain of about 6.65%. Karmakar and Kulkarni<sup>15</sup> used UV-rich visible light for grafting of polypropylene with various monomers such as acrylic acid, methacrylic acid, acrylamide, and acrylonitrile etc., and studied the effect of sensitizers such as ferric chloride and benzophenone. They showed a significant increase in graft yield on sensitizer pretreated polypropylene fibers. They also reported synergistic effects in case of grafting of mixtures of monomers.

Grafting is, essentially, a surface phenomenon.<sup>16</sup> A large surface area, therefore, must be provided to

Correspondence to: M. S. Inamdar (milindinamdar2001@yahoo.co.in).

access maximum amount of initiator and monomer and hence maximum and uniform swelling of fiber is essential. In our present investigation, therefore, emphasis is placed on the swelling of I.P.P. fiber by various techniques such as toluene, 1,1',2,2'tetrachloroethane, and ultrasound by chemical method of grafting using benzoyl peroxide initiator. In the present work we used both chemical as well as irradiation methods of grafting of I.P.P. to study various properties such as dyeability towards cationic dyes, ion exchange, thermal stability etc.

## MATERIALS AND METHODS

Experiments were carried on Isotactic polypropylene filament yarns (Denier: 210, No. of Filaments: 36; obtained from Sumilon Industries, Surat, India). To remove oil and dirt, polypropylene hank (2 g) was subjected to scouring with nonionic detergent, Lissapol-N (2 gpl) at 90°C for 1 h and then washed thoroughly. It was then oven dried at 80°C, stored in desiccator and weighed accurately. This was named as "Ref. P.P."

### Chemicals

Various chemicals such as monomer, initiator, and solvents used were L.R. grade, freshly procured, and used without further purification in our experiments.

### Grafting technique

Polypropylene hanks (2 g) were given [I] pretreatment with toluene, 1,1',2,2'tetrachloroethane (TCE), ultrasound, and UV-rich visible light respectively, and then subjected to [II] grafting with acrylic acid.

#### Pretreatments

*Chemical pretreatment with: (a) Toluene and (b) TCE.* Ref. P.P. hanks were treated for 2 h with (i) Toluene : Water (20 : 80 v/v) and (ii) TCE : Water (20 : 80 v/v) respectively. The solvents were then removed from hanks completely by treating with boiling water, hydro extracted and then used directly for grafting.

*Pretreatment under ultrasound.* Ref. P.P. hanks were immersed separately in (i) Water, (ii) Toluene, and (iii) TCE contained in stoppered conical glass flasks. These flasks were then placed in a water bath of ultrasound cleaner (freq. 40 kHz; Vibronics, Mumbai, India) for sonication at room temperature for varying sonication times.

The sonicated fibers were then washed thoroughly with nonionic detergent (Lissapol N, 2 gpl) to remove organic solvents. These samples were then used directly for graft copolymerization.

*Photoirradiation of polypropylene fibers.* Ref. P.P. fibers and pretreated polypropylene fibers with toluene : water and TCE : water were exposed to UV-rich visible light obtained from MBTF lamp (500 W) at 60°C for various times. The irradiation was carried out at about 8 in. away from the light source in a closed chamber.

### Grafting (polymerization) procedure

Above pretreated polypropylene filaments hanks were introduced separately into stoppered 150-mL stainless steel pot containing required amount of acrylic acid, benzoyl peroxide, and distilled water. The reaction systems were run at room temperature for 5 min and then placed in thermostatic water bath at 90°C for 4 h, under reflux. The contents were stirred occasionally during grafting.

The optimized recipe is

|  |        |
|--|--------|
| Ref. Polypropylene (g)                                     | 2      |
| Acrylic acid (% owf)                                       | 100    |
| Benzoyl peroxide (Bz <sub>2</sub> O <sub>2</sub> ) (% owf) | 0.3    |
| [Predissolved in benzene, conc. 10%]                       |        |
| Material weight to liquor ratio                            | 1 : 30 |
| Temperature (°C)   | 90     |
| Time (h)   | 4      |

After polymerization, the samples were washed with boiling water for 2 h and rinsed thoroughly with cold running water to remove homopolymer. The washed samples were then oven dried, stored in desiccator, and weighed.

The graft add-on was calculated using formula:

$$\% \text{ Graft add-on} = \frac{W_2 - W_1}{W_1} \times 100$$

where,  $W_1$  = weight of grafted polypropylene fibers,  $W_2$  = weight of Ref. P.P. fibers.

### Determination of tenacity of polypropylene fibers<sup>17</sup>

The tenacity of grafted polypropylene and Ref. P.P. were measured on Stelometer (SITRA, Coimbatore, India). The breaking load (kg) and elongation at break were obtained directly from scale. The samples were then collected and weighed. The tenacity (average of 50 readings) was calculated using following formula.

$$\text{Tenacity} = \frac{\text{Breaking load (kg)} \times 1.5 \times 10}{\text{Sample weight (mg)}}$$

$$\text{Sample length} = 1.5 \text{ cm.}$$

### Dyeing of grafted polypropylene

Grafted polypropylene fibers were dyed with basic dyes, viz, C.I.Basic Blue-16, C.I.Basic Green-1, and C.I.Basic Violet-16 respectively, of 1% shade (o.w.f.) with material to liquor ratio 1 : 50 at 85°C for 60 mins.

**TABLE I**  
Effect of Solvent Concentration in Pretreatment  
Liquor on Graft Yield

| Sr. no. | Pretreatment liquor concentration<br>Solvent : Water | Graft add-on (%)       |                    |
|---------|--|------------------------|--------------------|
|         |  | Toluene : Water system | TCE : Water system |
| 1       | Ref. PP  | 02.30                  | 02.30              |
| 2       | 00 : 100   | 10.41                  | 10.41              |
| 3       | 20 : 80  | 19.45                  | 20.05              |
| 4       | 40 : 60  | 22.65                  | 21.45              |
| 5       | 60 : 40  | 21.33                  | 21.86              |
| 6       | 80 : 20  | 22.74                  | 21.74              |
| 7       | 100 : 00   | 23.58                  | 23.45              |

The pH of the dye bath was maintained to 5.5 using acetic acid. The dyed samples were then taken out, rinsed with fresh water followed by soaping with nonionic detergent (Lissapol N = 2 gpl) at 70°C and rinsed again and air dried.

The K/S value of dyed sample was determined on Spectroscan5100 Computer Color Matching System (Premier Colorscan, Thane, India).

#### Water hardness measurement<sup>18</sup>

This test was used to study the ion exchange capacity of grafted polypropylene. A known volume (50 mL) of water sample was taken in a conical flask. Two mL of ammonia buffer and one to two drops of indicator (Erichrome Black T) were added and titrated against M/50 EDTA solution till wine color of solution turned to blue. The hardness expressed as CaCO<sub>3</sub> PPM was calculated using following formula.

Total hardness

$$= \frac{\text{mL of EDTA solution} \times 10^3}{\text{Volume of sample}} \quad (\text{as CaCO}_3 \text{ ppm})$$

#### Determination of melting temperature of polypropylene fibers

Melting temperature of Ref. P.P. and grafted polypropylene were determined on Kofler Hot Plate (Hem-Tech, Vadodara, India).

