

# Graft Copolymerization of Glycidylmethacrylate onto Modified Nylon-6 Fibers

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**ABSTRACT:** The graft copolymerization of glycidylmethacrylate (GMA) onto modified nylon-6 fibers containing polydiallyldimethylammonium chloride (PDADMAC) groups in the presence of  $(\text{Cu}^{2+}-\text{K}_2\text{S}_2\text{O}_8)$  as a redox initiating system was carried out, with very high extent and almost without homopolymer formation. The mechanism of the graft polymerization induced by this system was suggested. The rate of grafting was determined by varying the monomer,  $\text{K}_2\text{S}_2\text{O}_8$ , and cupric ion concentrations as well as the amount of PDADMAC. The kinetic investigation revealed that the rate of graft-

ing ( $R_p$ ) of GMA onto modified nylon-6 fibers is proportional to  $[\text{GMA}]^{1.83}$ ,  $[\text{CuSO}_4 \cdot 5\text{H}_2\text{O}]^{0.46}$ ,  $[\text{PDADMAC}]^{0.4}$ , and  $[\text{K}_2\text{S}_2\text{O}_8]^{1.43}$ . The overall activation energy was 134.7 kJ/mol. The fine structure and thermal properties of the grafted nylon-6 fibers were investigated. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 613–618, 2006

**Key words:** nylon; graft copolymers; glycidylmethacrylate (GMA); quaternary ammonium groups (QAG); kinetics (polym.)

## INTRODUCTION

Nowadays there is widespread use of fibers of synthetic origin because they are relatively inexpensive, can be easily processed, have high surface area, and have excellent physical and chemical properties. However, for a number of applications their surface properties need to be modified to make them suitable for use.

In recent years, the scientific literature has revealed a growing interest in graft copolymerization on polyamide fibers<sup>1–5</sup> as a desirable method of modifying their properties and consequently expanding their applications. One of the new fields of applications of polyamide fibers is the preparation of ion exchangers. A number of such materials, based on grafted nylon-6 fibers with different vinyl monomers, have been prepared.<sup>6,7</sup> However, technical and economical constraints remain important factors in the search for the so-called best available technology not including excessive cost.

Most of the methods presently used for grafting vinyl monomers onto polyamide fibers have limited usefulness because of (1) low rate of grafting reaction, (2) homopolymer formation, (3) irreproducibility in graft yields, and (4) inapplicability on an industrial scale.

Because the ion-exchange capacity is considered one of the basic parameters for selecting the ion exchangers, the preparation of grafted fibers using a method ensuring that the grafting reaction proceeds with a

high rate and without homopolymer formation is thus an absolute necessity. Al-Balakocy<sup>8</sup> reported that the graft copolymerization reaction proceeds with a higher rate and without homopolymer formation only when polyamide contains functional groups that are capable of forming a complex with the initiator on the fibers. Further decomposition of the obtained complex leads to the formation of free radicals on the fibers, thus facilitating direct grafting with a high rate and without formation of homopolymer.

Glycidylmethacrylate (GMA) is considered one of the more important vinyl monomers because of the presence of epoxy groups that have the ability to undergo consecutive modification, which leads to introducing basic or acidic groups to the fibers. This, in turn, leads to the formation of cationic, anionic, or amphoteric ion-exchange fibers.

With respect to these considerations, the object of the work described in this article was to study the grafting of GMA onto modified nylon-6 fibers, containing grafted polydiallyldimethyl ammonium chloride (PDADMAC) in the presence of  $(\text{K}_2\text{S}_2\text{O}_8-\text{Cu}^{2+})$  as a redox initiating system, to verify the role of quaternary ammonium groups (QAG) on the rate and mechanism of the grafting reaction. The fine structure and thermal properties of the grafted nylon-6 fibers were also investigated.

