

Grafting of 2-(Dimethylamino) Ethyl Methacrylate onto Gamma Irradiated Polypropylene Fabric

S. M. GAWISH,^{1,*} A. KANTOUCH,¹ A. M. EL NAGGAR,² and S. MOSLEH¹

¹Textile Division, National Research Center, Tahrir Str., Dokki, Cairo, Egypt, and ²National Center for Radiation, Research and Technology, Nasr City, Cairo, Egypt

SYNOPSIS

Polypropylene fabric was gamma pre-irradiated at doses of 1, 2, and 3 Mrads. The irradiated fabric was grafted with an aqueous solution of 2-(dimethylamino) ethyl methacrylate. The graft yield was studied as a function of the different variable conditions such as storage time, monomer concentration (10–40%), reaction time, and temperature (50, 70, 100°C). The grafted polypropylene was further quaternized with dimethyl sulphate or monochloroacetic acid. The grafted and quaternized fabrics were dyed with an acid dye. The fixation properties of the dyed samples were determined by DMF extraction. The moisture regain and mechanical properties were also measured.

INTRODUCTION

Polypropylene (PP) has excellent mechanical properties and chemical resistance, and is inexpensive if compared to other synthetic fibers. In addition, PP fibers have many applications such as upholstery, blankets, apparel fabrics (for sweaters, swim-, sport- and underwear), ropes, wire cable coating, and geotextiles (for road construction, drainage, coastal and riverbank protection).

The disadvantages of PP fibers are poor hygroscopicity, paraffinic feel, and high crystallinity. These fibers bear no reactive functional groups and have no affinity for normal dyestuffs. In order to improve these properties, PP fibers are modified by various techniques to allow easy dyeing. One of these methods involves activation of PP substrates by peroxidation, ozonation, or irradiation with UV, gamma rays, or electron beam where grafting of active polar monomers with dye-receptive sites can take place.

A review of the literature revealed that the American Cyanamid Co.¹ improved the dyeability of PP fibers modified with vinyl pyridine by treatment with anionic solutions of dodecyl sulfate (0.25–4% OWF)

with pH less than 6 at 140–250°F. The treated fibers can be dyed with acid, basic, or vat dyes. Caldo² studied the dyeing properties of PP fibers modified by the introduction of amino groups. He found the highest acid dye absorption with fibers containing piperazine amino groups, followed by those with an aliphatic tertiary amino moiety. Montecatini³ improved the dyeing characteristic of isotactic PP by incorporating 1–25% by weight of a polymeric basic nitrogen compound followed by halogenation. Hsieh⁴ grafted *N*-vinyl 2-pyrrolidinone on PP by gamma irradiation in different swelling solvents such as dimethyl sulfoxide, pyridine, and dimethyl formamide. The same grafted monomer⁵ improved moisture regain, melting points, and dye absorption of PP fibers. In a previous work⁶ PP preirradiated by electron beam was grafted with 2(morpholino)ethyl methacrylate. The fabric was dyed with a series of acid and disperse dyes.

The aim of the present study is to improve the physical properties and to increase the affinity to dyeing of PP fabric by creating active dyeing sites onto the backbone chains using pre-irradiation grafting technique. An aqueous solution of the cationic monomer, 2-(dimethylamino) ethyl methacrylate (DMAEM) was used.

The different variables affecting the grafting reaction (including irradiation doses, storage time, monomer concentration, reaction time and temper-

* To whom correspondence should be addressed.

ature) were studied, as well as quaternization of the grafted tertiary amino groups.

EXPERIMENTAL

Materials

Polypropylene fabric (100%) was obtained from Montedison Co. The fibers are highly isotatic with the specifications, warp 238 dtex, fill 251 dtex. The monomer 2-(dimethylamino) ethyl methacrylate (DMAEM), purity 98%, stabilized by 0.1% hydroquinone, was supplied by Merck Co. and used without further purification. The alkylating agents dimethyl sulfate (DMS) and monochloroacetic acid were supplied by Merck Co. The acid dye Irganol yellow 5GLS was supplied by Ciba Geigy, and a nonionic wetting agent, Hostopal CV-ET, was supplied by Hoechst Co.

Technical Procedures

Fabric Washing

Before irradiation, the fabric was thoroughly washed to remove PP additives such as UV stabilizers and antioxidants, which are considered to be inhibitors of the irradiation process. The procedure was reported earlier.⁶

Radiation Source

The irradiation of samples was carried out in a ⁶⁰Co gamma chamber at the National Center for Radiation, Cairo, Egypt. A pre-irradiation method was adopted. The dry fabric was exposed to irradiation of 1–3 Mrad in the presence of air (dose rate, 0.64 Mrad/h).

