# Modification of Polyamide Fibers (PA6) by Grafting Polyacrylamide (PAM)

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## SYNOPSIS

The grafting of polyacrylamide (PAM) onto PA6 knitted fabric in aqueous systems under the atmosphere of nitrogen or air was examined. The grafting process was initiated by oxidation with air oxygen, forming hydroperoxide groups. Effects of time and temperature of oxidation and of the grafting conditions, such as concentration of monomer, temperature, and time, on the rate and degree of grafting were determined. The optimum grafting conditions, ensuring the minimum amount of homopolymer, were found (oxidation temperature 413 K, oxidation time 10 min, grafting temperature under nitrogen 353–373 K, grafting time 1 h, monomer concentration 0.7 mol/dm$^3$). The activation energy of the grafting under nitrogen and air at 313–373 K was found to be 25.74 and 42.25 kJ/mol, respectively. The hydroscopicity, capillarity, disperse dye absorption, and electrical resistance of the modified PA-6 fabrics were determined. Some improvement of these properties was observed, depending on the degree of PAM grafting and the type of posttreatment with hydrazine and 3-bromopropionic acid. © 1995 John Wiley & Sons, Inc.

## INTRODUCTION

Previous articles[1-4] concerned the modification of polyamide fibers by grafting vinyl monomers (acrylic and itaconic acids and 2-vinylpyridine) using either thermal[5] or chemical initiation.[4] Although modification by grafting makes it possible to obtain many various, new properties of polyamide fibers, most studies have been focused on the most urgent problems to be solved such as elimination of static electricization, improvement of fiber dyeability, wearing comfort, and hygienic properties of textiles. Hygroscopic properties of fibers depend on polar hydrophilic groups present in the fiber-forming polymer as well as on the supermolecular structure of fibers. The low hygroscopicity of polyamide fibers as compared with natural fibers results from the lack of hydrophilic groups in the polyamide macromolecule. The terminal groups of polyamide such as carboxyl and amine groups which can combine in water are in too low quantities to be able to bring about a satisfactory hygroscopicity of polyamide. As follows from the above considerations, the hygroscopicity of polyamide fibers can be improved by introducing to polyamide another polymer containing a considerable amount of hydrophilic groups. It has been attempted to solve this problem by grafting, among other things, acrylamide[6-11] onto polyamide fibers, which, according to some authors,[12,13] improves the hygroscopicity of these fibers to the level of cotton fibers. According to Japanese researchers,[14] the grafting itself is not enough to bring about a satisfactory increase in hygroscopicity of polyamide textiles. The modification should include grafting of polyacrylamide (PAM) up to 10% by wt followed by treating the grafted fibers with some hydrophilic compounds, e.g., hydrazine. The hygroscopicity of such modified polyamide textiles is increased to 7.4% under standard conditions. The present study is the next stage of our studies in this field and takes into account a practical aspect of improving the performance properties of polyamide fibers as well as theoretical consideration of the grafting kinetics.

## EXPERIMENTAL

### Materials

A polyamide (PA6) shirt knitted fabric of a domestic make, prepared as in Ref. 5, was used in the study. The following reagents were used for the grafting:

- Acrylamide, a Japanese make, with a melting point of 353–358 K. After being crystallized three times in analar-grade benzene, the melting point of this compound was 357–358 K.

- Nitric acid, methyl alcohol, benzene, potassium bromide, potassium bromate, potassium iodide, sodium thiosulfate, sulfuric acid, and glacial acetic acid, all analar grade of "Ciech," Gliwice.

- Hydrazine, a product of the former USSR.

- 3-Bromopropionic acid of Koch Light Laboratory.

- Nitrogen of "Chemitex-Stilon," Gorzów Wlkp.

- A disperse dye, Blue 2RL, of "Boruta," Zgierz, Poland.

## Procedures

### Grafting of Acrylamide onto Polyamide Knitted Fabric

Knitted fabric samples with a weight of 2 g ± 0.1 mg each, prepared as in Ref. 5, were oxidized within the temperature range 393–433 K for various times. The oxidized samples were grafted in a 250 cm³ reactor provided with a stirrer, a thermometer, and a reflux condenser, including a nitrogen inlet. The knitted fabric samples, dried to a constant weight, were immersed in an aqueous solution of acrylamide in 0.3$N$ nitric acid and kept under specific conditions. The grafting process was carried out under nitrogen or air. The ratio of the weight of the polyamide sample to the bath was 1 : 30 in all the experiments.

### Determination of the Degree of Grafting and the Amount of Homopolymer Formed During the Process

The grafted samples were extracted with hot water for 0.5–4 h, depending on the degree of grafting of PAM on PA6 knitted fabric. The degree of grafting was determined gravimetrically after a thorough extraction and drying to a constant weight.

The homopolymer present in the postreaction solution and that after extraction of grafted fabrics was determined also by the gravimetric method, following water and unreacted acrylamide evaporation at the temperature of 313 K. At the same time, the unreacted acrylamide in the postreaction bath and that after extraction of the grafted fabrics were determined by the bromate–bromide analytical method.[15]

The degree of PAM grafting ($x$, $x_1$) was calculated from the following relationships:

$$x = \frac{m_k - m_0}{m_0} \times 100\% \text{ by wt} \qquad (1)$$

or

$$x_1 = \frac{x}{M_{ac}} \times 10^{-2} \text{ mol/g PA} \qquad (2)$$

where $m_0$ is the sample weight before grafting (g); $m_k$, the sample weight after grafting, extraction and drying (g); and $M_{ac}$, the molecular weight of acrylamide (g). The amount of homopolymer ($y$) was calculated from the relationship

$$y = \frac{m_H + m_E}{m_A} \times 100\% \qquad (3)$$

where $m_H$ is the weight of homopolymer present in the postreaction bath (g); $m_E$, the weight of homopolymer extracted from the grafted fabric (g); and $m_A$, the weight of acrylamide used in the grafting process (g).

