Grafting and Quaternization of 2-(Dimethylamino)Ethyl Methacrylate onto Polyamide-6 Fabric Pretreated with Acetone

A. M. RAMADAN, S. MOSLEH, S. M. GAWISH

National Research Centre, Textile Division, Tahrir Street, Dokki, Cairo, Egypt

Received 29 November 1999; accepted 5 September 2000

ABSTRACT: Grafting of polyamide (PA-6) pretreated with acetone was done using 2-(dimethylamino)ethyl methacrylate (DMAEM). It was found that the percentage graft yield of acetone-pretreated PA fabric was higher than the untreated and there was a difference of 4% under the same conditions. The graft yield was studied as a function of the different variable conditions such as monomer concentration, reaction time, and temperature. The pretreated and grafted DMAEM-PA fabric was then quaternized with different alkylating agents including ethyl iodide, benzyl chloride, and epichlorohydrin. The grafted and quaternized fabrics had a significant increase in dyeability. The quaternized fabric showed higher moisture regain compared to the ungrafted one and that could enhance the antistatic effect of such fibers. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 81: 2318–2323, 2001

Key words: grafted polyamide fabric; redox catalyst; quaternization

INTRODUCTION

Grafting of polyamide (PA-6) fabric with 2-(dimethylamino) ethyl methacrylate (DMAEM) in the presence of a redox catalyst was studied.[1] The shrinkage properties of the modified fibers, hygroscopicity, handle, and static charge were measured and discussed.

The grafting of PA-6 fibers with DMAEM at low temperature in the presence of a redox catalyst was also investigated.[2] A wool-like handle and good hygienic properties were obtained for the fibers.

The DMAEM (**I**) was grafted onto polycaprolactam containing a small amount of quaternary ammonium groups.[3] The graft yield of the copolymers (**II**) was ≤10–12% when $K_2S_2O_8$ or Cu^{2+} alone was used as the initiator. The reaction rate and the yield of **II** were increased in the copolymer initiated by a $K_2S_2O_8$-Cu^{2+} system. The mechanism of the grafting and initiation using Cu^{2+} was discussed.

Graft coplymerization of acrylic acid onto PA fibers was performed using $K_2S_2O_8$ as an initiator and $CuSO_4$ as a catalyst.[4] The method of grafting was based on complexation of $K_2S_2O_8$ with PA fibers containing a surfactant in the presence of Cu^{2+} ions. The reaction kinetics and mechanism of the grafting reactions were discussed.

Radiation induced graft copolymerization of 4-vinyl pyridine (VP) and a binary mixture of VP and acrylonitrile onto the PA-6 fibers and the optimum reactions conditions leading to a maximum percentage of grafting were studied. Also, the IR spectra, TGA, and dyeing behavior of grafted and ungrafted fibers were discussed.[5]

Correspondence to: S. Mosleh.

Journal of Applied Polymer Science, Vol. 81, 2318–2323 (2001)

Pretreated PA-6 with dimethyl formamide (DMF) was grafted by acrylamide.[6] An initiation system consisting of $K_2S_2O_8$ and cupric ions was used for graft copolymerization. The X-ray diffraction pattern identified that the change occurred in the fine structure of the pretreated PA-6 fiber.

The present work sought to facilitate the grafting reaction of PA-6 by fabric pretreatment with acetone. The tertiary amino groups of the grafted DMAEM side chain were quaternized with a series of alkylating agents: ethyl iodide, benzyl chloride, and epichlorohydrin. The improved affinity of the copolymerized PA-6-DMAEM was investigated for increase moisture regain and dyeing with acid dye.

EXPERIMENTAL

Materials

The PA-6 fabric (warp 42 ends/cm, weft 36 picks/cm) was obtained from El Nasr (Shorbagy) Co. The DMAEM monomer (purity 98%) stabilized by 0.1% hydroquinone was supplied by Merck Co. and used without further purification. The fabric was pretreated with acetone. The initiators potassium persulfate ($K_2S_2O_8$) and copper sulfate ($CuSO_4 \cdot 5H_2O$) were used as pure grade chemicals. The alkylating agents were ethyl iodide, benzyl chloride, and epichlorohydrin. The PA-6 grafted fabrics were further dyed with acid dye (C.I. Acid Red 1).