## EXPERIMENTAL

### Materials

Nylon-6 fibers used throughout this study (210 denier/135 filament, density 1.14 g/cm<sup>3</sup>) were gener-

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ously supplied by Misr Rayon Co. (Kafr El-Dawar, Egypt). The fiber samples were scoured at 80°C for 45 min with a solution containing 2 g/L nonionic detergent and 2 g/L sodium carbonate, washed with cooled water, squeezed, and finally air dried.

Pure-grade GMA was rendered inhibitor-free by vacuum distillation at 75°C and 10 mmHg before using. Potassium persulfate ( $K_2S_2O_8$ ), copper sulfate ( $CuSO_4 \cdot 5H_2O$ ), and nonionic detergent, under the commercial name Antrox CC730, were all pure-grade chemicals.

## Methods

### Preparation of nylon-6 fibers containing PDADMAC

The modification was carried out according to the method described by Al-Balakocy.<sup>8</sup>

### Grafting process

*Treatment with potassium persulfate.* The modified nylon-6 samples were treated with a solution containing  $K_2S_2O_8$  (2%) at room temperature for 30 min using a material to liquor ratio of 1 : 50. After this treatment, the fibers were thoroughly washed several times with cold water and dried at room temperature.

*Graft copolymerization.* The  $K_2S_2O_8$ -treated nylon-6 sample thus obtained was charged to a 100-mL stoppered Erlenmeyer flask containing an aqueous solution of GMA and copper sulfate. Polymerization was allowed to proceed at required temperature and duration. At the end of the reaction the sample was completely removed, washed with water, dried in an oven at 105°C for 2 h, and cooled to room temperature in a desiccator until attaining constant weight. The dried sample was then repeatedly Soxhlet extracted with methyl ethyl ketone (MEK) to remove the homopolymer of poly-GMA, dried again as previously indicated, and weighed. The percentage graft yield was calculated as follows:

$$\% \text{ Graft/yield} = \frac{P - P_0}{P_0} \times 100$$

where  $P$  is the dry weight of grafted nylon-6 fibers and  $P_0$  is the dry weight of nylon-6 fibers containing PDADMAC.

## Analysis

### Determination of potassium persulfate concentration

Potassium persulfate concentration in solution and the dried nylon-6 fibers was measured according to the method described by Jenkins.<sup>9</sup>

### Thermal analysis

Differential thermal analysis (DTA) was carried out using a thermal analyzer (Shimadzu, Kyoto, Japan). The rate of heating was adjusted at 15°C/min. Thermograms were recorded from 25 to 250°C under normal atmosphere.

### X-ray diffraction (XRD)

X-ray investigation was carried out using a Siemens D-5000 (computer controller) X-ray diffractometer, with Cu target ( $\lambda = 1.542 \text{ \AA}$ ) and Ni filter. A continuous-scan mode was used to scan  $5^\circ < 2\theta < 65^\circ$  in  $0.05^\circ$  increments. The samples were in powder form.

## RESULTS AND DISCUSSION

It is known that effectiveness of redox systems in graft polymerization processes can be considerably enhanced by fixing one of its components onto the fibers.<sup>10</sup> Therefore grafting was found to proceed, but with a low graft yield (48 and 70% after 10 and 60 min, respectively), when  $K_2S_2O_8$  was adsorbed onto nylon-6 fibers through pretreatment in an aqueous persulfate solution. On the other hand, the graft yield increased significantly (two- to threefold) under the same conditions when nylon-6 fibers were grafted with PDADMAC before the polymerization reaction, which signifies the role of grafted QAG. A substantial increase in the weight of nylon-6 fibers was observed after polymerization, even after several extractions of the fibers with MEK, which is the solvent of poly-GMA. The increase in weight arises from the inclusion of poly-GMA within nylon-6 fibers. The mechanism of such incorporation is believed to be grafting by vinyl addition to polyamide (PA) radicals formed during the polymerization process.

Hahn et al.<sup>11</sup> reported the formation of ionic complex of the cationic monomer with anionic peroxide initiators. Thus, when the nylon-6 fibers containing grafted QAG were immersed in aqueous  $K_2S_2O_8$  solution, a similar complex might be formed and become trapped inside the matrix. This complex dissociates to produce PA macroradicals, as shown by the reactions in Scheme 1.

