

# Use of Sulfonation Procedure for the Development of Thermally Stabilized Isotactic Polypropylene Fibers Prior to Carbonization

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**ABSTRACT:** Thermally stabilized isotactic polypropylene fibers were developed using sulfonation procedure prior to carbonization stage. Sulfonation was performed to make the fibers infusible, intractable, and insoluble with concentrated sulfuric acid (approx. 95–97% conc.) at a temperature of 120°C for sulfonation times ranging from 0.5 to 8 h. Sulfonation results in highly crosslinked structures which are thermally stabilized thus making the structure suitable to withstand the high temperatures involved in the carbonization stages. Structural characterization of sulfonated polypropylene fiber was carried out using combination of elemental analysis, differential scanning

calorimetry, thermogravimetric analysis, and infra-red spectroscopy techniques with the aim of following the structural developments at a molecular level. Precursor fibers sulfonated for sulfonation times of 6 h or longer retained up to 46% of their mass at 1000°C. DSC and IR-spectroscopy observations indicate the gradual loss of isotacticity and crystallinity with the progress of sulfonation treatment. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 123: 234–245, 2012

**Key words:** isotactic polypropylene fiber; sulfonation; crystallinity; DSC; TGA; IR-spectroscopy

## INTRODUCTION

Due to the green house effect and continuously decreasing world energy sources, humankind is pursuing alternative energy sources. Renewable energy which is produced from natural resources such as sunlight, wind, rain, tides, and geothermal heat<sup>1</sup> became popular in the last decade or so in developed countries. In particular, wind energy is becoming more and more popular in the developed world due to its low maintenance costs. The necessity to use lightweight wind-turbine blades became evident for producing low cost electricity. Carbon fiber reinforced composites became the ideal choice for this kind of applications due to its light weight nature and durability under hostile atmospheric conditions.

There is also a greater need for the passenger vehicles and airplanes to increase fuel efficiency by reducing fuel consumption with the intention of reducing harmful greenhouse gases released into the atmosphere. Use of structural components made of carbon composites results in weight savings of up to

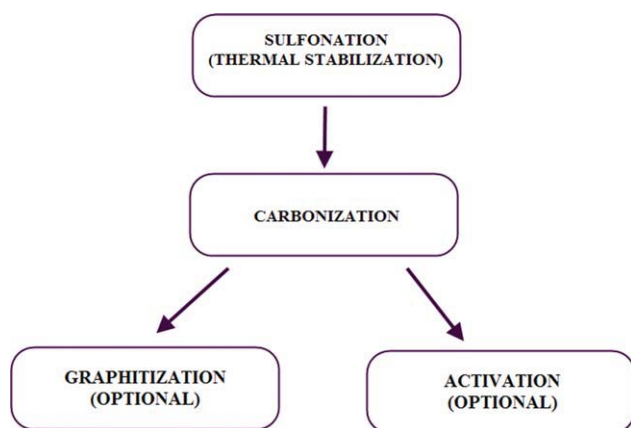
50% in comparison with steel components and are 30% lighter than aluminum components.<sup>2</sup> German car maker BMW<sup>®</sup> has announced plans to use carbon fiber composites for its first series production electric car scheduled for launch in 2013.<sup>2</sup>

According to the automobile industry experts, every 10% reduction in vehicle weight yields about 5% increase in fuel economy.<sup>3</sup> This means that every 50% weight reduction corresponds to 25% fuel economy. The reduction in weight can only become the real possibility if much lighter, stiffer, and corrosion resistant carbon reinforced composites are used instead of heavier metal structures. The trend in the use of renewable energy sources and the necessity to use lightweight land and air transportation systems necessitates the use of much more reliable carbon fiber composites. In particular, the latest models of Airbus<sup>®</sup> A380 and Boeing<sup>®</sup> B787 passenger planes are reported to be using significant proportions of carbon fiber reinforced composites.<sup>4</sup>

At present, commercial carbon fibers are produced from viscose rayon,<sup>5</sup> mesophase pitch,<sup>6</sup> and polyacrylonitrile.<sup>7</sup> High-strength carbon fibers are generally based on polyacrylonitrile, whereas high modulus carbon fibers are produced from mesophase pitch. Due to its low mechanical performance, viscose rayon based carbon fiber has a small share of the market and is mainly used for the activated carbon fiber manufacture. Potential precursor fibers such as Kevlar<sup>®</sup> (poly(*p*-phenylene terephthalamide)),<sup>8</sup>

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**Figure 1** The main production stages of graphitized or activated carbon fiber. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

chitosan,<sup>9</sup> Zylon<sup>®</sup> (poly(*p*-phenylene 2,6-benzobisoxazole),<sup>10</sup> PBZT (poly(*p*-phenylene benzobisthiazole),<sup>11</sup> Saran<sup>®</sup> (polyvinylene chloride-polyvinyl chloride copolymer),<sup>12</sup> PVA (polyvinylalcohol),<sup>13</sup> PBI (polybenzimidazole),<sup>14</sup> polystyrene,<sup>15</sup> and PE (polyethylene)<sup>16–21</sup> based carbon fibers were produced for scientific interest only but never succeeded commercially.

Postema and coworkers<sup>19</sup> produced carbon fiber from linear low density polyethylene by thermally stabilizing with chlorosulfonic acid. In this way, amorphous carbon fibers with a tensile strength of 1.15 GPa, extension at break of 3%, and elastic modulus of 60 GPa were produced.

In a series of publications<sup>16–18</sup> researchers at the University of Tennessee reported the production of carbon fibers from thermally stabilized commercially available gel-spun polyethylene fibers. These investigators obtained carbon fibers with an elastic modulus of 210 GPa and a tensile strength of 2.1 GPa.<sup>16</sup> Horikiri and coworkers<sup>21</sup> suggested the use of concentrated sulfuric acid, chlorosulfonic acid, or fuming sulfuric acid for the thermal stabilization of polyethylene and the temperature of at least 1000°C for the carbonization stage. They claimed that for good mechanical properties, the carbonization temperature should be at least 1200°C. It is reported that the mechanical properties of carbon fibers produced from low density polyethylene fiber can be strongly dependent on the fiber diameter.<sup>20</sup> These investigators showed that isotropic carbon fibers with a diameter of 13 μm having tensile strength of 2.16 GPa and elastic modulus of 148 GPa could be produced.

In the present investigation, in the search for a low cost alternative precursor material, melt-extruded isotactic polypropylene fiber is suggested as one of the most suitable carbon fiber precursors, due to its high carbon content, commercial availability, relatively low cost, recyclability, and easy processability. According to the latest published figures,<sup>22</sup> the latest polyolefin production in 2009 reached 2.6 million tons

per annum for filaments and staple fibers. This figure is very much higher than the annual production rate of polyacrylonitrile fibers. By the end of 2009, acrylic production of filaments and staples stood at 1.9 million tons per annum.<sup>22</sup>

Polypropylene can easily compete and complement the production of carbon fibers manufactured from PAN, mesophase pitch, and viscose rayon precursors. Carbon fiber production involves thermal stabilization followed by carbonization and optional activation or graphitization (Fig. 1) stages.<sup>5</sup> In the case of polyolefin fibers, especially, with polypropylene fibers, sulfonation treatment with highly concentrated sulfuric acid or fuming sulfuric acid is the most suitable choice for achieving a thermally stable structure prior to the carbonization stage.