Technical Procedures

Fabric Washing

The PA-6 fabric was washed for 0.5 h with a 2 g/L nonionic detergent solution at 45°C and air dried at room temperature.

Pretreatment

The PA fabric was pretreated with acetone in a stoppered glass bottle using a liquor ratio of 1 : 50 with occasional shaking. The treatment was carried out at 50°C for 1 h; the samples were filtered under suction and thoroughly washed with running water at room temperature. The sample were then resuctioned and air dried at room temperature.

Grafting Procedure

The pretreated PA-6 fabric (0.5 g) with acetone was immersed in 2% aqueous $K_2S_2O_8$ solution for 20 min at room temperature. The sample was then squeezed, thoroughly washed with water, and squeezed again until almost dry. The sample was then introduced into a stoppered flask containing 50 mL water, 0.47–0.94 mol/L monomer, two drops of nonionic detergent as an emulsifier, and 1.4 mmol/L copper sulfate at a definite temperature (80, 85, and 90°C) for 2–30 min. The samples were washed with hot and cold water and finally extracted with acetone to remove any residual homopolymer. The samples were dried, and the percentage graft yield (G_o) was calculated as follows:

$$G_o = \frac{W_g - W_o}{W_o} \times 100 \quad (1)$$

where W_g is the weight of the dry grafted PA-6 fabric and W_o is the weight of the dry ungrafted PA-6 fabric.

Quaternization of Grafted Tertiary Amino Groups

Quaternization was achieved by immersing the grafted sample fabric in 30 mL of ethyl alcohol containing an excess of 3 times the theoretical amount of alkylating agent, including ethyl iodide, benzyl chloride, or epichlorohydrin (the latter in alkaline pH 8). The sample was stirred at reflux temperature for 2 h, then removed and thoroughly washed with ethanol and cold and hot water. Finally, the sample was dried and the actual weight increase due to the quaternization reaction (W_1) was noted. The quaternization reaction completion was calculated as follows:

$$\text{quaternization completion (\%)} = \frac{W_1}{W_2} \times 100 \quad (2)$$

where W_2 is the theoretical weight of the alkylating agent needed for complete quaternization of grafted DMAEM.

The weight of the grafted DMAEM and the theoretical amount of alkylating agent required were calculated as follows:

$$\text{wt DMAEM} = \frac{\text{graft yield} \times \text{sample wt}}{100} \quad (3)$$

wt alkylating agent

$$= \frac{\text{MW alkylating agent} \times \text{wt DMAEM}}{\text{MW DMAEM}(157)} \quad (4)$$

Physical Tests

Moisture Regain

The samples were conditioned at room temperature for 4 days in a desiccator containing a saturated solution of sodium nitrite to achieve a relative humidity of 65%. The samples were weighed and dried, and the moisture regain was calculated as follows:

$$\text{moisture regain } (\%) = \frac{W - W_o}{W_o} \times 100 \quad (5)$$

where W is the conditioned sample weight and W_o is the dry sample weight.

Dyeing Technique

The ungrafted, grafted, and quaternized PA-6 samples were dyed separately using a dye–liquor ratio of 1 : 100 and 3% acid dye calculated on the fabric weight. The pH of the dye was adjusted to pH 4 by the addition of acetic acid. The dyeing was started at 50°C and the temperature was gradually raised to 90°C in 1 h.

The dyed sample was washed with water followed by extraction with 50% aqueous DMF.

The color strength (K/S) of the dyed sample after extraction with DMF solution were determined using a spectrophotometer (Perkin–Elmer Lambda 3B) and applying the Kubelka–Munk equation[7] as follows:

$$K/S = \frac{(1 - R)^2}{2R} - \frac{(1 - R_o)^2}{2R_o} \quad (6)$$

where K is the absorption coefficient; S is the scattering coefficient; and R and R_o are the reflectance decimal fractions of the dyed and undyed samples, respectively.

RESULTS AND DISCUSSION

Previous work investigated that pretreatment of PA-6 fabric with solvent caused a significant change in the fine structure of PA-6 fabric, leading to an increase in d spacing[8] (the distance between sets of parallel planes). For this reason, we attempted to carry out the graft polymerization reaction with DMAEM into PA-6 fabric pretreated with acetone.

