

# Chemical Grafting of 2-Ethyl Methacrylate Phosphoric Acid onto Nylon 6 Fabric

S. MOSLEH

Department of Proteinic and Synthetic Fibers, Textile Research Division, National Research Center, El-Tahrir St., Dokki, Cairo, Egypt

**ABSTRACT:** Graft copolymerization of 2-ethyl methacrylate phosphoric acid (EMPA) onto nylon 6 fabric is carried out using the  $K_2S_2O_8/CuSO_4$  system as reaction initiators. The most important factors affecting the graft yield are monomer concentration, reaction time and temperature. It was found that the graft yield increased with increasing EMPA concentration, grafting time, and temperature. The grafted nylon 6 fabric shows an increase in moisture regain to reach a maximum of 8.01% with increasing the graft yield to 35.6%. Also, the dyeability with the basic dye was significantly increased due to grafting with EMPA. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 77: 1357–1361, 2000

**Key words:** graft polymerization; 2-ethyl methacrylate phosphoric acid; nylon 6; monomer concentration; reaction time; temperature; moisture regain; dyeability

## INTRODUCTION

Nylon 6 can be grafted with various vinyl monomers with the view to increase surface water absorption, dyeability, solvent and chemical resistance, electrical conductivity light or heat resistance, and adhesion to rubber.<sup>1–12</sup>

Grafting copolymers of acrylamide to polyamide 6 is known to increase the sorption and the antistatic characteristics of nylon, the adhesion, and the improvement of other important properties.<sup>12–15</sup>

Thus, the graft copolymerization of vinyl monomers onto nylon 6 fabric can be affected by chemical initiation that produces free radicals followed by formation of covalent bonds between the fabric and the grafted monomer. Initiation can be undertaken by the use of several reagents such as cerium,<sup>16–24</sup> manganese, and vanadium salts, or other redox system.<sup>25</sup>

Persulphate has been extensively used to initiate graft copolymerization of acrylonitrile onto nylon 6. Shalaby et al.<sup>25,27</sup> used the same previous technique for grafting acrylic acid onto nylon

6 fibers and explained the grafting method on the basis of complexation of persulfate with polyamide in the presence of a surface active agent. Addition of copper sulfate to the grafting liquor has been reported to minimize or eliminate the formation of homopolymer.<sup>9</sup>

The aim of the present study is to improve the physical properties of nylon such as the moisture regain and to increase the affinity of nylon 6 fabric to basic dyes, by creating new active acidic sites onto the backbone chains using the chemical grafting technique of aqueous anionic monomer 2-ethylmethacrylate phosphoric acid (EMPA) as vinyl monomer and potassium persulfate copper sulfate redox system as a graft initiator for the reaction.

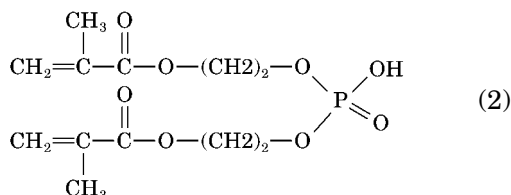
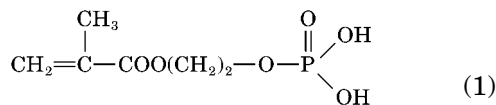
## EXPERIMENTAL

### Materials

Nylon 6 knitted fabric (120 g/m<sup>2</sup>) was obtained from the Egyptian El-Nasr Co., Cairo, for spinning, weaving, and knitting.

Monomer: 2-ethylmethacrylate phosphoric acid (EMPA) a mixture of mono (70%) and diester

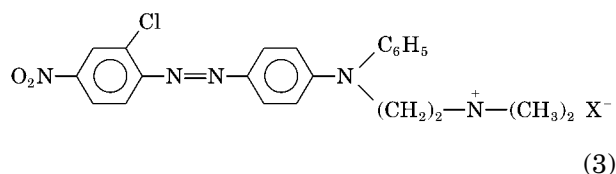
(30%) of the following chemical schematic configurations.



It was stabilized by 20 ppm methyl hydroquinone and was used without further purification.

Copper sulfate and potassium persulfate were used as pure grade chemicals initiators for the reaction.