#### Infrared spectroscopy

Infra Red Spectra were recorded on Shimadzu FTIR Spectrophotometer (Model: 8300) in the range of wave number 4000–500 cm<sup>-1</sup>.

#### Thermal analysis (TGA and DTA)

TGA and DTA studies were carried out on a T.A. Instrument (Model 5000/2960) thermo balance under nitrogen atmosphere. The test samples were first chopped into powder and then subjected to heating

under nitrogen atmosphere. The heating was carried out at uniform heating rate of 10°C/min starting from room temperature to 700°C.

## RESULTS AND DISCUSSION

### Effect of solvent pretreatment on graft yield

For grafting of acrylic acid on polypropylene fibers (as mentioned in *Experimental* section), various pretreatment baths were prepared using two solvents, namely, toluene and TCE along with polar solvent i.e., water (double distilled) in different compositions, followed by grafting (Table I). It can be seen from results that the Ref. P.P. and polypropylene that pretreated with water alone also show some graft yield. The pretreated fibers with toluene or TCE show substantial increase in graft yield. The increase in concentration solvents above 20 : 80, however, does not seem to have any substantial influence on graft yield.

Owing to the absence of any H-bonding groups and no intermolecular crosslinking, the Ref. P.P. is effectively in a permanently swollen state.<sup>19</sup> This is believed to permit the diffusion of small amount of monomer (along with initiator) and give the graft yield. Efficient grafting can be achieved only if the rate of diffusion of monomer and initiator is greater than the rate of polymerization. The inverse will, however, result into homopolymerization of monomer.<sup>5</sup> Greater extent of swelling can enhance the rate of diffusion of monomer. The swelling efficiency of solvent is characterized by solubility parameter ( $\delta$ ), which should be similar to that of polymer.<sup>20,21</sup> The  $\delta$  value of toluene ( $\delta = 8.9$ ) and TCE ( $\delta = 9.7$ ) are nearer to that of polypropylene ( $\delta = 9.2$ ).<sup>22</sup> Therefore these solvents can easily penetrate into and open up the fiber structure to much greater extent, especially at elevated temperature. This is why it was chosen as pretreatment solvent. This can facilitate the higher diffusion of initiator and monomer into the swollen polypropylene and give maximum graft yield. The swelling of polypropylene can be evidenced from the increased denier because of toluene and TCE treatment (Table II).

Swelling is confined, mostly, to the amorphous region of fiber.<sup>22</sup> Once the utmost swelling of fiber is

**TABLE II**  
Effect of Solvent Pretreatment on Fiber Denier

| Sr. no. | Solvent concentration in pretreatment liquor<br>Solvent : Water | Denier                 |                    |
|---------|---|------------------------|--------------------|
|         |   | Toluene : Water system | TCE : Water system |
| 1       | Ref. PP   | 221.7                  | 221.7              |
| 2       | 00 : 100  | 225.0                  | 225.0              |
| 3       | 20 : 80   | 234.0                  | 240.0              |
| 4       | 40 : 60   | 234.9                  | 232.4              |
| 5       | 60 : 40   | 233.4                  | 232.0              |
| 6       | 80 : 20   | 236.7                  | 232.6              |
| 7       | 100 : 00  | 229.8                  | 225.0              |

**TABLE III**  
Effect of Pretreatment Time on Graft Add-On

| Sr. no. | Pretreatment time (h) | Graft add-on (%)                     |                                  |
|---------|-----------------------|--------------------------------------|----------------------------------|
|         |                       | Toluene : Water system (20 : 80 v/v) | TCE : Water system (20 : 80 v/v) |
| 1       | 0 (Ref. PP)           | 2.3                                  | 2.3                              |
| 2       | 1                     | 16.19                                | 17.20                            |
| 3       | 2                     | 19.45                                | 20.07                            |
| 4       | 3                     | 18.90                                | 19.82                            |
| 5       | 4                     | 17.42                                | 18.84                            |

reached, further increase in concentration of solvent in pretreatment bath will not increase further extent of swelling of fiber and hence also the graft yield.

#### Effect of solvent pretreatment time on graft add-on

At an optimum concentration of pretreatment liquor (i.e., Toluene or TCE : Water, 20 : 80 v/v), the effect of duration of pretreatment on graft yield is shown in Table III. It can be seen that with increase in pretreatment time up to 2 h, the graft yield increases. However, after prolong treatment a slight decrease in graft add-on is anticipated. The increase in graft yield with increase in pretreatment time is believed to be due to increased extent of swelling, which can provide large surface area to access maximum initiator and monomer for grafting. A decline in graft yield in prolong pretreated polypropylene fiber may be due to the partial dissolution of fibers in organic solvents.<sup>20</sup>

#### Effect of solvent used with initiator

The initiator i.e., benzoyl peroxide ( $Bz_2O_2$ ) is added to the polymerization system, usually, in solution form using suitable solvent. The type of solvent used for dissolution of benzoyl peroxide seems to play a very important role in grafting. The graft yields as a function of type of solvent, viz, acetone and benzene, for benzoyl peroxide is shown in Table IV. This table also shows the effect of concentration of monomer i.e., acrylic acid on the graft yield. Here at each concentra-

tion level of monomer, benzene proves to be the most suitable solvent than acetone for benzoyl peroxide. The graft add-on in case of benzoyl peroxide in benzene method increases almost linearly with increase in concentration of monomer i.e., acrylic acid. The graft add-on in case benzoyl peroxide in acetone, however, is very low and anomalous to the concentration of monomer.

The solution of benzoyl peroxide in acetone was added to the polymerization system. Acetone, because of its solubility in water, goes into the solution leaving insoluble benzoyl peroxide dispersed in aqueous system. Therefore, the only few particles of benzoyl peroxide that are in proximity to fiber can create active sites for grafting. This situation may lead to poor graft yield and higher homopolymerization. In case of benzoyl peroxide in benzene system, benzene is believed to act as a carrier for transport of benzoyl peroxide into the fiber matrix. Benzene being immiscible in water does not allow the benzoyl peroxide to spread out in the bulk. The solubility parameter<sup>22</sup> of benzene ( $\delta = 9.2$ ) being very much matching with that of polypropylene ( $\delta = 9.2$ ), they have strong intermolecular forces of attraction. This leads to the diffusion of benzene along with benzoyl peroxide into the swollen polypropylene.<sup>20,21</sup> At elevated temperature, benzene evaporates leaving only benzoyl peroxide in the proximity of fiber molecules that create higher number of active sites on the fiber for graft copolymerization. Use of such water immiscible volatile organic solvents for the dissolution of initiator is mentioned.<sup>15,19,23,24</sup>

#### Effect of initiator concentration on grafting

Initiator, e.g., benzoyl peroxide on dissociation, because of heat or radiation energy, produces free radicals; the number of free radicals generated may directly influence the grafting efficiency. Therefore, the concentration of initiator is believed to play a very important role on the grafting efficiency. Table V shows the influence of benzoyl peroxide concentration on the graft add-on of polyacrylic acid onto polypropylene. Results show Trommsdorff peak at 0.3% benzoyl peroxide concentration for both the systems.