Sulfonation, one of the most common surface modification methods, has been commonly used for the thermal stabilization of polyolefins to produce insoluble, infusible, intractable, and crosslinked structure. Surface sulfonation of polyolefins has been usually performed using highly concentrated sulfuric acid,<sup>23–28</sup> fuming sulfuric acid,<sup>29–31</sup> sulfonyl chloride,<sup>32</sup> chlorosulfonic acid,<sup>19–21,33–36</sup> dry gaseous mixture of sulfur trioxide and chloride,<sup>37</sup> mixture of sulfur dioxide and oxygen,<sup>38</sup> and solutions of sulfur trioxide in the presence of inert chlorinated hydrocarbon based solvents (i.e., methylene chloride, carbon tetrachloride, perchloroethylene, and ethylene dichloride),<sup>39</sup> gas phase sulfur trioxide in nitrogen.<sup>40</sup>

Apart from crosslinking and thermal stabilization, sulfonation as a surface modification technique has been shown to enhance several surface properties including dyeability,<sup>41–43</sup> adhesion,<sup>40,44,45</sup> wettability,<sup>46,47</sup> metallization,<sup>48</sup> electrostatic charge dissipation,<sup>49</sup> and barrier properties.<sup>50–52</sup> Thermal stabilization is needed to withstand the high temperatures involved in both carbonization and graphitization stages (Fig. 1). Thermally stable precursors can then be easily carbonized in an inert atmosphere at temperatures up to about 1500°C<sup>5</sup>.

The aim of the present investigation is to characterize the structure of sulfonated isotactic polypropylene fiber prior to carbonization using combination of differential scanning calorimetry, thermogravimetric analysis, and infra-red spectroscopy techniques with the ultimate aim of establishing the most suitable conditions for the production of isotactic polypropylene-based high performance carbon fibers.

## EXPERIMENTAL

### Fiber production

The melt spinning of isotactic polypropylene fibers were carried out using Barnag<sup>®</sup> CF spinning machine operating at an extrusion temperature of

235°C with a constant throughput of 9.12 g/min. In the present investigation, extrusion speed of 2500 m/min was employed. Basell Polyolefins isotactic polypropylene granules with a melt flow index of 35 g/10 min, with weight average molecular weight of 179,000 and polydispersity ( $M_w/M_n$ ) of 4.6 were utilized to produce fibers. The melt-extruded filaments were immediately solidified with the assistance of cooling air blow with a speed of 40–70 m/s and a cooling air blow temperature of 18–19°C. During the melt-extrusion stage, a spinneret pressure of 60–70 bar and spinneret hole diameter of 200–400  $\mu\text{m}$  was utilized. Filaments had a trilobal cross-sectional shape. Melt extrusion was performed with environmental conditions having the typical characteristics of 70% relative humidity and 15°C local temperature.

### Sulfonation procedure

Sulfonation of melt-extruded isotactic polypropylene fiber produced with a take-up speed of 2500 m/min was carried out using highly concentrated sulfuric acid (95–97% conc.) at a temperature of 120°C. Sulfonation was performed in a stainless steel heater bath with an electrical resistance controller to vary the temperature up to the desired sulfonation temperature with a heating rate of at least 0.5°C/min. Higher heating rate (i.e., 1°C/min) resulted in a degradation of the sample due to the negative effects of rapid heating. The sulfonation temperature was also externally controlled with an alcohol based thermometer. The samples were wound onto a stainless steel frame with the aim of constraining the samples to prevent shrinkage and subsequently were inserted into the sulfonation bath. The sulfonation bath temperature was then slowly heated to 120°C and kept there for various amounts of times. After the sulfonation treatment for a predetermined time, the samples were taken out, rinsed in three steps by aqueous sulfuric acid solutions with weight percentage of 62.5, 48.5, and 35.5% for 30 min and finally in pure water. The rinsed samples were dried at 120°C for 1–2 h until the weight is constant.

## EXPERIMENTAL DATA COLLECTION

### Thermal analysis

The differential scanning calorimetry (DSC) experiments were carried out using a Perkin–Elmer Diamond DSC system. Typical sample weights used were approximately 5 mg. The heating rate of 10°C/min and an upper temperature range of 250°C were selected. Indium (m.p. 156.6°C and  $\Delta H = 28.45 \text{ J/g}$ ) was used for heat flow calibration. Indium and zinc (m.p. 419.51°C) standards were used for temperature calibration. The specimens were always tested under a nitrogen flow rate of 50 mL/min.

Thermogravimetric analysis (TGA) thermograms were collected using a Perkin–Elmer Diamond thermogravimetric/differential thermal analyzer. Typical sample weights used in the measurements were approximately 4–6 mg. The heating rate of 10°C/min and an upper temperature range of 1150°C were selected. The temperature calibration of TG/DTA was carried out using the melting points of indium (m.p. 156.6°C), tin (m.p. 231.88°C), zinc (419.51°C), aluminum (m.p. 660.1°C), and gold (m.p. 1064.18°C) standards. The weight balance calibration was performed by using a standard weight of 20 mg at room temperature in both systems. Experiments were performed under a nitrogen flow of 200 mL/min. Data from TGA was used in the evaluation of weight loss and percent carbon yield for untreated and sulfonated samples.

### Infra-red spectroscopy measurements

Perkin–Elmer® Spectrum 400 FT-IR spectrometer was employed for infrared measurements using single reflection diamond crystal based GladiATR® model ATR attachment. ATR-IR technique is known to be a surface characterization technique and is known to be sensitive to about a few microns into the surface of the samples. In some cases depth of beam penetration can be as much as 1.66  $\mu\text{m}$  at 1000  $\text{cm}^{-1}$  for diamond ATR crystals and 0.65  $\mu\text{m}$  at 1000  $\text{cm}^{-1}$  for germanium ATR crystals.<sup>53</sup> All the spectra were collected in the mid-IR range (i.e., 4000–400  $\text{cm}^{-1}$ ) at a resolution of 2  $\text{cm}^{-1}$ . In all cases, 50 interferograms of a sample were averaged and transformed with medium Norton–Beer apodization function. Each sample spectrum was ratioed against a corresponding number of background scans using the same instrument settings. Finally, all the spectra were analyzed using the OMNIC software® to obtain accurate peak parameters.

### Determination of gel fraction

The measurement of gel fraction shows the fraction of crosslinked polymer chains insoluble in its own solvent. In the case of isotactic polypropylene, xylene is used as an organic solvent. Sulfonated samples were cut into small pieces and about 100 mg of crosslinked sample was immersed in a boiling xylene (bp 135  $\pm$  2°C) for 12 h. The percentage of the insoluble portion in the original sulfonated sample gave the gel fraction.<sup>54</sup> Gel fraction was measured by using the eq. (1).

$$\% \text{ gel fraction} = \frac{w_2}{w_1} \times 100 \quad (1)$$

where  $w_1$  is the original sample weight (i.e., about 100 mg) and  $w_2$  is the gel weight after extraction with pure xylene.

### Elemental analysis

Chemical elemental analysis for C, H, S, and O was carried out by combustion in a LECO<sup>®</sup> TruSpec Micro Elemental Analyzer. For sulfonated samples high temperature combustion was used as the means of removing the elements from the material. In the process of combustion, the sample was encapsulated in a tin capsule with an average weight of 2 mg. The sample was placed in the sample loading chamber and held there until a dose of oxygen had been released. The sample was then dropped into the furnace. The sample was combusted in the heated oxygen rich environment. Calibration was performed with sulfamethazine for CHNS test and benzoic acid for oxygen test.