Grafting Procedure

The preirradiated samples were weighed and immersed in hermetically closed pyrex tubes containing aqueous 2-(dimethylamino) ethyl methacrylate solution of different concentrations (10–40%). The solution was purged with nitrogen gas for 5 min to insure an oxygen-free solution. The tubes were thermostated at different temperatures (50, 70, 100°C) for specific periods. The grafted samples were thoroughly washed with warm then cold water and finally extracted with acetone to remove any residual homopolymer. The samples were dried and the graft yield was calculated either based on the initial weight (W_0) or the grafted sample weight (W_g) as follows:

$$G_0 = \frac{W_g - W_0}{W_0} \times 100, \quad G_g = \frac{W_g - W_0}{W_g} \times 100$$

where G_0 is the percentage graft yield calculated on W_0 and G_g is the percentage graft yield calculated on W_g .

Quaternization of Grafted Tertiary Aminogroups

Quaternization was achieved by immersing a known weight of the grafted fabric in ethyl alcohol containing an excess of three times the calculated weight of the alkylating agent, dimethyl sulfate or monochloroacetic acid (with traces of NaOH). The sample was stirred at reflux temperature for 1 h, then removed and thoroughly washed with ethanol, cold and hot water. Finally, the sample was dried and the increase in weight (W_1) due to the quaternization reaction was noted. The completion of the quaternization reaction was calculated as follows:

$$\text{Percentage reaction completion} = \frac{W_1}{W_2} \times 100$$

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

The weights of DMAEM grafted and the alkylating agent required were computed as follows:

$$\text{Weight of DMAEM} = \frac{G_g \times \text{grafted sample weight}}{100}$$

Weight of alkylating agent

$$= \frac{\text{MW of alkylating agent} \times \text{wt DMAEM}}{\text{MW of DMAEM}}$$

Dyeing Procedure

Dyeing was carried out at pH 5.5, with a fabric to liquor ratio of 1 : 100, and both nonionic wetting agent and dye concentrations of 0.5 g/L. The dyeing was started at 50°C and the temperature was gradually raised to the boil in half an hour and maintained at this temperature for another half an hour. The dyed sample was washed with fresh water followed by extraction with 50% aqueous dimethylformamide.

The color strength (K/S) of the dyed sample before and after extraction with DMF solution, were determined using a spectrophotometer (Perkin Elmer Lambda 3B) and applying the Kubelka–Munk equation⁷ as follows:

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

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

Physical and Mechanical 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:

$$\% \text{ Moisture regain} = \frac{W - W_0}{W_0} \times 100$$

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

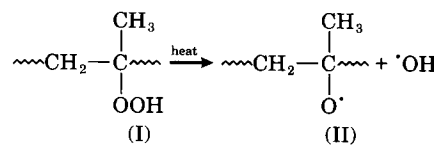
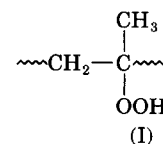
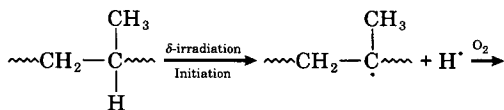
Tensile Strength and Elongation

Fabric tensile strength and elongation at break in the warp direction were determined by a fabric strength testing machine according to ASTM D-1682 standard method.

