Surface Modification of Nylon-6 Fibers for Medical Applications

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ABSTRACT: Hydroxyethylmethacrylate (HEMA) is considered to be one of the important vinyl monomers. The ability of polyhydroxyethyl-methacylate (PHEMA) graft sites to consecutive chemical modification makes the use of nylon-6 fibers grafted with PHEMA a feasible bed for immobilization of a wide range of biologically active reagents, specially enzymes, drugs, cells, and immunadsorbents. Stemming from the above discussions, in this article, the graft copolymerization of HEMA onto modified nylon-6 fibers containing Polydiallyldimethylammonium chloride (PDADMAC) in the presence of Cu^{2+}–$K_2S_2O_8$ as a redox initiating system was carried out, with very high rate and almost without homopolymer formation. The factors affecting the grafting reaction (monomer, $K_2S_2O_8$ and cupric ion concentrations, the amount of PDADMAC as well as the reaction temperature) were studied. Kinetic investigation revealed that the rate of grafting (R_p) of HEMA onto modified nylon-6 fibers is proportional to $[HEMA]^1$, $[CuSO_4.5H_2O]^{0.7}$, $[PDADMAC]^{0.4}$, and $[K_2S_2O_8]^{1.4}$. The overall activation energy was calculated (71 KJ/mol). The fine structure, surface topography, thermal and electrical properties of parent and grafted nylon-6 fibers were investigated. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 104: 3788–3796, 2007

Key words: nylon-6 fibers; graft copolymerization; hydroxyethylmethacrylate (HEMA); polyhydroxyethylmethacrylate (PHEMA); polydiallyldimethylammonium chloride (PDADMAC); X-ray; SEM; DSC–TGA; electrical properties

INTRODUCTION

In recent years, scientific reports on synthetic fibers have revealed a continuously growing interest in polymers and fibers suitable for medical applications. Any biomaterial that is to be clinically used for the next generation should have excellent properties both in bulk and surface. However, it is very rare that a material with good bulk properties also possesses the surface characteristics required for medical applications. This is the reason why surface modification is in many cases essential for a material to be applied in medicine. The surface of the materials used for medical applications is modified for at least two purposes; one to render the material surface biocompatible, and the other to give it physiological activity.

The manufacture of bioactive polyamide fibers can be accomplished by the modification of readymade fibers followed by their treatment with bactericidal agents,[1–5] or by addition of bactericides to polymer chips before fiber formation.[6] For the medical purpose, addition and blending technologies are not recommended since the additives will leach out, causing cytotoxicity. Surface modifications through covalent bonding without bulk deterioration are most desirable for biomaterials. Among these methods surface grafting is especially important, because the interface properties of fibers can be designed to the requirements of many very diverse applications (ion-exchanging, filtration, separation, and biological technology).[7]

The graft polymerization of acrylic acid (AA) on polyamide-6 (PA-6) yarns was carried out. The resultant fibers were additionally modified with penicillin, neomycin, or gentamycin to obtain antibacterial fibers.[5] Protoporphyrin IX-ethylenediamine (PPIX-ED) and zinc protoporphyrin IX-ethylenediamine (Zn-PPIX-ED) have been grafted onto nylon surface with pregrafted polyacrylic acid polymer chain. This technique has proved to be a consistent and reliable method for permanently attaching light-activated antimicrobial molecules to nylon surface.[8] Nylon particles were grafted with diethylene glycol dimethacrylate (DGMA) and treated with hexamethylene diamine (HMDA). The aminoalkylated particles were activated with Glutaraldehyde and finally, penicillin G acrylase (PA) was immobilized to these activated particles.[9]

The problem with grafting approach is that a large number of graft sites must be available for attaching the bactericidal agents, where as the number of potential graft sites on the surfaces of most noncellulosic polymers is very small.

Hydroxyethylmethacrylate (HEMA) is considered to be one of the important vinyl monomers. The ability

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of polyhydroxyethylmethacylate (PHEMA) graft sites to consecutive chemical modification makes the use of nylon-6 fibers grafted with PHEMA a feasible bed for immobilization of a wide range of biologically active reagents, specially enzymes, drugs, cells, and immunoadsorbents. But nowadays, the available methods for grafting nylon-6 fibers with HEMA proceed with low rate and are accompanied with homopolymer formation.[10] Stemming from the discussions above, a method ensuring increasing the number of graft PHEMA sites with a high rate and without homopolymer formation is thus an absolute necessity.