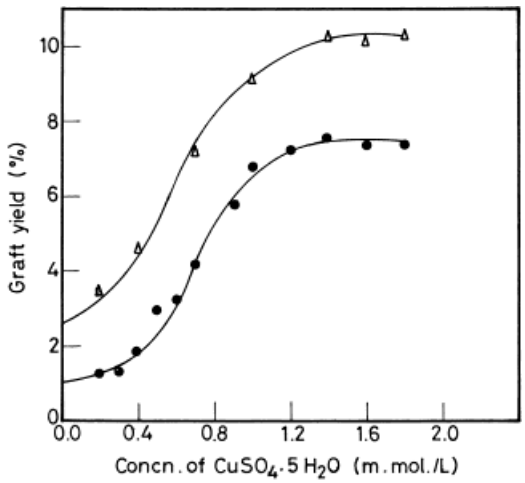


Figure 1 The effect of the $CuSO_4 \cdot 5H_2O$ concentration on the percentage graft yield of DMAEM onto the PA-6 fabric. Grafting conditions: 1.84×10^{-5} mol/L $K_2S_2O_8$, 0.712 mol/L DMAEM, temp. 80°C, liquor ratio 1 : 50. (●) Untreated fabric and (△) acetone-pretreated fabric.

Factors Affecting Grafting

Effect of Copper Sulfate

The effect of the copper sulfate concentrations on the percentage graft yield of DMAEM onto PA is clear in Figure 1. For the untreated fabric the graft yield was found to increase gradually with increasing copper sulfate concentration and reached about 7.5% at 1.4 mmol/L $CuSO_4$, while it attained 10.3% for the acetone-pretreated PA fabric.

Effect of DMAEM

In general, the graft yield increased with increasing monomer concentration, which is demonstrated in Figure 2. The enhancement in graft yield associated with increasing DMAEM concentration could be attributed to the diffusion of excess monomer into the PA fabrics under the chosen reaction conditions. Also, the acetone-pretreated PA fabric gave a higher graft yield (15.8%) than the untreated PA (11.8%) under the same conditions of grafting.

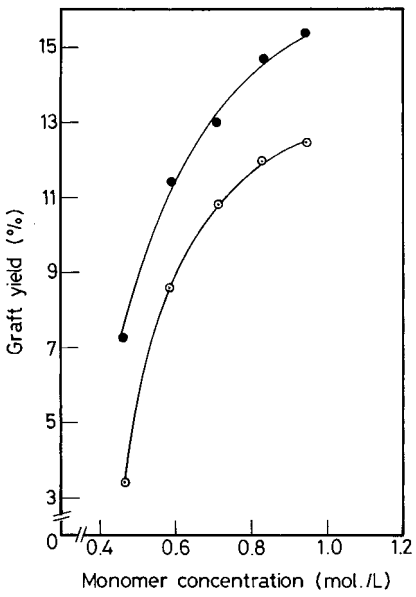


Figure 2 The effect of the DMAEM concentration on the percentage graft yield: Grafting conditions: 1.84 $\times 10^{-5}$ mol/L $K_2S_2O_8$, 1.4 mmol/L $CuSO_4 \cdot 5H_2O$, temp. 90°C, liquor ratio 1 : 50. (⊙) untreated PA-6 fabric and (●) acetone-pretreated PA-6 fabric.

Effect of Temperature and Time

The effect of temperature (80–90°C) on the percentage graft yield of acetone-pretreated and untreated PA fabrics is shown in Figure 3. At all temperatures used (80–90°C) there was an increase in graft yield with increasing time, and after 10 min the curves tended to level off (Fig. 3). The graft yield of the acetone-pretreated PA fabric increased with the reaction time and the maximum values of 10, 10.5, and 13.4% were attained at 80, 85, and 90°C, respectively. Further, the grafting of the untreated polyamide at the same temperatures reached maximum values of 6.8, 7.5, and 10.8%, respectively, compared to the previous values. We concluded that the untreated PA gave a lower percentage graft yield than the pretreated PA under the same conditions of grafting.

The increase in graft yield of the acetone-pretreated sample may be explained by the change in the microfine structure of fabrics due to the solvent effect before the grafting reaction.

