

# Photograft Copolymerization of Methyl Methacrylate on Viscose Fiber Using Titanium(III) Chloride–Potassium Persulfate Redox Initiator in a Limited Aqueous System

TARUN KUMAR MAJI and AMAR NATH BANERJEE\*

Department of Plastics and Rubber Technology, Calcutta University, Calcutta-700 009, India

## SYNOPSIS

The graft copolymerization of methyl methacrylate (MMA) onto viscose fibers were studied under photoactive conditions with visible light using titanium(III) chloride–potassium persulfate as redox initiator in a limited aqueous system. Polymerization carried out in the dark at  $40 \pm 1^\circ\text{C}$  produced little graft copolymer whereas that in the presence of light at  $40 \pm 1^\circ\text{C}$  produced significant grafting. Percent grafting, percent total conversion, and grafting efficiency (%) were studied by varying time, initiator concentration, monomer concentration, solvent composition, and pH of the medium. High percent grafting ( $\sim 200\%$ ), high grafting efficiency ( $\sim 98\%$ ), and percent total conversion ( $\sim 47\%$ ) were obtained with little homopolymer formation. A suitable mechanism for grafting has been discussed and also the characterization of the grafted fibers were studied by Fourier transform infrared (FTIR) spectroscopy, thermogravimetry and scanning electron microscopy (SEM). © 1992 John Wiley & Sons, Inc.

## INTRODUCTION

The application field of graft copolymerization onto textile fibers for improving properties has been enlarging continuously in recent years. Grafting of vinyl monomer onto viscose rayon has improved various properties.<sup>1,2</sup> Various methods have been employed for graft copolymerization of vinyl monomers onto viscose fibers such as high-energy radiations,<sup>2–5</sup> redox systems,<sup>6–11</sup> etc. The use of ceric salts and persulfate have also been reported.<sup>12,13</sup>

The graft copolymerization of vinyl monomers onto viscose fiber under visible light has not been investigated so much, and further investigations in this area are still open. Besides for industrial purposes, minimization of homopolymer formation is desirable. Recently we have reported<sup>14</sup> iron (II)–potassium persulfate initiated graft copolymerization of methyl methacrylate on viscose fibers in limited aqueous system under visible light. The present work has been undertaken to investigate the grafting of

methyl methacrylate onto viscose fiber using a combination of titanium(III) chloride–potassium persulfate as redox initiator under visible light.

## EXPERIMENTAL

### Materials

Processed viscose staple fibers ( $1.5 \times 51$  mm; Grey staple, bright bleached, Nagda) were supplied by Jayasree Textiles, Rishra, Hooghly, West Bengal. Potassium persulfate (AR grade) and titanium(III) chloride (15% solution in 10% HCl) from E. Merck, Germany, were used directly. Other reagents used were of analytical grade. Purification of monomer, grafting procedure, and homopolymer separation have been reported in our previous communication.<sup>14</sup>

### Measurements

The FTIR spectra have been recorded on a Perkin-Elmer (model FTIR-1600) instrument.

The thermal behavior has been examined on a Perkin-Elmer Delta series TGA-7 instrument under

\* To whom correspondence should be addressed.

**Table I Polymerization of MMA on Viscose Rayon<sup>a</sup>**

Initiator System	Conditions of Polymerization	Formation of PMMA <sup>b</sup>	
		Free	Grafted
K <sub>2</sub> S <sub>2</sub> O <sub>8</sub> /TiCl <sub>3</sub>	Dark, 40 ± 1°C, 3 h	+	+
K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	Dark, 40 ± 1°C, 3 h	+	-
TiCl <sub>3</sub>	Dark, 40 ± 1°C, 3 h	-	-
K <sub>2</sub> S <sub>2</sub> O <sub>8</sub> /TiCl <sub>3</sub>	Photo, 40 ± 1°C, 3 h	+	++
K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	Photo, 40 ± 1°C, 3 h	+	+
TiCl <sub>3</sub>	Photo, 40 ± 1°C, 3 h	-	-

<sup>a</sup> Initiator system: K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, (1.08 mg); [TiCl<sub>3</sub>] 3 × 10<sup>-3</sup> M; MMA 1 mL; water 0.7 mL; pH 0.30.

