Egyptian Journal of Chemistry
http://ejchem.journals.ekb.eg/

Preparation of Nylon-6 Textile Materials for Special Applications Part 1: Polymerization of 2-Methacryloxy Ethyl Trimethyl Ammonium Chloride with Nylon-6 Nonwoven Fabric Using $K_2S_2O_8$ As Initiator

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In the present work, a novel method was designed to develop an efficient and generally applicable technique for the creation of quaternary ammonium groups in nylon-6 macromolecules via polymerization of 2-methacryloxy ethyltrimethyl ammonium chloride (VQAs) in the presence of nylon-6 nonwoven fabrics using potassium persulphate ($K_2S_2O_8$) as initiator. In addition factors affecting the extent and rate of polymerization (Rp) were investigated and the apparent activation energy was calculated. The reaction mechanism was suggested. Characterization of the grafted with PVQAs Nylon-6 nonwoven fabrics was investigated by X-ray, SEM, and FT-IR.

Key Words: Nonwoven nylon-6 fabric, Grafting, VQAs, PVQAs

Introduction

Nylon is one of the oldest synthetic fiber materials and was initially developed as substitute to silk in women's hosiery. Polyamide fibers or the finished articles produced from them have the following advantages: (i) high breaking resistance; (ii) high abrasion resistance and high durability; and (iii) good resistance to biological influences. However, these fibers suffer from some inherent drawbacks such as: a-poor moisture content; b -high pilling tendency; c- poor heat and thermal resistance; d- low inflammability. e-poor resistance to light and weather; and f- poor resistance to alkalis and concentrated acids.

Physical or chemical modifications have been used to impart fibers some desirable properties. Scientific literature revealed that, different methods have been applied for physical modification of polyamide fibers [1-11].

Chemical modification of nylon-6 fibers was carried out through chemical bonding of the finishing reagents by the modification of these fibers for increasing the content of functional groups or creating on the fiber new ones which have the ability to react with the finishing reagents.

Grafting reaction has been expensively investigated for imparting new properties to synthetic macromolecules. Different techniques for grafting polyamide fibers have been used. The most important among them are : initiation by irradiation [12-17], by plasma treatments [18] and by chemical methods [20-31].

In spite of considerable research has been carried out on graft polymerization reaction onto nylon-6 fabrics using irridiation methods, very few techniques have been used on industerial scale.

Much interest has been focused on vinyl graft copolymerization of PA fibers through chemical

initiation. Many redox systems have been used for grafting different vinyl monomers onto polyamide fibers and fabrics [19-30].

Recently, the scientific literature has revealed a growing interest in modifying nylon-6 properties, and consequently, expanding their applications. The preparation of antimicrobial fabrics [27-29] and ion exchangers based on nylon-6 textile materials is one of the new fields which gained a great interest in the last years. A great number of such ion-exchangers were developed by grafting nylon-6 with different vinyl monomers such as methyl vinyl pyridine (MVP) [31].

Technical and economic aspects are very important factors in finding best and cheap technology for modifications of nylon-6 fibers. Chemical modification of nylon-6 nonwoven fabrics using graft copolymerization with vinyl monomers could be carried out on industerial scale if this process takes place with high rate and without formation of homopolymer.

To achieve this, fabrics should contain reactive groups able to form ionic complex on the fabrics with initiator. The following decomposition of this complex leads to free radical formation on the fibers. This facilitates direct grafting without homopolymer formation. Shalaby etal reported the graft copolymerization of DMAEMA [32], HEMA [33], GMA [34], onto modified nylon-6 fibers containing polydiallyl dimethyl ammonium chloride (PDADMAC) in the presence of Cu^{2+}–$K_2S_2O_8$ as a redox initiating system, with very high rate and almost without homopolymer formation.

It is important to mention that this method in spite of the fact that it directly provides the creation of the QAGs within PA macromolecule, it suffers from a number of drawbacks that prevent its application on industerial scale.

Therefore, another method has been suggested. It consists of the creation of dimethylal kylbenzyl ammonoium chloride (DMABAC) in nylon-6 textile fabrics followed by treatment the fabrics in a solution containing $K_2S_2O_8$-Cu^{2+} at room temperature. The so obtained nylon-6 fabrics were introduced in an aqueous solution of GMA [35], DMAEMA [36], MAA [37] containing metallic ion. Grafting of each of these vinyl monomers was accomplished under required temperature and duration with high rate and almost without homopolymer formation.

The use of vinyl quaternary ammonium salt (VQAs) (vinyl benzyl chloride (VBC) [15], vinyl benzyl trimethyl ammonium chloride (VBTAC) [14], methacryloxy ethyl trimethyl ammonium chloride (METAC) [27], methacryloxy ethyl dimethyl dodecyl ammonium bromide (CATAL) [28]) as a grafting monomer with its QAGs is likely to create lots number of active sites on nylon-6 surfaces to enhance the grating reaction and for imparting higher and chemically stable (durable) antimicrobial properties to the final nylon-6 nonwoven fabrics than previously prepared in presence of poly diallyl dimethyl ammonium chloride (PDADMAC) or dimethyl alkylbenzyl ammonium chloride (DMABAC).

The present work aims at preparation and characterization of modified nylon-6 nonwoven fabrics containing quaternary ammonium groups. The method is based on creation of these groups in nylon-6 macromolecules by polymerization of 2-methacryloxy ethyl trimethyl ammonium chloride (VQAs) using $K_2S_2O_8$ as initiator. This paves the way for further grafting nylon-6 nonwoven fabrics with suitable vinyl monomers for the preparation of antimicrobial fabrics and ion-exchangers. The feature of this method is that grafting reaction occurs with high rate and almost without homopolymer formation.

Experimental Work

Materials

• Nylon-6 fibers, was manufactured from nylon-6 fibers (denier 14) were kindly supplied by Misr Company for spinning and weaving, El Mahalla El-kobra, Egypt. These fibers were converted into nonwoven fabrics at FiberTex Co., 6th October City, Egypt.

• [2- (Methacryloyloxy) ethyl] trimethyl ammonium chloride (VQAs) in the form of 75 wt % aqueous solution was purchased from Sigma-Aldrich.

• Potassium persulphate ($K_2S_2O_8$) used was of analytical grade chemicals.