**TABLE IV**  
Effect of Monomer Concentration on Graft Yield

| Concentration of acrylic acid (% owf) | Graft add-on (%)                     |                      |                                  |                      |
|---------------------------------------|--------------------------------------|----------------------|----------------------------------|----------------------|
|                                       | Toluene : Water system 20 : 80 (v/v) |                      | TCE : Water system 20 : 80 (v/v) |                      |
|                                       | $Bz_2O_2$ in Acetone                 | $Bz_2O_2$ in Benzene | $Bz_2O_2$ in Acetone             | $Bz_2O_2$ in Benzene |
| 25                                    | 2.83                                 | 4.73                 | 0.26                             | 5.11                 |
| 50                                    | 3.17                                 | 11.01                | 1.86                             | 13.29                |
| 75                                    | 3.43                                 | 16.21                | 2.98                             | 17.20                |
| 100                                   | 4.04                                 | 19.45                | 1.82                             | 20.07                |
| 125                                   | 2.68                                 | 21.03                | 1.64                             | 24.23                |
| 150                                   | 4.51                                 | 24.40                | 2.27                             | 26.36                |

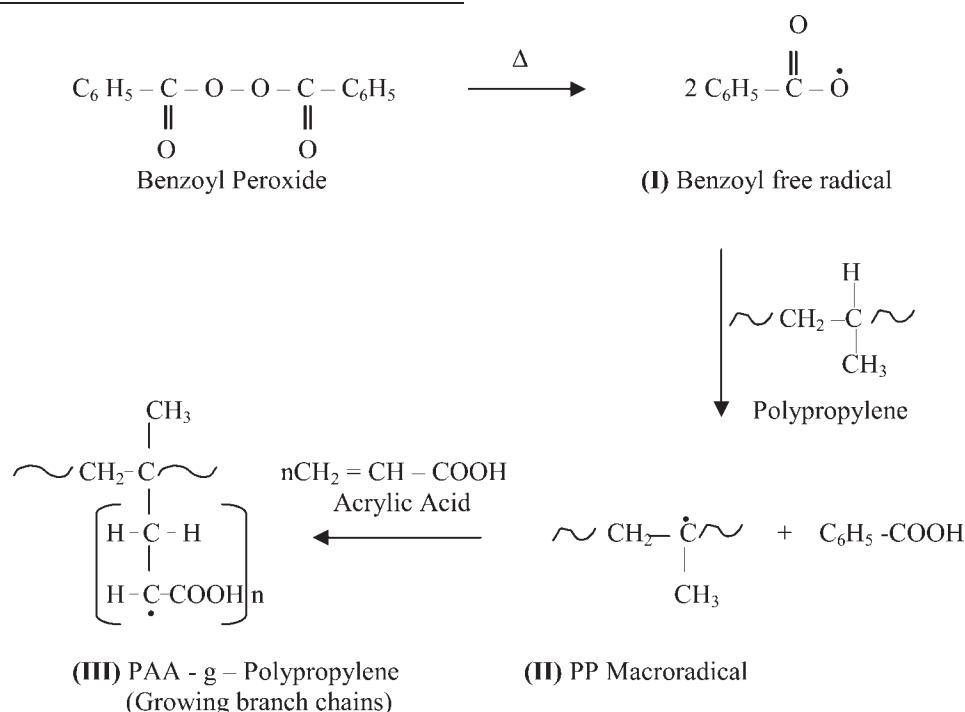
**TABLE V**  
Effect of Initiator Concentration on Grafting

| Concentration of benzoyl peroxide (% w/v) | Graft add-on (%)                     |                                  |
|---|--------------------------------------|----------------------------------|
|   | Toluene : Water system 20 : 80 (v/v) | TCE : Water system 20 : 80 (v/v) |
| 0.1                                       | 12.45                                | 12.32                            |
| 0.2                                       | 15.40                                | 16.48                            |
| 0.3                                       | 19.45                                | 20.07                            |
| 0.4                                       | 19.20                                | 19.81                            |
| 0.5                                       | 18.07                                | 19.34                            |
| 0.6                                       | 18.00                                | 19.10                            |

The increase in percent graft with increase in concentration of initiator in the first stage may be attributed to the increased number of free radicals formed by the decomposition of initiator. The higher the number of free radicals, higher the chain transfer to polymer backbone, so higher will be the graft yield. However at concentration of initiator beyond this peak, the homopolymerization of acrylic acid may be predominant and reduction in graft yield will result. The higher concentration of initiator is also believed to cause termination of growing side chains due to chain transfer resulting into decreased average molecular weight of side chains.<sup>10,15,25</sup> Therefore an attempt has been made to propose the mechanism of such grafting.

### Proposed mechanism

The overall mechanism of graft copolymerization of acrylic acid onto polypropylene can be described in the following four steps.<sup>15,26,27</sup>



### Decomposition of initiator

The free radicals may be produced when initiators such as benzoyl peroxide is decomposed by heat, light, radiations, or electron beam. The initiation of free radical reaction is usually dependent on unimolecular homolytic dissociation of weak bonds by heating or by irradiations.

### Creation of active sites on polypropylene backbone

The free radicals formed, by decomposition of initiator, abstract the labile hydrogen atom from polypropylene macromolecule giving rise to fiber macroradical. In polypropylene, the labile hydrogen from tertiary carbon atom is abstracted.

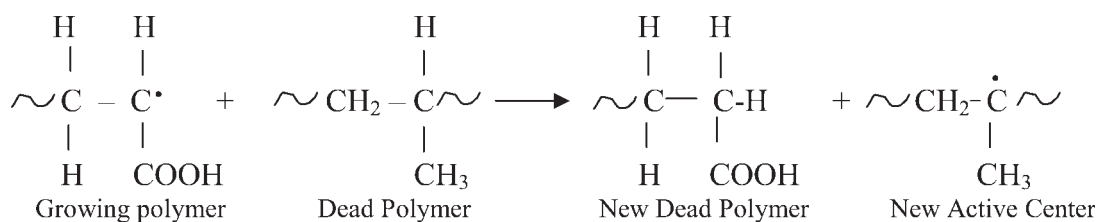
The readiness of hydrogen of tertiary carbon atom of polypropylene for the abstraction by benzoyl free radical may be due to low electron density on this tertiary carbon atom. Mostly due the inductive effect, electrons from tertiary carbon atom are shifted towards adjacent methyl and methylene groups resulting in the decrease in electron density. This may result into weak covalent bond formation between hydrogen and tertiary carbon. Such views were also reported earlier.<sup>28</sup>

### Propagation

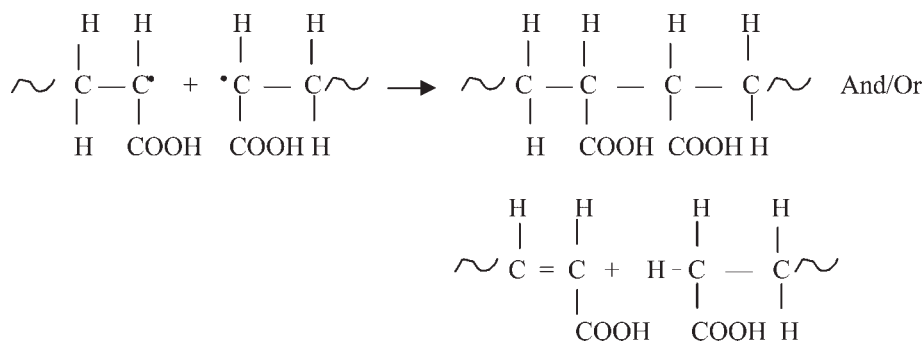
The polypropylene macroradical then reacts with monomer (acrylic acid) and initiates its polymerization and, as a consequence, growing of branches of polyacrylic acid out of the trunk chain of polypropylene takes place.