Basic dye: CI Red 18, of the following chemical structure—



## Technical Procedures

### Pretreatment

Nylon 6 knitted fabric was washed with 2 g/L nonionic surfactant at 40°C for 1 h, thoroughly rinsed, and air dried at room temperature.

Nylon 6 knitted fabric was further treated by magnetic stirring with 2% solution of  $\text{K}_2\text{S}_2\text{O}_8$  for 20 min at room temperature. The excess persulfate was removed by washing with distilled water, squeezed, and dried at room temperature.

### Graft Copolymerization

The persulfate pretreated knitted fabric (0.5 g) was immersed in hermetically closed Pyrex tubes containing different amounts of monomer ( $0.47 \times 10^{-2}$  to  $1.19 \times 10^{-1}$  mol/L) and 0.35m mol/L of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ . The tubes were thermostated at different temperatures (75, 85, 90°C) for a specific period. The grafted samples were thoroughly washed with warm followed by cold water, and finally extracted with acetone to remove any residual homopolymer.

The samples were dried at 105°C and the graft yield was calculated as follows:

$$G_0 = (W_g - W_0) \times 100/W_0 \quad (4)$$

where  $W_0$  is the initial sample weight,  $W_g$  the grafted sample weight, and  $G_0$  the graft yield referred to the untreated sample.

### Dyeing Procedure

Dyeing was carried out at pH 4, with a fabric to liquor ratio (1:100) and dye concentration 0.1 g/L. The dyeing was started at 50°C and the temperature was gradually raised to the 80°C in 1 h.

The dyed samples were further extracted with a hot N, N-dimethylformamide(DMF)/water mixture at 90°C.

The color strength ( $K/S$ ) of the dyed samples before and after extraction with DMF solution, were determined using a spectrophotometer (Perkin Elmer Lambda 3 B); the Kubelka–Munk equation was applied as follows:

$$K/S = \frac{(1 - R)^2}{2R} - \frac{(1 - R_0)^2}{2R_0} \quad (5)$$

where  $K$  is the absorption coefficient,  $S$  the scattering coefficient, and  $R$  and  $R_0$  are the reflectance decimal fractions of the dyed and undyed samples, respectively.

### Physical Tests

#### Moisture Regain

The samples were conditioned at room temperature for four 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:

$$\% \text{ Moisture regain} = \frac{W - W_0}{W_0} \times 100 \quad (6)$$

where  $W$  is the conditioned sample weight and  $W_0$  is the dry initial weight.

## RESULTS AND DISCUSSION

### Factors Affecting EMPA Grafting onto Nylon 6 Knitted Fabric

#### Effect of Cupric Ion Concentration

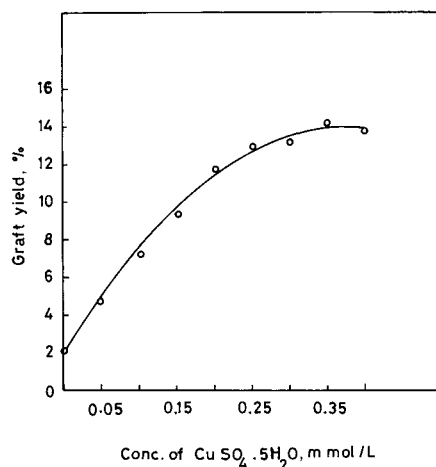
The effect of incorporating various concentration of copper sulfate upon grafting 2-ethylmethacry-

late phosphoric acid onto pretreated fabric is shown in (Fig. 1). It was observed that the presence of cupric ion in the system had a significant role in affecting the grafting reaction. An increase in the graft yield could be achieved when  $\text{Cu}^{2+}$  ion was used in the reaction. A graft yield of 4.8% was attained in the presence of 0.05m mole/L, in comparison to 1.8% in absence of  $\text{Cu}^{2+}$  ion.