Methods

Treatment of nylon-6 with VQAs

The nylon-6 nonwoven fabric was padded at room temperature with completely soluble padding solution of (VQAs) containing different

amounts of potassium persulphate. The nit was removed from the pad bath, squeezed to a suitable wet pick-up% using a laboratory padder, dried in an air oven at 105°C for 15min, then the samples were cured at temperature (115-130 °C). After the elapsed reaction time, the treated nonwoven fabric was cooled to room temperature in a dessicator until attaining a constant weight. The dried samples were then repeatedly soxhlet extracted with warm water to remove the homopolymer of poly vinyl quaternary ammonium salt (PVQAs), dried again in an oven at 105°C for 2 hours, cooled again and weighed.

The percentage of grafted PVQAs was calculated as follows:

$$\% \, \text{Graft yield} = \frac{P - P_\circ}{P_\circ} \times 100$$

Where P: dry weight of grafted nylon-6 nonwoven fabrics.

$P_\circ$: dry weight of untreated nylon-6 nonwoven fabrics.

Analysis

Nitrogen percentage determination

Nitrogen was determined by the Cole and Parks modifications of the semi-micro Kjeldahl method [Cole, J.O.; et al] [38].

X-ray diffraction

Both grafted and ungrafted nylon-6 samples have been investigated by X-ray diffraction technique, using Siemens D-5000 (computer controller) X-ray diffractometer, with Cu target (λ = 1.542 A°) and Ni filter. A continuous scan mode was used to scan 5°< 2θ < 65° in 0.05 step. The samples were in the powder form.

Scanning Electron Microscope (SEM) examination

The sample (nylon-6 nonwoven fabric) was mounted on a standard specimen stub and examined in an JEOL-Model JSM-T20 SEM operating at 19 KV. A thin coating (~ 10 nm) of gold was deposited onto the sample, and attached to the stub , prior to examination in the SEM, to enhance the conductivity and secondary electron emission characteristics of the over growth.

Fourier-Transform Infrared Spectroscopy (FTIR)

The chemical structure was determined using the Fourier transformation infrared (FT-IR)

spectrometer, model NEXUS 670, NICOLET USA. The measurements were carried in spectral range from 4000 cm^{-1} to 500 cm^{-1}. Reflection percentage measurement technique was applied (R %) to all investigated samples.

Results and Discussion

The aim of the present work is the development of an applicable method for creation of QAGs in nylon-6 nonwoven fabrics. To achieve this the following trials were carried out:

1-The nylon-6 sample was introduced into thermostated reaction solution consisting of H_2O and VQAs. The polymerization reaction was proceeded at the required temperature for the desired reaction time. After this the contents were filtered, washed with water, dried at 105°C. The samples were then cured at temperature (130°C), cooled to room temperature and weighted. The obtained results revealed that no grafting occurs under these conditions.

2-Nylon-6 sample was immersed in aqueous $K_2S_2O_8$ solution for the desired duration at room temperature. The sample was then squeezed, washed, and introduced into the thermostated reaction solution consisting of :

a- H_2O / VQAs

b- H_2O/ VQAs /Cu^{2+}

The polymerization reaction was carried out according to the conditions indicated above. In this case it was observed that no grafting occurs neither when nylon-6/VQAs/$K_2S_2O_8$/H_2O nor when nylon-6 /VQAs/$K_2S_2O_8$/Cu^{2+}/H_2O systems were used. In both systems homopolymers formation took place.

3- Nylon-6 sample was treated with an aqueous solution of VQAs with subsequent compression and heat treatment at 115-130°C for the desired time. It was observed that no grafting occurs when this system was used, but a substantial amount of homopolymer was formed.

4- The nylon-6 sample was treated with aqueous $K_2S_2O_8$ solution, followed by subsequent treatment with an aqueous solution of VQAs with subsequent compression and heat treatment at 115-130°C for the desired time. It was observed that no grafting occurs when this system was used, but a substantial amount of homopolymer was formed.

5- The nylon-6 sample was treated with an aqueous VQAs solution containing different amounts of $K_2S_2O_8$, squeezed, and heat, treatment at 115-130°C for the desired time. It was noticed that there was a substantial increase in weight of the sample, and that a part of this increase in weight was still existing even after several extractions of the PVQAs with hot water. This mainly is due to the inclusion of PVQAs within the treated sample.

In this work, the graft yield was calculated by the increase in weight and by nitrogen content in the samples (Table 1).

$$2[H_2C=C(CH_3)COOCH_2CH_2N-(CH_3)_3Cl+K_2S_2O_8$$

$$[N^+..S_2O_8^{-2}...N^+] + 2KCl \qquad (1)$$

$$2M^+ + S_2O_8^{-2} \rightarrow [M^+.....S_2O_8^{-2}.......M^+] \qquad ....(2)$$
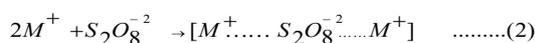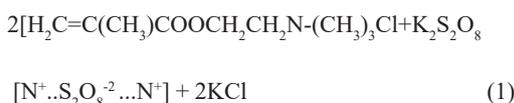
Shalaby etal [37] have suggested the formation of ionic complex of the cationic monomer with anionic peroxide initiator. when nonwoven fabrics were padded in the aqueous solution of VQAs containing $K_2S_2O_8$ the complex formed becomes trapped inside the matrix. During the thermal treatment of treated nylon-6 sample several reactions are taking place simultaneously.

Primary radical formation
a- The monomer initiator complex formed (equation1) decomposes faster than unbonded initiator, and yield sulphate radicals as suggested by Shalaby etal [35].

b- Redex reaction takes place between persulphate molecules and chloride ions to yield cl• and $So_4^{•-}$ as follows:

$$S_2O_8^{2-} + 2Cl^- \rightarrow SO_4^{•-} + Cl^• + SO_4^{2-} \qquad ....(3)$$
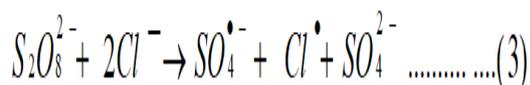
Homopolymerization
The resulted and in the medium (Equation 3) are expected to lead to homopolymer formation (PVQAs) as follows:

Initiation

$$SO_4^{•-} + M \rightarrow SO_4M^{•-} ....(4)$$

$$Cl^• + M \rightarrow ClM^• ....(5)$$
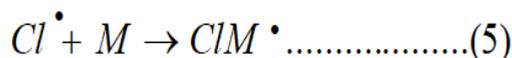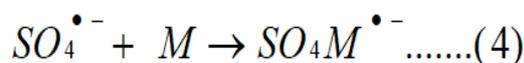
Where M= VQAs

Propagation

$$P^• + M \rightarrow P_L^• \qquad ....(6) \text{ linear propagation}$$
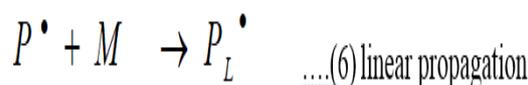
where

P$^•$ = polymer radical

P$_L$$^•$ = linear polymer radical

Termination

by combination reaction:

$$2P_L^• \rightarrow P_L - P_L ....(7)$$

Graft copolymerization
Based on the above mentioned findings the following mechanism could be suggested for the graft copolymerization of VQAs onto nylon-6 nonwoven fabrics using $K_2S_2O_8$ as initiator.

Macroradical formation
The free radicals are produced on nylon-6 backbone by its reaction with and formed in equations (2) and (3). This generally occurs through abstracting a hydrogen atom from amide group in the macromolecule to produce nylon-6 macroradicals, which initiate copolymerization reactions as follows:

$$Nylon\cdots CONH\cdots Nylon + R^• \rightarrow Nylon\cdots CON^•\cdots Nylon + RH \text{ (8)}$$

Where R • = SO_4 • – or Cl•

Initiation

$$\cdots Nylon\cdots^• + M \xrightarrow{Ki} \cdots Nylon\cdots M^• ....(9)$$

macroradical   growing chain

$$M + R^• \rightarrow M^• + RH ....(10)$$

$$Nylon\cdots Nylon + M^• \xrightarrow{Chain \leftrightarrow Transfer} \cdots Nylon^•\cdots + M ....(11)$$

Termination

$$\cdots Nylon \cdots M_1^{\bullet} + M \xrightarrow{Kp} \cdots Nylon \cdots M_2^{\bullet} \quad \ldots\ldots\ldots\ldots\ldots (12)$$

$$\cdots Nylon \cdots M_{(n-1)}^{\bullet} + M \xrightarrow{Kp} \cdots Nylon \cdots M_n^{\bullet} \ldots\ldots (13)$$

$$M^{\bullet} + M \to M_2^{\bullet} \quad \ldots\ldots\ldots \ldots\ldots\ldots (14)$$

$$M_{n-1}^{\bullet} + M \to M_n^{\bullet} \quad \ldots\ldots\ldots \ldots\ldots (15)$$

Factors affecting the graft yield
Potassium persulphate concentration

$$\cdots Nylon \cdots M_n^{\bullet} + \cdots Nylon \cdots M_n^{\bullet} \xrightarrow{Kt} Graft\ copolymer \ldots\ldots (16)$$

$$\cdots Nylon \cdots M_n^{\bullet} + M_n^{\bullet} \xrightarrow{Kt} Graft\ copolymer \ldots (17)$$

$$\cdots Nylon \cdots M_n^{\bullet} + R^{\bullet} \xrightarrow{Kt} Graft\ copolymer \quad \ldots (18)$$

$$M_n^{\bullet} + M_n^{\bullet} \xrightarrow{Kt} Homopolmer \ldots\ldots (19)$$

$$M_n^{\bullet} + R^{\bullet} \xrightarrow{Kt} Homopolmer \ldots\ldots (20)$$
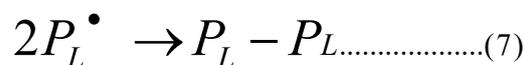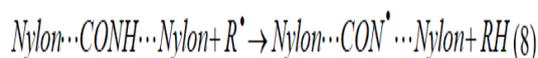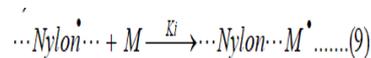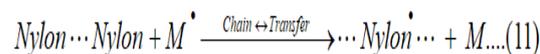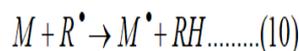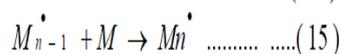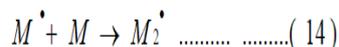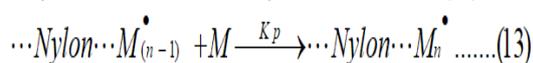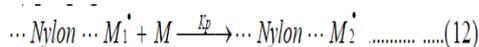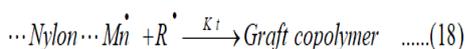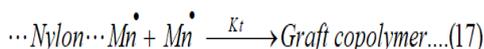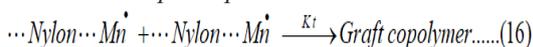
It has been reported that when $K_2S_2O_8$ is added to VQAs solution as ionic complex of cationic monomer with anionic peroxide initiator is formed. This complex decomposes to yield sulphate radicals () (equation 3). Besides, redox reaction takes place between $S_2O_8^{-2}$ and Cl^- to yield and (equation 3). and radicals seem to increase by increasing $K_2S_2O_8$ concentration. So, one can conclude that the maximum abstraction of hydrogen atom from Nylon-6 backbone by these free radicals, as well as, the formation of similar Nylon-6 macroradicals via chain transfer from growing homopoly (VQAs) took place at $K_2S_2O_8$ equal to 5.52×10^{-2} mol/l.

The increase of $K_2S_2O_8$ concentration abovementioned before value, will lead to abundance of free radicals formation. These free radicals will contribute at the same time in grafting and termination reactions. This will lead to decrease in the amount of graft yield.

The relation between $K_2S_2O_8$ concentrations and the rate of grafting of VQAs onto nylon-6 fabrics was studied (Table 3). The obtained results revealed that, grafting is characterized by an initial fast rate, followed by a slower one, and then levels off. This is observed regardless of the concentration of $K_2S_2O_8$ used.

Kinetic investigation (Table 4) revealed that, the rate of grating (Rp) of VOAs onto nylon-6 nonwoven fabrics is proportional to 0.47 power of $K_2S_2O_8$ concentration. (R_p α $[K_2S_2O_8]^{0.47}$)

Vinyl quaternary ammonium salt concentration
The effect of `VQAs concentration on polymer add-on is shown in Table 2. It can be seen that, the graft yield increases up to 0.8 mole of VQAs/100gr. fabric. Further increase in monomer concentration leads to a reduction in polymer add-on. That is, concentration of 0.8 mole/100gr. Fabric constitutes the optimal concentration for achieving maximum polymer add-on.