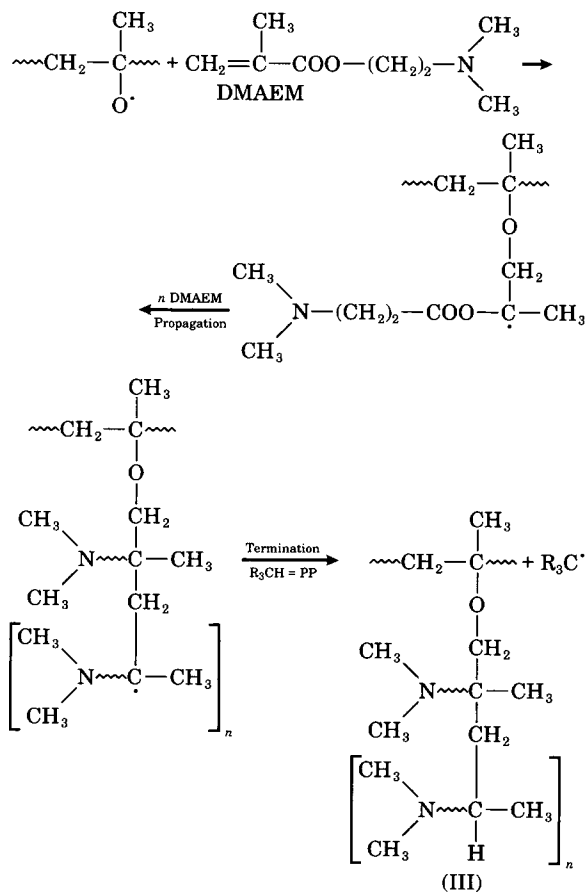
RESULTS AND DISCUSSION

A pre-irradiation technique was carried out on PP in the presence of air. The graft copolymerization of gamma irradiated samples was done with aqueous DMAEM solution at different temperatures. Active free radical centers are formed on the labile tertiary hydrogen of PP chains. These active centers react with the air oxygen leading to the formation of hydroperoxides (I) at ambient temperature. These in turn are decomposed by heat in presence of nitrogen to give alkoxide radicals (II) able to bind the monomer to the PP macromolecules. The overall reaction can be summarized as follows:

1. Gamma irradiation and free radical formation onto PP:



2. Grafting of 2-(dimethylamino) ethyl methacrylate to gamma irradiated fabric:



Grafting Factors

Effect of Storage Time

The gamma irradiated samples were stored at room temperature for one or five days. The stored samples were grafted with aqueous DMAEM solution. The variation of the graft yield with monomer concentration after storage of the irradiated PP is illustrated in Figure 1. For the same dose of irradiation

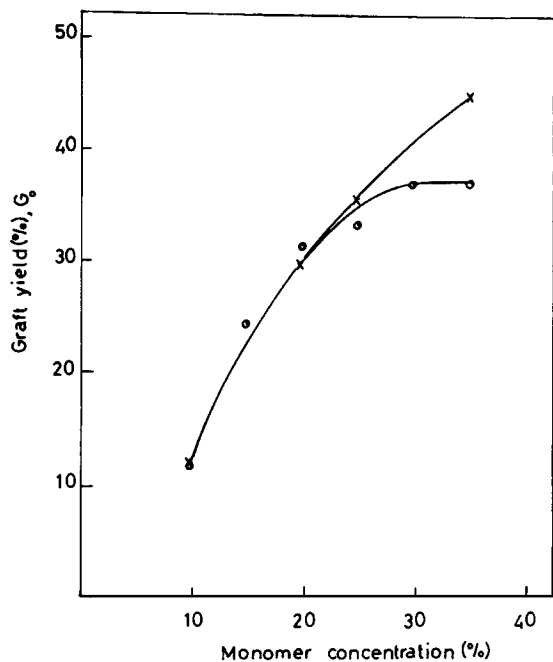


Figure 1 Effect of DMAEM concentration on the graft yield of 3 Mrad preirradiated PP fabric, at 100°C and after varying storage time: (x) one day, (o) 5 days.

(3 Mrad), there is a very slight decrease in the graft yield of PP samples stored for five days compared to one day. Prolonged storage time has been reported

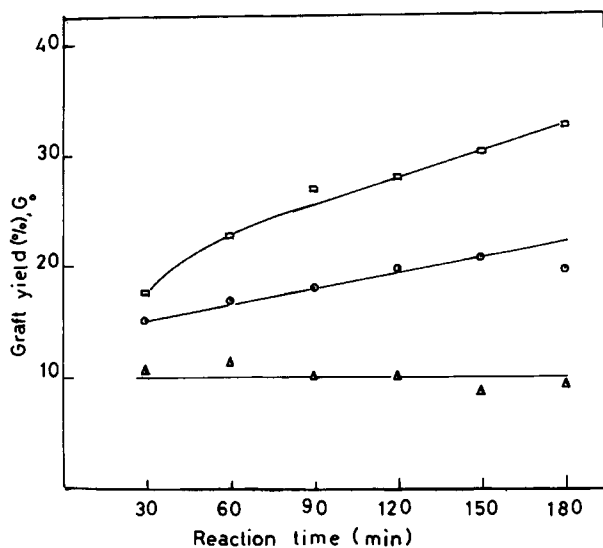


Figure 2 Effect of reaction time on the graft yield of 2 Mrad preirradiated PP fabric at different monomer concentrations, reaction temperature 70°C: (Δ) 10%; (o) 20%; (□) 30%.