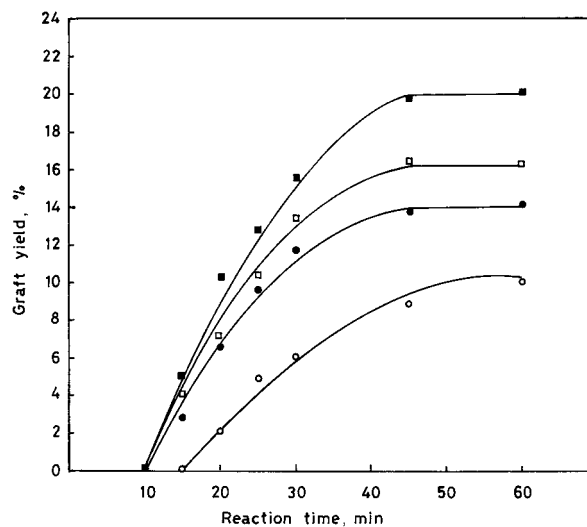
The extent enhancement of grafting was depended on the  $\text{Cu}^{2+}$  ion concentration. The graft yield increased gradually with increasing  $\text{Cu}^{2+}$  ion concentration and reached about 14% at  $\text{Cu}^{2+}$  ion concentration of 0.35m mole/L.

### Effect of Monomer Concentration

The percentage graft yield rate of 2-ethylmethacrylate phosphoric acid onto nylon 6 knitted fabric was studied using different concentrations of monomer. It is observed from Figure 2 that the grafting reaction proceeded via an induction period ranging from 10 to 15 min, which may be attributed to the lower diffusion of 2-ethyl methacrylate phosphoric acid into the knitted fabric at the beginning of the reaction. As the monomer concentration increases in the range  $0.7 \times 10^{-2}$  to  $1.19 \times 10^{-1}$  mol/L, the graft yield increases with time and then tends to level off after 45–60 min of the reaction. Leveling off of grafting is in accordance with previous investigations, which is due to the depletion in monomer concentration and the reduction in active free radicals of the polyamide backbone.<sup>28,29</sup>



**Figure 1** Effect of  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  concentration on percentage graft yield EMPA onto nylon 6 knitted fabric. Potassium persulfate:  $2.25 \times 10^{-4}$  mol/L; monomer [EMPA] concentration:  $0.71 \times 10^{-2}$  mol/L; temperature: 75°C; liquor ratio: 1:50.



**Figure 2** Effect of reaction time on the rate of grafting at various EMPA concentrations. (○)  $0.47 \times 10^{-2}$  mol/L, (●)  $0.71 \times 10^{-2}$  mol/L, (□)  $0.95 \times 10^{-2}$  mol/L, (■)  $1.19 \times 10^{-1}$  mol/L EMPA.  $\text{K}_2\text{S}_2\text{O}_8$  concentration:  $2.25 \times 10^{-4}$  mol/L;  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  concentration: 0.35 m mol/L; liquor ratio: 1:50.

### Effect of Time and Temperature

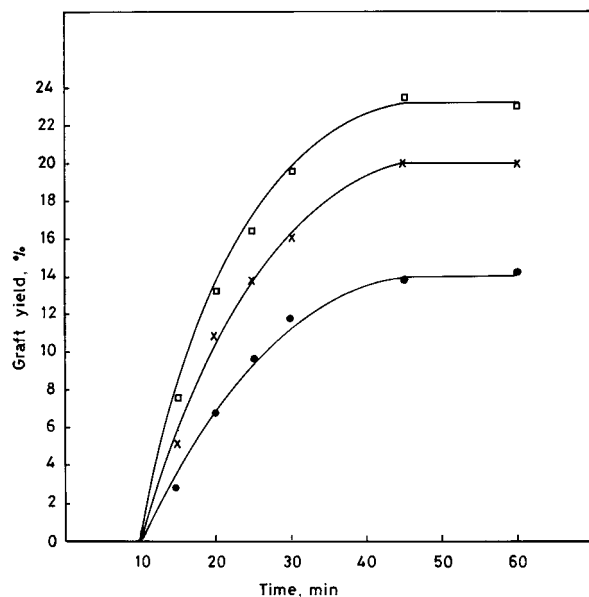
The graft copolymerization reaction of 2-ethylmethacrylate phosphoric acid onto nylon 6 knitted fabrics was carried out at different temperatures (75–90°C) for different periods of time 10–60 min (Fig. 3). In general, it was found that the grafting reaction proceeded via an induction period of about 10 min; then grafting increased with reaction time and attained the maximum value after 45 min.