At lower VQAs concentration (up to 0.8 mole/100gr. fabric) the effect of (a) abstraction of hydrogen atom from nylon-6 backbone via the formation of nylon-6 macroradical capable of initiating grafting with VQAs [equation8], (b) propagation according to (equations 13,15), (c) termination process with growing polymer chains [equation 16], and (d) the combination of growing polymer chains with growing PVQAs [equation 17] and with primary radicals ($R^{\bullet}$) [equation 18] seems to prevail over the combination effect of (e) direct attack on VQAs by primary radicals ($R^{\bullet}$) [equation10], and (f) the combination of VQAs macroradicals by coupling [equation19] and by primary radicals ($R^{\bullet}$) [equation 20]. All these factors will increase the graft yield. The increase in monomer concentration more than the abovementioned value will decrease the values of the graft yield.

The relation between VQAs concentration and the rate of grafting (Rp) onto nylon-6 nonwoven fabrics was investigated (Table 3). It is clear that the increase in the monomer concentration from 0.2 to 0.8 mole/ 100 gr. fabric leads to an enhancement in the extent and rate of grafting. The obtained results also revealed that, the grafting proceeds at the initial stage with fast rate, followed by a slower one then levels off. The leveling off of the grafting could be associated with reduction in the available sites for grafting on the nylon-6 backbone as the reaction proceeds.

Kinetic investigation (Table 4) of the dependence of the rate of graft copolymerization (Rp) reaction on the VQAs concentration revealed that the (Rp) is proportional to 1.038 power of the monomer (VQAs) concentration. (R_p α $[VQAs]^{1.038}$). The rate of grafting belongs to a first order reaction which is in full agreement with traditional equation of free radical polymerization.

TABLE 1. Graft yield (G.Y) of Poly (VQAS) calculated by weight and nitrogen content in the nylon- 6 samples

G.Y by Weight (%)	Theoretical nitrogen content (mol./100g. fabric)	Nitrogen Content determined by titration (mol./100g .fabric)	Add-On Calculated by nitrogen content (%)	$\dfrac{Add-on(by\ nitrogen)}{Add-on(by\ weight)}x100$
1.0	0.07	0.06	0.9	89.0
1.5	0.10	0.09	1.4	91.3
2.0	0.13	0.12	1.8	91.5
2.5	0.17	0.16	2.4	95.6
3.5	0.23	0.22	3.3	95.4
5.0	0.33	0.32	4.8	95.8

TABLE 2. Effect of reaction conditions on the graft yield% of PVQAs onto nylon-6 nonwoven fabrics

^{A} [K$_2$S$_2$O$_8$], mol/l	
[K$_2$S$_2$O$_8$], mol/l	Graft Yield %
1.84×10^{-3}	1.7
3.7×10^{-3}	3.3
1.84×10^{-2}	3.5
3.68×10^{-2}	4.0
5.52×10^{-2}	5.0
7.36×10^{-2}	3.9
1.22×10^{-1}	1.7
^{B}[VQAS],mol/100gr.fabric	
[VQAS],mol/100gr.fabric	Graft Yield %
0.1	1.1
0.2	2.6
0.4	2.7
0.6	3.2
0.8	5.0
1.0	3.4
1.2	2.9

Reaction conditions:

^{A}[VQAs], 0.8 mol/100gr.fabric; Reaction Temperature, 130ºC; Reaction Time, 150Sec.

^{B} [K$_2$S$_2$O$_8$], 5.52×10^{-2} mol/l; Reaction Temperature, 130ºC;Reaction Time, 150 Sec.

Reaction temperature

The effect of temperature on the extent and rate of grafting was studied. The samples were treated with an aqueous VQAs solution containing fixed amount of $K_2S_2O_8$, squeezed, and heat treated at four temperatures in the range 115-130°C. The data listed in Table 3 revealed that, the amounts of graft yield and the values of (Rp) increase with increasing the reaction temperature up to 130°C. Maximum graft yield is obtained at 130°C. This is in accordance with previous studies [34] and may be attributed to:

a- faster rate of monomer initial complex decomposition;

b- enhancement in fabrics swellability;

c- increased mobility of the VQAs molecules;

d- higher diffusion of VQAs into nylon-6 nonwoven fabrics;

e- reaction between the growing homopolymer chain radical reaction with **nylon** and /or the nylon-6 macroradicals; and

f- increasein the rate of initiation and propagation of copolymerization reaction.

Besides the above factors, **nylon** attains its glass transition temperature (Tg) at 50°C [Beaman, R. G.] [39]. At this temperature the nylon-6 segments became more mobile and the reactivity increases. This is resulting in raising the polymer add-on.

The results listed in Table 4 were used for calculation of the apparent activation energy of grafting by plotting Ln Rp versus 1/T. It was found to be: 35.1 KJ.mol^{-1}

Characterization of modified Nylon-6 nonwoven fabrics
Internal structure of modified nylon-6 nonwoven fabrics

X-ray diffraction patterns for ungrafted nylon-6 nonwoven fabrics and fabrics grafted with PVQAs (Nylon-6-gr- PVQAs) were investigated. Two different planes (2θ ~19.8 and 23.7) which are specific and characterized to crystlline area of nylon-6 polymer have been chosen for comparison. Table 5 shows the d-spacing and crystallinity of the modified nylon-6 nonwoven fabrics. According to these measurements and observations, the following can be concluded:

1-The parent and modified samples have the same diffraction patterns. This points to that, all the samples have the same unit cell type. This type is similar to that mentioned by Suehiro et al [40] a pseudo- hexagonal structure;

2-The d–spacing values fluctuate depending on the type and amount of modification ;

3- The same diffraction patterns for the parent and modified fabrics, verify that a chemical reaction took place and that, grafted polymers rather than a mixture of two polymers; have been obtained ; and

4- The degree of crystallinity of the modified nylon-6 nonwoven fabrics is less than that of parent one. The trend a decrease depends upon the amount of the grafted polymer.