The present article aims at the grafting of HEMA to the surface of nylon-6 fibers based on a new technique which paves the way for proceeding reaction with high rate and without homopolymer formation. Moreover, the properties of grafted nylon-6 fibers with polyhydroxyethyl-methacylate (PHEMA) were studied. The immobilization of biologically active reagents onto nylon-6 grafted with PHEMA and the antimicrobial effectiveness of these materials will be the subject of forthcoming publication.

EXPERIMENTAL

Materials

Nylon-6 fibers used throughout this study (210 denier/135 filament, density 1.14 g/cm^3) were kindly supplied by Misr Rayon Co. (Kafer El-Dawar, Egypt). The fibers were scoured at 80°C for 45 min with solution containing 2 g/L nonionic detergent and 2 g/L sodium carbonate, washed with cooled water, squeezed, and finally air dried.

Hydroxyethylmethacrylate (HEMA), Potassium persulphate ($K_2S_2O_8$), and Copper sulfate ($CuSO_4 \cdot 5H_2O$), were all of pure grade chemicals.

Methods

Preparation of nylon-6 fibers containing Polydiallyldimethyl-ammonium chloride (PDADMAC) was carried out according to the method described by Shalaby.[11]

Grafting Process

The modified nylon-6 samples containing PDADMAC 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 : 100. After this treatment, the fibers were thoroughly washed several times with cold water, and dried at room temperature.

The so-obtained $K_2S_2O_8$-treated nylon-6 sample was introduced in 100 mL stoppered Erlenmeyer flask containing an aqueous solution of HEMA and copper sulfate. Polymerization was allowed to proceed at required temperature and duration. At the end of the reaction the sample was removed, thoroughly washed with water, dried in an oven at 105°C for 2 h, and cooled to room temperature in a dissecator until attaining constant weight. The dried sample was then repeatedly soxhlet extracted with methanol to remove the homopolymer of PHEMA, dried again as previously indicated and weighed. The percentage graft yield was calculated as follows:

$$\% \text{ Graft yield} = \frac{P - P_0}{P_0} \times 100 \quad (1)$$

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

Analysis

Potassium persulphate concentration in solution and the dried nylon-6 fibers was measured according to the method described by Jenkins.[12]

X- ray investigation was carried out using Siemens D-5000 (computer controller) X-ray diffractometer, with Cu target ($\lambda = 1.542$ Å) and Ni filter. A continuous scan mode was used to scan $5^\circ < 2\theta < 75^\circ$ in 0.05° increments. Samples were in powder form.

Thermogravimetric analysis (TGA) for parent and grafted nylon-6 samples were carried out using TGA-50 Shimadzu thermal analyzer. The rate of heating was adjusted at 10°C/min. Thermograms were recorded from 25°C to 600°C under nitrogen atmosphere.

Differential scanning calorimetry (DSC) for parent and grafted nylon-6 samples was carried out using DSC-50 Shimadzu thermal analyzer. The rate of heating was adjusted at 10°C/min. Thermograms were recorded from 25°C to 400°C under nitrogen atmosphere.

Surface topography of nylon-6 fibers was examined in an JEOL JXA-84OH Electron Probe Microanalyzer JAPAN operating at 19 kVA thin coating (~ 10 nm) of gold was deposited onto the sample, and attached to the stub, prior to examination in the SEM.

A.C. Electrical properties [Resistance (Ω), Capacitance (CpF), and electrical loss factor (tan δ)] for both parent and modified nylon-6 fibers were measured with the help of computerized a.c. bridge [HIOKI3532 LCR HITESTER] in the frequency range 5–50 MHz and temperature from room 25°C–100°C. Samples were in the form of tablets and silver past was used as electrodes.

RESULTS AND DISCUSSION

The chemical modification of polyamide fibers via grafting with vinyl monomers, could be applicable on

industrial scale, only when the grafting process proceeds with higher rate and without homopolymer formation. These limitations could be fulfilled only when polyamide contains function groups which are capable of formation of 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 paving the way for direct grafting almost without the formation of homopolymer. It is well known that quaternary ammonium groups (QAG) can form complexes with peroxides.[13] Stemming from this, a simple method for creation of such groups in nylon-6 macromolecule was adopted.[11] In previous investigations,[14–16] the reliability of applying polyamide fibers containing QAG, rather than the application of pure ones, for grafting with methacrylic acid,[14] acrylamide,[14] 2,2 dimethylaminoethylmethacrylate[15] and glycidyl-methacrylate,[16] was verified.

In this work, we report on the results of graft copolymerization of HEMA onto nylon-6 fibers, containing PDADMAC, by using Cu^{2+}–$K_2S_2O_8$ redox system. Moreover, the fine structure, surface topography, thermal and electrical properties of parent and grafted fibers were evaluated.