The quantities of the homopolymer determined by gravimetric and analytical methods are given in Table I. It can be seen that the results obtained by both methods are comparable and the systematic error is approximately constant. Therefore, in further experiments, only the gravimetric method was used since the bromate–bromide method is a laborious one and can be used only in the case of low concentrations of acrylamide in solution.

### Treatment of the Grafted Fabric

The grafted knitted polyamide fabrics were impregnated with a hydrazine or methanol solution of 3-bromopropionic acid with variable concentration at

**Table I  Quantities of Homopolymer Formed on Grafting, Determined by Gravimetric and Analytical Methods**

| Sample No. | Homopolymer Determined by | |
|---|---|---|
| | Gravimetric Method % by Wt | Analytical Method % by Wt |
| 1 | 42.7 | 40.4 |
| 2 | 52.2 | 48.9 |
| 3 | 64.6 | 61.0 |
| 4 | 69.7 | 66.3 |

various temperatures for different periods of time. The extent of reaction between these compounds and the grafted fabric was also determined gravimetrically.

### Determination of Physical and Chemical Properties of Modified Knitted Fabrics

Hydrophilic properties of the modified samples were examined by determining the absorption of water for 4 h at 65 or 100% RH by the deccicator method according to Polish Standard PN-71-P-04635 and the capillarity of fabric according to PN-67-P-04633. The samples were air-conditioned according to PN-71-P-04602. The amount of absorbed water was determined gravimetrically.

The dyeability of modified samples was examined by dyeing with Disperse Blue 2 RL. The procedure was the same as in Ref. 2. The extinction was measured with a "Specol" spectrophotometer (Carl Zeiss Jena). The absorption maximum for Blue 2 RL was at $\lambda$ = 590 nm.

Antistatic properties of the modified fabrics were examined by the determination of electric resistance with a Megohmeter IM5e of Radiometer (Denmark). Samples in the form of a 50 × 15 mm tape,

air-conditioned for 24 h under standard conditions (RH 65%, temperature 293 ± 2 K, PN-71-P-04602), were fixed between electrodes and their resistance in M$\Omega$ was read from the meter. Ten measurements were taken for each kind of the modified fabric and the average value was then calculated.

## RESULTS AND DISCUSSION

### Effect of Oxidation Conditions on the Degree of PAM Grafting onto PA6 Knitted Fabric

Samples of the knitted fabric were oxidized with hot air[5] at various temperatures from 393 to 433 K and variable time from 5 to 30 min, while the conditions of grafting for these series were constant: temperature 353 K, time 1 h, and acrylamide concentration, 0.7 mol/dm$^3$, pH 0.5 (corresponding to 0.3$N$ HNO$_3$).

It has been found previously[5] that under the above conditions of oxidation the number of hydroxyl groups formed is sufficient to initiate the grafting process on PA6. The active oxygen content in the oxidized PA6 knitted fabrics is given in Table II. The grafting process was carried out under nitrogen or air. Results of these experiments are shown

**Table II  Active Oxygen Content in Polyamide Knitted Fabric Samples Oxidized with Hot Air**

| Sample No. | Oxidation Time (min) | Oxidation Temperature (K) | Molar Content of OOH Groups × 10$^4$ mol/g |
|---|---|---|---|
| Untreated initial sample | | | 1.0780 |
| 1 | 5 | | 1.2792 |
| 2 | 10 | | 1.6444 |
| 3 | 15 | 393 | 1.5217 |
| 4 | 20 | | 1.8551 |
| 5 | 30 | | 1.6780 |
| 6 | 2 | | 1.2910 |
| 7 | 5 | | 1.6833 |
| 8 | 10 | 413 | 1.9590 |
| 9 | 15 | | 2.1527 |
| 10 | 20 | | 2.2021 |
| 11 | 30 | | 4.6053 |
| 12 | 2 | | 1.5351 |
| 13 | 5 | 423 | 3.7465 |
| 14 | 10 | | 4.1953 |
| 15 | 15 | | 4.8324 |
| 16 | 2 | | 3.0060 |
| 17 | 5 | 433 | 4.6910 |
| 18 | 10 | | 7.1617 |
| 19 | 15 | | 7.1058 |

in Figures 1 and 2, illustrating the dependence of the grafting degree and the homopolymer content on temperature (Fig. 1) and time (Fig. 2) of the oxidation process.

It is seen from these diagrams that the grafting under nitrogen results in higher degrees of grafting of PAM on PA6 and lower homopolymer contents than those under air. This could be due to deactivation of the active centers, formed by oxidation, under the air atmosphere, as well as to the fact that acrylamide penetrates into individual filaments of the knitted fabric in a more difficult way because of the considerable amount of homopolymer being formed under air.

## Effect of Temperature and Time of Grafting on the Degree of Grafting of PAM on PA6

The following parameters were constant in this series: temperature of oxidation 413 K, oxidation time 10 min, acrylamide concentration 0.7 mol/dm³, and pH 0.5. The time of grafting in the first series of experiments was also constant (1 h), while the grafting temperature varied from 313 to 373 K. In the second series, the grafting time ranged from 0.5 to 5 h at the constant temperature of 353 K. The process was carried out under nitrogen or air. The results obtained in these two series are shown in Figures 3 and 4.
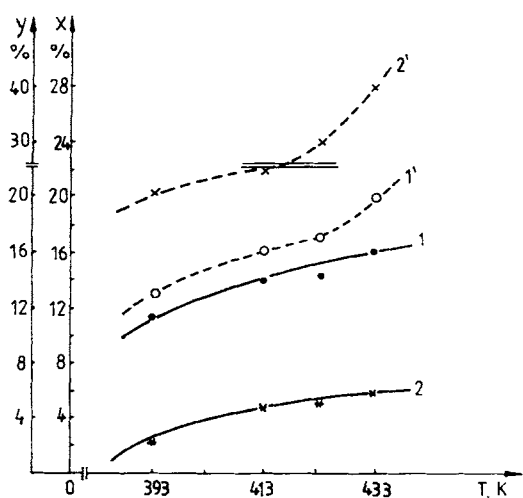
**Figure 2** Dependence of the degree of grafting of PAM on PA6 knitted fabric (x) and homopolymer content (y) on the time of its oxidation (τ). Oxidation temperature, 413 K; monomer concentration, 0.7 mol/dm³, pH 0.5; grafting temperature, 353 K; grafting time, 1 h. Notations of the curves as in Figure 1.