The graft yield increased with increasing temperature in the range 75, 85, and 95°C, and the maximum value of graft values obtained were 14, 20, and 23.2%, respectively. This finding can be explained by the effect of temperature increase to influence the diffusion of the monomer into the polymer matrix. Also, this can be attributed to the adsorption of the monomer onto the fabric and finally its bonding with the nylon molecules to create the new induced monomer reactivity.

### Physical Properties of Grafted Fabric

#### Moisture Regain

The grafting of nylon 6 fabric with EMPA greatly improves its moisture regain, which increases gradually with increasing grafting from 4.3 for



**Figure 3** Effect of reaction time on graft yield EMPA onto nylon 6 knitted fabric at different reaction temperatures: (●) 75°C, (×) 85°C, and (□) 90°C.  $K_2S_2O_8$  concentration:  $2.25 \times 10^{-4}$  mol/L;  $CuSO_4 \cdot 5H_2O$  concentration: 0.35 m mol/L; liquor ratio: 1:50.

the ungrafted sample to 8.01% for 35.6% graft yield (Table I).

The improvement in moisture regain is attributed to the hydrophilic nature of the added grafted EMPA containing phosphate groups.

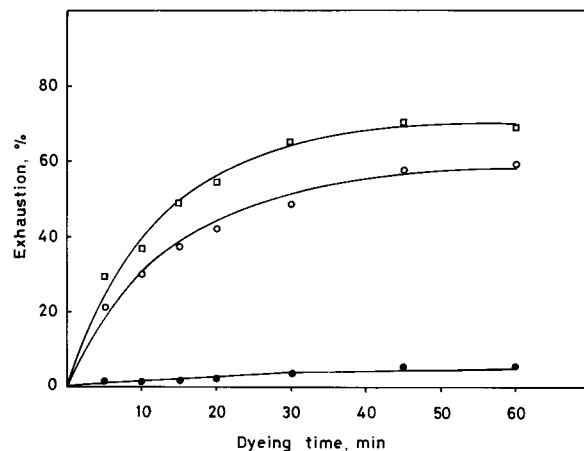
### Dyeing

The exhaustion rate of basic dye red 18 to nylon 6 knitted fabric grafted with EMPA was shown in (Fig. 4).

The extent of dye exhaustion onto EMPA grafted fabrics is higher than the ungrafted sample. Also, it is observed that the rate of dye exhaustion of grafted nylon fabric proceeded fast in the early stage of dyeing process and finally lev-

**Table I** Moisture Regain of EMPA Grafted Nylon 6 at 20°C and 65% Relative Humidity

Grafting Calc. on the Initial Weight %	Moisture Regain %
0	4.3
10	4.9
16.8	5.8
24.7	7.5
35.6	8.01



**Figure 4** Effect of dyeing time of grafted and ungrafted nylon 6 of knitted fabric on the percentage exhaustion of basic dye red 18. One percent on weight fabric; pH 4; liquor ratio: 1:100 at 80°C. (●) Control, (○), 16.4%, and (□) 24.4% graft yield.

eled off. Thus a maximum dye exhaustion of 70% and 58% was attained for 24.4% and 16.4% EMPA grafted samples respectively compared to 6% dye exhaustion for the ungrafted control one.

The color strength ( $K/S$ ) of ungrafted fabric is very low compared to that of grafted samples (Table II). Extraction of dyed fabrics with DMF indicates strong chemical bond formation between the grafted phosphate groups and the dye molecule.

The above finding revealed a strong ionic bond formation between the grafted negatively charged phosphate groups and the cationic part of the dye, leading to strong salt formation onto the nylon 6 fabric. Thus the grafting of nylon 6 fabric with EMPA greatly improves its affinity for basic dye.

The author expresses deep thanks and gratitude to Dr. Samiha Gawish, Professor of Textile Chemistry at Na-

**Table II** Dyeing Properties of EMPA-Grafted Nylon 6 Fabrics

Graft Yield (%)	Color Strength ( $K/S$ )	
	Dyed Fabric	Dyed and Extracted Fabric
0 (Blank)	0.488	0.469
13.1	6.5	6.28
20.2	6.97	6.84
34.6	7.1	6.73

tional Research Center for her valuable assistance of this work.