It was observed that no grafting occurs when nylon-6/HEMA/Cu^{2+}/H_2O or nylon-6/HEMA/$K_2S_2O_8$/Cu^{2+}/H_2O systems were used irrespective of the conditions of the reaction. Under these conditions tremendous amount of homopolymer formation observed with the latter system. Grafting was found to proceed, but with a low graft yield (22.5% after 60 min at 90°C), when $K_2S_2O_8$ was adsorbed onto nylon-6 fibers through pretreatment in an aqueous persulphate solution. On the other hand the graft yield increased significantly under the same conditions when nylon-6 fibers were grafted with PDADMAC prior to the polymerization reaction; a point which signifies the role of grafted QAG. It was observed that, there was a substantial increase in the weight of nylon-6 fibers after polymerization even after several extractions of the fibers with methanol which is the solvent of PHEMA. The increase in weight is due to inclusion of PHEMA within nylon-6 fibers. The mechanism of such incorporation is believed to be grafting by vinyl addition to polyamide radicals formed during the polymerization process, and is similar to that indicated in a pervious paper.[16]

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

Cupric ion concentration

Figure 1 and Table I show the effect of incorporation of various concentrations of copper sulfate on the extent and rate of grafting. At first glance, the presence of Cu^{2+} causes an outstanding enhancement in the extent and rate of grafting. This enhancement

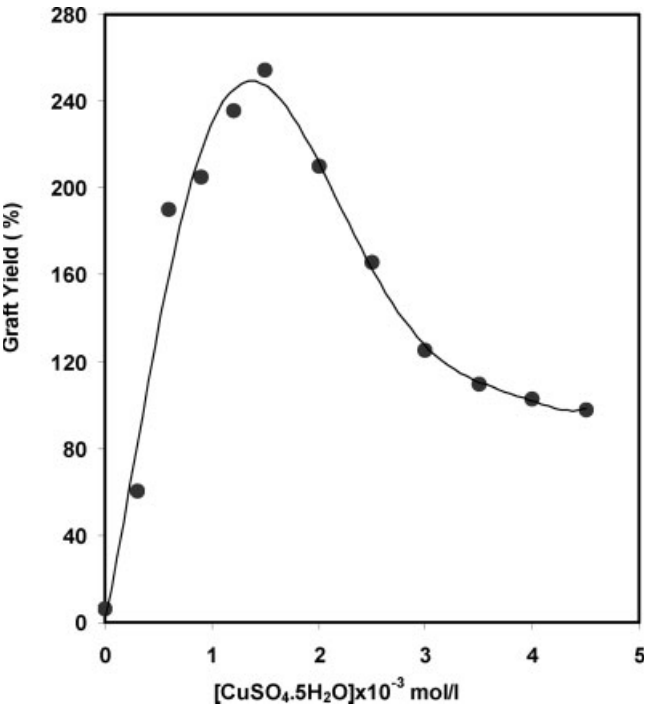

Figure 1 Effect of [$CuSO_4 \cdot 5H_2O$] on graft yield % of PHEMA onto nylon-6 fibers. Reaction Conditions: [HEMA], 2.46×10^{-1} mol/L; [$K_2S_2O_8$], 2.96×10^{-4} mol/L; [PDADMAC], 9.9×10^{-3} mol/100 g fibers; Reaction time, 60 min; Reaction temperature, 90°C; Material : Liquor ratio, 1 : 100.

depends on the concentration of Cu^{2+} ion. The graft yield increases with increasing $CuSO_4 \cdot 5H_2O$ concentration up to 1.5×10^{-3} mol/L. Thereafter, the graft yield decreases as the Cu^{2+} ion concentration increases. However, regardless of the Cu^{2+} ion concentration used in this work, the graft yield obtained in the presence of Cu^{2+} is much greater than in its absence. The implication of this is that the presence of copper sulfate up to a certain concentration in the polymerization system helps the decomposition of $K_2S_2O_8$ to yield efficient $SO_4^{\bullet}-$ for grafting. At relatively high copper sulfate concentration, the Cu^{2+} ions seem to participate in the termination of growing grafted chain radicals and nylon-6 macroradicals.

Kinetic investigation of the dependence of the rate of grafting (R_p) of HEMA onto nylon-6 fibers, containing PDADMAC, revealed that R_p is proportional to 0.69 power of $CuSO_4 \cdot 5H_2O$ concentration.