### EXPERIMENTAL DATA ANALYSIS

#### Evaluation of DSC crystallinity from melting enthalpy values

Assuming a two-phase model consisting of crystalline and noncrystalline (i.e., amorphous) phase, the degree of DSC crystallinity can be evaluated from the melting enthalpies using the eq. (2)

$$\chi_c = \frac{\Delta H}{\Delta H_m} \times 100 \quad (2)$$

where  $\chi_c$  is the degree of crystallinity evaluated by the DSC method,  $\Delta H$  is the melting enthalpy of the sulfonated sample and  $\Delta H_m$  is the melting enthalpy of 100% crystalline sample and is taken as 165 J/g as published in the literature.<sup>55</sup>

#### Evaluation of aromatization index from differential scanning calorimetry

DSC based aromatization index is evaluated using eq. (3).

$$\text{Aromatization index (\%)} = \frac{\Delta H_o - \Delta H}{\Delta H_o} \quad (3)$$

where  $\Delta H_o$  is the melting enthalpy of pristine sample and  $\Delta H$  is the melting enthalpy of sulfonated sample, respectively.

#### Evaluation of tacticity from IR-spectroscopy measurements

The value of isotacticity has been measured by means of the absorbance ratios of the IR bands at 841, 973, and 998  $\text{cm}^{-1}$ . 973  $\text{cm}^{-1}$  band has been used as an internal standard due to its presence in the IR spectrum of melted polymer.<sup>56</sup> The absorbance ratios examined in the present investigation are  $A_{998}/A_{973}$  and  $A_{841}/A_{973}$ . Assuming the absence of syndiotactic propylene sequences in the polymer

**TABLE I**  
Results from Color Change and Elemental Composition (%) of Untreated and Sulfonated Isotactic Polypropylene Fibers

Sulfonation time (h)	Color change	C (%)	H (%)	O (%)	S (%)
0	White	85.7	14.3	0	0
0.5	Dark Brown	82.4	13.4	4.1	0.1
1	Black	82.0	13.6	3.1	1.3
2	Black	72.8	11.5	12.9	2.8
3	Black	68.0	9.9	17.3	4.8
4	Black	60.0	8.0	26.3	5.7
6	Black	46.6	4.9	40.9	7.6
8	Black	43.6	3.7	46.6	6.1

chain, the tacticity is calculated as the sum of the fraction of isotactic and atactic propylene sequences; hence atacticity is calculated using the eq. (4)

$$\chi_{\text{atacticity}} = 1 - \chi_{\text{isotacticity}} \quad (4)$$

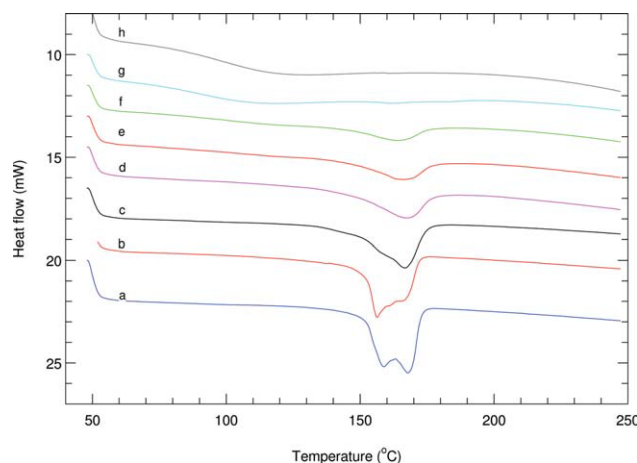
### RESULTS AND DISCUSSION

Isotactic polypropylene fiber was sulfonated with concentrated sulfuric acid at an isothermal temperature of 120°C for various amounts of times under constrained condition to prevent shrinkage and also to prevent loss of molecular orientation. The sulfonated samples changed color with the progress of sulfonation. For example, the sulfonation experiments performed at 120°C for 30 min, the color changed from white for the untreated sample to dark brown and with higher sulfonation times exceeding 1 h, the color was black all the way through (Table I). To check whether the sulfonation temperature may or may not play a role with the formation of lighter colors, sulfonation at 105°C was performed and it was observed that the color was light yellow for the sample sulfonated for 1 min only and the color changed to dark yellow and brown with the sulfonation times of 5 and 10 min. It showed conclusively that the sulfonation at 120°C indeed lead to dark colors showing the real effect of the sulfonation at this temperature. With the progress of sulfonation, the darkening of sulfonated samples suggests the formation of conjugated C=C double bonds with subsequent carbonization taking place at higher treatment times.<sup>26</sup>

#### Assessment of differential scanning calorimetry data

DSC thermograms of untreated [Fig. 2(a)] and sulfonated [Fig. 2(b–h)] isotactic polypropylene fibers for different sulfonation times are presented in Figure 2. With the progress of sulfonation, melting peaks show



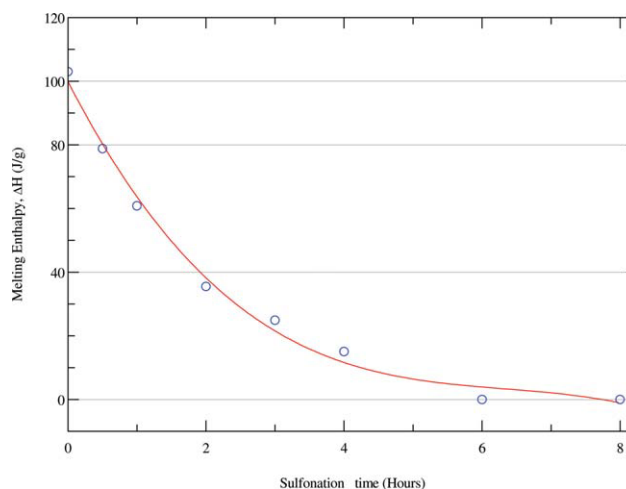


**Figure 2** DSC thermograms of sulfonated isotactic polypropylene fibers extruded at a take-up speed of 2500 m/min as function of sulfonation time: (a) untreated; (b) 120°C, 30 mins; (c) 120°C, 1 h; (d) 120°C, 2 h; (e) 120°C, 3 h; (f) 120°C, 4 h; (g) 120°C, 6 h; (h) 120°C, 8 h. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

the tendency of broadening with accompanying reduction in the area under the melting endotherm (Fig. 3).

DSC thermograms presented in Figure 2 show that the precursor fiber reaches the full stabilization in about 6 h at 120°C as indicated by the disappearance of the melting peaks. In essence, the disappearance of the melting peaks is an unquestionable positive proof of the full crosslinking of chain segments which takes place during the sulfonation stage.

DSC thermogram of the sample sulfonated for 30 min shows a shift of melting temperature from 159 to 156°C corresponding to the low temperature peak whereas high temperature peak is shifted from 168 to 167°C. When the sulfonation time of 1 h is reached, low temperature side of the melting endotherm is gradually lost. At this point, it is highly likely that the amorphous phase followed by the paracrystalline (or smectic) structure is crosslinked with the progress of sulfonation and the remaining  $\alpha$ -monoclinic phase is still intact. This means that the crosslinking starts first with the amorphous phase followed by the paracrystalline structure and finally by the well-ordered  $\beta$ -mono-



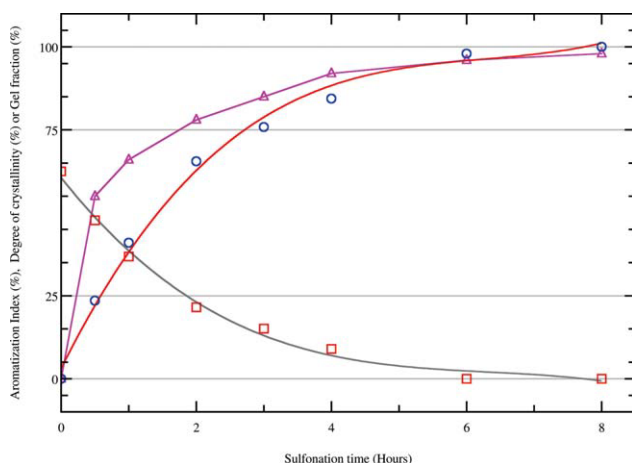
**Figure 3** Variation of melting enthalpy ( $\Delta H$ ) of sulfonated isotactic polypropylene fibers extruded at a take-up speed of 2500 m/min as function of sulfonation time. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

clinic phase. This may be explained in terms of the diffusion of sulfonation agent into the relatively free regions between polymer chains in the amorphous and paracrystalline phase where the polypropylene chains are less well packed.