### Termination

The growing chains may be terminated by a phenomenon known as chain transfer. In this process, the active center abstracts an atom from the same chain



Termination with an inhibition of the radical center and growing polymer chain may also occur by coupling



(backbiting), another chain, monomer or the initiator. The active center on growing chain becomes inactive and a new free radical is produced in each of these chain transfer reactions.

pling with other growing radical and/or by disproportionation.

### Grafting of ultrasound pretreated polypropylene

Ultrasound is the sound with frequency above threshold human hearing i.e. 18 KHz. These are longitudinal waves and propagate in the direction of vibration.<sup>29</sup> Such vibrational energy has been increasingly utilized for dyeing textile fibers.<sup>30-33</sup> No work, however, has been reported where ultrasound can be used as a probable means of grafting. Therefore, an attempt has been made here to graft polyacrylic acid on ultrasound pretreated polypropylene fiber (Table VI).

The results show a maximum graft yield for the fibers sonicated in organic solvents. Sonicated fibers in water require longer time to get satisfactory results. High graft values of polypropylene sonicated in organic solvents may be attributed to the greater pene-

tration of these solvents into the fiber structure causing swelling. Factors such as solubility parameter values of solvents and fiber, intensity of ultrasound, vapor pressure of solvents, and temperature are believed to play vital roles on the efficacy.<sup>30</sup>

### Grafting of photoirradiated polypropylene

Ultraviolet radiation or UV-rich visible light, ionizing radiations like  $\gamma$ -rays and high energy electrons can also be used for grafting of polypropylene. Both simultaneous irradiation and preirradiation methods for grafting of polypropylene have been carried out earlier.<sup>15,34,35</sup>

In case of preirradiation in air method, the grafting of polypropylene is believed to take place through the formation of hydroperoxide at tertiary carbon atom. The formations of free radical sites at tertiary carbon atom through hydroperoxide route have been described.<sup>13,36,37</sup> The proposed mechanism for grafting of photoirradiated polypropylene is summarized as below.

Polypropylene in pure state does not usually absorb light in the spectral region above 3000 Å. However, the processed polypropylene contains traces of impurities, which, in presence of light or heat, permits a polypropylene radical to be formed at tertiary carbon atom.

TABLE VI  
Effect of Sonication Time on Graft Add-On

| Sr. no. | Sonication medium | Sonication time (h) | Graft add-on (%) |
|---------|-------------------|---------------------|------------------|
| 1       | Water             | 0                   | 2.3              |
| 2       | Water             | 3                   | 15.42            |
| 3       | Water             | 4                   | 17.36            |
| 4       | Water             | 5                   | 17.58            |
| 5       | Toluene           | 3                   | 19.95            |
| 6       | TCE               | 3                   | 22.98            |



TABLE VIII  
Effect of Graft Add-On on Tensile Properties of Polypropylene

| Sr. no. | Toluene : Water system (20 : 80) |                  |                         | TCE : Water system (20 : 80) |                  |                         |
|---------|----------------------------------|------------------|-------------------------|------------------------------|------------------|-------------------------|
|         | Graft add-on (%)                 | Tenacity (g/tex) | Elongation at break (%) | Graft add-on (%)             | Tenacity (g/tex) | Elongation at break (%) |
| 1       | 0.00 (Ref. PP)                   | 7.85             | 23                      | 0.00 (Ref. PP)               | 7.85             | 23                      |
| 2       | 2.83                             | 8.16             | 20                      | 0.26                         | 8.24             | 20                      |
| 3       | 3.17                             | 7.68             | 23                      | 2.98                         | 8.37             | 23                      |
| 4       | 4.04                             | 8.03             | 20                      | 5.11                         | 6.76             | 20                      |
| 5       | 4.73                             | 7.83             | 21                      | 13.29                        | 7.57             | 22                      |
| 6       | 11.01                            | 7.02             | 23                      | 17.20                        | 7.42             | 22                      |
| 7       | 19.45                            | 6.54             | 24                      | 20.07                        | 7.09             | 24                      |
| 8       | 21.03                            | 6.37             | 23                      | 24.23                        | 6.56             | 21                      |
| 9       | 24.40                            | 6.55             | 23                      | 26.36                        | 6.51             | 23                      |

the grafted polymer is essentially an amorphous substance with no regular arrangement.<sup>16</sup> In the case when it is attached to backbone chains constituting inner layers of fiber in sufficient amount, the fiber structure becomes more or less disordered. Therefore, the graft copolymerization by suitable monomer modifies mechanical, thermal and physicochemical properties of polypropylene.

### Tensile properties

The change in tenacity and elongation at break of polypropylene due to polyacrylic acid grafting at different graft yields are shown in Table VIII and in Figure 1. It can be seen that the tenacity and elongation at break change substantially at each level of graft with respect to that of reference polypropylene under a particular pretreatment condition. Tenacity of polypropylene increases gradually and reaches to maximum at about 4–5% graft add-on level, and decreases then after. Conversely, the elongation at breaks drops and attains minimum at about 4–5% graft add-on level and then increases with further increases in graft add-on.

These observations led us to believe that, at lower degree of grafting, crosslinking of polypropylene chain with short chain of polyacrylic acid takes place. This is believed to impart strength but reduces slippages of fiber molecules and also the elongations. In case, when the grafting is carried out in sufficient amount, the fiber structure become more and more disordered and results into decreased strength. The increased elongation at higher graft yield may be attributed to the plasticizer effect of long polyacrylic acid chains. Such views were reported earlier.<sup>7,10,15,16,19,23</sup>

### Effect of grafting on melting temperature of polypropylene

Heating of polymer causes the motion/oscillation of the segments in the molecular chains and those seg-

ments that possess adequate energy will break away from the crystallites and become a part of amorphous region. Thus the term melting point, in the case of polymers, refers to the temperature at which crystallinity disappears. Thus any changes in crystallinity of the fiber are reflected through its melting temperature.<sup>23,38,39</sup>

It can be observed (Table IX) that there is some drop in melting point of grafted polypropylene from that of reference polypropylene. However, the extent of graft add-on does not seem to play any substantial effect on melting temperature.