PDADMAC add-on

Table I shows the effect of reaction time on the degree and rate of grafting of HEMA onto nylon-6 fibers, containing different PDADMAC add-on. It can be seen that, regardless of PDADMAC add-on used, grafting increases significantly by increasing reaction time to 45 min. Further increase in reaction time above 45 min seems to display little effect on the graft yield. The R_p

TABLE I
Effect of [$CuSO_4.5H_2O$], [PDADMAC], [$K_2S_2O_8$], and [HEMA] on the Extent and Rate of Grafting (R_p)

	Reaction Time (S)									
	600		1200		1800		2700		3600	
[$CuSO_4.5H_2O$], (mol/L) [a]	G.Y (%) (1)	R_p (mo1 L^{-1} Sec^{-1}) (2)	G.Y (%) (3)	R_p (mo1 L^{-1} Sec^{-1}) (4)	G.Y (%) (5)	R_p (mo1 L^{-1} Sec^{-1}) (6)	G.Y (%) (7)	R_p (mo1 L^{-1} Sec^{-1}) (8)	G.Y (%) (9)	R_p (mo1 L^{-1} Sec^{-1}) (10)
0.0									6	1.3×10^{-6}
0.6×10^{-3}	25	3.2×10^{-5}	80	5.1×10^{-5}	125	5.3×10^{-5}	180	5.1×10^{-5}	190	4.1×10^{-5}
0.9×10^{-3}	36	4.6×10^{-5}	100	6.4×10^{-5}	150	6.4×10^{-5}	200	5.7×10^{-5}	205	4.4×10^{-5}
1.2×10^{-3}	42	5.4×10^{-5}	120	7.7×10^{-5}	180	7.7×10^{-5}	230	6.6×10^{-5}	236	5.0×10^{-5}
1.5×10^{-3}	50	6.4×10^{-5}	132	8.5×10^{-5}	202	8.6×10^{-5}	250	7.1×10^{-5}	255	5.4×10^{-5}
[PDADMAC], (mol/100 gr. Fibers)[b]	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)
0.0									23	4.9×10^{-6}
3.1×10^{-3}	25	3.2×10^{-5}	71	4.6×10^{-5}	110	4.7×10^{-5}	186	5.3×10^{-5}	200	4.3×10^{-5}
6.2×10^{-3}	35	4.5×10^{-5}	80	5.1×10^{-5}	150	6.4×10^{-5}	219	6.2×10^{-5}	225	4.8×10^{-5}
7.4×10^{-3}	45	5.8×10^{-5}	100	6.4×10^{-5}	175	7.5×10^{-5}	235	6.7×10^{-5}	240	5.1×10^{-5}
9.9×10^{-3}	50	6.4×10^{-5}	132	8.5×10^{-5}	202	8.6×10^{-5}	250	7.1×10^{-5}	255	5.4×10^{-5}
[$K_2S_2O_8$], (mol/L)[c]	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)
2.03×10^{-4}	36	4.6×10^{-5}	100	6.4×10^{-5}	165	7.1×10^{-5}	219	6.2×10^{-5}	224	4.8×10^{-5}
2.40×10^{-4}	43	5.5×10^{-5}	122	7.8×10^{-5}	183	7.8×10^{-5}	232	6.6×10^{-5}	232	5.0×10^{-5}
2.96×10^{-4}	50	6.4×10^{-5}	132	8.5×10^{-5}	202	8.6×10^{-5}	250	7.1×10^{-5}	255	5.4×10^{-5}
[HEMA] (mol/L)[d]	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)
0.5×10^{-1}	10	1.3×10^{-5}	23	1.5×10^{-5}	32	1.4×10^{-5}	40	1.1×10^{-5}	50	1.1×10^{-5}
1.48×10^{-1}	28	3.6×10^{-5}	53	3.4×10^{-5}	88	3.8×10^{-5}	109	3.1×10^{-5}	124	2.6×10^{-5}
1.97×10^{-1}	37	4.7×10^{-5}	80	5.1×10^{-5}	127	5.4×10^{-5}	165	4.7×10^{-5}	189	4.0×10^{-5}
2.46×10^{-1}	50	6.4×10^{-5}	132	8.5×10^{-5}	202	8.6×10^{-5}	250	7.1×10^{-5}	255	5.4×10^{-5}