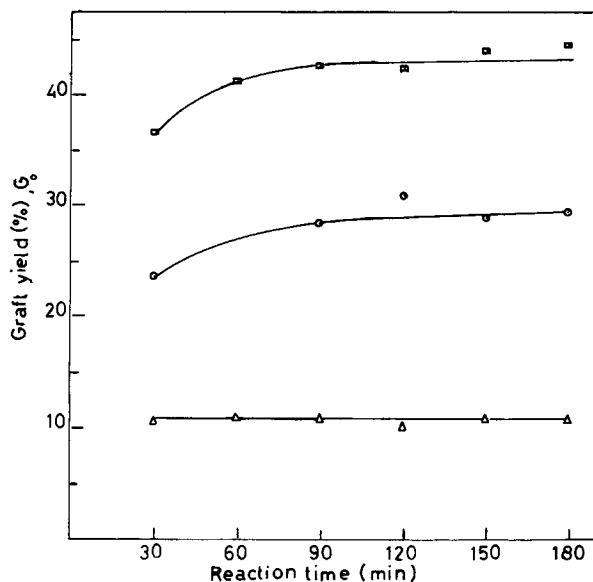


Figure 3 Effect of reaction time on the graft yield of 2 Mrad preirradiated PP fabric at different monomer concentrations, reaction temperature 100°C: (Δ) 10%; (o) 20%; (□) 30%.

by Sundari⁵ to decrease the graft yield and was explained on the basis of decay of hydroperoxide radicals with time.

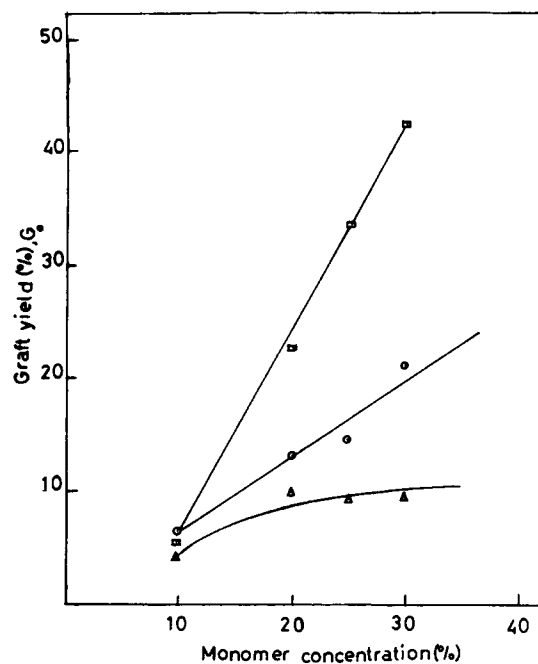


Figure 4 Effect of DMAEM concentration on the graft yield of 1 Mrad preirradiated PP at different reaction temperatures: (Δ) 50°C; (o) 70 and (□) 100°C.

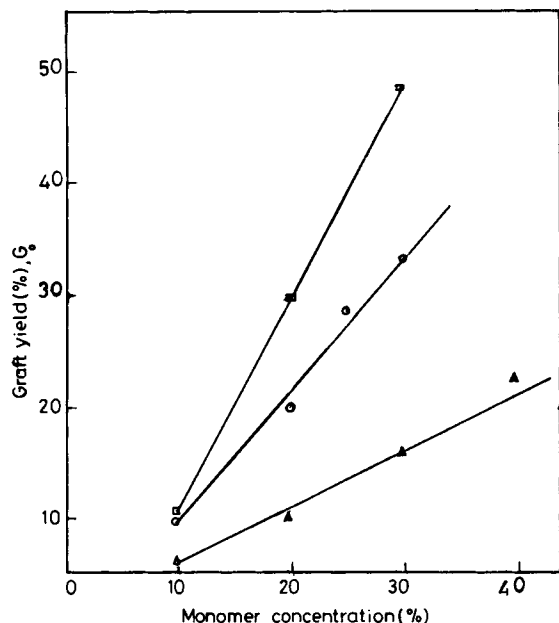


Figure 5 Effect of DMAEM concentration on the graft yield of 2 Mrad preirradiated PP at reaction temperatures (Δ) 50°C; (\odot) 70°C; (\square) 100°C.