As the grafting takes place in the amorphous region of the fiber, the increase in graft add-on can change only the apparent crystallinity without affecting the inherent crystallinity of the backbone polypropylene. Mukharji and Gupta<sup>11</sup> have demonstrated this by grafting polypropylene with PMMA by simultaneous irradiation method under inert atmosphere. In this case, however, the grafting of polypropylene with acrylic acid was carried out by chemical method in which benzoyl peroxide was used as initiator. The action of this initiator on polypropylene during the graft copolymerization process seemed to be the most

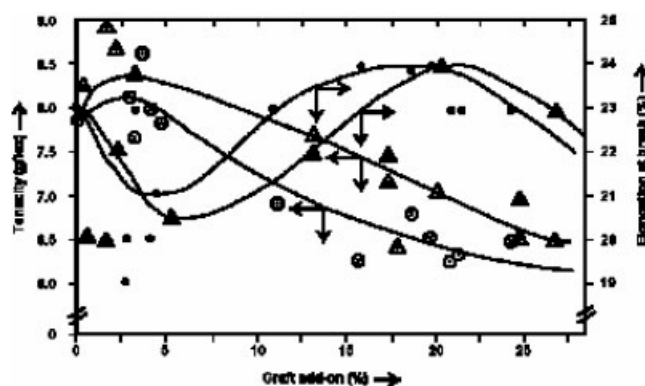


Figure 1 Effect of polyacrylic acid grafting on tenacity and elongation at break of Polypropylene. Tenacity – (○) Toluene : Water system, (Δ) TCE : Water system. Elongation at break – (●) Toluene : Water system, (▲) TCE : Water system.



TABLE IX  
Effect of Grafting Melting Temperature of Polypropylene

| Sr. no. | Toluene : Water system (20 : 80 v/v) |                    | TCE : Water system (20 : 80 v/v) |                    |
|---------|--------------------------------------|--------------------|----------------------------------|--------------------|
|         | Graft add-on (%)                     | Melting temp. (°C) | Graft add-on (%)                 | Melting temp. (°C) |
| 1       | 0.00 (Ref. PP)                       | 168–170            | 0.00 (Ref. PP)                   | 168–170            |
| 2       | 4.73                                 | 161–164            | 5.11                             | 161–164            |
| 3       | 11.01                                | 161–166            | 13.29                            | 161–166            |
| 4       | 16.02                                | 160–163            | 17.2                             | 160–163            |
| 5       | 19.45                                | 160–162            | 19.85                            | 160–162            |
| 6       | 21.03                                | 161–164            | 24.23                            | 161–164            |
| 7       | 24.40                                | 162–164            | 26.36                            | 162–164            |

Measured on Kofler hot plate.

probable cause for decrease in melting temperature of grafted polypropylene. The possibility of chain scission in polypropylene backbone due to oxidative degradation by benzoyl peroxide during polymerization may be very high. It was also presumed by Sundardi<sup>40</sup> that the radical, generated during initiation step mostly locate for longer time at boundaries of crystalline region. Because of this reason it may be possible that the oxidative degradation occurs at the boundaries of crystallites resulting into decreased crystallinity. Thus the possible oxidative degradation occurred at crystalline boundaries and the less crystal perfection due to grafting may be presumed to be main cause for decreased melting temperature of polyacrylic acid-grafted polypropylene.

Owing to the same concentration of benzoyl peroxide used in grafting reactions for all concentrations of acrylic acid, the extent of oxidative degradation of polypropylene at amorphous-crystalline interphase may possibly remain constant. Thus, it is the benzoyl peroxide (and its concentration) and not the graft yields that alter the melting temperature of polypropylene. Oxidative degradation of polypropylene has been reported earlier.<sup>19,36,37</sup>

#### Properties of ultrasound-aided polyacrylic acid-grafted polypropylene

Ultrasound energy can cause intermolecular tearing, surface scrubbing, polymer degradation etc.<sup>30,41</sup> With this idea in mind, we studied various properties such

as tensile properties and melting temperature of ultrasound aided polyacrylic acid-grafted polypropylene (Table X). It can be seen that the tenacity of polypropylene sonicated in water medium decreased by about one unit with respect to Ref. P.P. With increase in sonication time to 5 h, the tenacity decreases only slightly. The tenacity of sonicated polypropylene in toluene and TCE decreases to somewhat higher extent. In all these cases, tenacity is reduced after grafting the sonicated polypropylene fibers. The melting points of sonicated polypropylene are almost unchanged as compared to that of reference polypropylene. The sonication time and type of medium do not show any influence on melting temperature. However, there is a substantial drop in melting temperature of polypropylene after grafting. The melting temperatures are almost similar after grafting, irrespective of sonication time and graft yield.

The decreased tenacity of polypropylene during sonication may be attributed to the intermolecular tearing or rupture occurred as a result of high frequency shocks. The type of solvent medium used also seems to play the important role. The solvents that have similar solubility parameters ( $\delta$ ) (e.g., toluene and TCE) to that of polypropylene can penetrate into and open-up the fiber structure to greater extent under ultrasound vibrations and also may cause intermolecular rupture in the polymer backbone.

The mechanism of degradation of polymer under ultrasound can briefly be described as the polymer

TABLE X  
Tenacity and Melting Point of Ultrasound Aided Grafted Polypropylene

| Sr. no. | Sonication medium | Sonication time (h) | Graft add-on (%) | Tenacity (g/tex) (EAB, %)* |                | Melting temp. (°C) |                |
|---------|-------------------|---------------------|------------------|----------------------------|----------------|--------------------|----------------|
|         |                   |                     |                  | Before grafting            | After grafting | Before grafting    | After grafting |
| 1       | (Ref. PP)         | –                   | 2.3              | 7.851(23)*                 | 9.22(20)       | 168–170            | 162–164        |
| 2       | Water             | 3                   | 15.42            | 6.87(23)                   | 6.35(23)       | 167–169            | 161–164        |
| 3       | Water             | 4                   | 17.36            | 6.67(23)                   | 6.36(24)       | 166–170            | 161–163        |
| 4       | Water             | 5                   | 17.58            | 6.68(23)                   | 6.29(23)       | 166–169            | 160–164        |
| 5       | Toluene           | 3                   | 19.95            | 6.51(24)                   | 6.05(22)       | 165–169            | 160–163        |
| 6       | TCE               | 3                   | 22.98            | 6.23(24)                   | 6.06(21)       | 165–168            | 162–165        |

\*Values inside parentheses indicate elongation at break abbreviated as EAB.