## REFERENCES

1. Varma, D. S.; Ravishankar, S. *Angew Makromol Chem* 1973, 28, 191.
2. Varma, D. S.; Ray, N. D. *Angew Makromol Chem* 1973, 32(1), 163.
3. Varma, D. S.; Ray, N. D. *Chem Abstr* 1973, 79, 106039r.
4. Gilber, N. A.; Robert, J. P.; Richard, N. M. *Text Res J* 1971, 41, 113.
5. Shalaby, S. E.; Gabrielyan, G. A.; Rogovin, Z. A. *Vysokomol Sod Ser B* 1982, 24(3), 222.
6. Shalaby, S. E.; Afanceva, I. S.; Gabrielyan, G. A.; Druzhinina, T. V. *Khim Volokna* 1982, No 2, 30.
7. Shalaby, S. E.; Piankova, A. B.; Gabrelyan, G. A.; Druzhinina, T. V.; Rogovin, Z. A. *Khim Volokna* 1982, No 3, 10.
8. Shalaby, S. E.; Afanaceva, I. S.; Gabrielyan, G. A.; Druzhinina, T. V.; Rogovin, Z. A. *Vysokomol Sod Ser B* 1982, 24(4), 288.
9. Shalaby, S. E.; El-Shahed, M. F.; Hebeish, A. *Acta Polym* 1984, 35(4), 321.
10. Naik, S. R.; Lokhande, H. T.; Pauland, R.; Borse, N. K. *Am Dyest Rep* 1997, 86(5), 20, 22–24.
11. Kaur, I.; Misra, B. N.; Barsola, R. *Angew Makromol Chem* 1996, 234, 1.
12. Buchanska, J. *J Appl Polym Sci* 1996, 60(4), 519.
13. Flath, H. J.; Feldt, D.; Morgenstern, J.; Pässler, H. *Textiltech* 1980, 30, 444.
14. Ravishankar, S.; Kumar, R.; Nigam, J. K. *Ind J Textile Res* 1977, 2(3), 85.
15. Ravishankar, S.; Kumar, R.; Nigam, J. K. *Chem Abstr* 1979, 91, 58560C.
16. Venkatakrishnan, S.; Santappa, M. *Makromol Chem* 1958, 27, 51.
17. Lalitha, J.; Santappa, M. *Vijnana Parishad Anusandhan Patrica* 1961, 4, 139.
18. Lalitha, J.; Santappa, M. *Chem Abstr* 1962, 57, 3607h.
19. Ananthanarayanan, V. S.; Santappa, M. *Indian J. Chem* 1964, 2, 330.
20. Ananthanarayanan, V. S.; Santappa, M. *Chem Abstr* 1964, 61, 16158f.
21. Narita, H.; Machida, S. *Makromol Chem* 1966, 97, 209.
22. Narita, H.; Okamoto, S.; Machida, S. *Makromol Chem* 1969, 125, 15.
23. Narita, H.; Okamoto, S.; Machida, S. *Makromol Chem* 1968, 111, 14.
24. Narita, H.; Okamoto, T.; Machida, S. *Makromol Chem* 1972, 157, 153.
25. Hebeish, A.; Guthrie, J. T. *Polymers, Vol. 4: The Chemistry and Technology of Cellulosic Copolymers*; Springer Verlag: Berlin, New York, 1981.
26. Shalaby, S. E.; Kantouch, A.; Bendak, A.; Ramadan, A. M. *Bull Natl Res Cent (Egypt)* 1993, 18(3) 189.
27. Shalaby, S. E.; Kantouch, A.; Bendak, A.; Ramadan, A. M. *Chem Abstr* 1995, 122, 267947g.
28. Gawish, S. M.; Kantouch, A.; El-Naggat, A. M.; Mosleh, S. *J Appl Polym Sci* 1995, 57, 45–53.
29. Gawish, S. M.; Kantouch, A.; El-Naggat, A. M.; Mosleh, S. *J Appl Polym Sci* 1992, 44, 1671–1677.