Aromatization index evaluated using the eq. (3), which in effect describes the degree of crosslinking density by differential scanning calorimetry, shows an increasing trend (Table II and Fig. 4). As the sulfonation time reaches 6 h, the structure seems to be 100% crosslinked. This is supported by the gel-fraction results shown on the same figure. It seems that gel-fraction can also be described as a means of measuring the degree of crosslinking by chemical means shows an increasing trend with increasing sulfonation time. At high sulfonation times of 6 and 8 h, the sulfonated samples become practically insoluble in boiling xylene. The results presented in Figure 4 shows low gel fraction at low sulfonation time followed by a rapid increase with increasing treatment time. It may be concluded that the degree of crosslinking measured by both aromatization index and gel fraction shows a direct proportionality

**TABLE II**  
Thermal Characteristics of Sulfonated Isopropylene Fibers Melt-Spun at 2500 m/min

Sulfonation time (h)	Melting endotherm peak (1) (°C)	Melting endotherm peak (2) (°C)	Aromatization index (%)	Gel-fraction (%)	DSC ( $\chi_c$ )
0	159	168	0.00	0	62.5
0.5	156	167	23.5	55	47.8
1	156	167	41.0	66	36.9
2	–	167	65.5	78	21.5
3	–	167	75.8	85	15.1
4	–	167	84.4	92	9
6	–	–	100.0	96	0
8	–	–	100.0	98	0



**Figure 4** Variation of aromatization index (O), degree of crystallinity (□), and gel fraction (Δ) of sulfonated isotactic polypropylene fibers extruded at a take-up speed of 2500 m/min as a function of sulfonation time. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

with sulfonation time. This means that the higher the sulfonation time, the higher is the crosslinking density.

This shows that as a result of extensive sulfonation, the samples become fully infusible, intractable, and insoluble in pure xylene. The increase in the crosslink density is in line with reduced crystallinity as shown in Figure 4. The degree of crystallinity using eq. (2) based on the melting enthalpy obtained from DSC thermograms shows a decreasing trend with an increasing sulfonation time. When the sulfonation time of 6 h is reached, the crystallinity of the samples seems to be totally lost. When all the results are put together, it shows that the sulfonation mechanism progresses with the elimination of ordered regions starting possibly from easily accessible amorphous and paracrystalline regions followed by the highly ordered  $\alpha$ -monoclinic phase.

### Assessment of TGA data

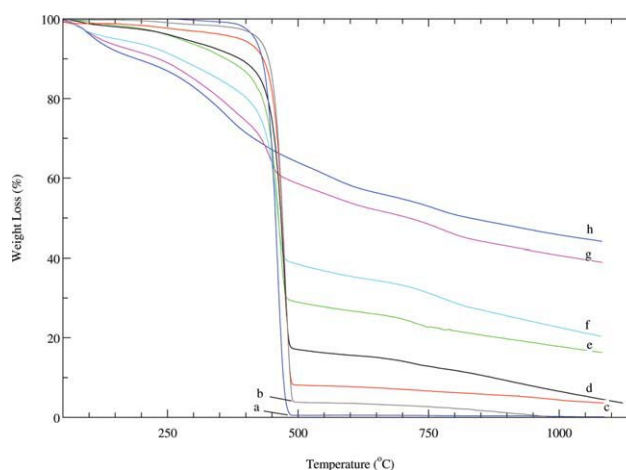
Thermogravimetric analysis technique is most often considered an effective and efficient method for determining the thermal stability of isotactic polypropylene fibers. Relatively deeper and narrower temperature distribution reflects faster decomposition reactions and the resulting weight losses are likely to be considerably large, which in turn results in lower carbon yields. Conversely, wider temperature distribution related weight losses show moderate reactions and consequently result in higher carbon yields. Thermal decomposition in terms of weight loss and the rate of weight loss can be used to compare the relative yields of carbonization behavior.

The untreated polypropylene (extruded at 2500 m/min) [Fig. 5(a)] sample remains stable from 50 to 250°C, where there is no visible sign of weight loss. This zone of thermal stability is followed by a slow

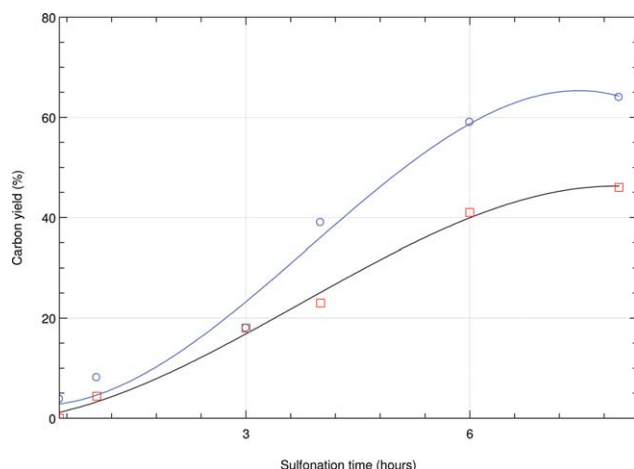
rate of decomposition from 250 to 400°C. In this slow decomposition zone, there is a slight weight loss of about 2.5%. A faster rate of decomposition starts after this zone until the sample is fully decomposed at about 500°C. At this temperature a net weight loss of about 99.5% has been observed. This means that the untreated sample is characterized by a carbon yield of 0.5%.

TGA thermograms of sulfonated samples are plotted in Figure 5(b–g). The TGA thermograms confirm the findings of the DSC thermograms. As expected, TGA thermograms show decreasing weight loss with increasing sulfonation time indicating decreasing weight loss and increasing carbon yield due to the increasing degree of crosslinking density. Untreated sample loses weight over a narrow temperature range whereas sulfonated samples lose weight over a wide temperature range due to the effect of increased thermal stabilization. Weight retention in TGA thermograms is usually regarded as a useful measure of the extent of thermal stabilization. In effect, normally thermally stabilized samples do not decompose during heating stage in an inert nitrogen or argon atmosphere. Thermally stabilized samples are observed to lose weight as the samples acquire carbonized form resulting in the elimination of organic materials as pyrolysis by-products. Usually noncarbon elements such as hydrogen, oxygen, carbon monoxide, carbon dioxide, and water vapor are eliminated up to 600°C and beyond.