G.Y, Graft Yield.
R_p, Rate of Grafting.
[a] [HEMA], 2.46×10^{-1}mol/L; [$K_2S_2O_8$], 2.96×10^{-4} mol/L; [PDADMAC], 9.9×10^{-3} mol/100 gr.Fibers; Temp., 90°C; M : L, 1 : 100.
[b] [HEMA], 2.46×10^{-1}mol/L; [$CuSO_4 \cdot 5H_2O$], 1.5×10^{-3} mol/L; [$K_2S_2O_8$], 2.96×10^{-4}; Temp., 90°C; M : L, 1 : 100.
[c] [HEMA], 2.46×10^{-1}mol/L; [$CuSO_4 \cdot 5H_2O$], 1.5×10^{-3} mol/L; [PDADMAC], 9.9×10^{-3} mol/100 gr.Fibers; Temp., 90°C; zM : L, 1 : 100.
[d] [$CuSO_4 \cdot 5H_2O$], 1.5×10^{-3} mol/L; [$K_2S_2O_8$], 2.96×10^{-4} mol/L; [PDADMAC], 9.9×10^{-3} mol/100 gr.Fibers; Temp., 90°C; M : L, 1 : 100.

also increases with increasing reaction time up to 30 min, thereafter it decreases as the duration increases. On the other hand, the higher the PDADMAC add-on, the higher is the rate and the degree of grafting. The accelerating effect of PDADMAC could be attributed to the formation of complex with $K_2S_2O_8$ and the decomposition of this complex.

The logarithmic relationship between the rate of grafting R_p and PDADMAC add-on revealed that R_p is proportional to 0.44 power of PDADMAC concentration.

$K_2S_2O_8$ concentration

Table I shows the effect of reaction time on the degree and rate of grafting, at constant aqueous HEMA concentration, onto nylon-6 fibers containing PDADMAC over a range of 1.66 to 2.96 $\times$ 10^{-4} mol/L $K_2S_2O_8$. It can be seen that the graft yield and R_p increase with increasing the reaction time for all the studied concentrations. However, at longer reaction time the degree of grafting levels off and the R_p decreases. Moreover, the graft yield and R_p increase as the $K_2S_2O_8$ concentration increases.

Kinetic investigation of the effect of $K_2S_2O_8$ concentration on the R_p revealed that the latter is proportional to 1.42 power of $K_2S_2O_8$ concentration. Similar observations were reported by Shalaby when dimethylaminoethyl-methacrylate[15] and glycidylmethacrylate[16] were grafted onto nylon-6 fibers containing PDADMAC in the presence of redox system $K_2S_2O_8$–Cu^{2+}, and by Bogoeva[17] in case of grafting acrylamide onto polycaproamide in the presence of $K_2S_2O_8$/$Na_2S_2O_3$ redox system. The elevated order of initiator concentration shows the involvement of $K_2S_2O_8$ in the reaction of chain break and its transfer onto the monomer.

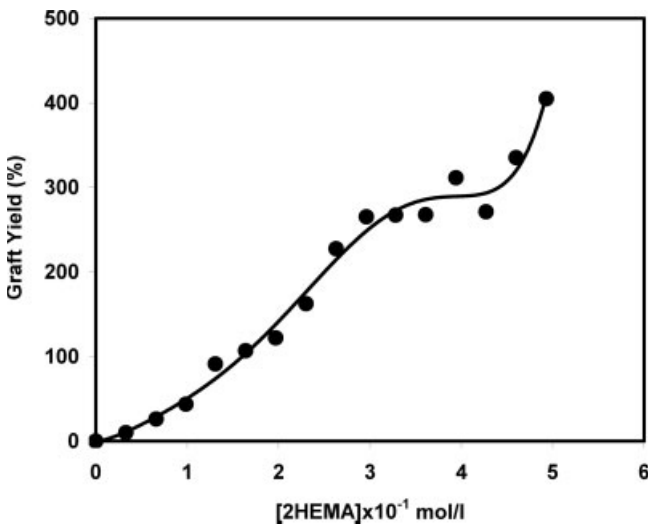

Figure 2 Effect of HEMA on the graft yield % of PHEMA onto nylon-6 fibers. Reaction Conditions: [$CuSO_4.5H_2O$], 1.5 $\times$ 10^{-3} mol/L; [$K_2S_2O_8$], 2.96 $\times$ 10^{-4} mol/L; [PDADMAC], 9.9 $\times$ 10^{-3} mol/100 g fibers; Reaction time, 30 min; Reaction temperature, 90°C; Material : Liquor ratio, 1 : 100.

HEMA concentration

The effect of HEMA concentration on grafting was investigated within the range 0.33 $\times$ 10^{-1} to 4.6 $\times$ 10^{-1} mol/L, while keeping other experimental conditions constant (Fig. 2). It was observed that the graft yield increased steadily with an increase in HEMA concentration. Moreover, at a shorter grafting time (45 min.), there is a significant increase in the degree of grafting with increasing HEMA concentration (Table I). However, further increase in the reaction time has a little effect on the graft yield, especially when lower monomer concentration is used. The dependence of the R_p on monomer concentration, calculated from logarithmic relationship between the R_p and [HEMA], was found to be first-order dependence.