The data shows that there is a very significant effect of grafting temperature on the degree of grafting of PAM on PA6. The degree of grafting increases with temperature, which is accompanied by the increase in homopolymer content, especially within the temperature range from 353 to 373 K. There again is observed a higher degree of PAM grafting and lower homopolymer content under nitrogen than under air.

Following the effect of grafting time (Fig. 4), one can also observe here higher degrees of grafting under nitrogen than in air. The grafting degree in-

**Figure 1** Dependence of the degree of grafting of PAM on PA6 knitted fabric (x) and homopolymer content (y) on the temperature of its oxidation (T). Oxidation time, 10 min; monomer concentration, 0.7 mol/dm³, pH 0.5; grafting temperature, 353 K; grafting time, 1 h (1) grafting under nitrogen; (1') homopolymer content; (2) grafting under air; (2') homopolymer content.
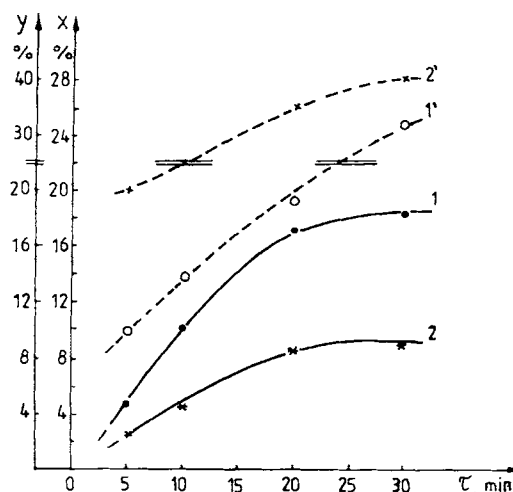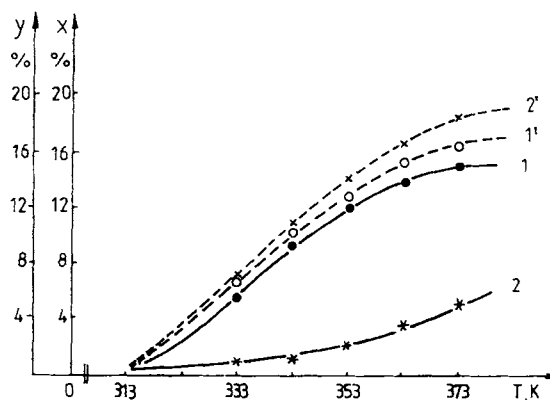
**Figure 3** Dependence of the degree of grafting of PAM on PA6 knitted fabric (x) and homopolymer content (y) on the grafting temperature (T). Oxidation at 413 K for 10 min. Grafting time, 1 h; monomer concentration, 0.7 mol/dm³, pH 0.5. Notations of the curves as in Figure 1.
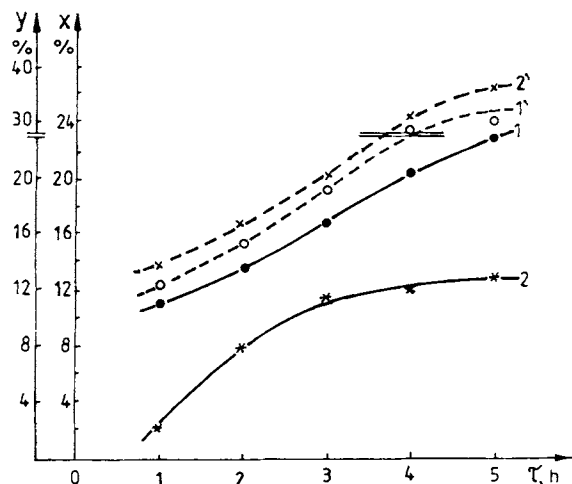
**Figure 4** Dependence of the degree of grafting of PAM on PA6 knitted fabric $(x)$ and homopolymer content $(y)$ on the grafting time $(\tau)$. Oxidation at 413 K for 10 min; grafting temperature, 353 K; monomer concentration, 0.7 mol/dm³, pH 0.5. Notations of the curves as in Figure 1.

creases gradually after 2 h of the process duration under nitrogen, while under air, some equilibrium is established. Extension of the reaction time in this case does not affect significantly the degree of grafting. This is due to the formation of considerable quantities of homopolymer when grafting under air.

### Effect of the Monomer Concentration on the Degree of Grafting of PAM on PA6

The following conditions were constant in this series: oxidation temperature 413 K, oxidation time 10 min, grafting temperature 353 K, grafting time 1 h, and pH 0.5. The process was carried out under nitrogen or air. The concentration of acrylamide ranged from 0.14 to 2.1 mol/dm³. The results obtained are shown in Figure 5. The degree of grafting is significantly affected by the monomer concentration in the reaction system. At the low concentrations up to 0.35 mol/dm³, a low degree of grafting and quite low homopolymer content are observed. When using acrylamide concentrations of 0.7 mol/dm³ or higher, a gradual increase in the degree of PAM grafting on PA6 is observed. At the same time, the homopolymer content increases both under nitrogen and air. The much lower grafting degrees obtained when carrying out the process under air can be explained in a similar way as previously by the deactivation of active centers in air and also by the formation of considerable quantities of homopolymer, which makes it difficult for the unreacted acrylamide to penetrate inside the PA6 fabric.