Quaternization Reactions

The tertiary amino groups of the grafted DMAEM chains were subsequently quaternized with the appropriate alkylating agent (ethyl iodide, benzyl chloride, and epichlorohydrin) to yield the corresponding quaternary cationic PA fabric (Table I).

The quaternization reaction can be represented as follows:

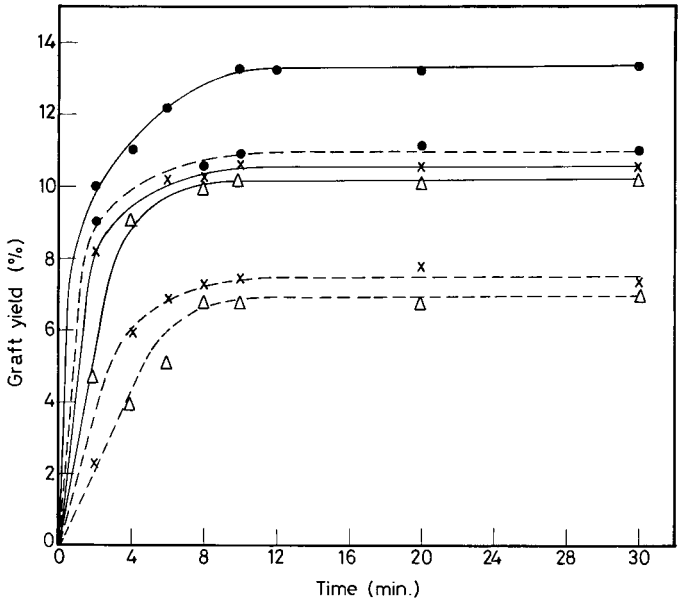
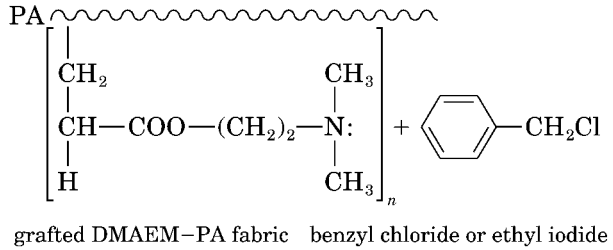


Figure 3 The effect of the temperature on the percentage graft yield of (—) untreated PA-6 and (—) acetone-pretreated PA-6. Grafting conditions: 1.84 $\times 10^{-5}$ mol/L $K_2S_2O_8$, 1.4 mmol/L $CuSO_4 \cdot 5H_2O$, 0.712 mol/L DMAEM, liquor ratio 1 : 50; temperatures (°C): (△) 80, (×) 85, (●) 90.

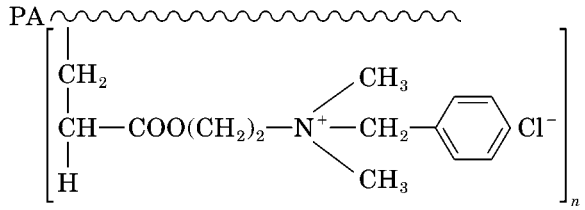
Table I Properties of PA Grafted with DMAEM (MW 157) and Quaternized with Different Alkylating Agents

Alkylating Agent	G_o (%)	W_1 (%)	W_2 (%)	Quaternization Completion (%)
Ethyl iodide (MW 156)	15.3	10.3	15.6	67.94
Benzyl chloride (MW = 126.6)	18.2	8.22	14.6	56.30
Epichlorohydrin (MW 92.5)	20.35	4.9	11.9	41.2

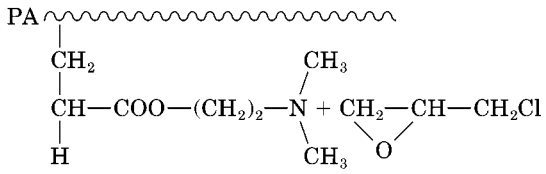
G_o, graft yield; W_1, the weight increase by quaternization; W_2, the theorical weight increase by quaternization.