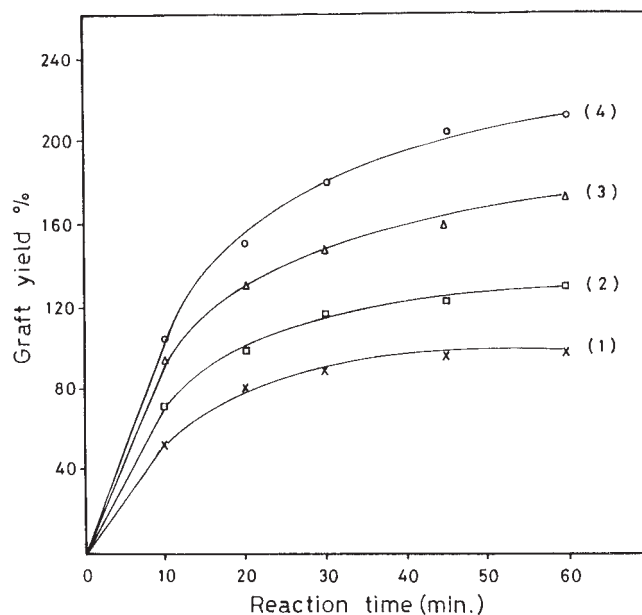
The formation of  $SO_4^{\cdot -}$  and  $Cl^{\cdot}$  in the reaction medium [eqs. (2) and (3)] is expected to lead to homopolymer formation. Indeed, this was found to be the case and necessitates use of  $Cu^{2+}$  ion along with the polyamide grafted with the PDADMAC/ $K_2S_2O_8$ /GMA/ $H_2O$  system.

Given below are the different factors that affect the graft add-on.

### Cupric ion concentration

It was observed that a substantial increase in the graft yield could be achieved when  $Cu^{2+}$  ion was included





**Figure 1** Effect of [PDADMAC] on rate of grafting ( $R_p$ ) of GMA onto nylon-6 fibers. Reaction conditions: [PDADMAC] ( $\times 10^{-3}$  mol/100 g fibers): (1) 1.5, (2) 3.1, (3) 6.2, (4) 9.3; [CuSO<sub>4</sub>·5H<sub>2</sub>O]:  $1.5 \times 10^{-3}$  mol/L; [K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>]:  $2.96 \times 10^{-4}$  mol/L; [GMA]:  $3.02 \times 10^{-1}$  mol/L; reaction temperature: 85°C; material : liquor ratio: 1 : 100.

Kinetic investigation of the dependency of the rate of grafting ( $R_p$ ) of GMA onto nylon-6 fibers on the add-on of PDADMAC revealed that  $R_p$  is proportional to the 0.40 power of PDADMAC concentration.

#### Potassium persulfate concentration

The effect of K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> concentration on the rate of grafting of GMA onto nylon-6 fibers containing QAG was investigated over a range of 1.66 to  $2.96 \times 10^{-4}$  mol/L. Figure 2 illustrates that the graft yield increases as the K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> concentration increases. A graft yield of 213.8% was attained, at a potassium persulfate concentration of  $2.96 \times 10^{-4}$  mol/L.

Kinetic investigation of the effect of K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> concentration on the rate of graft polymerization ( $R_p$ ) revealed that the latter is proportional to the 1.43 power of K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> concentration. Similar observations were reported by Hahn et al.,<sup>11</sup> in the case of radical homopolymerization of PDADMAC, and by Bogoeva et al.<sup>14</sup> when acrylamide was grafted onto polycapraamide in the presence of the K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>/Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> redox system. The elevated order in initiator concentration shows the involvement of K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> in the reactions of chain breakage and its transfer onto the monomer.

#### GMA concentration

The effect of GMA concentration on grafting was investigated within the range 0.75 to  $3.78 \times 10^{-1}$  mol/L.