The fiber topography of modified nylon-6 nonwoven fabrics

The SEM examinations were carried out on the parent nylon-6 nonwoven fabrics and the modified ones. The modified samples include nylon-6 grafted with poly vinyl quaternary ammonium salt [Nylon-6-gr. PVQAs]. Figure 1 shows the electron micrographes corresponding to different investigated samples. The surface topographical changes in parent nylon-6 nonwoven fabrics (Fig.1) indicated the smoothing of the nonwoven fabric surface and continuous dark parallel lines inside the nonwoven fabric. The edge of the fabric is more transparent than its main part. When these fabrics were modified by PVQAs (1.0 %) the fabric surface appeared comparatively smooth and some elongated particles parallel to the fabric axis can be seen (Fig.1). When the amount of grafted PVQAs increased up to 5.0%, the nylon-6 developed roughness periodically running vertical to the fabric axis and edge of the nonwoven fabric became empty (Fig. 1).

It is important to emphases, that no significant deposition of grafted polymer exists on the outside of the nonwoven fabrics.

Infrared properties (FTIR)

The chemical structure of fabrics was determined using the Fourier-Transform Infrared spectroscopy (FTIR) (Table 6).According to the obtained results, we can conclude the following:

1-The obtained spectrum of parent nylon-6 nonwoven fabrics have absorption bands at 1662–1531, 3083, and 2920–2852 cm^{-1}, which are belong to those of >C=O in CONH, NH_2, N——H stretching and C——H stretching, respectively.

TABLE 3. Effect of reaction conditions on the rate of grafting (Rp) of VQAs onto nylon-6 nonwoven fabrics

[A] $[K_2S_2O_8]$, mol/l	Reaction Time (min.)					
	0.5	1.00	1.5	2.00	2.5	
3.7×10^{-3}	0.7	2.4	2.6	3.2	3.3	
1.84×10^{-2}	1.5	3.0	3.4	3.5	3.5	
3.68×10^{-2}	2.1	3.3	3.6	3.8	4.0	
5.52×10^{-2}	2.5	3.4	3.9	4.5	5.0	
[B] **[VQAS], mol/100gr.fabric**						
	0.5	**1.00**	**1.5**	**2.00**	**2.5**	Graft Yield %
0.2	0.6	2.1	2.4	2.5	2.6	
0.4	1.6	2.3	2.6	2.7	2.7	
0.6	2.1	2.6	3.0	3.0	3.2	
0.8	2.5	3.4	3.9	4.5	5.0	
[C] **Reaction Temperature, (°C)**						
	0.5	**1.00**	**1.50**	**2.00**	**2.50**	
115	1.7	2.2	2.5	2.6	2.7	
120	1.9	2.6	2.8	2.9	3.0	
125	2.3	3.2	3.5	3.8	3.9	
130	2.5	3.4	3.9	4.5	5.0	

Reaction conditions:

[A] [VQAs], 0.8 mol/100g. fabric; Reaction Temperature, 130ºC.

[B] $[K_2S_2O_8]$, 5.52×10^{-2} mol/l; Reaction Temperature, 130ºC.

[C] [VQAs], 0.8 mol/100gr.fabric; $[K_2S_2O_8]$, 5.52×10^{-2} mol/l;

TABLE 4. Dependence of the rate of grafting (Rp) of VQAs onto nylon-6 nonwoven fabrics on the reaction conditions

[A] $[K_2S_2O_8]$, mol/l	Ln $[K_2S_2O_8]$	Ln$[K_2S_2O_8]$ +6	PVQAs (%)	PVQAs (g/ 100 g. Fabric)	PVQAs (mol/ 100 gr. Fabric)	$Rp\times10^{-4}$ Mol/100 g. Fabric. $L^{-1}.Sec^{-1}$	Ln Rp	LnRp+10
3.7×10^{-3}	-5.6	0.4	0.7	0.7	3.4×10^{-3}	1.12	-9.10	0.91
1.84×10^{-2}	-4.0	2.0	1.5	1.5	7.2×10^{-3}	2.41	-8.33	1.67
3.68×10^{-2}	-3.3	2.7	2.1	2.1	1.0×10^{-2}	3.37	-8.00	2.00
5.52×10^{-2}	-2.9	3.1	2.5	2.5	1.2×10^{-2}	4.00	-7.82	2.18
[B] [VQAS], mol/100 gr. Fabric	Ln [VQAs]	Ln [VQAs] +2	PVQAs (%)	PVQAs (g/100 g. Fabric)	PVQAs (Mol/ 100 g. Fabric)	Rp Mol/100 g. Fabric. $L^{-1}.Sec^{-1}$	LnRp	LnRp+10
0.2	-1.609	0.391	0.6	0.6	2.9×10^{-3}	9.6×10^{-5}	-9.247	0.753
0.4	-0.916	1.084	1.6	1.6	7.7×10^{-3}	2.6×10^{-4}	-8.266	1.734
0.6	-0.510	1.490	2.1	2.1	1.0×10^{-2}	3.7×10^{-4}	-7.995	2.005
0.8	-0.223	1.776	2.5	2.5	1.2×10^{-2}	4.0×10^{-4}	-7.820	2.180
[C] Reaction Temperature, (°C)	T+273	1000/T	PVQAs (%)	PVQAs (g/100 g. Fabric)	PVQAs (mol/100 g. Fabric)	$Rp\times10^{-4}$ Mol/100 g. Fabric. $L^{-1}.Sec^{-1}$	Ln Rp	Ln Rp+9
115	388	2.58	1.7	1.7	8.2×10^{-3}	2.7	-8.21	0.79
120	393	2.54	1.9	1.9	9.1×10^{-3}	3.0	-8.10	0.90
125	398	2.51	2.3	2.3	1.1×10^{-2}	3.7	-7.90	1.10
130	403	2.48	2.5	2.5	1.2×10^{-2}	4.0	-7.82	1.18

Reaction conditions:

[A] [VQAs],0.8 mol/100g. fabric; Reaction Temperature, 130 ºC; Reaction Time, 30 Sec.

[B] $[K_2S_2O_8]$, 5.52×10^{-2} mol/l; Reaction Temperature, 130 ºC; Reaction Time, 30 Sec.

[C] [VQAs],0.8 mol/100g. fabric; $[K_2S_2O_8]$, 5.52×10^{-2} mol/l; Reaction Time, 30 Sec.