Polymerization temperature

Table II shows the effect of temperature on the extent and rate of grafting of HEMA on nylon-6 fibers, containing PDADMAC. It is clear that, both the extent and R_p increase as the reaction temperature increases from 65°C to 90°C. The enhancement in grafting by raising the polymerization temperature could be attributed to the softness and flexibility of the polyamide structure close to the glass transition temperature (60°C).[18] Above this temperature, the diffusion of the monomer and the decomposition of PDADMAC–$K_2S_2O_8$ complex are greatly enhanced.

Based on the results of Table II the apparent activation energy of grafting of HEMA onto nylon-6 containing PDADMAC was calculated using the Arhenius equation by plotting ln R_p versus $1/T$. The apparent activation energy was found to be 71 KJ/mol^{-1}.

Characterization of modified nylon-6 fibers

Internal structure

The internal structure of parent and modified nylon-6 fibers was investigated by XRD technique. Two different planes (2θ $\sim$ 21° and 24°), which are well defined and much more intense, have been selected for comparison. Based on the above-mentioned measurement and observation, (Table III) the following can be concluded:

1. The nylon-6 fibers and its all modified samples have the same diffraction patterns, irrespective of the type and amount of modification. This means that we have the same unit cell type. On other

TABLE II
Effect of Temperature on the Extent and Rate of Grafting (R_p)

Temperature (°C)	10^3/T	Reaction Time (Sec.) 600 G.Y (%)	600 R_p(mol L^{-1} Sec^{-1})	1200 G.Y (%)	1200 R_p (mol L^{-1} Sec^{-1})	1800 G.Y (%)	1800 R_p (mol L^{-1} Sec^{-1})	2700 G.Y (%)	2700 R_p (mol L^{-1} Sec^{-1})	3600 G.Y (%)	3600 R_p (mol L^{-1} Sec^{-1})
65	3.00	6	7.7×10^{-6}	17	1.1×10^{-5}	30	1.3×10^{-5}	46	1.3×10^{-5}	50	1.1×10^{-5}
70	2.91	15	1.9×10^{-5}	35	2.2×10^{-5}	72	3.1×10^{-5}	90	2.6×10^{-5}	100	2.1×10^{-5}
80	2.83	30	3.8×10^{-5}	80	5.1×10^{-5}	150	6.4×10^{-5}	210	6.0×10^{-5}	225	4.8×10^{-5}
90	2.75	50	6.4×10^{-5}	132	8.5×10^{-5}	202	8.6×10^{-5}	250	7.1×10^{-5}	255	5.4×10^{-5}

G.Y., Graft Yield.
R_p, Rate of Grafting;
[HEMA], 2.46×10^{-1}mol/L; [$CuSO_4.5H_2O$], 1.5×10^{-3} mol/L; [$K_2S_2O_8$], 2.96×10^{-4} mol/L.
[PDADMAC], 9.9×10^{-3} mol/100 gr. fibers; Material : Liquor ratio, 1 : 100.

hand, this verifies that a chemical reaction took place and that we are dealing with a grafted polymer rather than a mixture of polymers.

2. The degree of crystallinity of the modified nylon-6 fibers was found to be less than that of the parent one. The trend of decrease depends upon the type and the amount of the grafted polymer. The higher the amount of the grafted PHEMA, the lower the degree of crystallinity of nylon-6 fibers.

The fiber topography

Fiber surface topography of nylon-6 fibers was studied using SEM. The electron micrographs, corresponding to different investigated samples, are depicted in Figure 3. Before grafting, the surface of nylon-6 fiber has a smooth and relatively homogenous appearance. Grafting of 1.5% of PDADMAC developed roughness running vertical to the fiber axis. After HEMA grafting onto nylon-6 fiber, the surface has gained a heterogeneous appearance, which shows another proof of grafting. In case of samples containing PDADMAC and grafted with PHEMA the micrographs provide an excellent view of the distribution of the regular parallel transparent lines which are perpendicular to the edge of the fiber. Moreover, the density of these lines increases with increasing the amount of grafted PHEMA from 10 to 50%. Also, it can be seen from Figure 3, that no significant deposition of grafted polymer exists on the outside of the fibers.