Effect of Grafting Time

The variation of the graft yield with reaction time at 2 Mrad (after 24-h storage) carried out at 70°C and 100°C is shown in Figures 2 and 3.

At 70°C, using 10% aqueous monomer solution, the graft yield attained a constant value of 10% with increasing reaction time, indicating a steady state reached in a short time (30 min). At higher monomer concentrations (20, 30%), the graft yield increased with increasing reaction time.

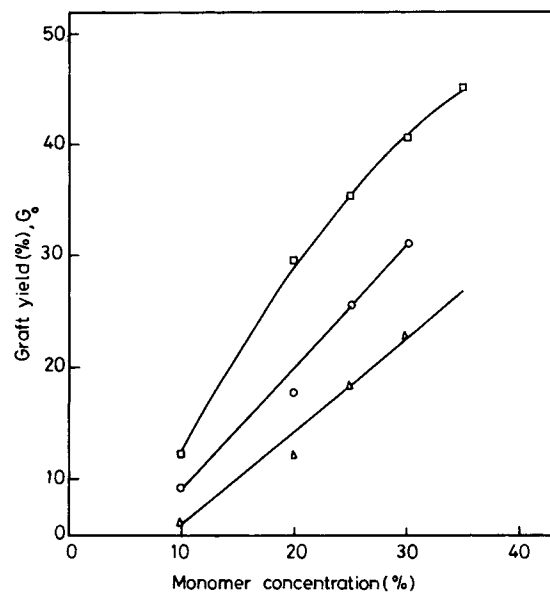


Figure 6 Effect of DMAEM concentration on the graft yield of 3 Mrad preirradiated PP at different reaction temperatures: (Δ) 50°C; (\odot) 70°C; (\square) 100°C.

At higher temperature (100°C) and concentrations (20, 30%) there is an increase in graft yield with increasing time and then the figure tends to level off after 60–90 min reaction, indicating an almost steady graft yield and constant hydroperoxide radical formation.

Effect of Monomer Concentration and Temperatures

The effect of DMAEM concentration on the graft yield carried out at 50, 70, 100°C, for different ir-

Table I Properties of PP-Grafted 2-(dimethylamino) Ethyl Methacrylate (MW 157) and Quaternized with Different Alkylating Agents

Property	Alkylating Agent	
	Dimethyl Sulfate (MW, 126)	Chloroacetic Acid (MW, 94.5)
% Graft (G_g)	25.00	19.7
% Actual weight increase by quaternization	18.44	11.8
% Theoretical weight increase by quaternization	20.11	11.8
% Reaction completion	91.70	100.0
% Moisture regain of grafted sample	1.01	0.8
% Moisture regain of quaternized sample	2.88	1.5
% Increase in moisture regain due to quaternization	1.87	0.7

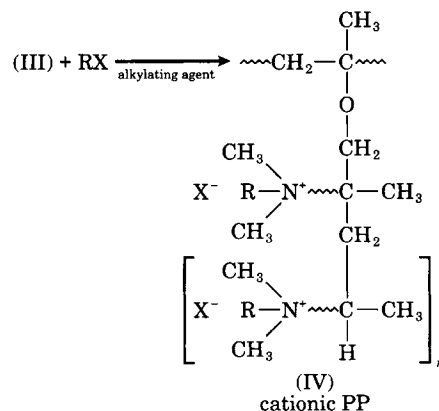
Table II Moisture Regain of DMAEM-Grafted Polypropylene Fabric

% Graft Yield (Go)	% G _g	% Moisture Regain
15.93	13.74	0.63
19.70	16.46	0.70
24.5	19.7	0.80
28.15	22.0	0.89
33.3	25.0	1.01
37.10	27.06	1.00
45.62	31.33	1.20

radiation doses (1, 2, and 3 Mrads) are shown in Figures 4 to 6. In general, at a given irradiation dose, the graft yield increases with increasing monomer concentration. This fact could be explained by the easy diffusion of excess monomer to PP fabric. Also, it is observed that the graft yield increases with increasing irradiation dose due to higher amounts of formed hydroperoxide groups. The enhancement in graft yield associated with increasing temperature may be explained by the increase of the liberated free radicals from their corresponding hydroperoxide groups.

Quaternization Reactions

The tertiary amino groups of the grafted side chains are quaternized with the alkylating agents dimethyl sulfate or monochloroacetic acid to yield the corresponding cationic PP fabric (Table I). The quaternization reaction can be represented as follows:



The reaction was 92% and 100% complete for dimethyl sulfate and monochloroacetic acid respectively. The creation of both the hydrophilic grafted tertiary amino group and the quaternary salt moiety greatly improves the moisture regain of the grafted and quaternized PP fabric.