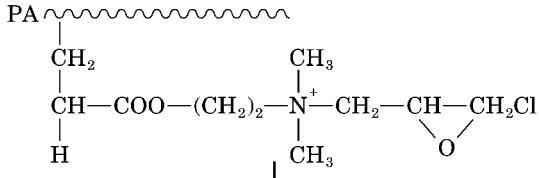
grafted DMAEM–PA fabric benzyl chloride or ethyl iodide



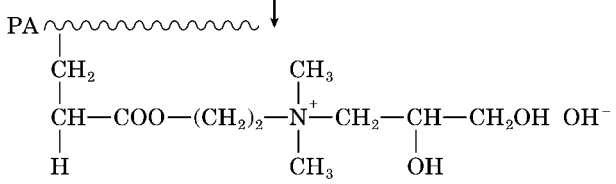
quaternized PA fabric (**I**)



epichlorohydrin



NaOH



quaternized PA fabric (**II**)

The quaternization reaction completion was 41.2, 56.30, and 67.94% for epichlorohydrin, benzyl chloride, and ethyl iodide, respectively. The PA fabric grafted with DMAEM quaternary ammonium salt can be also used as an ion exchanger.

A similar quaternization reaction on grafted synthetic fabric to prepare strongly basic anion exchangers was reported by Gawish et al.[9] and Lysenko et al.[10]

Physical Properties of Grafted Fabric

Moisture Regain

The moisture regain of the fabric was highly improved by grafting and subsequent quaternization (Table II). It attained 6.6, 8.02, and 8.4%, respectively, for ethyl iodide, benzyl chloride, and epichlorohydrin quaternized samples compared to 4.3% for the ungrafted one.

In general, the amount of moisture regain was found to increase with the quaternization of PA and the type of alkylating agent used.

Dyeing

The color strength of grafted and quaternized PA compared to the ungrafted PA-6 is shown in Table III. Note that quaternization of the grafted DMAEM tertiary amino group with ethyl iodide,

Table II Moisture Regain of Grafted and Quaternized DMAEM

Graft Yield (%)	Moisture Regain (%)
0 (Blank, ungrafted)	4.3
15.3 (Graft and quaternized with ethyl iodide)	6.6
18.2 (Graft and quaternized with benzyl chloride)	8.02
20.3 (Graft and quaternized with epichlorohydrin)	8.4

Table III Dyeing Properties of DMAEM Grafted PA Fabric

Graft Yield (%)	Color Strength of 3% Dyed Fabric
0 (Blank, ungrafted)	8.83
19.1 (Graft sample)	9.4
15.3 (Graft and quaternized with ethyl iodide)	10.13
18.2 (Graft and quaternized with benzyl chloride)	10.39
20.3 (Graft and quaternized with epichlorohydrin)	10.13

benzyl chloride, and epichlorohydrin and subsequent dyeing resulted in higher dye absorption. This was reflected in an increase of color strength with the increase of the percentage of grafted quaternary ammonium salt in comparison with the grafted and blank samples.

The above finding revealed a strong ionic bond formation between the positively charged quaternary nitrogen and the anionic dye, leading to strong salt formation onto the PA fabrics.

REFERENCES

1. Derbisher, V. E.; Elfimova, L. V.; Zhltobryukhov, V. F.; Khardin, A. P.; Shiganova, Z. S. Tekhnol Legkoi Promyshlennosti 1984, 27(4), 33.
2. Khardin, A. P.; Zheltobryukhov, V. F.; Tatarnikov, M. K. Khimi Volokna 1984, 26(3), 33.
3. Shalaby, S. E.; Afanaseva, I. S.; Gabrielyan, G. A.; Druzhinina, T. V.; Rogovin, Z. A. Vysokomol Soed Ser B 1982, 24, 288.
4. Shalaby, S. E.; Kantouch, A.; Bendak, A.; Ramadan, A. M. Bull NRC Egypt 1993, 18, 189.
5. Kaur, I.; Misra, B. N.; Barsola, R.; Angew Makromol Chem 1996, 234, 1–2; Chem Abstr 1996, 124, 204738K.
6. Ramdan, A. M. Bull NRC Egypt 2000, 25, 1.
7. Kubelka, P.; Munk, F. Z Technol Phys 1981, 12, 593.
8. Ramadan, A. M. Ph.D. Thesis, Cairo University, 1995.
9. Gawish, S. M.; Kantouch, A.; El-Naggar, A. M.; Mosleh, S. J Appl Polym Sci 1992, 44, 1671.
10. Lysenko, A. A.; Eets, L. V.; Mezentseva, G. B. Chem Abstr 1982, 97, 110.