Sulfonated samples starting with sulfonation time of 30 min shows a much less severe thermal decomposition between 400 and 500°C with a net weight loss of 96.3% which leads to a net carbon yield of 3.7%. As shown in Figure 5, the weight loss between 50 and 500°C progressively decreases with



**Figure 5** TGA thermograms of untreated and sulfonated isotactic polypropylene fibers: (a) untreated; (b) 120°C, 30 mins; (c) 120°C, 1 h; (d) 120°C, 2 h; (e) 120°C, 3 h; (f) 120°C, 4 h; (g) 120°C, 6 h; (h) 120°C, 8 h. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



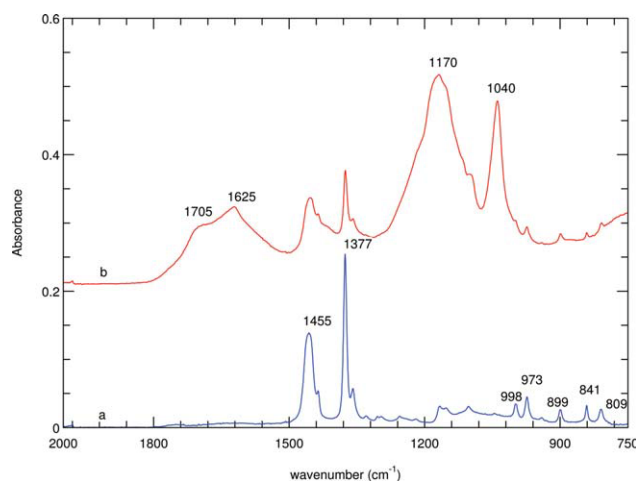
**Figure 6** Variation of carbon yield (%) with sulfonation time for the untreated and sulfonated isotactic polypropylene fibers (O) at 500°C and (□) at 1000°C. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

increasing sulfonation time. When the sulfonation time of 6 h is reached, net weight loss reaches 41% at 500°C and 59% at 1000°C, respectively.

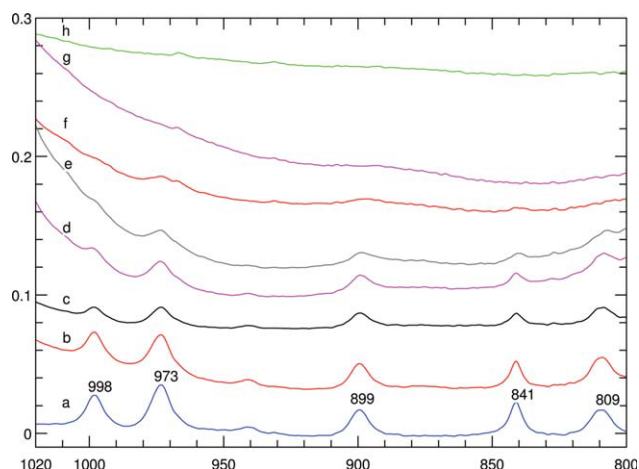
The results show that sulfonated samples acquire high thermal stability as a result of sulfonation based crosslinking. Figure 6 shows the carbon yields at 500 and 1000°C for the untreated and sulfonated isotactic polypropylene fibers. The results show an increasing carbon yield with increasing sulfonation time and it reaches a maximum value of 46% at 1000°C for the sample sulfonated for 8 h at 120°C.

### Assessment of FT-IR spectroscopy data

Qualitative examination of infra-red spectra of sulfonated samples shown in Figures 7 and 8 indicates



**Figure 7** IR spectrum of untreated (a) and sulfonated isotactic polypropylene (b) fiber in the 2000–750  $\text{cm}^{-1}$  range showing characteristic band positions. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



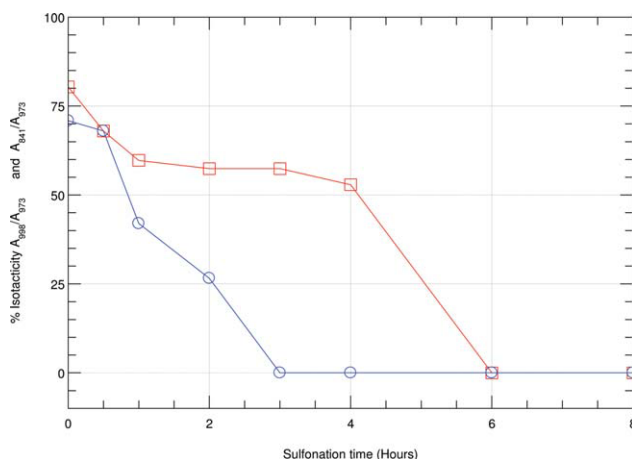
**Figure 8** IR-spectrum of untreated and sulfonated isotactic polypropylene fibers in the 1020 to 800  $\text{cm}^{-1}$  range: (a) untreated; (b) 120°C, 30 mins; (c) 120°C, 1 h; (d) 120°C, 2 h; (e) 120°C, 3 h; (f) 120°C, 4 h; (g) 120°C, 6 h; (h) 120°C, 8 h. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

that significant structural changes have taken place during the sulfonation treatment. A deeper understanding on the effects of sulfonation of isotactic polypropylene fibers may be obtained by analyzing the structural changes which may vary with increasing sulfonation time.

FT-IR spectra of untreated and sulfonated isotactic polypropylene in the frequency range of 2000–750  $\text{cm}^{-1}$  are presented in Figure 7. The standard bands of untreated polypropylene occur at 1455, 1377, 1359, 1256, and 1104  $\text{cm}^{-1}$ . The IR peaks located at 1220, 1168, 1104, 1044, 998, 899, 841, and 809  $\text{cm}^{-1}$  are characteristic of the threefold helical structure present in crystalline polypropylene. These bands are known as regularity bands arising from the presence of helical chains.<sup>57</sup> These regularity bands are either absent or very weak in intensity in amorphous polypropylene, and hence, should provide indications of structural changes taking place during the sulfonation stage. Assignments of the IR bands in the 4000–800  $\text{cm}^{-1}$  region are listed in Table IV.

Many investigations showed that specific regularity bands are related to the critical length of isotactic sequences. It was found that the absorption intensity of the 998  $\text{cm}^{-1}$  band disappears as the sequence length becomes less than 10 monomeric units. The other regularity bands were found to disappear<sup>58</sup> up on melting. It is shown that<sup>59</sup> only 841 and 998  $\text{cm}^{-1}$  bands remain for monomeric sequence lengths less than 10 in the IR spectra of isotactic copolymer and deuteropropylene copolymers. Although the 998  $\text{cm}^{-1}$  band is still observed to exist at 220°C, its intensity is seen considerably weakened but a small portion is found to remain.<sup>60</sup>

With increasing sulfonation time, the regularity bands arising from the crystalline regions lose their



**Figure 9** Variation of % isotacticity values of untreated and sulfonated isotactic polypropylene fibers (O)  $A_{998}/A_{973}$  and (□)  $A_{841}/A_{973}$ . [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

intensity with increasing sulfonation time as shown in Figure 8. As a result, the  $998\text{ cm}^{-1}$  band disappears completely after 3 h of exposure to sulfonation treatment; in the same way, the  $841\text{ cm}^{-1}$  band disappears completely after 6 h and the  $809\text{ cm}^{-1}$  band disappears after 4 h, whereas the average band due to the combination of amorphous and crystalline phase located at  $973\text{ cm}^{-1}$  does not disappear completely even after 8 h of treatment (Fig. 8).