TABLE XI  
Tenacity and Melting Point as a Function of Photoinduced Grafting

| Sr. no. | Pretreatment    | Irradiation time (h) | Graft add-on (%) | Tenacity (g/tex) (EAB, %) |                | Melting Temp. (°C) |                |
|---------|-----------------|----------------------|------------------|---------------------------|----------------|--------------------|----------------|
|         |                 |                      |                  | Before grafting           | After grafting | Before grafting    | After grafting |
| 1       | Ref. PP         | 0                    | 2.3              | 7.851(23)                 | 9.23(20)       | 168–170            | 162–164        |
| 2       | Ref. PP         | 2                    | 12.22            | 7.55(23)                  | 7.03(23)       | 167–170            | 161–163        |
| 3       | Ref. PP         | 4                    | 13.54            | 7.11(22)                  | 6.74(23)       | 167–168            | 161–164        |
| 4       | Ref. PP         | 6                    | 15.65            | 5.18(8)                   | 5.11(10)       | 165–169            | 158–162        |
| 5       | Ref. PP         | 8                    | 16.75            | 5.12(8)                   | 5.03(8)        | 166–168            | 157–162        |
| 6       | Toluene : Water | 4                    | 20.3             | 7.25(23)                  | 6.63(22)       | 166–169            | 160–164        |
| 7       | TCE : Water     | 4                    | 21.39            | 7.41(22)                  | 6.39(22)       | 165–169            | 160–163        |

chains being caught in the rapid flow of solvent molecules caused by the collapse of cavitations bubbles. A second cause of solvent movement is the shock waves generated after the implosion of the bubbles. The chains are thus subjected to extremely large shear forces resulting in stretching of the chain and if force is sufficiently large, breakage of bond in the chain occurs.<sup>30</sup> Price and Smith<sup>42</sup> have reported the effect of ultrasound on polymer degradations in terms decrease in molecular weight.

The decreased tensile strength after grafting may be attributed to the structural disorder caused by the high graft yield, discussed earlier in toluene : water and T.C.E. : water methods.

Almost no change in melting point of polypropylene after sonication indicates the degradation of polymer may occur only in amorphous region and keeping the crystalline region intact. Substantial drop in melting point of polypropylene after grafting of sonicated fibers may, once again, be attributed to the oxidative degradation of polypropylene backbone during initiation step of graft copolymerization.

#### Properties of photoinitiated polyacrylic acid-grafted polypropylene

It has been known for long time that polypropylene is least resistant to sunlight or UV-rich light of all common fibers.<sup>7,15,16,36</sup> It may, therefore, be possible that tensile properties and crystallinity of polypropylene alter due to photoinduced grafting. Relevant properties such as tenacity and melting point as a function of photoinduced graft, therefore, are studied in our experiment (Table XI). It can be seen that the tenacity of photoirradiated polypropylene with respect to original polypropylene changes with change in irradiation time. There is slight decrease in strength up to 4 h. exposure and a substantial deterioration then after. The elongation at break also decreases on prolong exposure. The strength still decreases after grafting these preirradiated polypropylene fibers. The melting point of photoirradiated polypropylene fibers are not much changed up to 4 h exposures, only a slight drop in

melting temperature noticed on longer exposure. The melting temperature, however, decreases significantly after grafting these photoirradiated samples.

The deterioration in strength of photoirradiated polypropylene may be due to photo oxidative degradation i.e., photolysis. The resistance of polypropylene to photo oxidation in the comparatively shorter period may be conferred to the stabilizing action of photo stabilizer incorporated during fiber manufacturing. Supporting results are reported earlier by Pajgrt,<sup>16</sup> Nito et al.<sup>35</sup> and Wishman and Haggler.<sup>36</sup> The deterioration in strength after grafting, as discussed earlier, may be due to the structural disorder in polypropylene backbone caused by grafted polyacrylic acid.

No significant alteration in melting temperature of photoirradiated polypropylene suggests the photo oxidation degradation of polypropylene occurs mostly in amorphous region. Nevertheless, a slight degradation in crystalline region due to photo oxidation may be possible on prolong exposure, as is reflected by a slight change in melting temperature. A substantial drop in melting temperature of photoirradiated PAA-grafted polypropylene, here also, may be regarded to the oxidative degradation due to decomposition of benzoyl peroxide during initiation step of graft copolymerization. The mechanism for photo oxidative degradation is discussed elsewhere.<sup>16,36,37</sup>

#### Ion exchange properties of acrylic acid-grafted polypropylene

The grafts of monomers bearing anionic functional groups such as carboxylates are capable of reacting with different cations. Thus the grafted polypropylene fibers are expected to act as ion exchanges.<sup>19</sup>

Owing to the rapid and complete dissociation of sodium carboxylates than that of parent carboxylic acid grown on acrylic acid-grafted polypropylene, the fibers were first neutralized with 1% sodium hydroxide solution at room temperature for 1 h. The alkali-treated fibers were washed thoroughly with distilled water until the wash liquor showed neutral to pH paper. Then exactly 1 g of above alkali-treated fiber sam-

**TABLE XII**  
**Ion Exchange/Chelation Capacity of Grafted Polypropylene (Tol : Water System)**

| Sr. no. | Graft add-on (%) | Hardness of water (ppm) | Decrease in hardness (ppm) |
|---------|------------------|-------------------------|----------------------------|
| 1       | Initial Bath     | 474                     | —                          |
| 2       | Ref. PP          | 477                     | —                          |
| 3       | 5.03             | 454                     | 20                         |
| 4       | 18.3             | 440                     | 34                         |
| 5       | 29.8             | 410                     | 64                         |

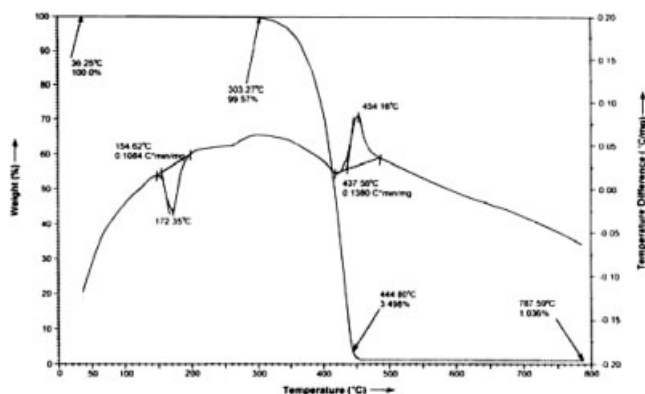
ple was immersed in 100 mL water of known hardness and kept for 24 h. The hardness of water was then estimated. The absorption of  $\text{Ca}^{2+}$  ions (i.e., reduction in hardness of water) by grafted polypropylene of different add-on is shown in Table XII.