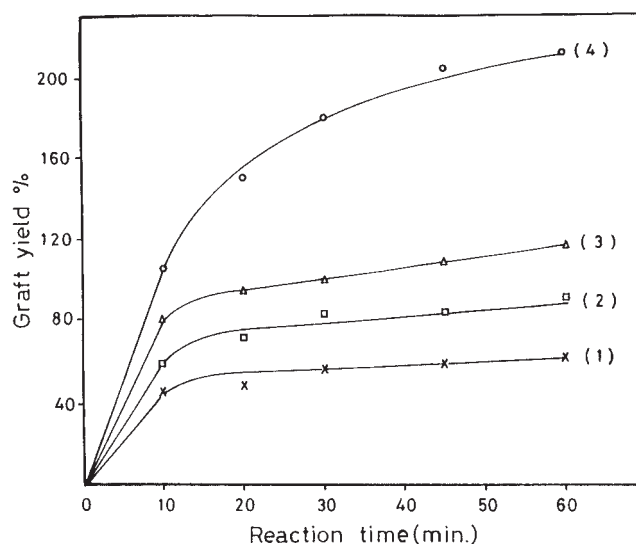
It was found that concentration of  $3.02 \times 10^{-1}$  mol/L constitutes the optimal concentration for achieving maximum graft yield. At higher monomer concentrations, the rate of monomer diffusion was progressively affected by the polymer deposit formed, which of course grows most rapidly when high concentrations of monomer are used. Similar observations have been reported in the grafting of acrylamide onto nylon-6 fibers using trivalent manganese as initiator.<sup>15</sup>

It was found that increasing the reaction time causes a significant increase in the graft yield (Fig. 3). The grafting reaction is characterized by an initial fast rate, followed by a slower one, after which it levels off. This is observed regardless of the GMA concentration used.

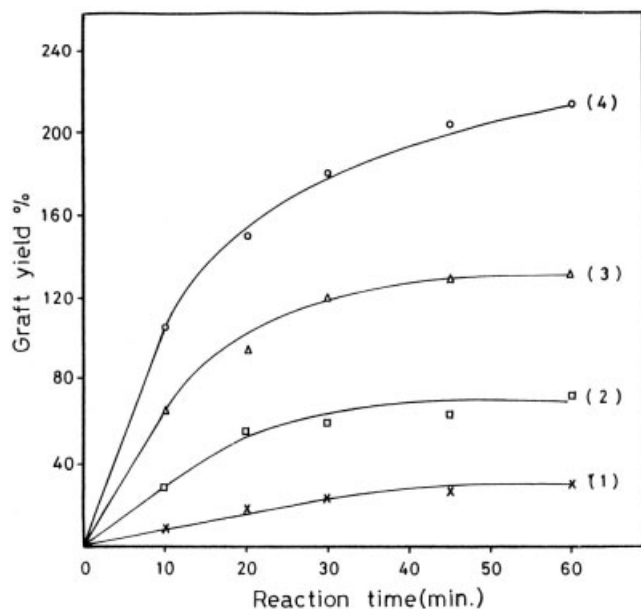
Kinetic investigation of the effect of GMA concentration on the rate of graft polymerization ( $R_p$ ) revealed that the latter is proportional to the 1.83 power of monomer concentration. This provides solid evidence supporting the possibility of the participation GMA in the initiation reaction and is in full harmony with earlier postulation.<sup>5</sup>

#### Polymerization temperature

The graft copolymerization reaction of GMA onto nylon-6 fibers containing PDADMAC was carried out at four temperatures between 70 and 85°C. It was found that the percentage of graft yield increases with increasing temperature (Fig. 4). In a complex system like this, several reactions might be taking place simultaneously such as: (1) a faster rate of PDADMAC-



**Figure 2** Effect of [K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>] on the rate of grafting of PGMA onto nylon-6 fibers. Reaction conditions: [K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>] ( $\times 10^{-4}$  mol/L): (1) 1.664, (2) 2.034, (3) 2.404, (4) 2.96; [PDADMAC]:  $9.3 \times 10^{-3}$  mol/100 g fibers; [CuSO<sub>4</sub>·5H<sub>2</sub>O]:  $1.5 \times 10^{-3}$  mol/L; [GMA]:  $3.02 \times 10^{-1}$  mol/L; reaction temperature: 85°C; material : liquor ratio: 1 : 100.