In the previous series, the acrylamide concentration 0.703 mol/dm³ was constant. It is difficult to estimate from Figure 5 if this value of concentration has been selected correctly in relation to the obtained result. In this connection, some additional data are given in Table III, such as grafting efficiency $(E)$, extent of reaction $(K)$, and grafting ratio $(R)$,[16] for the processes carried out at various monomer concentrations from 0.14 to 2.11 mol/dm³ under nitrogen or air. They would allow selection of optimum conditions to carry out the PAM onto PA6 fabrics. The grafting efficiency expresses the ratio of grafted polymer to monomer in % by wt, thus determining the amount of monomer being grafted in relation to the initial amount of monomer introduced to the process and is expressed by the relationship

$$E = \frac{m_k - m_0}{m_A} \times 100\% \qquad (4)$$

The extent of reaction $(K)$ takes into account the amount of monomer grafted and the amount of homopolymer in relation to the monomer used:

$$K = \frac{(m_k - m_0) + H}{m_A} \times 100\% \qquad (5)$$

The grafting ratio $(R)$ describes which part of the monomer used has been grafted and at the same time characterizes competitive processes: grafting and homopolymerization. When an ideal grafting
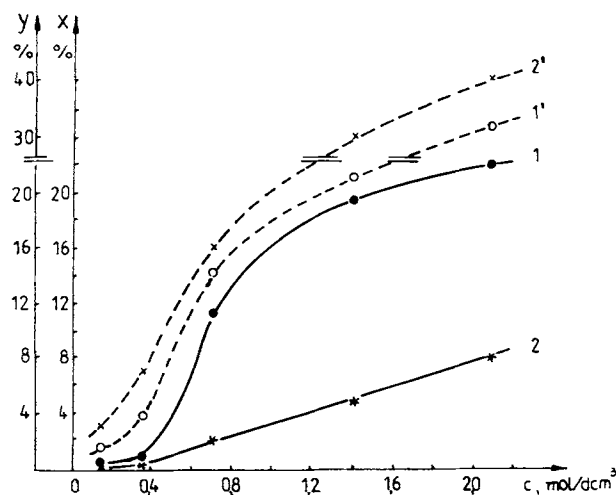


**Figure 5** Dependence of the degree of grafting of PAM on PA6 knitted fabric $(x)$ and homopolymer content $(y)$ on the monomer concentration in aqueous solution $(c)$. The conditions of oxidation and grafting are given in the text. Notations of the curves as in Figure 1.

**Table III    Efficiency, Extent of Reaction, and Ratio of Grafting Under Nitrogen and Air**

| Concentration of Acrylamide (mol/dm³) | Efficiency % by Wt | | Extent of Reaction % by Wt | | Grafting Ratio % by Wt | |
|---|---|---|---|---|---|---|
| | $N_2$ | Air | $N_2$ | Air | $N_2$ | Air |
| 0.14 | 0.096 | 0.083 | 1.990 | 3.083 | 4.838 | 2.702 |
| 0.35 | 0.588 | 0.188 | 4.405 | 7.647 | 7.692 | 4.730 |
| 0.70 | 7.727 | 1.400 | 21.751 | 17.400 | 35.520 | 8.045 |
| 1.40 | 6.495 | 1.700 | 26.495 | 31.684 | 24.551 | 5.365 |
| 2.11 | 4.837 | 1.770 | 37.314 | 42.340 | 13.115 | 4.198 |

proceeds, no homopolymer is formed; $H = 0$, then $R = 100\%$:

$$R = \frac{E}{K} \times 100\% = \frac{m_k - m_0}{(m_k - m_0) + H} \times 100\% \quad (6)$$

where $m_k$ is the sample weight after grafting, $g$; $m_o$, the sample weight before grafting, $g$; $m_A$, the monomer weight used in the process, $g$; and $H$, homopolymer weight, $g$.

As follows from Table III, the highest grafting efficiency is obtained when using a 5% acrylamide content in the reaction system under nitrogen (0.7 mol/dm³). At this monomer level, the highest grafting ratio is also observed. Although the extent of reaction increases with increasing acrylamide concentration, this result is brought about first of all by the increase in homopolymer quantity during grafting. Thus, the selection of the acrylamide concentration of 0.7 mol/dm³ in the grafting bath in the previous series was correct.

## Effect of Conditions on the Grafting Rate

The grafting rate is expressed as a ratio of the grafting degree to grafting time.[17] Figures 6–8 show the dependencies of grafting rate of PAM on temperature and time of fiber oxidation as well as on grafting temperature. It results from the given relationships that the grafting rate increases considerably with both temperature (Fig. 6) and time of fiber oxidation (Fig. 7). This is associated with the formation of hydroxyl groups in a high amount under the conditions of polyamide activation and decomposition



**Figure 6**    Dependence of the grafting rate ($V$) on the oxidation temperature ($T$). The conditions of grafting and notations of the curves as in Figure 1.