The results show that with increase in graft add-on, the hardness of water decreased. It was 64-ppm decrease in hardness by 29.8% graft add-on sample. This value corresponds to 6.4 mg equiv/g of fiber. This value is sufficiently high for a normal ion exchanger.<sup>43</sup> The ion absorption onto solid ion exchanger is generally considered to involve liquid-solid phase reaction. The ions first diffuse through the solid solution to the surface of solid absorbent, followed by diffusion of ions within the solid phase. Then the chemical reaction between ion and functional groups takes place and finally the exchanged ions diffuse to surface of the absorptions and to the solution.<sup>44</sup> Further, the carboxylate groups on grafted polypropylene can also be converted in to chelating functional fibers by reactions with various amines. Development of such ion exchangers may find many applications in waste management systems.<sup>45,46</sup>

## CHARACTERIZATION

### IR spectroscopy

The chemical groups inserted through grafting envisaged by IR spectroscopy analysis. As in all grafting



**Figure 2** TGA-DTA thermograms of reference polypropylene.

processes polyacrylic acid is grafted on different pre-treated polypropylene fibers, the chemical changes expected to be the same. The IR spectrum of grafted polypropylene shows following changes from that of IR spectrum of reference polypropylene:

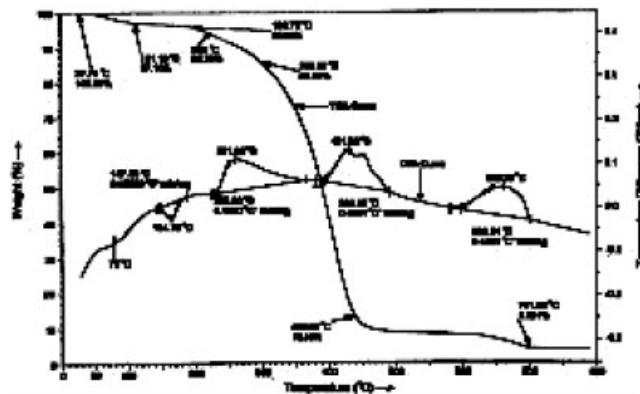
- Appearance of peak at wave number  $1750\text{--}1700\text{ cm}^{-1}$  may be attributed to the carbonyl group.<sup>10,11</sup>
- Broadening of peak at wave number  $2920\text{ cm}^{-1}$  indicates the diminishing of C-H bond at tertiary carbon atom.<sup>47</sup>
- Twin peaks at wave number  $2350\text{ cm}^{-1}$  and  $2330\text{ cm}^{-1}$ , which are characteristics of carbon-carbon double bonds ( $\text{--C=C--}$ ).<sup>39</sup>

These observations indicate the introduction of polyacrylic acid as a graft onto polypropylene with attachment at tertiary carbon atom. The presence of double bond indicates that the chain transfer to monomer is taking place and causing the termination with the end group containing double bond.

### Thermo gravimetric analysis (TGA)

Usually any chemical modifications including grafting are believed to alter the thermal stability of polymer. Mostly monomers containing carboxylic acid groups e.g., acrylic acid, methacrylic acid etc. or anhydrides are believed to improve the thermal stability of polymer after grafting.<sup>11,13,40</sup> With this idea in mind, we conducted a study on thermal behavior of polyacrylic acid-grafted polypropylene by thermogravimetric analysis.

Thermograms of reference polypropylene and polyacrylic acid-grafted polypropylene at different graft yields are presented in Figures 2 and 3. From these thermograms various inflection points indicating initial decomposition temperature (IDT), integral procedure decomposition temperature (IPDT), the temperature at which the sample under goes 50% decomposition ( $T_{50}$ ) and final decomposition temperature (FDT)



**Figure 3** TGA-DTA thermograms of PAA-grafted PP (Graft add-on 29%).

TABLE XIII  
Thermogravimetric Analysis of Polyacrylic Acid Grafted Polypropylene

| Graft add-on (%) | Inflection 1                 | Inflection 2                 | IDT (°C) | $T_{50}$ (°C) | IPDT (°C) | FDT (°C) | Residue left after complete decomposition (%) |
|------------------|------------------------------|------------------------------|----------|---------------|-----------|----------|---|
|                  | Dehydration temperature (°C) | Cyclization temperature (°C) |          |               |           |          |   |
| O (Ref. PP)      | –                            | –                            | 303.27   | 415           | 444.80    | 450.00   | 1.036   |
| 5.03             | 110.0                        | 204.01                       | 334.66   | 439           | 468.73    | 490.00   | 1.403   |
| 18.3             | 111.1                        | 218.87                       | 331.00   | 420           | 457.78    | 639.56   | 2.377   |
| 29.81            | 111.1                        | 196.79                       | 299.37   | 390           | 439.60    | 701.89   | 3.776   |

i.e., the temperature after which the residue showed a constant weight, were evaluated. These data are presented in Table XIII.

The inflection-1 inflection at about 110°C in thermograms of grafted polypropylene sample (which is absent in that of reference polypropylene) may be due to the removal of free moisture (moisture regain due to carboxylic groups) from the fiber. The absence of this inflection in reference polypropylene indicates the hydrophobicity of polypropylene.

The inflection-2 in thermograms of grafted samples (around 200°C) may be due to the dehydration from polyacrylic acid chains resulting into the formation of cyclic six member anhydride rings. These cyclic anhydrides are believed to impart the thermal stability to the fiber, which is manifested by thermogravimetric indices such as IDT,  $T_{50}$ , IPDT, and FDT values. Beside this cyclization reaction, the improved thermal stability may also be attributed to the abstraction of labile hydrogen atom from tertiary carbon atom of polypropylene followed by grafting of polyacrylic acid at the site generated. This interpretation also confirms introduction of graft at tertiary carbon atom of polypropylene.

However, no significant changes in IDT,  $T_{50}$ , and IPDT values of polypropylene at very high value i.e., 29.8% indicate no alteration in fiber backbone. The reason may be, the higher viscosity of liquid (due to homopolymerization) at higher monomer concentration of monomer and also certain amount of graft formation acting as diffusion barrier lead to the grafting confined mostly to surface without deep penetration into the fiber matrix.<sup>15</sup>

The TGA thermograms also indicate a progressive increase in FDT and the residue left after maximum decomposition. This, once again, may be attributed to

the existence of more thermally stable polyacrylic acid on polypropylene backbone.

### Differential Thermal analysis (DTA)

Differential Thermal Analysis method is well suited for studying the process that brings about changes in inner structure of polymer by analyzing various endothermic and exothermic peaks. Usually inflection points and endothermic peaks refer to transition points such as glass transition temperature ( $T_g$ ) and melting point ( $T_m$ ). Whereas, exothermic peaks refer to decomposition reactions.<sup>6,48</sup> DTA curves for reference polypropylene and polyacrylic acid-grafted polypropylene are shown in Figures 2 and 3. The temperature at inflections and various endothermic and exothermic peaks so evaluated from above DTA curves are summarized in Table XIV.

The inflection point at about 78°C for higher graft yields indicates the  $T_g$  of polyacrylic acid-grafted on polypropylene, which closely corresponds to the  $T_g$  value of polyacrylic acid earlier determined by Klein and Heitzmann<sup>49</sup> by DTA method. Such inflections are absent in parent polypropylene ( $T_{gpp} = -15^\circ\text{C}$ ).<sup>36</sup> The indication of  $T_g$  of polyacrylic acid at higher graft yields (i.e., above 18%) led us to assume that the polyacrylic acid chains grow out of polypropylene backbone independently even though they are attached to polypropylene backbone by covalent bonds.

The endothermic peaks (161–172°C) correspond to the melting temperatures of grafted and ungrafted polypropylene. These results agree with the melting temperatures determined earlier by Kofler Hot Stage method.