<sup>b</sup> +, low, ++, high, - nil.

nitrogen atmosphere at a heating rate of 20°C/min. The morphological structure has been investigated by scanning electron microscope (model Philips P SEM-500).

## RESULTS AND DISCUSSION

Preliminary investigations indicated (Table I) that the rate of polymerization, for polymerization done in the dark at 40 ± 1°C, was lower compared to that in the presence of light. Hence all experiments were carried out under photoactive conditions.

The results showing the effect of variation of time, monomer concentration, and solvent composition are presented in Figures 1-3, and the effect of variation in initiator concentration, pH, are given in Tables II and III.

**Table II Effect of Variation of K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> and TiCl<sub>3</sub> Contents on Photograft Copolymerization of MMA on Viscose Fiber in Limited Aqueous System<sup>a</sup>**

K <sub>2</sub> S <sub>2</sub> O <sub>8</sub> (mg)	[TiCl <sub>3</sub> ] × 10 <sup>-3</sup> M	Grafting (%)	Total Conversion (%)	Grafting Efficiency (%)
0.674	3.0	64.25	13.69	100.00
0.808	3.0	58.81	13.05	95.00
1.213	3.0	78.67	17.78	94.20
1.347	3.0	79.14	17.57	96.00
1.078	2.0	49.12	10.46	100.00
1.078	3.0	70.86	17.15	87.96
1.078	3.5	102.14	22.67	96.00
1.078	4.0	62.08	16.03	82.48
1.078	4.5	68.81	18.46	79.48

<sup>a</sup> Viscose rayon 0.2 g, MMA 1 mL; time 1 h; pH 0.30; temperature 40 ± 1°C.

**Table III Effect of Variation of pH on Photograft Copolymerization of MMA on Viscose Rayon at 38 ± 1°C in Limited Aqueous System Using Ti<sup>3+</sup>/S<sub>2</sub>O<sub>8</sub><sup>2-</sup> Redox System<sup>a</sup>**

pH of the Medium	Grafting (%)	Total Conversion (%)	Grafting Efficiency (%)
0.30	62.92	14.58	91.97
0.54	109.16	24.19	95.86
0.75	115.36	25.16	97.46
1.87	102.84	22.10	97.18

<sup>a</sup> Initiator system: K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, 1.08 mg; [TiCl<sub>3</sub>], 3 × 10<sup>-3</sup> M; MMA 1 mL; water 0.7 mL; time 1 h.

### Effect of Variation of Polymerization Time

The results are shown in Figure 1. Both percent grafting and percent total conversion increases over the time period (1-5 h) studied. Grafting efficiency first increases sharply up to 1 h and finally levels off around 93%.

### Effect of Variation of Monomer Concentration

Related results are shown in Figure 2. Percent grafting and percent total conversion increased expectedly over the range of monomer concentration studied. Grafting efficiency first increases and then it levels off.

### Effect of Variation of Potassium Persulfate Content

Related results are shown in Table II. At fixed titanium(III) chloride concentration, an increase in

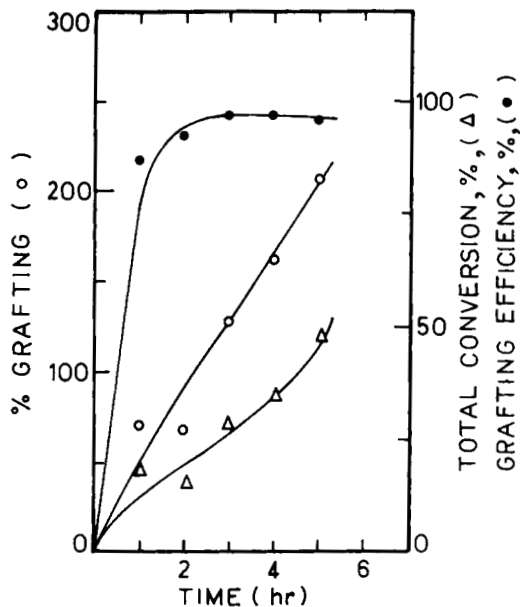


Figure 1

the amount of  $K_2S_2O_8$  shows a slow increasing trend in percent grafting and percent conversion initially, but latter it tends to level off. Grafting efficiency remains more or less steady around 96%. The increasing trend in the lower concentration range is due to increase in the number of active sites on the viscose fiber backbone while the leveling off tendency may be due to the saturation of active sites.