In the present investigation, for the quantitative characterization of tacticity of sulfonated isotactic polypropylene fibers,  $998$ ,  $841$ , and  $973\text{ cm}^{-1}$  absorption bands are selected.  $998$  and  $841\text{ cm}^{-1}$  absorption bands are usually assigned to the crystalline phase, whereas  $973\text{ cm}^{-1}$  band is assigned to both crystalline and amorphous chains in helical conformations and is often used as an internal reference band.<sup>56,61</sup>  $973\text{ cm}^{-1}$  band is associated with the presence of short isotactic helices apparently still present in the melt or in the atactic material. The regularity band at  $841\text{ cm}^{-1}$  showed the lowest peak width in comparison with the other helical bands.<sup>62</sup> It has been assigned to long helical chains with an average length of 12–14 units.<sup>57</sup> Molecular orientation parameters calculated using this peak for isotactic polypropylene films showed excellent agreement and correlation with the x-ray diffraction measurements.<sup>62,63</sup> It was suggested that in the absence of x-ray diffraction data this peak may be used for the determination of orientation quite safely.

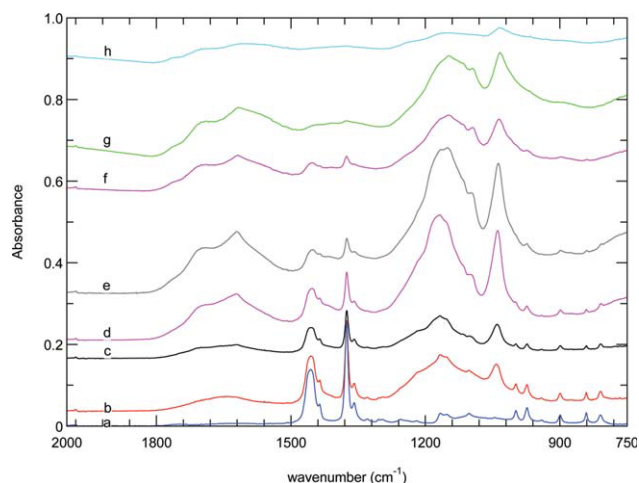
Tacticity values for the sulfonated samples evaluated from the absorbance ratios of  $A_{998}/A_{973}$  and  $A_{841}/A_{973}$  are presented in Figure 9. Values of isotacticity (%) arising from the absorbance ratio of  $A_{998}/A_{973}$  decreases to zero after the sulfonation time of 3 h, whereas the absorbance ratio of  $A_{841}/A_{973}$  decreases to zero after the sulfonation time of

**TABLE III**  
Percent Isotacticity and Atacticity Values of Melt-Spun Isotactic Polypropylene Fibers Sulfonated at  $120^\circ\text{C}$

Sulfonation time (h)	$A_{998}/A_{973}$ Isotacticity (%)	$A_{998}/A_{973}$ Atacticity (%)	$A_{841}/A_{973}$ Isotacticity (%)	$A_{841}/A_{973}$ Atacticity (%)
0	70.9	29.1	80.4	19.6
0.5	68.0	32.0	68.00	32.00
1	42.0	58.0	59.7	40.3
2	26.6	73.4	57.4	42.6
3	0	100.0	57.4	42.6
4	0	100.0	52.9	47.1
6	0	100.0	0	100
8	0	100.0	0	100

6 h. It shows that with increasing sulfonation time, untreated isotactic polypropylene chains gradually lose their original crystalline structure, most probably, as a result of crosslinking. Assuming the presence of all the isotactic propylene segments in the crystalline phase, the results indicate the gradual loss of crystallinity and the gradual increase of atactic structure (Table III) with the increase in sulfonation time.

Number of characteristic IR bands due to sulfonic acid groups appear in the  $1280$  to  $1000\text{ cm}^{-1}$  range. The IR bands in the  $1280$  to  $1080\text{ cm}^{-1}$  region and at  $1040\text{ cm}^{-1}$  can be assigned to  $\text{O}=\text{S}=\text{O}$  stretching vibrations.<sup>25</sup> It is possible to assume that sulfonations give rise to sulfonic acid groups ( $-\text{HSO}_3$ ), sulfones, and sulfate groups as  $\text{O}=\text{S}=\text{O}$  containing products. Therefore, it can be assumed that the bands in the  $1280$ – $1080\text{ cm}^{-1}$  range can be assigned to one of these vibrational groups.



**Figure 10** IR spectrum of untreated (a) and sulfonated isotactic polypropylene fiber in the  $2000$ – $750\text{ cm}^{-1}$  range. Sulfonation at  $120^\circ\text{C}$  for (b) 30 mins; (c) 1 h; (d) 2 h; (e) 3 h; (f) 4 h; (g) 6 h; (h) 8 h. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

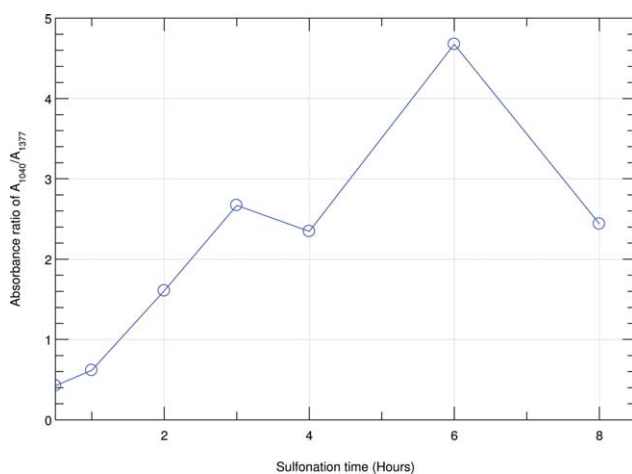


**TABLE IV**  
IR Vibrations of Isotactic Polypropylene Fibers

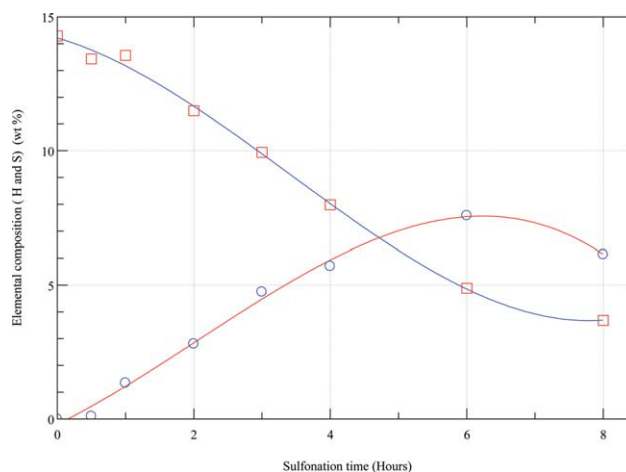
Wavenumber (cm <sup>-1</sup> )	Assignment <sup>30,68</sup>
809	CH <sub>2</sub> rocking + C—C stretching + C—H stretching
841	CH <sub>2</sub> rocking + C—CH <sub>3</sub> stretching
973	CH <sub>3</sub> rocking + C—C chain stretch
998	CH <sub>3</sub> rocking + CH <sub>2</sub> wagging + CH bending
1040	O=S=O symmetrical stretch
1170	O=S=O asymmetrical stretch
1377	CH <sub>3</sub> symmetric bending + CH <sub>2</sub> wagging
1455	CH <sub>2</sub> bending
1625	C=C stretch
1705	C=O stretch
3000–2800	C—H stretch
3400	OH stretch

In this region there is another band located at 1104 cm<sup>-1</sup> as a weak band (C—C chain stretching + CH<sub>3</sub> rocking + CH<sub>2</sub> wagging + CH twisting + CH bending) which is most likely due to the untreated polypropylene. Figure 10 shows the steady build-up of the concentration of sulfonic acid groups as a function of sulfonation time as indicated by the increase of the absorbance values of the bands positioned at 1170 and 1040 cm<sup>-1</sup>, respectively.