**Figure 7**    Dependence of the grafting rate ($V$) on the oxidation time. The conditions of grafting and notations of the curves as in Figure 2.
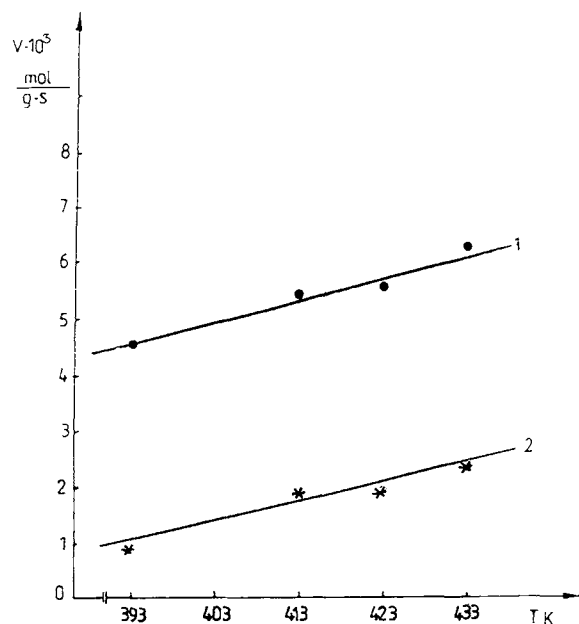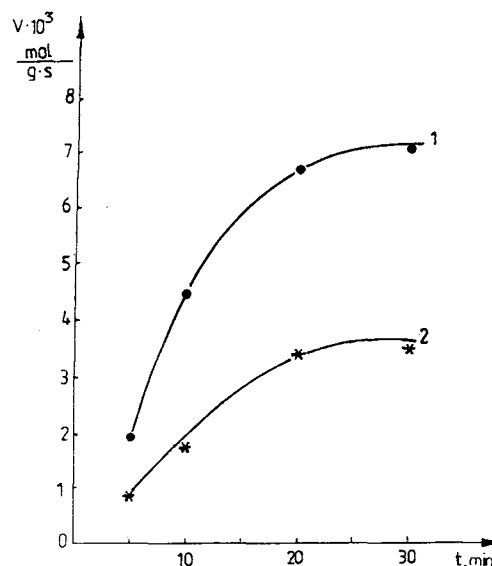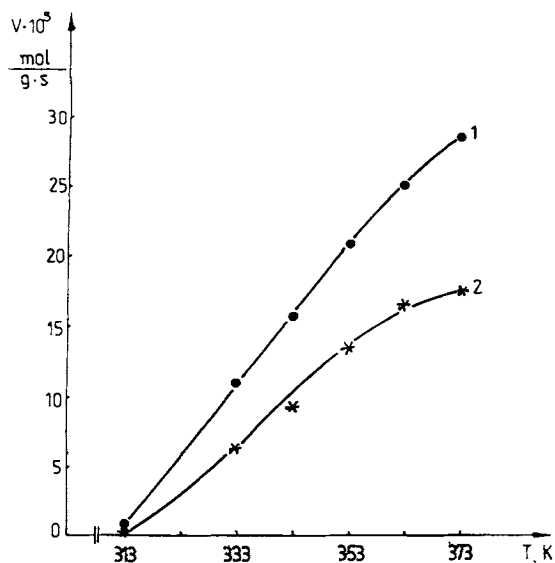
**Figure 8** Dependence of the grafting rate ($V$) on the grafting temperature ($T$). The conditions of grafting and notations of the curves as in Figure 3.



**Figure 9** The function $\log V = f(1/T)$ for grafting PAM on PA6 knitted fabric. Notations of the curves as in Figure 1.

of these groups, thus the formation of a high number of active centers under the conditions of grafting.[5] There is a considerable effect of oxidation time within the range from 5 to 20 min on the grafting rate of PAM, especially when carrying out the process under nitrogen (Fig. 7). This is probably because, within short time of oxidation, an insufficient amount of hydroxyl groups is formed, which is also accompanied with their recombination and formation of a considerable amount of homopolymer; the
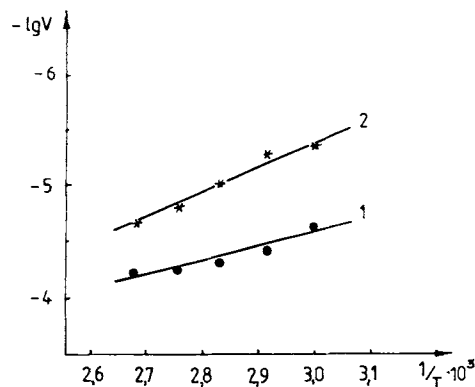
latter makes it difficult for acrylamide to access the active centers, especially when they are not easy to approach.

When running the grafting process under air, much lower grafting rates are observed. This is associated with a higher deactivation of macroradicals under the influence of the homopolymer formed in the process.

## Activation Energy of Grafting PAM on PA6

To check whether the discussed processes are applicable to the Arrhenius equation, i.e., whether the activation energy could be calculated, the dependence of the reaction rate logarithm on the temperature reciprocal was determined (Fig. 9 and Table IV). These data can be used to calculate the acti-

**Table IV** Values of the Preexponential Constant ($A$) from Arrhenius Equation and Activation Energy ($E_a$) of the Grafting of PAM on PA6 (Acrylamide Concentration 0.7 mol/dm$^3$)

| Grafting Temperature (K) | $1/T \times 10^3$ (k$^{-1}$) | Grafting Rate $V \times 10^6$ (mol/g s) | log $V$ | $A$ | $E_a$ (kJ/mol) |
|---|---|---|---|---|---|
| N$_2$ | | | | | |
| 313 | 3.1948 | 1.368 | −5.8640 | | |
| 333 | 3.0030 | 21.885 | −4.6599 | | |
| 343 | 2.9150 | 38.103 | −4.4191 | 1346.10 | 25.7421 |
| 353 | 2.8328 | 47.286 | −4.3253 | | |
| 363 | 2.7548 | 55.102 | −4.2589 | | |
| 373 | 2.6809 | 59.389 | −4.2263 | | |
| Air | | | | | |
| 313 | 3.1948 | 0.391 | −6.4049 | | |
| 333 | 3.0030 | 3.947 | −5.4038 | | |
| 343 | 2.9150 | 4.885 | −5.3112 | 2209.56 | 42.2545 |
| 353 | 2.8328 | 8.676 | −5.0617 | | |
| 363 | 2.7548 | 15.046 | −4.8226 | | |
| 373 | 2.6809 | 20.321 | −4.6924 | | |

Table V   Absorption of Moisture by Various Fabrics According to PN-71-P-04635
(4 h Storing in a Deccicator)

| Sample No. | Fabric | Degree of Grafting % by Wt | Hygroscopicity % | |
|---|---|---|---|---|
| | | | 65% RH | 100% RH |
| 1 | Viscose fabric | — | 7.11 | 13.60 |
| 2 | Cotton fabric | — | 3.99 | 9.06 |
| 3 | PA6 untreated knitted fabric | — | 3.00 | 6.55 |
| 4 | PA6 knitted fabric grafted with PAM | 5.27 | 3.55 | 7.13 |
| | | 10.11 | 3.89 | 7.30 |
| | | 14.39 | 4.16 | 7.71 |
| | | 20.09 | 4.66 | 7.91 |

vation energy of grafting PAM under nitrogen and air according to Ref. 18. The results of calculation of the constants appearing in the Arrhenius equation given in Table IV should be considered approximate since the grafting processes take place in a heterogeneous system. It follows from the calculation that the activation energy of the grafting process in air is much higher than that of the grafting under nitrogen ($E_{nitrogen} < E_{air}$).