Electrical properties

The effect of grafting nylon-6 fibers, containing PDADMAC, with HEMA on electrical resistance (RΩ), electrical capacitance (Cp), and electrical loss factor (tan δ) of the modified fibers was studied (Table III). Based on the obtained data, one can conclude the following:

1. Grafting with HEMA leads to a decrease in the value of $R(\Omega)$ for all grafted nylon-6 fibers. Moreover, the magnitude of decrease depends upon the amount of grafted PHEMA, irrespective of the values of the temperature and frequency used in measurements. The increase in temperature, at constant frequency, did not affect the value of $R(\Omega)$, the fact which indicates that the physical structural of the tested samples did not change within the range of temperature used. On the other hand, it was found that the increase in frequency, at constant temperature, leads to a significant decrease of R (Ω) for parent and modified nylon-6 fibers. This indicates that, during testing the increase in frequency is accompanied with a

TABLE III
d-Spacing and Crystallinity of Parent and Modified Nylon-6 Fibers

Sample	*d*-spacing (Å)		2θ	Crystallinity (%)	
	1st peak	2nd peak	1st peak	2nd peak	
Nylon-6	4.344	3.777	21.0	24.0	59.2
Nylon-6-gr.PDADMAC (1.5%)	4.377	3.752	21.0	24.0	52.0
Nylon-6-gr.PDADMAC (1.5%)-gr. PHEMA (10%)	4.407	3.747	20.5	24.5	53.6
Nylon-6-gr.PDADMAC (1.5%)-gr. PHEMA (30%)	4.354	3.695	21.0	24.5	47.99
Nylon-6-gr.PDADMAC (1.5%)-gr. PHEMA (50%)	4.407	3.728	20.5	24.5	46.2

significant increase in movement of ions in the fine structure of polymer and thereby increasing the electrical conductivity. Moreover, the decrease of $R(\Omega)$ of grafted nylon-6 fibers with the increase of graft yield of PHEMA is mainly due to: (a) the presence of polar OH groups in the grafted nylon-6 fibers, and (b) to the increase in moisture content of the modified samples.

2. In general, it was found that grafting with HEMA leads to an increase in capacitance (Cp) of modified samples as compared with the parent nylon-6 fibers: The higher the (Cp), the higher the grafted amount of PHEMA, irrespective of the temperature and frequency used during testing. While the change in temperature, within the range of frequency used, did not affect the value of electrical capacitance, the latter for all samples increases with increasing frequency at a constant temperature.

   Based on the fact, that the presence of grafted PHEMA leads to an increase in the electrical capacitance, the grafted samples are more capable of getting rid of the static charges. The verification of this comes from the results of SEM examination for grafted samples. SEM revealed the presence of ripples which increase with increasing the amount of grafted PHEMA.
3. Grafting of nylon-6 fibers, containing PDADMAC, with HEMA leads to a decrease in electrical loss factor (tan δ). The higher the graft yield, the greater the decrease of tan δ. Irrespective of type of tested fibers, the increase in frequency is accompanied with a noticeable decrease in tan δ.

Thermal properties (DSC-TGA)

The thermal properties of parent and nylon-6 grafted fibers were investigated by studying their DSC curves and TGA thermograms. The results are presented in Table IV, which indicate the following:

1. No individual T_g and T_m points corresponding to the graft PDADMAC and PHEMA were observed, indicating thereby that the graft copolymer mainly exists in the form of grafted chain on the surface of nylon-6 fibers. Moreover, it is apparent that, the T_g and T_m temperatures of nylon-6 fibers are changed due to modification with PDADMAC and PHEMA. This is in agreement with x-ray investigation, which revealed that grafting of PHEMA decreases the crystallinity of the nylon-6 fibers.
2. The initial decomposition temperature (IDT) decreases with increasing the percentage of grafted PHEMA.
3. With an increase in the graft level, the decomposition temperature (T_D) decreases continuously in the cases of weight loss percentage from 20 to 60%, as compared to that of parent nylon-6 fibers. Apon increase of weight loss over 60% the tem-