2-An additional absorption bandat1704 cm^{-1}was observed in the spectrum of grafted nylon-6 with PVQAs nonwoven fabrics. This band can be attributed to >C=O in COOH of PVQAs. The presence of such band verifies the grafting of poly 2-methacryloxy ethyl trimethyl ammonium chloride onto nylon-6 nonwoven fabrics.

3-The absorption band corresponding to N——H group at 3080 cm^{-1} has gradually reduced with the increase of the graft yield. This supports that, the grafting reaction took place on the nitrogen atom of amide group (CONH) in nylon-6 molecules.

Conclusion

A novel method was designed to develop an efficient and generally applicable technique for the creation of quaternary ammonium groups in nylon-6 macromolecules via polymerization of 2-methacryloxy ethyl trimethyl ammonium chloride (VQAs) in the presence of nylon-6 nonwoven fabrics using potassium persulphate (K$_2$S$_2$O$_8$) as initiator. In addition factors affecting the extent and rate of polymerization (Rp) were investigated and the apparent activation energy was calculated. The reaction mechanism was suggested. It was found that, increasing the K$_2$S$_2$O$_8$ concentration up to 5.52×10^{-2}mol/100gr. fabric is accompanied by an increase in the polymer add-on. Further increase in initiator concentration causes a marked fall in the amount of grafted PVQAs. The graft yield was found to increase as the concentration of VQAs increases up to 0.8 mole/100gr.fabric,and a reduction in the polymer add-on was observed by further increase in monomer concentration. That is, concentration of 0.8 mole/100gr. fabric. nonwoven fabrics constitutes the optimal concentration for achieving maximum polymer add-on. The effect of temperature on the graft polymerization reaction was studied at four temperatures in the range 115-130°C. It was noticed that, the higher the reaction temperature, the higher the percent of the graft yield. Kinetic investigation revealed that, the rate of grafting (Rp) of VQAs onto nylon-6 nonwoven fabrics is proportional to [K$_2$S$_2$O]$^{0.47}$, and [VQAs]$^{1.038}$. The apparent activation energy of grafting was calculated and was found to be 35.1 KJ.mol^{-1}.

Characterization of parent and modified nylon-6 nonwoven fabrics was investigated. Internal structure of nylon-6 fabrics was investigated by using x-ray diffraction technique. It was found that, the parent fabric and its all modified samples have the same diffraction patterns, irrespective of the amount of grafted PVQAs. The d-spacing values fluctuate depending on the percentage of grafted polymer. The degree of crystallinity of the modified nylon-6 nonwoven fabrics is found to be less than the apparent one. The SEM examinations revealed that, no significant deposition of grafted polymer exists on the outside of the nonwoven fabrics. The chemical structure of fabrics was determined using the Fourier-Transform Infrared spectroscopy (FTIR). The spectrum of grafted nylon-6 with PVQAs nonwoven fabrics shows an additional absorption band at1704cm^{-1} that can be attributed to >C=O in COOH of PVQAs. The presence of this band verifies that the grafting of poly 2-methacryloxy ethyl trimethyl ammonium chloride to nylon-6 nonwoven fabrics has occurred as expected. The absorption corresponding to N——H group at 3080 cm^{-1} has gradually weakened with the increase of grafting. This leads to the suggestion that, the grafting reaction happened on the nitrogen atoms of amide groups (CONH) in nylon-6 molecules.
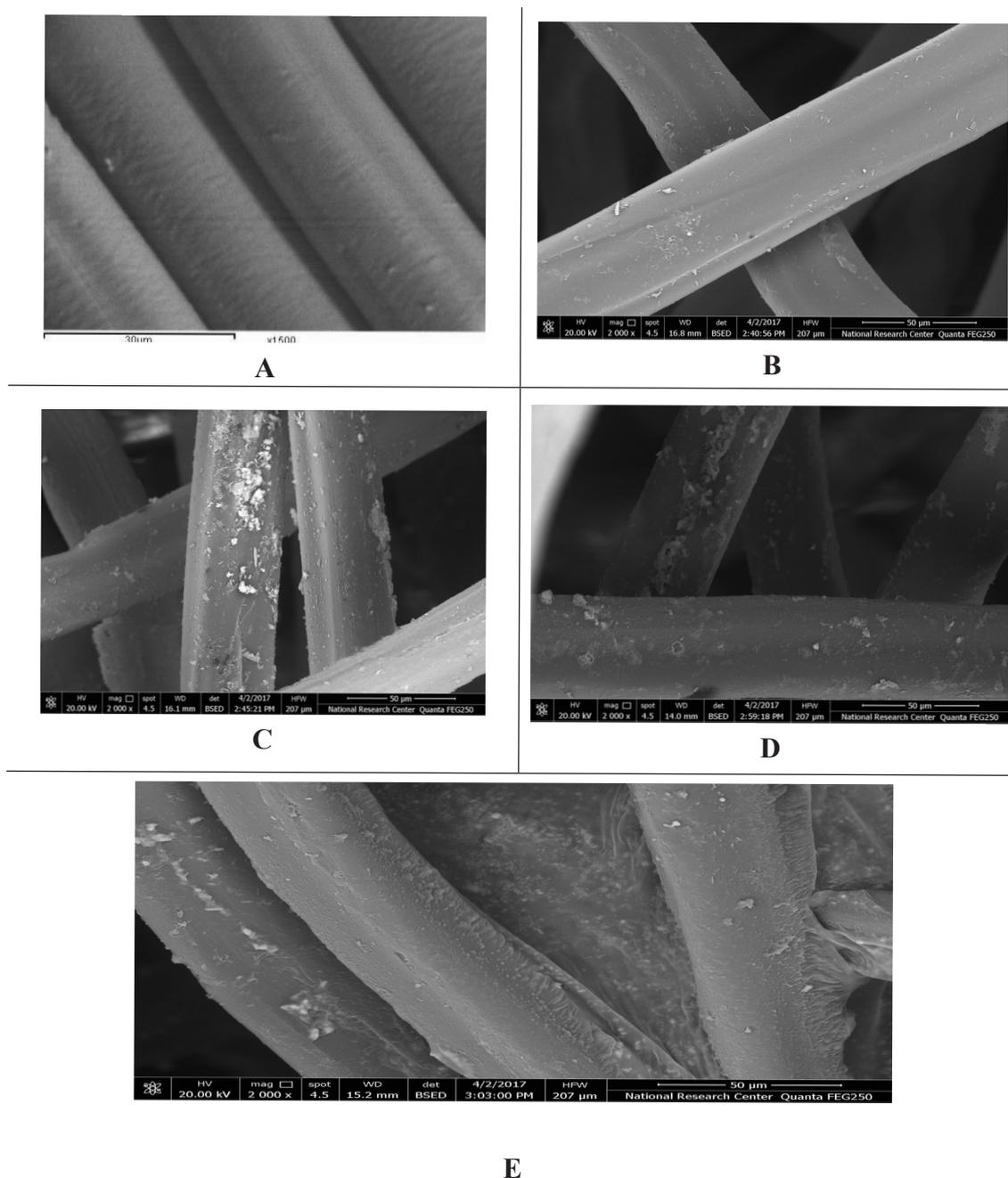
Fig. 1. SEM of blank nylon-6 nonwoven fabrics and grafted with PVQAs (2000x)