**Effect of Variation of Titanium(III) Chloride Concentration**

Related results are shown in Table II. At fixed  $K_2S_2O_8$  concentration, when concentration of  $TiCl_3$  is increased gradually from a lower range of concen-

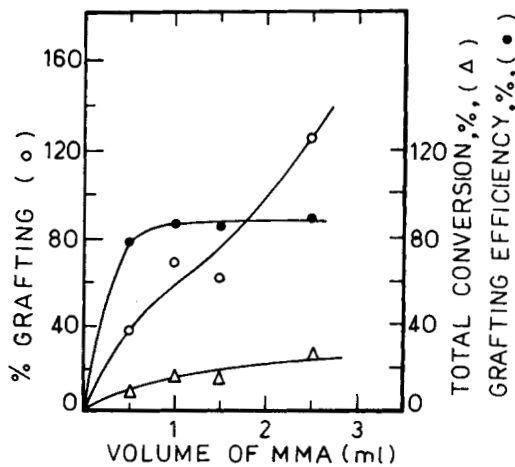


Figure 2

tration, a gradual enhancement in percent grafting, percent total conversion is observed up to a certain concentration and thereafter a falling trend in percent grafting, percent total conversion is observed. Grafting efficiency decreases over the range of concentration studied.

At higher concentration of  $TiCl_3$ , probably the rate of termination prevails over initiation and propagation and therefore rate of polymerization decreases. A similar observation was reported by Bataille et al.<sup>15</sup> for the emulsion polymerization of styrene at higher  $Ti^{3+}$  concentration using  $Ti^{3+}/S_2O_8^{2-}$  redox system.

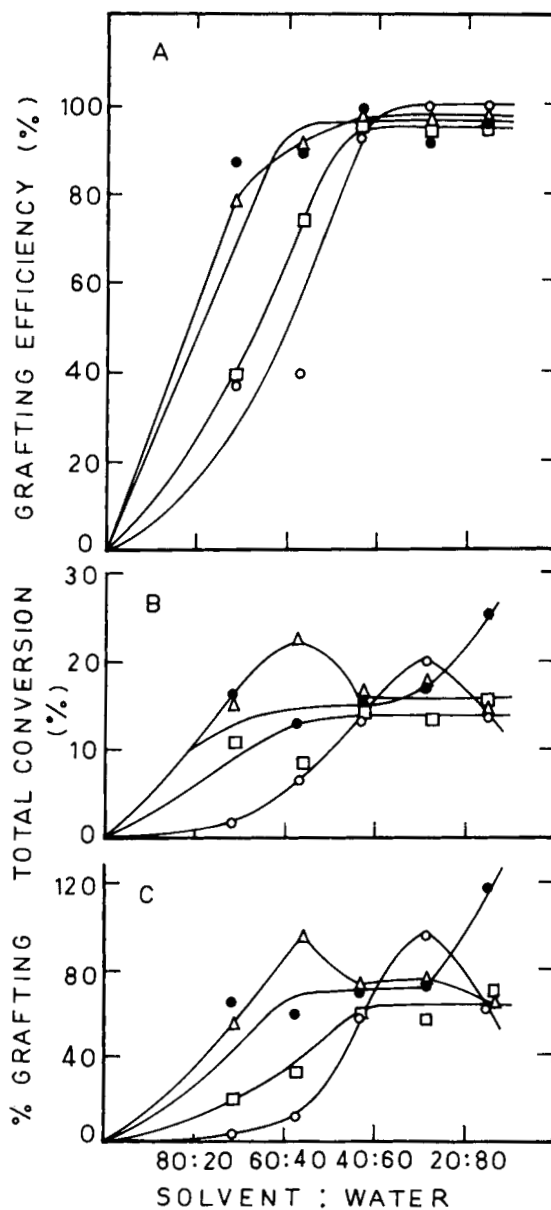


Figure 3

### Effect of Variation of pH

The results are shown in Table III. An enhancement in percent grafting, percent total conversion is observed up to 0.75 pH and then both decrease gradually. Grafting efficiency increases initially and then it levels off around 97%.