Due to its isolated position and lack of its overlapping nature with the neighboring bands, the band around 1040 cm<sup>-1</sup> is normalized against the methylene group vibration at 1377 cm<sup>-1</sup> to monitor the structural changes taking place during the sulfonation treatment.<sup>25</sup> Due to the presence of several overlapping peaks in the 1309–1072 cm<sup>-1</sup> region (Fig. 10), the band around 1170 cm<sup>-1</sup> is found to be unsuitable for the present quantitative analysis. 1850–900 cm<sup>-1</sup> region was used as the baseline



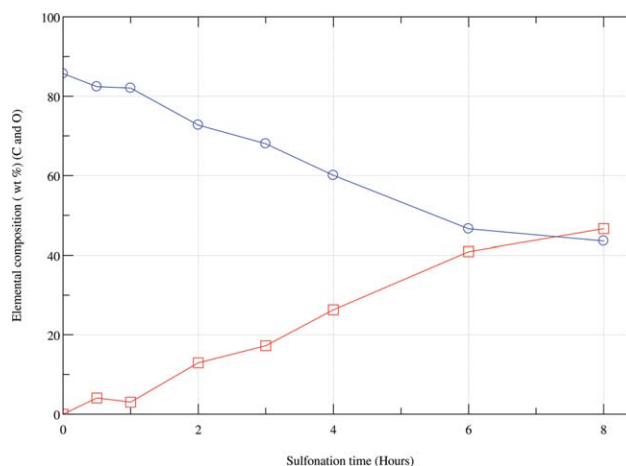
**Figure 11** Variation of absorption ratio of A<sub>1040</sub>/A<sub>1377</sub> of sulfonated isotactic polypropylene fibers. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



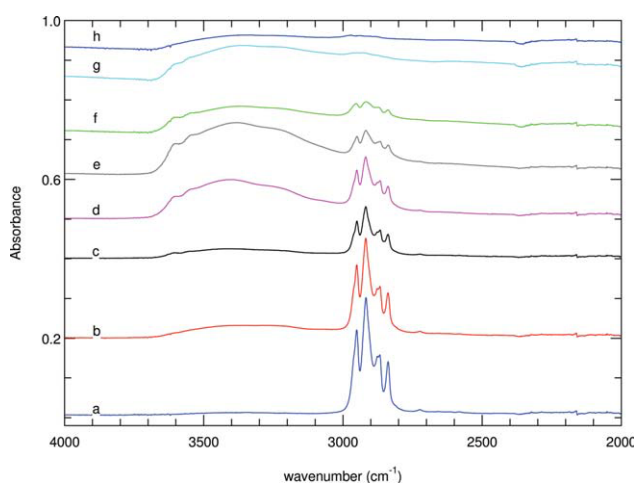
**Figure 12** Elemental composition (in weight %) of sulfonated isotactic polypropylene fibers as a function of sulfonation time: sulfur content (○) and hydrogen content (□). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

boundaries above which the absorbance values were determined.

The absorbance ratio of A<sub>1040</sub>/A<sub>1377</sub> as a function of sulfonation time plotted in Figure 11 shows a continuous upward trend up to the sulfonation time of 3 h, with a slight decrease at about 4 h followed by a continuous upward increase until the sulfonation time of 6 h. There appears to be a decrease in the absorbance ratio at about 8 h of sulfonation time. It seems that some kind of desulfonation reaction takes place as a result of the loss of sulfonic acid groups as indicated by the loss of absorbance values of the bands assigned to the sulfonic acid groups after the sulfonation time of 3 h.



**Figure 13** Elemental composition (in weight %) of sulfonated isotactic polypropylene fibers as a function of sulfonation time: carbon content (○) and oxygen content (□). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]



**Figure 14** IR spectrum of untreated (a) and sulfonated isotactic polypropylene fiber in the 4000–2000  $\text{cm}^{-1}$  range. Sulfonation at 120°C for (b) 30 mins; (c) 1 h; (d) 2 h; (e) 3 h; (f) 4 h; (g) 6 h; (h) 8 h. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

Chemical composition of sulfonated samples was determined by elemental analysis. Carbon (C), hydrogen (H), oxygen (O), and sulfur (S) contents are listed in Table I. Figure 12 shows sulfur and hydrogen content of sulfonated samples as a function of sulfonation time. The sulfur content for the sulfonated samples increased from 0.1 to 7.6% while the sulfonation time increased from 0.5 to 6 h. The sulfur content for the sulfonated sample with the sulfonation time of 8 h is reduced to 6.1%. Meanwhile, hydrogen content is seen to decrease with increasing sulfonation time from an initial value of 14.3% to 3.7% after 8 h. Figure 13 shows carbon and oxygen content as a function of sulfonation time. The carbon content comes down from 85.7% to 43.6% after 8 h of sulfonation whereas oxygen content increases to 46.6% after 8 h of sulfonation.

The results indicate a significant increase in the sulfonic acid ( $-\text{HSO}_3$ ) groups that are incorporated to the polypropylene polymer chains during the sulfonation stage. Loss of carbon may have occurred as CO or  $\text{CO}_2$  emission during the sulfonation stage. The increase in sulfur and oxygen content is in agreement with the results obtained from the IR absorbance ratio of  $A_{1040}/A_{1377}$  as a function of sulfonation time plotted in Figure 11. When the sulfonation time exceeds 3 h, desulfonation reaction seems to be taking place while forming new functional groups containing elemental sulfur and oxygen atoms. It has been suggested that the formation of C=C double bonds occurs by the desulfonation reaction following the formation of sulfonic acid<sup>64–66</sup> groups.

Sulfonic acid bands around 1250–1000  $\text{cm}^{-1}$  region indicate the presence of a weak peak, as a shoulder, located at about 1170  $\text{cm}^{-1}$  (C–C chain stretching +  $\text{CH}_3$  rocking + CH bending), clearly visible in the

spectrum of sulfonated sample at 120°C for 30 min [Fig. 10(b)], which is a characteristic polypropylene band. The 1280–1080  $\text{cm}^{-1}$  region contains several overlapping bands and can best be resolved into several peaks with positions at 1200, 1167, 1152, 1114, and 1084  $\text{cm}^{-1}$ . This shows the possibility of different vibrational groups incorporating O=S=O units other than sulfonic acid groups. It is pointed out that besides the formation of sulfonic acid groups during the sulfonation reactions other reactions are likely to produce sulfones.<sup>66</sup> Characteristic polypropylene bands at 1455 and 1377  $\text{cm}^{-1}$  keep their presence felt until about the treatment time of 4 h and afterward lose their intensity altogether after 6 and 8 h, respectively.

As can be seen in Figure 10, there are characteristic absorption bands in the 1800–1600  $\text{cm}^{-1}$  region. The band located around 1700  $\text{cm}^{-1}$  can best be attributed to carbonyl (C=O) groups present in ketones, aldehydes, and carboxylic acids.<sup>30</sup> It has been pointed out that the sulfonation of polyolefins with fuming sulfuric acid and hot sulfuric acid results in the formation of carbonyl groups due to the oxidation reaction in the sulfonation treatment.<sup>23–25,44</sup> The band at 1605  $\text{cm}^{-1}$  may be assigned to the C=C double bonds.

The IR spectra shown in Figure 10 reveal that the absorption bands around 1700 and 1650  $\text{cm}^{-1}$  increase in intensity with increasing sulfonation time. The same behavior is also observed with the sulfonic acid bands located at 1170 and 1040  $\text{cm}^{-1}$ . This indicates the possibility of formation of carbonyl (C=O) and C=C double bonds at the same time with the sulfonation treatment.