The exothermic peaks may be categorized in to three-temperature zones. The peaks in the first zone

TABLE XIV  
Differential Thermal Analysis of Polyacrylic Acid Grafted Polypropylene

| Graft add-on (%) | Inflection point (°C) | Endothermic peak (°C) | Exothermic peak (°C) |        |        |
|------------------|-----------------------|-----------------------|----------------------|--------|--------|
|                  |                       |                       | 1                    | 2      | 3      |
| O (Ref. PP)      | –                     | 172.32                | –                    | 454.16 | –      |
| 5.03             | –                     | 162.39                | 222.00               | 477.12 | –      |
| 18.3             | 78                    | 161.08                | 251.09               | 477.60 | –      |
| 29.81            | 79                    | 164.70                | 261.04               | 431.29 | 662.39 |

TABLE XV  
Dyeability of Polyacrylic Acid Grafted Polypropylene

| Sr. no. | Sample  | Graft add-on (%) | K/S values           |                    |                    |
|---------|---|------------------|----------------------|--------------------|--------------------|
|         |   |                  | C.I. Basic Violet-16 | C.I. Basic Blue-16 | C.I. Basic Green-1 |
| 1       | Ref. PP   | –                | 1.8224               | 4.5025             | 1.9755             |
| 2       | Grafted PP (Tol. : Water System)                  | 5.05             | 30.8341              | 21.7987            | 31.9023            |
| 3       | Grafted PP (Tol. : Water System)                  | 18.3             | 30.0254              | 22.0629            | 28.2825            |
| 4       | Grafted PP (TCE. : Water System)                  | 19.21            | 31.4059              | 23.7573            | 33.0352            |
| 5       | Photoinduced Grafted PP (Tol.Pretreated)          | 22.3             | 32.8914              | 23.7741            | 32.1162            |
| 6       | Photoinduced Grafted PP (TCE Pretreated)          | 21.39            | 32.1734              | 22.8216            | 26.3614            |
| 7       | Grafted PP Ultrasound pretreated (Water medium)   | 18.41            | 27.4009              | 21.8050            | 32.5844            |
| 8       | Grafted PP Ultrasound pretreated (Toluene medium) | 19.41            | 29.9684              | 21.4610            | 32.4628            |
| 9       | Grafted PP Ultrasound pretreated (TCE medium)     | 22.98            | 30.2997              | 22.1018            | 30.7503            |
| 10      | CDPET   | –                | 28.7051              | 20.3047            | 26.6328            |

(i.e. 222°C–261.04°C) in the DTA of grafted samples may represent the dehydrations from polyacrylic acid. The area under this curve corresponds to amount of dehydration,<sup>6</sup> which increases with increase in graft add-on. The absence of exothermic peak in the first temperature zone of reference polypropylene and the presence of that in grafted polypropylene support the assumption of introduction of carboxylic groups, due to grafting, onto the polypropylene fiber. The exothermic peaks in the second temperature zone (i.e. 431–477°C) may be correlated to IPDT in TGA study i.e., decomposition of polypropylene backbone or in other words its thermal stability. Here, thermal stability increases up to 18.3% graft yield, which supports the presumption of modification in polypropylene backbone structure by abstracting labile hydrogen from tertiary carbon atom and introduction of new moiety i.e., polyacrylic acid. In case no improvement in thermal stability of polypropylene backbone at 29.8% graft yield may be attributed to the grafting being confined mostly onto surface with the result that the parent polypropylene backbone remains intact. So at higher yield the polyacrylic acid-grafted polypropylene behaves as a two-phase material. This assumption is also supported by a peak observed in third zone (at 662.39°C), which may be related to the decomposition of polyacrylic acid. The occurrence of third peak also supports the increased FDT. Earlier studies conducted by Mehta et al.<sup>13</sup> and Sundardi et al.<sup>39</sup> in this regard support our observations.

#### Dyeing properties of polyacrylic acid-grafted polypropylene

Presuming the introduction of anionic carboxylic groups of polyacrylic acid into the polypropylene fiber by means of grafting, dyeability towards basic dyes is expected. The dyeing results evaluated in terms of K/S values of grafted polypropylene in comparison with CDPET (which are also dyed with basic dyes) are presented in Table XV.

Table XV shows the excellent dyeability of grafted polypropylene towards basic dyes, irrespective of the pretreatment method used. The commercial dyeing of polypropylene can be obtained in full depth when grafted at about 5% graft add-on. The results are very much comparable to that with CDPET fibers.

#### CONCLUSIONS

Chemical modification of polypropylene through grafting offers an effective means for introducing some desirable properties into polymer without adversely affecting the nature of polymer backbone. The following conclusions may be drawn from the present investigation.

- i. Irrespective of the method used, the extent of swelling seems to play a vital role on the efficiency of grafting. Choice of proper swelling agent is an important criterion. Pretreatment of polypropylene with either toluene or TCE have similar effects on graft yields. However, TCE has the advantage of fire safety.
- ii. Ultrasound aided grafting can be a promising technique and the results obtained are quite satisfactory and comparable. Moreover, the electrical energy involved in producing the ultra sonic effects is relatively low, the technique is energy efficient. In this method also, choice of proper sonication medium is most important. TCE is most suitable and safe while water requires longer sonication time.

In case of photoirradiation method, preswollen fibers give comparable results. Detailed studies in this area are still in progress.

- iii. Grafting efficiency and its reproducibility is highly dependant on process parameters. That is finalized as mentioned in the text. Benzene is found to be an effective solvent studied for initiator, benzoyl peroxide. This seems to be a good carrier to bring the initiator deep into the

fiber matrix due to the similar solubility parameter to that of polypropylene. Also, due to low boiling point (80.10°C), its removal from the fiber at polymerization temperature is easy.

- iv. Excessive increased concentration of monomer and reaction time shows a level-off type curves while the initiator concentration curve shows Tromonsdorff peak at 0.3%.
- v. The introduction of carboxyl groups and attachment of polyacrylic acid at tertiary carbon atom are confirmed through IR spectroscopy.
- vi. Various properties of polypropylene are found to be changed due to grafting. The tenacity is increased at low graft add-on (4–5%) and then decreased at higher graft add-on. The decrease in tenacity due to grafting up to about 20% add-on, however, is still in tolerable limit as compared to ungrafted polypropylene. Therefore the grafting can safely be carried out up to 20% graft add-on.

Thermal stability of polypropylene fiber as studied by TGA/DTA is found to be increased markedly because of grafting with acrylic acid. The reason is well described. This study also reveals the system at high graft yield behaves as a two phase material. The melting temperature of PAA-grafted polypropylene, however, is dropped, which may be due to the oxidative degradation of polypropylene by initiator.

Polyacrylic acid-grafted polypropylene is found to exhibit ion exchange property due to presence of carboxyl groups of acrylic acid. The grafted polypropylene fibers (about 30% graft add-on) may replace conventional styrene based on exchange resins. The fibrous ion exchanger is believed to be more efficient due to higher surface area.

The polyacrylic acid-grafted polypropylene shows excellent dyeability toward cationic dyes even at low add-on such as 4–5%.

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