This behavior is due to the change in oxidation potential of  $Ti^{3+}$  with a change in HCl concentration. At higher acid concentration, i.e., at lower pH, the reducing ability of  $Ti^{3+}$  decreases, and the radical generation process is retarded, which affects the percent grafting. At higher pH, titanium(III) chloride hydrolyses readily and the above study becomes difficult.

### Effect of Solvent Composition

The effect of different types of solvents (of varying composition) on grafting are shown in Figure 3. A decrease in solvent-water composition has a role on graft copolymerization. Among the composition studied, a solvent-water ratio of 28.5 : 71.5 for formic acid, a ratio of 57 : 43 for dioxane, a ratio of 43 : 57 for methanol, and a ratio of 15 : 85 for tetrahydrofuran seems to be most favorable composition for

grafting. For tetrahydrofuran, a slow increasing trend in percent total conversion is observed. For formic acid, percent total conversion increases up to the ratio of 28.5 : 71.5, and for dioxane and methanol it levels off after an initial increment. In all the cases, grafting efficiency levels off after an initial increment.

The increasing trend may be due to the following factors: (i) capability of swelling the fibers, (ii) miscibility of the monomer, (iii) formation of solvent radical or hydroxyl radicals from water under the influence of primary radical species of the initiating systems, and (iv) contribution of these solvents or hydroxyl radicals in the activation of rayon.

The decreasing tendency may be due to the premature termination of the growing chain radical by the solvent or water via chain transfer.

### Mechanism

The radical generating process in the present graft copolymerization system is complicated because of the involvement of various factors including the heterogeneous nature of the system. The most likely primary radicals to be generated in this system are

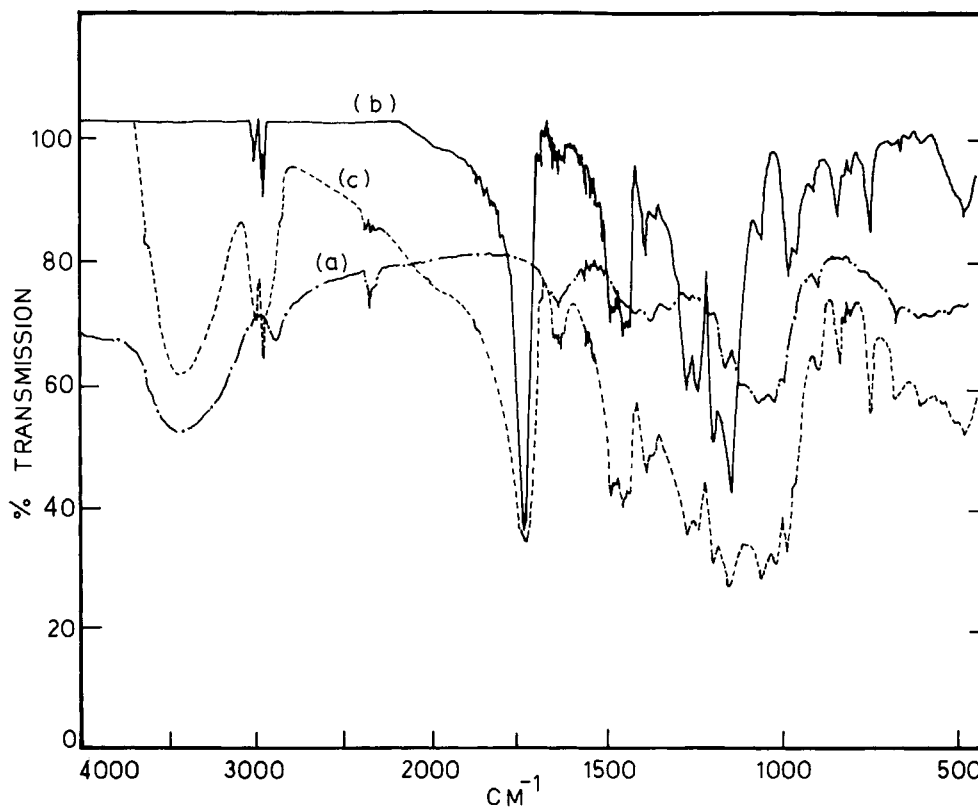
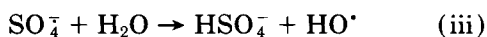
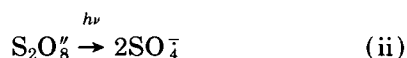
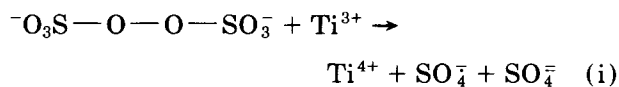
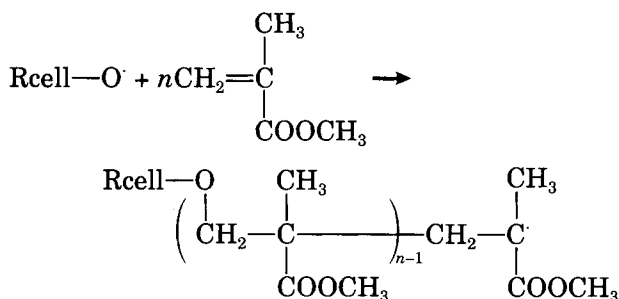
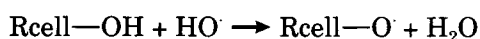