[A]Nylon-6 (Blank)
[B]Nylon-6 grafted with PVQAs (G. Y % =1.0%)
[C]Nylon-6 grafted with PVQAs (G. Y % =1.5%)
[D]Nylon-6 grafted with PVQAs (G. Y % =3.5%)
[E]Nylon-6 grafted with PVQAs (G. Y % =5.0%)

References

1. Shayestehfar, S.;Yazdanshenas, M. E.; Khajavi, R.; Rashidi, A., Physical and Mechanical Properties of Nylon-6/TiO$_2$ Micro and Nano-Composite Multifilament Yarns, *Journal of Engineered Fibers and Fabrics,* **9**, 3, p.158 (2015).

2. Phumelele, K.; Carminita, L. F.; Zenixole, R. T.; Nelson T., Electrospun Nylon-6 Nanofibers Incorporated with 2-Substituted *N*-alkylimidazoles and their Silver(I) Complexes for Antibacterial Applications, *Journal of Applied Polymer Science,* **131**, 2, p.39783 (2014).

3. Yuranova, T.;Rincon, A. G.; Bozzi, A.; Parra, S.; Pulgarin, C.; Albers, P.; Kiwi, J., Antimicrobial Textiles Prepared by RF Plasma and Vacuum – UV Mediated Deposition Silver, *J Photochem Photobiol.* A **161**, 27 (2003).

4. Radetic, M;Ilic, V.; Vodnik, V.; Dimitrijevic, S.; Jovancic, P.; Saponjic Z.; Nedeljkovic, J., Antibacterial Effect of Ag NPs Deposited on Corona-Treated Polyester and Polyamide Fabrics, *Polym Advan Technol,* **19**, 1816 (2008).

5. Son,Y.A.; Sun,G., Durable Antimicrobial Nylon 6,6 Fabrics: Ionic Interactions with Quaternary Ammonium Salts, *J. Appl Polym Sci,* **90** 2194–2199 (2003).

6. Shalaby, S. E.; Al-Balakocy, N. G.; Beliakova, M. K.; Elshafei, A. M. Imparting Durable Antimicrobial Properties to Regular Nylon-6 Fibers via Reaction in Polymer chain, *International Journal of Applied Chemistry,* **10**, 2, 169-183 (2014).

7. Kanellia, M.;Vasilakosb, S.; Ladasc, S.; Symianakisc, E.; Christakopoulosd, P.; Topakasa, E., Surface Modification of Polyamide 6.6 Fibers by Enzymatic Hydrolysis, *Process Biochemistry,* **59**,97–103 (2017).

8. Song, J.E.; and Kim, H. R., Improvement in Nylon Fabrics Reactivity via Enzymatic Functionalization, *The Journal of The Textile Institute,* **108**, 2, 155–164 (2017).

9. Kobayashia, T.;Arisawaa, M.; Ngoca, N. L.; Tranga, T.C.; Myoubudanib, H., Surface Modification of Polymer Textiles by Thermally Dried Ozone, *Journal of Adhesion Science and Technology,* **25**,1849–1859 (2011).

10. Zhao, Q.;Gu, X.; Zhang, S.; Dong, M.; Jiang, P.; Hu, Z., Surface Modification of Polyamide 66 fabric by Microwave Induced Grafting with 2-Hydroxyethyl Methacrylate, *Surface and Coatings Technology,* **240**,197–203 (2014).

11. Bahtiyari, M. I.; Laser modification of polyamide fabrics, *Optics and Laser Technology,* **43**, 114–118 (2011).

12. Armstrong, A. A.; Jr.; Walsh, W. K. ; Rutherford, H. A., A Vapor-Phase Technique for Radiation-Induced Grafting of Vinyl Monomers to Fibers ,*U. S. At. Energy Comm.* NCSC-2477-1 I (1963).

13. Malcom B. H.; Randal, W. R., Characterization of A nylon- 6/poly(methyl acrylate) Copolymer Produced by Radiation Grafting, *J. Appl. Polym. Sci.,* **25**, 25 13 (1980).

14. Kolhe, S.M.; Kumar, A., Radiation-Induced Grafting of Vinyl Benzyl Trimethyl Ammonium Chloride onto Nylon-6 Fabric, *Radiation Physics and Chemistry,* **76**, 901–906 (2007).

15. Ting,T.M.; Nasef, M. M.; Hashim, K., Modification of Nylon-6 Fibres by Radiation-Induced Graft Polymerization of Vinylbenzyl Chloride, *Radiation Physics and Chemistry,* **109**,54-62 (2015)**.**

16. Mukerjee, A. K.; Sachdev, H. S.; Gupta, A., Photo induced Graft Copolymerization of Nylon-6 Fibers with Acrylamide. I. Effect of synthesis conditions, *J. Appl. Polym. Sci.,* **28**, 2125 (1983).

17. Lenka, S.; Nayak, P. L., Photo-induced Graft Copolymerization. IV. Graft copolymerization of Methyl Methacrylate onto Nylon-6 using N-bromosuccinamide as Photo initiator, *J. Appl. Polym. Sci.,* **27**,3625 (1982).

18. Shalaby, S. E.; Al-Balakocy, N. G.; Abo – Ola S.M.; Elshafei, A. M., Effect of Surface Activation of Nylon-6 Fabrics by Plasma and Grafting with Vinyl Monomers on its Functional Finishing with TiO$_2$ Nanoparticles, *Journal of Applied Sciences Research,* **9**, 3, 1743 – 1753 (2013).