## Physical and Chemical Properties of the Modified Knitted Fabric

The grafting of PAM on a PA6 knitted fabric introduces hydrophilic polar groups into the PA6 macromolecule. In this connection, one should expect to improve the hygroscopic and antistatic properties of the modified textiles. Therefore, the hydrophilic characteristics of the modified fabric were examined and the results are given in Table V. It can be seen that the hygroscopicity of the grafted knitted fabric is higher than that of an untreated fabric, being comparable with that of cotton under the same conditions.

In addition, the hygroscopicity of the modified knitted fabric was examined by determining capillarity since it plays an important role in the distribution of water to regions beyond the wetting spot. This parameter is of primary importance in the comfort of clothes in which the processes of absorption and desorption of moisture proceed via capillaries and pores in textiles. Results of the capillarity measurements are given in Table VI.

It follows from the measurements that the modified knitted fabric shows improved adhesive and capillary fixation of water. The highest capillarity is shown by the grafted fabric containing $0.095 \cdot 10^{-2}$ mol PAM per 1 g of the sample. At higher degrees

of grafting, the capillarity gradually dropped. The high increase in capillarity in modified fabrics with low degrees of grafting and quite low hydroscopicity could be explained by the fact that, probably, the grafting of low quantities of PAM results in an increased internal surface of the fabric, while higher quantities of another polymer introduced into the polyamide fabric can bring about plugging of the capillary system and, consequently, a decrease in capillarity.

Considering that the grafting of PAM brings about improved hydrophilic properties of the modified PA6 fabric, we can expect that the fabric dyeability with disperse dyes will also be increased. This was verified by test dyeing with Blue 2RL as a potential dye for dyeing the modified PA6 textiles by the method of sublimation print. The results of the

Table VI   Capillarity of PA6 Knitted Fabric Grafted with PAM

| Sample No. | Degree of Grafting | | Capillarity (mm) |
|---|---|---|---|
| | % by Wt | $10^2$ mol/g | |
| 1 | PA6 untreated knitted fabric | | 3.0 |
| 2 | 0.20 | 0.0028 | 22.0 |
| 3 | 1.11 | 0.0156 | 28.0 |
| 4 | 2.85 | 0.0400 | 30.0 |
| 5 | 2.90 | 0.0408 | 32.0 |
| 6 | 2.94 | 0.0413 | 42.0 |
| 7 | 3.10 | 0.0436 | 46.0 |
| 8 | 4.82 | 0.0678 | 56.0 |
| 9 | 6.76 | 0.0950 | 78.0 |
| 10 | 8.99 | 0.1264 | 49.0 |
| 11 | 10.10 | 0.1420 | 38. |

dye equilibrium absorption from the bath vs. the degree of grafting are shown in Figure 10. The point on the ordinate in this plot refers to the absorption of the dye by an unmodified PA fabric. It can be seen that, already with very low degrees of grafting PAM on PA6, almost 90% exhaustion of the dye is observed. This result could be considered useful in terms of savings as well as of environmental protection.

## Further Modification of the Grafted PA Fabric

It has been found that PAM grafted onto PA6 textiles in a quantity of about $0.14 \cdot 10^{-2}$ mol/g (10% by wt) brings about a still insufficient increase in hygroscopicity of these fibers. On the other hand, the grafting of high quantities of PAM (over 20% by wt) results in the required hygroscopicity, but the modified fabric becomes stiff. According to Japanese findings,[14] the grafting of PAM should be limited to optimal quantities and followed with a subsequent treatment of the grafted material with hydrophilic organic compounds. Such an approach was verified in the present study, using an aqueous solution of hydrazine for treating the grafted polyamide fabrics with the same degree of grafting (about 8% by wt). Several series of experiments were carried out with variable concentrations of hydrazine from 10 to 80% by wt, treatment time from 0.5 to 3 h, and temperature from 353 to 373 K.

The treated samples showed increased weight from 0.5 to 1.5% by wt, the highest weight increase
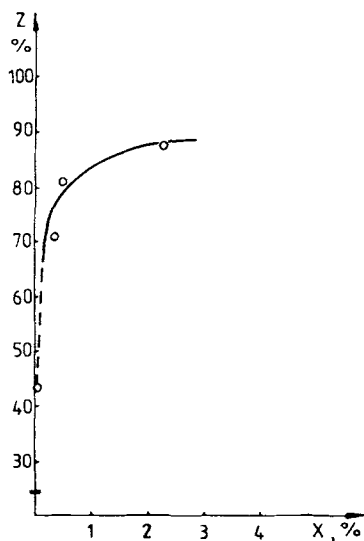


**Figure 10** Dependence of the absorption of a disperse dye ($z$) on the degree of grafting of PAM on PA6 fabric ($x$).

**Table VII Hygroscopic (65% RH; 4 h) and Antistatic Properties of PA6 Knitted Fabric Grafted with PAM and Treated with Hydrazine or 3-Bromopropionic Acid**