Figure 4

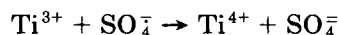
sulfate ion radical ( $\text{SO}_4^-$ ) and hydroxyl radicals ( $\text{OH}^\cdot$ ). End group analysis<sup>16</sup> of the free PMMA isolated from the gross polymers gave a positive test for sulfate and hydroxyl end groups. Thus the probable mechanism may be described as



Equation (i), (ii), and (iii) are faster in the presence of light compared to dark (Table I) as described earlier.



Furthermore, decrease in percent grafting with increase in  $\text{TiCl}_3$  content may be assumed to be caused by the consumption of  $\text{SO}_4^-$  by  $\text{Ti}^{3+}$  ion<sup>15</sup> according to the following equation:



### FTIR Spectra

The spectra of the grafted and ungrafted fiber are shown in Figure 4. In the spectra of the MMA polymer initiated by  $\text{Ti}^{3+}/\text{S}_2\text{O}_8^{2-}$  (curve b) and grafted fiber (curve c), the absorption band in the range of  $1733\text{--}1734\text{ cm}^{-1}$  is due to the presence of the ester group. The absorption band in ungrafted viscose fiber (curve a) and grafted fiber (curve c) in the range of  $3446\text{--}3448\text{ cm}^{-1}$  is due to the presence of hydroxyl group. As expected, the absorption band within the range of  $3446\text{--}3448\text{ cm}^{-1}$ , characteristic of hydroxyl group, should change with the amount of grafting. But this is not reflected because rayon contains a large number of hydroxyl group in its structure.