19. Varma, D. S.; Ray, N. D., Graft Copolymerization of Nylon 6 with Methylmethacrylate and Methylacrylate, I. Optimum Conditions of Grafting and Thermal Behaviour of the Copolymers, *Angew. Macromol. Chem.,* **32**, 81 (1973).

20. Sheela, B.; Kalaiarasi, K.; Vijayalakshmi, K.; Sudha, P. N.,Optimization of Grafting Parameters of Nylon-6-Graft-Acrylic Acid Copolymer Using Ceric Ammonium Nitrate as an Initiator, *International Journal of Applied and Advanced Scientific Research,* **1**, 2,9-16 (2016).

21. Bucheaska, J., Polyamide Fibers (PA6) with Antibacterial Properties, *Journal of Applied Polymer Science,* **61**, 567-576 (1996).

22. Li, X.; Gu, X.; Zhang, S,; Li, H.; Feng, Q.; Sun, J.; Zhao, Q., Improving the Fire Performance of Nylon 6,6 Fabric by Chemical Grafting with Acrylamide, *Journal of Applied Polymer Science,* **52**, 6, 2290–2296 (2013).

23. Khalil, M. I.; Abdel-Fattah, S. H.; Kantouch, A., Manganese(IV)-Initiated Graft Polymerization of Vinyl Monomers on Polyamide Fibers, *J. Appl. Polym. Sci.,* **19**, 2699 (1975).

24. Nayak, P. L.; Lenka, S.; Mishra,N. K.; Tripathy,A. K., Grafting Vinyl Monomers into Nylon-6. II. Graft Copolymerization of Methyl Methacrylate onto nylon-6 by Hexavalent Chromium Ion, *J. Appl. Polym. Sci.,* **26**, 2437 (1981).

25. El-Rafie, M. H.; Khalil, M. I.; Hebeish, A., Azo bis isobutyronitrile - Induced Vinyl Graft Polymerization onto Nylon 66, *J. Appl. Polym. Sci.,* **19**, 1677 (1975).

26. Pradhan, A. K.; Pati, N. C.; Nayak, P. L., Grafting Vinyl Monomers onto Nylon 6. IV. Graft copolymerization of Methyl Methacrylate onto Nylon 6 Using the V^{5+}–Thiourea Redox System, *J. Appl. Polym. Sci.,* **27,** 1839 (1982).

27. Saihi, D.; El-Achari, A.; Vroman, I.; Caze, C., Graft Copolymerization of Methacryloyloxyethyl Trimethyl Ammonium Chloride monomer onto Polyamide 6,6 Fibres, *Journal of Textile and Apparel, Technolgy,* **4**, 1,(2004).

28. Saihi, D.; El-Achari, A.; Vroman, I.; Perichaud, A.,Antibacterial Activity of Modified Polyamide Fibers, *J. Appl. Polym. Sci.,* **98**, 3,997-1000(2005).

29. Shalaby, S. E.; Al-Balakocy, N. G.; Beliakova, M. K. ; Abdel-Fatah O. M.; Elshafei, A. M., Antimicrobial Finishing of Regular and Modified Nylon-6 Fabrics, *J. Appl Polym Sci.,* **110**, 2, 738 (2008).

30. Dash, S. B.; Pradhan, A. K.; Pati, N. C.; Nayak, P. L., Grafting Vinyl Monomers onto Nylon 6. IX. Graft Copolymerization of Methyl Methacrylate onto Nylon-6 using Peroxydiphosphate–Cu(II) Redox System , *J. Appl. Polym. Sci.,* **28**, 8, 2673 (1983).

31. Druzhnina,T. V.; Nazarina, L. A.; Kardash, K. V., Sorption – Active Modified Chemical Fibers, *Fiber Chemistry,* **32**, 6, 407 (2002).

32. Shalaby, S. E.; Abdella, N. H.; Rabie, A. M., Chemical Modification of Polyamide-6 Fibers, Containing Chemically Bonded Quaternary Ammonium Groups, with 2-Dimethyl aminoethyl methacrylate, *1ˢᵗInternational Conference of Textile Research Division, National Research Centre, Cairo,* Egypt, March 2-4, (2004).

33. Shalaby, S. E.; Al-Balakocy, N. G.; Abo El-Ola, S. M., Surface Modification of Nylon-6 Fibers for Medical Applications, *J Appl Polym Sci,* **104**, 6, 3788-3796 (2007).

34. Shalaby, S. E.;Al-Balakocy, N. G.;Abo El-Ola, S. M., Graft Copolymerization of Glycidylmethacrylate onto Modified Nylon-6 Fibers, *J Appl Polym Sci,* **99**, 3, 613-618 (2006).

35. Shalaby, S. E; Al-Balakocy N. G; Beliakova, M. K. Simple Method for Grafting of Glycidyl Methacrylate onto Nylon-6 Nonwoven Fabrics for Ion Exchange Applications, *International Journal of Science and Research (IJSR) ,* **4**, 5 (2015).

36. Shalaby, S. E.; Balakocy, N. G; Abo EL-Ola, S.M; Beliakova, M. K. Development of Pilot Scale System for Production of Nylon-6 Fibers Grafted with Polydimethylaminoethylmathacrylate (PDMAEMA) for the Application as Ion Exchange. *Desalination and Water Treatment* (Accepted 2018).

37. Shalaby, S. E.; Abo EL-Ola, S.M; Balakocy, N. G; Beliakova, M. k.; Abas R. A. Development of Pilot Scale System for Production of Polyamide-6 Fibers Grafted with Polymethacrylic Acid for Ion Exchange Applications. *Egypt. J. Chem.* **61**, 6, 1097 - 1109(2018).

38. Cole, J.O; Parks, C. R; Ianni, J.D.D., *Ind. Eng. Chem., Anal.* Ed., **18**, 61 (1949).

39. Beaman, R.G., Correlation and Prediction of Polyamide Glass Transitions**,** *J. Polym. Sci.,* **9**, 12, 3949-3952 (1965).

40. Suehiro, K.; Egashira, T.; Imamura, K.; and Nagano, Y., Structural Studies on 6–66 and 6–68 Copolyamides, *Acta. Polym.*, **40**, 1, 4-8 (1989).