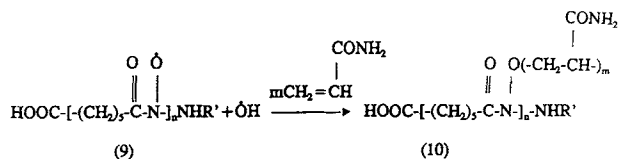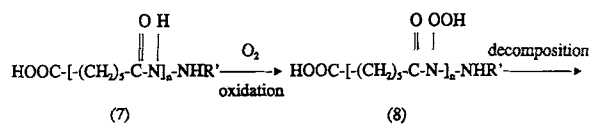| Type of Modification[a] | Hygroscopicity % by Wt | Electrical Resistance ($M_{ohm}$) |
|---|---|---|
| Untreated | 3.00 | $3.2 \times 10^{12}$ |
| Grafted with PAM (10.5%) | 3.89 | $1.8 \times 10^{11}$ |
| PAM-grafted + hydrazine (1.5%) | 5.10 | $1.2 \times 10^{11}$ |
| PAM-grafted + 3-bromopropionic acid (2.6%) | 8.0 | $2.7 \times 10^{9}$ |
| Grafted with PAA (10.7%) | 3.5 | $3.6 \times 10^{12}$ |
| Grafted with PAA (10.7%) and treated with $Na_2CO_3$ (6.5%) | 6.57 | $1.8 \times 10^{9}$ |

[a] In parentheses, degrees of PAM grafting or pickup of representative compound.

being for the sample treated with 80% hydrazine solution at 373 K for 3 h: 1.5% by wt. The hydrazine-treated samples of PA6–PAM fabrics were subjected to the hygroscopicity test under standard conditions according to PN-71-P-04635. The hygroscopicity was 5.10%, only slightly higher than that of the grafted sample before the hydrazine treatment.

Finally, the required increase in hygroscopicity up to about 8.0% under standard conditions and a simultaneous decrease in electrical resistance by several orders of magnitude was obtained by treating the PAM-grafted polyamide fabric with 3-bromopropionic acid. The treatment was carried out with a methanol solution of hydrazine at 333 K for 1–3 h. The hygroscopic properties and electrical resistance of the treated fabrics are listed in Table VII. For the purposes of comparison, the table contains also the values of electrical resistance of knitted fabrics grafted with poly(acrylic acid) and then treated with a sodium carbonate solution.[3]
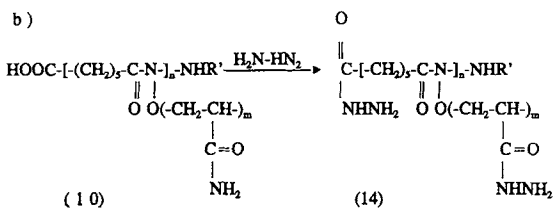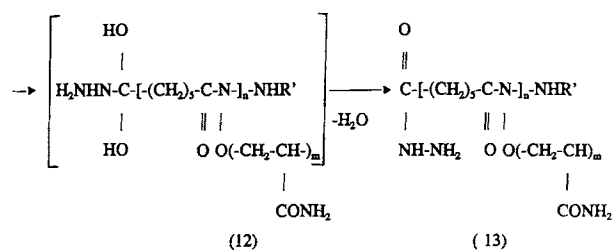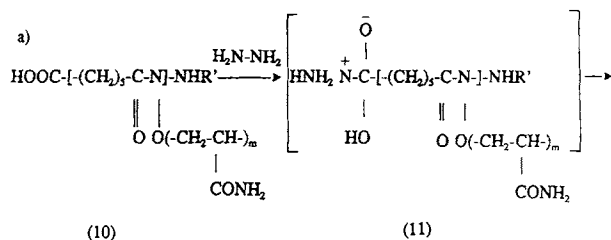
By comparing the value of hygroscopicity and electric resistance (Table VII) of the fibers PA6 grafted by PAM and impregnated additionally with a hydrazine or methanol solution of 3-bromopropionic acid and considering conditions of their modification, it is possible to suggest the following schema of reactions which take place during modifications of the fibers:

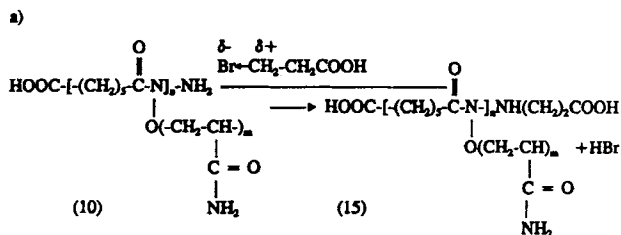**I.** Oxidation and grafting of knitted polyamide fabric[19]:

$$HOOC-[-(CH_2)_5-\overset{\overset{O}{\|}}{C}-\overset{\overset{H}{|}}{N}]_n-NHR' \xrightarrow[\text{oxidation}]{O_2} HOOC-[-(CH_2)_5-\overset{\overset{O}{\|}}{C}-N-]_n-NHR' \xrightarrow{\text{decomposition}}$$

(7)                                                    (8)

$$HOOC-[-(CH_2)_5-\overset{\overset{O}{\|}}{C}-N-]_n NHR'+\overset{\overset{\cdot}{O}}{O}H \xrightarrow[mCH_2=CH]{\overset{\overset{CONH_2}{|}}{}} HOOC-[-(CH_2)_5-\overset{\overset{O}{\|}}{C}-N-]_n-NHR'$$

(9)                                                    (10)

where $R'$ is — H or — $OCCH_3$ (the rest of stabilizing agent molecular weight of PA6); $n$, the degree of polymerization PA6; and $m$, the degree of polymerization PAM.