**Figure 3** Effect of [GMA] on the rate of grafting ( $R_p$ ) of GMA onto nylon-6 fibers. Reaction conditions: [GMA] ( $\times 10^{-1}$  mol/L): (1) 0.75, (2) 1.51, (3) 2.27, (4) 3.02; [PDADMAC]:  $9.3 \times 10^{-3}$  mol/100 g fibers;  $[\text{CuSO}_4 \cdot 5\text{H}_2\text{O}]$ :  $1.5 \times 10^{-3}$  mol/L;  $[\text{K}_2\text{S}_2\text{O}_8]$ :  $2.96 \times 10^{-4}$  mol/L; reaction temperature:  $85^\circ\text{C}$ ; material : liquor ratio: 1 : 100.

$\text{K}_2\text{S}_2\text{O}_8$  complex decomposition, giving rise to more free radicals; (2) enhancement in the swellability of nylon-6 fibers; (3) increased mobility of the monomer molecules; (4) higher rate of GMA diffusion from the reaction medium to the nylon-6 fibers; (5) possible reaction between the growing homopolymer chain with nylon-6 and/or nylon macroradicals; and (6) enhancement in the rate of initiation and propagation of the copolymerization reaction. The net effect of all these factors leads to higher grafting with increasing reaction temperature. Reduction of the percentage of polymer add-on during the latter stages of the reaction could be associated with: (1) depletion in monomer and initiator concentration as well as decrease in the available active sites on nylon-6 backbone; (2) fast rate of termination; and (3) prevention of monomer diffusion attributed to the abundant amount of internally deposited poly-GMA that occurred during the initial stages of polymerization.

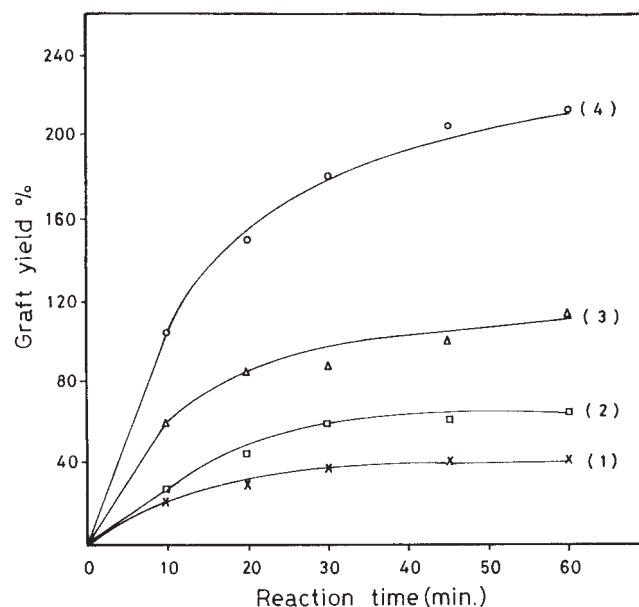
Based on the obtained results, the apparent activation energy of grafting of GMA onto nylon-6 fibers containing PDADMAC was found to be 134.7 kJ/mol.