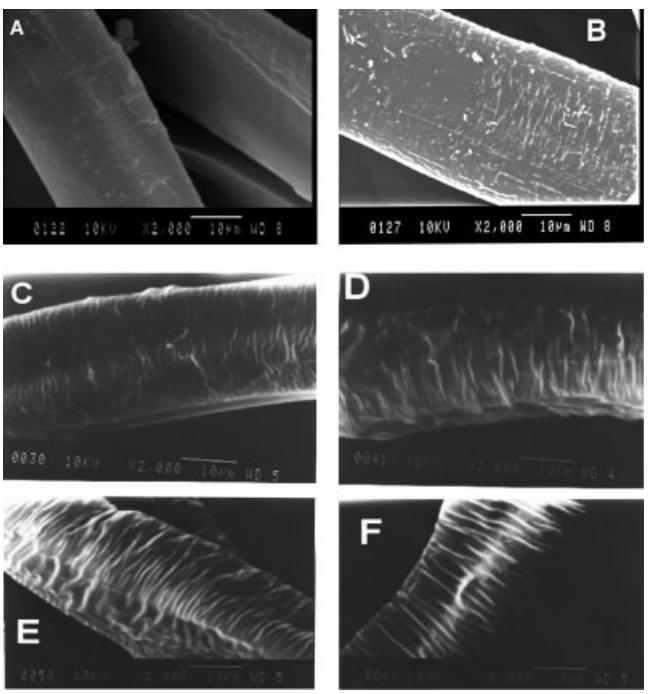

Figure 3 Scanning electron micrographs for nylon-6 fibers containing PDADMAC and grafted with PHEMA. (A) Nylon-6 fibers. (B) Nylon-6 fibers–gr PDADMAC (1.5%). (C) Nylon-6 fibers–gr PDADMAC–gr HEMA (10%). (D) Nylon-6 fibers–gr PDADMAC–gr HEMA (20%). (E) Nylon-6 fibers–gr PDADMAC–gr HEMA (30%). Nylon-6 fibers–gr PDADMAC–gr HEMA (50%).

TABLE IV
Effect of Grafting Nylon-6 containing PDADMAC, with HEMA on the Electrical Properties of the Fibers

Property	Temperature (°C)[a]	Frequency (KHz)[b]	Sample: Nylon-6	Nylon-6-gr-PDADMAC (1.5%)	Nylon-6-gr-PDADMAC (1.5%)-gr-PHEMA (10%)	Nylon-6-gr-PDADMAC (1.5%)-gr-PHEMA (30%)
Electrical resistance (RΩ)	40		–	1.7	1.5	1.3
	60		–	1.6	1.5	1.4
	80		1.7	1.6	1.4	1.3
	100		1.8	–	1.4	1.3
		50	6.2	5.5	5.1	3.4
		60	5.4	4.6	4.3	3.4
		80	2.1	1.9	1.8	1.6
		100	1.7	1.6	1.4	1.3
Capacitance (CpF) $\times 10^{-12}$	40		4.75	5.00	5.20	5.80
	60		4.75	5.00	5.20	5.80
	80		4.73	4.96	5.10	5.80
	100		4.75	4.96	5.10	8.86
		40	4.64	5.06	5.10	5.82
		60	4.77	4.96	5.10	5.81
		80	4.77	4.95	5.10	5.83
		100	4.73	4.96	5.10	5.80
Electrical loss factor (tan δ)	60		–	0.027	0.018	0.018
	80		0.23	0.027	0.018	0.016
	100		0.22	0.020	0.019	0.014
		80	0.027	0.026	0.021	0.017
		90	0.026	0.023	0.019	0.015
		100	0.023	0.023	0.018	0.015

perature at which the loss of weight in the grafted samples reaches 70–80% is noticeably higher than that for nylon-6 fibers. This happens irrespective of the amount of grafted PHEMA. This may be due to that, grafting nylon-6 fibers, containing PDADMAC, with HEMA leads to the formation of new structure which is able to resist the effect of thermal treatment under temperatures exceeding 450°C. This could be attributed to the formation of crosslinking between the macromolecules of grafted nylon-6 fibers or within the macromolecule itself. Similar behavior was observed in the decomposition of nylon-6 fibers grafted with polydimethylaminoethylmethacrylat (PDMAEMA).[15,19]

CONCLUSIONS

The graft copolymerization of hydroxyethylmethacrylate onto nylon-6 fibers, containing Polydiallyldimethylammonium chloride, in the presence of $K_2S_2O_8$–Cu^{2+} as redox initiating system was carried out with high rate and almost without homopolymer formation. The factors affecting the grafting reaction were studied. It was found that the rate of grafting (R_p) is proportional to $[HEMA]^1$, $[CuSO_4.5H_2O]^{0.7}$, $[PDADMAC]^{0.4}$, and $[K_2S_2O_8]^{1.4}$. The overall activation energy was calculated (71 KJ/mol). Grafting nylon-6 fibers, containing PDADMAC, with HEMA led to a decrease in the degree of crystallinity, T_g, T_m, IDT, T_D, $R(\Omega)$, tan δ and to an increase in Cp with increasing the percentage of grafted PHEMA. SEM examination for the grafted with PHEMA samples, revealed the presence of ripples on the surface of the fibers which increase with increasing the amount of grafted polymer.

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