**II.** Impregnation of the grafted fabric PA–PAM by hydrazine:

a)

$$HOOC-[-(CH_2)_5-C-N]-NHR' \xrightarrow{H_2N-NH_2} [HNH_2 \overset{+}{N}-C-[-(CH_2)_5-C-N-]-NHR'] \rightarrow$$

(10)                                                    (11)

$$\rightarrow [H_2NHN-C-[-(CH_2)_5-C-N-]_n-NHR'] \xrightarrow{-H_2O} C-[-(CH_2)_5-C-N-]_n-NHR'$$

(12)                                                    (13)

b)

$$HOOC-[-(CH_2)_5-C-N-]_n-NHR' \xrightarrow{H_2N-HN_2} C-[-CH_2)_5-C-N-]_n-NHR'$$

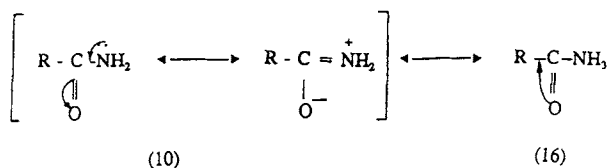(10)                                                    (14)

c) The hydrolysis reaction of the amide group PAM, added to carboxyl groups is not very probable, because hydrazine is a weak alkali. Hydrolysis of this group will be possible under the influence of a strong alkali in higher temperature.

**III.** Treatment of the grafted polyamide fabric of 3-bromopropionic acid:

a)

$$HOOC-[-(CH_2)_5-C-N]_n-NH_2 \xrightarrow{\overset{\delta- \quad \delta+}{Br-CH_2-CH_2COOH}} HOOC-[-(CH_2)_5-C-N-]_nNH(CH_2)_2COOH \ +HBr$$
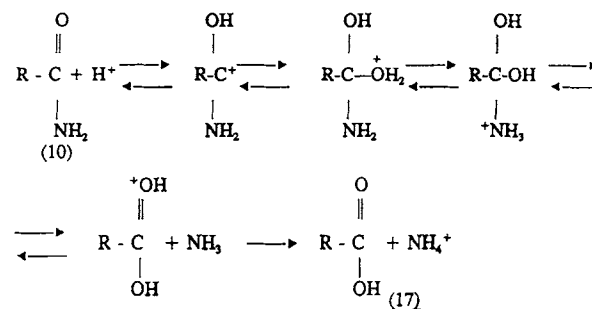
(10)                              (15)

b) The reaction of 3-bromopropionic acid with an amide group of the connected PAM chain is not very probable because a mezomeric structure of this group is possible, which makes impossible the connecting of this acid:

$$[R-C\overset{\overset{NH_2}{}}{\underset{O}{\|}} \longleftrightarrow R-C=\overset{+}{N}H_2 \ \underset{O^-}{|}] \longleftrightarrow R-\overset{\overset{C-NH_3}{\|}}{\underset{O}{}}$$

(10)                                    (16)

where $R$ is the polymeric rest of PAM–PA.

c) As the reaction of the treatment of the grafted polyamide fabric with the bromopropionic acid took place in alcohol which contained a minimal volume of water, accordingly, acid hydrolysis of amide group in the PAM chain connected to carboxyl groups can be expected, according to the reaction

$$R-\overset{\overset{O}{\|}}{\underset{NH_2}{C}}+H^+ \underset{\longleftarrow}{\longrightarrow} R-\overset{\overset{OH}{|}}{\underset{NH_2}{C^+}} \underset{\longleftarrow}{\longrightarrow} R-\overset{\overset{OH}{|}}{\underset{NH_2}{C-\overset{+}{O}H_2}} \underset{\longleftarrow}{\longrightarrow} R-\overset{\overset{OH}{|}}{\underset{+NH_3}{C-OH}} \underset{\longleftarrow}{\longrightarrow}$$

(10)

$$\underset{\longleftarrow}{\longrightarrow} R-\overset{\overset{+OH}{\|}}{\underset{OH}{C}}+NH_3 \longrightarrow R-\overset{\overset{O}{\|}}{\underset{OH}{C}}+NH_4^+$$

(17)

where $R$ is the polymeric rest PAM–PA.

Consequently, the grafted polyamide fabric treated with 3-bromopropionic acid, near structures (**15**) and (**17**), could be described as structure (**18**), too:

$$HOOC-[-(CH_2)_5-\overset{\overset{O}{\|}}{C}-N-]_n-NH(CH_2)_2-COOH$$

(18)
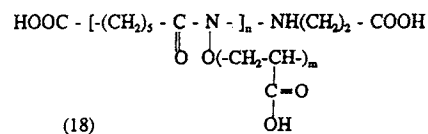
Creating the acid groups in the added PAM (formulas 15, 17, and 18) causes the higher growth of hygroscopicity and higher decrease of electric resistance of modified knitted fabric, in comparison with

the introduction of the additional alkaline groups —$NH_2$ into the polymeric chain, because groups —$COOH$ are more hygroscopic than are groups —$NH_2$. Accordingly, the grafted polyamide fabric additionally treated with 3-bromopropionic acid has better physical proporties.

## CONCLUSIONS

1. By examining the major dependencies of the grafting process on the conditions of its initiation and the grafting itself, the following optimal conditions have been found: temperature of PA6 knitted fabric oxidation, 413 K; oxidation time, 10 min; temperature of grafting under nitrogen, 353–373 K; grafting time, 1 h; and acrylamide concentration, 0.7 mol/dm$^3$.

2. The following approximate values of the activation energy of PAM grafting were calculated: 25.742 kJ/mol under nitrogen and 42.254 kJ/mol under air.

3. The grafting of PAM on PA6 fabrics in quantities up to $0.14 \cdot 10^{-2}$ mol/g brings about an insignificant increase in hygroscopicity, a high increase in capillarity, a small drop of electrical resistance, and considerable improvement of dyeability with disperse dyes. Although grafting higher quantities of PAM improves hygroscopicity and antistatic properties, it makes the fabric stiff.

4. A subsequent treatment of the PAM-grafted PA6 fabric with hydrazine improves the above-mentioned properties only to some small extent, but when 3-bromopropionic acid is used in the final treatment, the hydrophilic and antistatic properties of the modified polyamide fabric are considerably improved.

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