IR bands in the 4000–2000  $\text{cm}^{-1}$  range are shown in Figure 14. In the 3000–2800  $\text{cm}^{-1}$  range, standard bands of untreated isotactic polypropylene due to C–H stretching vibration are observed. At higher wavenumbers a broad band around 3450  $\text{cm}^{-1}$  assigned to the OH stretching was observed [Fig. 14(b–h)]. With the progress of sulfonation, the intensity of the CH stretching bands located around 3000–2800  $\text{cm}^{-1}$  decreases and totally disappears after about 6 h of sulfonation [Fig. 14(g)].

### Assessment of the sulfonation mechanism

Significant differences between the sulfonation mechanism of aliphatic and aromatic compounds are known. In the case of aromatic compounds, the sulfonation reaction is known to proceed relatively easier than the aliphatic compounds despite the fact that the dissociation energy of C–H bond is higher in aromatic (428 kJ/mol) than in aliphatic (374–384 kJ/mol) compounds.<sup>67</sup> It is clear that a maximum of three sulfonic acid groups ( $-\text{HSO}_3$ ) may be linked to one carbon atom of the aliphatic chain whereas only one sulfonic acid group may be linked to the carbon atom of the aromatic ring.

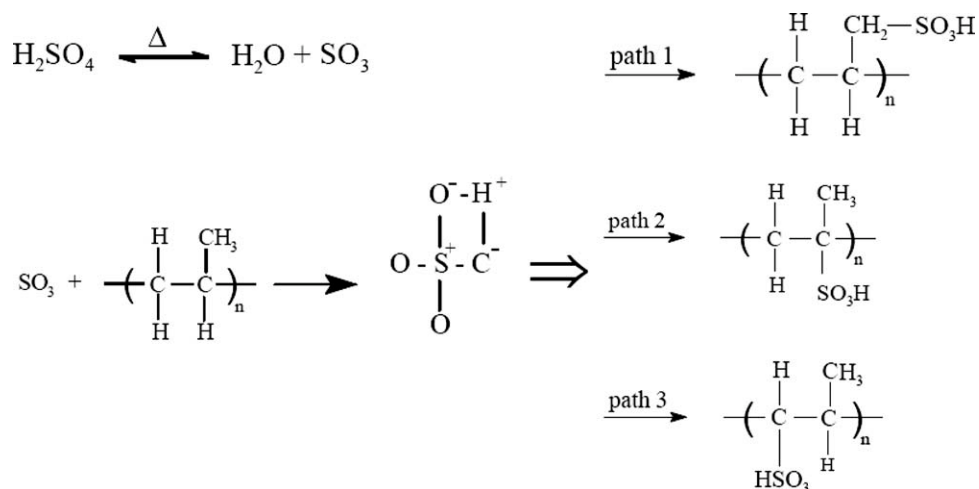


Figure 15 Reaction scheme of sulfonation of polypropylene.<sup>23</sup>

In terms of the sulfonation mechanism, the sulfonation reaction proceeds through electrophilic addition of  $\text{SO}_3$  to  $\text{C}=\text{C}$  bonds in the case of fully aromatic compounds. In the case of aliphatic compounds such as polypropylenes, several sulfonation mechanisms are involved. During the sulfonation treatment the hydrogen atom of the  $\text{C}-\text{H}$  group either from the main chain  $\text{C}-\text{C}$  backbone or from the methyl group ( $-\text{CH}_3$ ) is removed and replaced by  $\text{SO}_3$  group, which is subsequently hydrogenated to form a sulfonic acid ( $-\text{HSO}_3$ ) group at the site of attachment.<sup>40</sup>

Investigations carried out on the sulfonation of polypropylene<sup>23,25,30</sup> have revealed that the sulfonation treatment produces sulfonic acid ( $-\text{HSO}_3$ ) groups, although different reaction mechanisms are involved. These investigations demonstrated the generation of  $\text{C}=\text{C}$  double bonds arising from the desulfonation of polypropylene. According to Cameron and Main<sup>25</sup> sulfonation treatments tend to be accompanied by some oxidation reactions. As a result of sulfonation-desulfonation reactions, conjugated sequences of double bonds seem to be produced.

Tada and Ito<sup>23</sup> revealed that sulfur atoms act as electrophilic centers reacting with negatively charged C atoms of polypropylene through the electrophilic addition of  $\text{SO}_3$ . Due to the higher charge of the carbon atoms of the side methyl groups ( $-\text{CH}_3$ ), sulfonation treatment is thought to take place with the side methyl ( $\text{CH}_3$ ) groups rather than the C-atoms of the main chain (Fig. 15). According to this principle, paths 2 and 3 should be ruled out and only path 1 remains the only possibility for the attachment of sulfonic acid groups to the polypropylene chains. This is thought to make the polypropylene chains vulnerable to acid attack, but it seems that this is the case only for atactic polypropylene. Due to the highly crystalline nature of isotactic polypropylene, though, some kind of protection seems to be provided.<sup>25</sup>

According to the results obtained,<sup>23</sup> path 2 and path 3 should have much more activation energy than path 1, which results in a selective reaction site during the sulfonation of polypropylene (Fig. 15). Attachment of sulfonic acid ( $-\text{HSO}_3$ ) groups on to the polypropylene chains results in polypropylene ionomers, which makes it possible to be utilized in a wide range of commercial applications due to their relatively high reactivities.<sup>26</sup> The rules engaged in the selectivity explains the reasons why a significant proportion of conjugated  $\text{C}=\text{C}$  bonds, normally observed during the sulfonation of polyethylene, are not obtained in the case of polypropylene.

Kaneko and Sato proposed<sup>30</sup> another mechanism for the sulfonation of isotactic polypropylene film with fuming sulfuric acid, where a  $\text{C}=\text{C}$  double bond is formed first by hydride abstraction of  $\text{SO}_3$  and subsequently loss of proton is observed. Consequently,  $\text{SO}_3$  undergoes an electrophilic addition step to form a double bond. In the mechanisms mentioned already, electron-rich C-atoms are thought to play a key role in the addition step.<sup>43</sup>

## CONCLUSIONS

Sulfonation treatment using concentrated sulfuric acid was used to produce thermally stabilized isotactic polypropylene fibers prior to carbonization stage. Sulfonation was carried out at  $120^\circ\text{C}$  for treatment times ranging from 0.5 to 8 h. Sulfonated polypropylene samples showed color changes from dark brown to black with the progress of sulfonation. Elemental analysis, differential scanning calorimetry, thermogravimetric analysis, and infra-red spectroscopy techniques were used for the structural characterization. DSC thermograms showed the loss of crystallinity with increasing sulfonation time which is accompanied by an increasing crosslinking density as indicated by the increasing trend of aromatization index values. TGA thermograms showed decreasing loss of weight with increasing sulfonation time.

Decreasing weight loss observed in the TGA thermograms resulted in an increasing carbon yield of up to 46% at 1000°C for the sample sulfonated at 8 h. IR spectroscopy supported the findings of the DSC thermograms where the loss of crystallization and isotacticity was observed with the gradual loss of absorbances of regularity bands in the 1080–750 cm<sup>-1</sup> region with the progress of sulfonation. The results obtained from IR spectroscopy showed the formation of C=C double bonds, carbonyl band (C=O) due to oxidation, and sulfonation reactions which occur simultaneously as a result of sulfonation–desulfonation reactions.

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