### Thermal Decomposition Studies

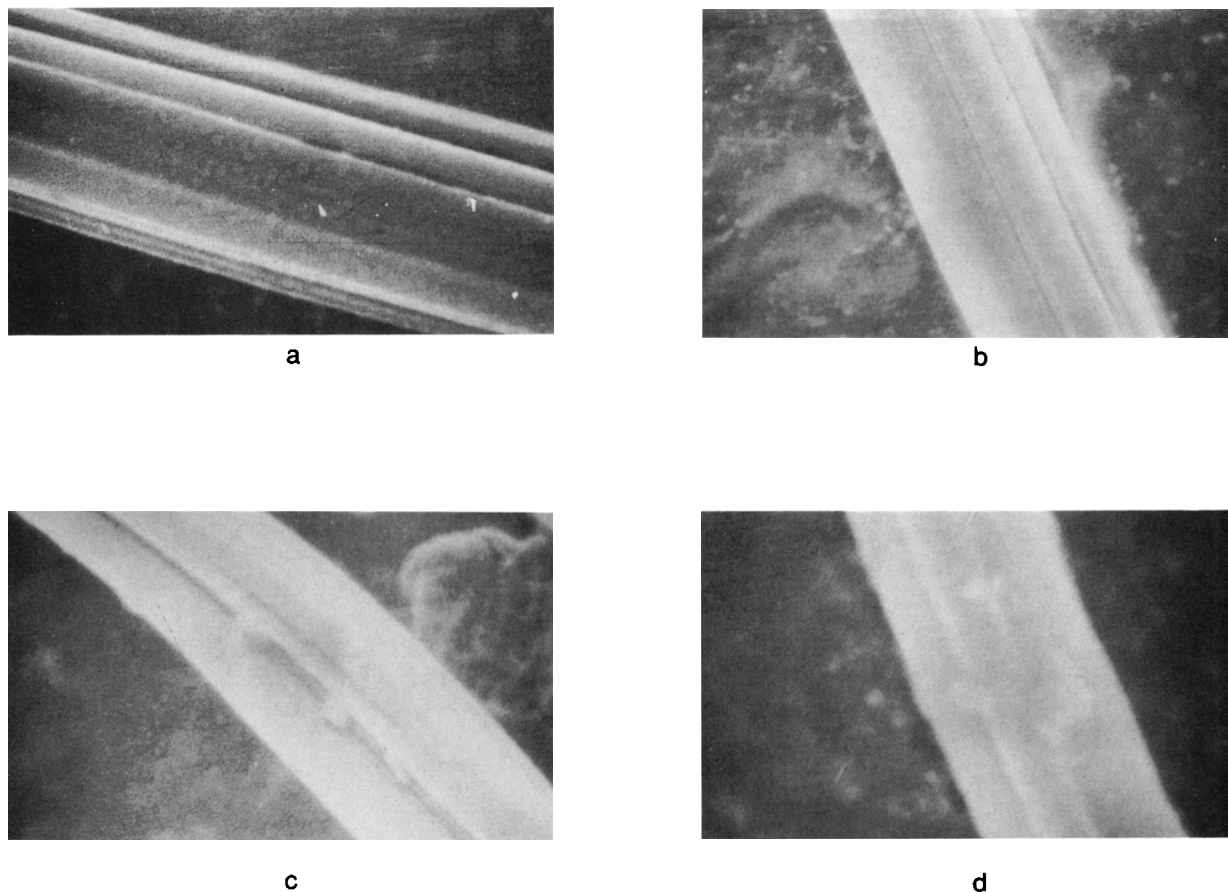
Thermogravimetric and differential thermogravimetric analysis (TGA, DTGA) studies of viscose fiber, PMMA homopolymer, MMA grafted viscose

Table IV Analysis of TGA and DTGA Curves

Sample Particulars	Inception <sup>a</sup> Temperature (°C)	Degradative <sup>b</sup> Weight Loss (%)	Peak Decomposition Temperature (°C)		Major Decomposition Temperature Range (°C)	Residual Weight (%)
			1st Peak	2nd Peak		
Viscose rayon	253	63.75	376	—	258–453 (177)	24.19
MMA homopolymer	270	97.30	—	420	284–450 (166)	Negligible
MMA grafted viscose fibers						
65.95% grafting	269	87.83	380	417	284–448 (164)	4.73
128.85 grafting	278	92.57	399	429	278–470 (192)	2.70
207.18 grafting	286	92.56	395	443	258–484 (226)	1.69
Mixture of rayon and PMMA (80 : 20)	254	86.44	386	416	250–468 (218)	8.78

<sup>a</sup> Starting degradation temperature derived from the derivative curve.

<sup>b</sup> Weight loss due to main degradation reaction as shown by TGA curve.



**Figure 5** Scanning electron micrographs of MMA grafted viscose fibers (3200 X). Graft yield (%), (a) 0, (b) 12.15, (c) 31.40, (d) 162.08.

fibers, with varying degree of grafting and a physical mixture of viscose fiber and PMMA (80 : 20) are computed in Table IV. From these studies it may be concluded that the grafting of MMA on viscose fiber (rayon) improves the thermal stability of the fiber.

### Morphological Structure

The morphological structures are shown in Figure 5. The surface of the ungrafted fiber is smooth. The presence of granules on the surface of the grafted fibers may be due to the PMMA, which is chemically bonded to the surface of the fiber [Fig. 5(c), (d)].

### CONCLUSION

Experimental data reveals that  $\text{TiCl}_3/\text{K}_2\text{S}_2\text{O}_8$  initiation system is unique for the graft copolymerization of MMA onto viscose fiber. The initiator sys-

tem has been found to be much more effective in the presence of visible light compared to same in dark (Table I). The pH dependence initiation for the graft copolymerization has also been explained in the experiment. Characterization of the grafted fibers by FTIR, TGA, and SEM indicate the evidence of grafting on fiber backbone. The stability of the fiber has also been increased by grafting as shown in thermogravimetric curves.

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