#### Characterization of modified nylon-6 fibers

The internal structure and the thermal properties of parent and modified nylon-6 fibers were investigated by an XRD technique and by diffraction thermal anal-

ysis. Based on the results obtained using these techniques (Table II), the following can be concluded:

1. The parent material and all of its modified samples have the same diffraction patterns with two well-defined and much more intense different planes at  $2\theta$  at  $20$  and  $24^\circ$ , irrespective of the type of fibers and amount of modifications. This verifies that a chemical reaction took place and that we are dealing with a grafted polymer rather than with a mixture of two polymers. On the other hand, this fact provides solid evidence supporting that we have the same unit cell type. This type is similar to a pseudohexagonal structure in a previous report.<sup>16</sup>
2. The degree of crystallinity of the modified nylon-6 fibers is found to be less than that of the parent one. The decreasing trend depends on the amount of the grafted PGMA. According to the matrix effect, we can assume that the grafted surface layers in the earlier stages of the grafting process, in contact with highly oriented surface layers of the nylon-6 matrix, will also have a certain degree of orientation. This effect decreases with increasing PGMA add-on.
3. No individual glass-transition ( $T_g$ ) and melting temperature ( $T_m$ ) values corresponding to the grafted PDADMAC and PGMA were observed, thus indicating that the graft copolymer mainly



**Figure 4** Effect of reaction temperature on the rate of grafting ( $R_p$ ) of GMA onto nylon-6 fibers. Reaction conditions: reaction temperature ( $^\circ\text{C}$ ): (1) 70, (2) 75, (3) 80, (4) 85; [PDADMAC]:  $9.3 \times 10^{-3}$  mol/100 g fibers;  $[\text{CuSO}_4 \cdot 5\text{H}_2\text{O}]$ :  $1.5 \times 10^{-3}$  mol/L;  $[\text{K}_2\text{S}_2\text{O}_8]$ :  $2.96 \times 10^{-4}$  mol/L; [GMA]:  $3.02 \times 10^{-1}$  mol/L; material : liquor ratio: 1 : 100.

TABLE II  
Effect of the Amount of Grafted PGMA on Crystallinity, Glass-Transition Temperature ( $T_g$ ), and Melting Point ( $T_m$ ) of Nylon-6 Fibers

Sample	2 $\theta$ value		Crystallinity (%)	$T_g$	$T_m$
	1st peak	2nd peak			
Nylon-6 fibers	18.0	23.7	37.9	57.5	222.7
Nylon-6-g-PDADMAC(1.5%)	20.3	23.6	33.9	57.2	219.6
Nylon-6-g-PDADMAC(1.5%)-g-PGMA(5%)	20.5	24.0	25.4	—	216.5
Nylon-6-g-PDADMAC(1.5%)-g-PGMA(16%)	20.5	24.0	23.6	51.3	211.6
Nylon-6-g-PDADMAC(1.5%)-g-PGMA(45%)	20.0	24.0	16.5	—	212.5
Nylon-6-g-PDADMAC(1.5%)-g-PGMA(80%)	20.0	24.0	13.8	41.2	189.7

exists in the form of grafted chains on the surface of nylon-6 fibers. It was apparent that  $T_g$  and  $T_m$  values of nylon-6 fibers decreased as a result of modification with PGMA. The decreasing trend depends on the amount of grafted polymer, which is in full agreement with the crystallinity of grafted samples.

### CONCLUSIONS

The graft copolymerization of glycidylmethacrylate onto modified nylon-6 fibers, containing polydiallyldimethylammonium chloride, in the presence of  $K_2S_2O_8-Cu^{2+}$  as a redox initiating system was carried out. It was found that the presence of quaternary ammonium groups in nylon-6 macromolecules facilitates the grafting reaction with a very high rate, and almost without homopolymer formation. Kinetic investigation revealed that the  $R_p \propto [GMA]^{1.83}$ ,  $[CuSO_4 \cdot 5H_2O]^{0.46}$ ,  $[PDADMAC]^{0.4}$ , and  $[K_2S_2O_8]^{1.43}$ . The apparent activation energy of grafting was calculated and was found to be 134.7 kJ/mol. The grafting of GMA onto nylon-6 fibers led to a decrease in the degree of crystallinity,  $T_g$ , and  $T_m$  of the fibers. The mode of decrement depends on the graft level.

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