It is worth mentioning that a similar quaternization reaction on grafted synthetic fibers has been reported by Lysenko et al.⁸ to prepare strongly basic anion exchangers.

Physical Properties of Grafted Fabric

Moisture Regain

The grafting of PP fabric with DMAEM improves its moisture regain, which increases gradually with increasing grafting (Table II).

On the other hand additional improvement of moisture regain is achieved by quaternization of the

Table III Mechanical Properties of DMAEM-Grafted Polypropylene Fabric

Polypropylene Sample	Graft %	Elongation at Break %	Tensile Strength kg	Loss in Tensile Strength %
Unirradiated	—	31	120	—
<i>1 Mrad irradiation</i>				
Irradiated	—	30	120	0.00
Irradiated and grafted	9.06	29	85	29.20
Irradiated and grafted	19.1	28	80	33.30
<i>2 Mrad irradiation</i>				
Irradiated	—	30	107	10.83
Irradiated and grafted	7.3	30	91	24.20
Irradiated and grafted	14.9	25	64	46.70
<i>3 Mrad irradiation</i>				
Irradiated	—	28	84	30.00
Irradiated and grafted	12.5	28	67	44.20

Table IV Dyeing* Properties of DMAEM-Grafted Polypropylene Fabrics

Graft Yield G_0 %	Color Strength (K/S)	
	Dyed Fabric	Dyed and Extracted Fabric
0 (Blank)	1.945	0.637
14.1	10.390	9.660
17.1	15.680	15.680
19.1	16.260	13.300
14.0 (Quaternized with dimethyl sulfate)	16.250	15.680
14.0 (Quaternized with chloroacetic acid)	19.850	19.010

* Dye: Irganol yellow 5GLS, 5% shade, reflectance measured at λ_{\max} 390 nm.

grafted samples. It attains 2.88% and 1.5%, respectively, for dimethyl sulfate and chloroacetic acid quaternized samples compared to 1.01% and 0.8% for the ones with unquaternized grafts (Table I).

Mechanical Properties

Elongation. The elongations at break (Table III) of the grafted samples slightly decreased compared to the untreated fabric indicating a slight rigidity effect due to irradiation and to grafting.

Tensile strength. The tensile strength of PP fabric decreased by simultaneous irradiation and grafting (Table III). The loss in tensile strength increased with increasing irradiation dose from 1 to 3 Mrad. For the same irradiation dose (2 Mrad), the irradiation decreased the tensile strength by 10.83%. As the graft yield increased from 7.3% to 14.9%, the loss in tensile strength increased from 24.2% to 46.7%.

Dyeing

The color strength (K/S) of untreated fabric is very low compared to that of grafted samples (Table IV). Extraction of dyed fabrics with DMF indicates strong chemical bond formation between the grafted amino group and the dye molecule. For the bright yellow acid color, the increase of K/S with increasing graft is highly pronounced.

Quaternization of the grafted tertiary amino

group of DMAEM with either dimethyl sulfate or chloroacetic acid and subsequent dyeing, results in higher dye absorption. This is reflected in color strength increase in comparison with that of grafted unquaternized sample. Extraction with DMF gave nearly the same value of K/S for the dyed 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 PP fibers. Thus, the grafting of PP fabric with DMAEM improves greatly its acid dye uptake.

REFERENCES

1. American Cyanamid Co. and J. M. Mecco, U.S. Patent 3,707,351 (1972).
2. C. Caldo, *Tintoria* **75**, 221-235 (1978).
3. E. Montecatini and V. Cappucio, U.S. Patent 3,482,926 (1969).
4. Y. L. Hsieh, *Polym. Mater. Sci. Eng.*, **51**, 646-650 (1984).
5. F. Sundari, *J. Appl. Polym. Sci.*, **22**, 3163-3176 (1978).
6. S. M. Gawish, L. Gavet, B. Chabert, and G. Nemoz, *Am. Dyestuff Reporter*, **79**, 22-32 (1990).
7. P. Kubelka and F. Munk, *Z. Technol. Phys.*, **12**, 593 (1931).
8. A. A. Lysenko, L. V. Eets, and G. B. Mezentseva, *Chem. Abstr.*, **97**, 110728 (1982).

Received August 15, 1990

Accepted May 28, 1991