

Benzoyl Peroxide-Induced Graft Polymerization of 2-Methyl-5-Vinylpyridine Onto Polyester/Wool Blend

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Synopsis

Graft polymerization of 2-methyl-5-vinylpyridine (MVP) onto polyester/wool blended fabric was carried out using benzoyl peroxide as initiator. The graft polymerization reaction was conducted under a variety of conditions. The graft yield increased by increasing benzoyl peroxide concentration from 0.559 mmole/l. to 1.657 mmole/l. Further increase in benzoyl peroxide concentration (i.e., up to 2.795 mmole/l.) decreased grafting. Increasing the MVP concentration from 4% to 10% caused a significant enhancement in grafting. The same held true for raising the polymerization temperature within the range of 65°–85°C. The grafting reaction proceeded initially at a fast rate and decreased with time to a slower rate. The grafted samples showed improved dyeability toward acid dye, increased density, and decreased moisture regain as compared with the untreated blend. Furthermore, a tentative mechanism for initiation of grafting was suggested.

INTRODUCTION

Chemical modification of wool via grafting polymerization can be achieved through either physical or chemical activation of wool.¹⁻³ Subjecting wool to high-energy radiation³⁻⁸ or low-energy radiation in the presence and absence of sensitizers^{6,9-14} produces wool macroradicals which are capable of initiating grafting. Similar wool radicals can be brought about by the action of redox systems,¹⁵⁻¹⁹ ceric ion,^{20,21} periodate ion,²² acetyl(acetonato) copper(II)-trichloroacetic acid complex,²³⁻²⁷ potassium permanganate,^{28,29} benzoyl peroxide,³⁰ dimethylaniline-benzyl chloride mixture,³¹ thiourea in acid medium,³² and other redox system such as Fe³⁺-thiourea,³³ di-*tertiary*-butyl peroxide-thiourea,³⁴ and hydrogen peroxide-thiourea.³⁵ Creation of free radicals on the wool backbone through chain transfer has also been possible.³⁶

Though much of these studies have been devoted to the kinetics of grafting, yet a substantial amount of information about the physicommechanical properties as well as dyeability of the grafted wool is available.^{1-3,6,37} Relatively little information, however, is available regarding the kinetics of polymerization and the modification effect on polyester, i.e., poly(ethylene terephthalate), though investigations on high-energy and ultraviolet radiation of this material have been carried out in the presence and absence of vinyl monomers.³⁸⁻⁴⁷ Chemical methods have also been used to initiate vinyl graft polymerization onto polyester.⁴⁸⁻⁵⁶ It should be emphasized that in both the radiation and chemical methods of grafting, the homopolymer of the vinyl monomer is to be expected,

but often can be suppressed by suitable additives.⁵⁷⁻⁶⁰ An improvement in dyeability elevation of melting point, and accentuation of antistatic properties of polyester could be achieved by grafting the latter with acrylic acid.⁶¹ Polyester copolymerized with 2-vinylpyridine could also be dyed with acid dyes.⁶²

The aim of the present work was to study the graft polymerization of MVP on polyester/wool blended fabric. The polymerization was initiated by benzoyl peroxide in aqueous medium. Variation in properties such as moisture regain, density, and dyeability of the grafted blend were evaluated.

EXPERIMENTAL

Materials

Merino wool fibers were purified by Soxhlet extraction with acetone for 24 hr, followed by washing with cold, distilled water and air drying.

Poly(ethylene terephthalate) fibers and fabrics, kindly supplied by Hoechst, 1.2 den/40 mm (cotton type), were purified by Soxhlet extraction with methanol for 24 hr, followed by washing with cold, distilled water and air drying.

Wool fabric and polyester/wool blended fabric (50:50), kindly supplied by Misr El-Mehala El-Kobra Company, were purified by a mild scouring treatment with Lissapol NX (Ciba) for 30 min at 50°C followed by washing for 30 min with cold, distilled water and air drying.

2-Methyl-5-vinyl pyridine (MVP) was pure-grade chemical and freshly distilled (75°C/13 mm Hg) before use.

Benzoyl peroxide was freshly prepared according to the method of Vanino and Herzer.⁶³ Kiton Fast Red B1 (Ciba), C.I., 17045, was used.

Grafting Procedure

Graft copolymerization was carried out under atmospheric oxygen in a 100-ml stoppered Erlenmeyer flask. The sample (0.5 g) was introduced into a 50-ml aqueous solution containing the monomer and the emulsifying agent (Emulsogen GG-Hoechst). The flask was immediately stoppered and placed in a thermostated water bath for a certain period till the required temperature was reached, and the initiator was then added. The reaction was allowed to proceed for different periods of time. The sample was washed with distilled water and Soxhlet extracted with methyl alcohol and dried. Extraction with alcohol and drying was repeated to constant weight. The graft yield was calculated on the basis of constant dry weight, determined by storing the substrate over phosphorus pentoxide at room temperature.

% graft yield

$$= \frac{\text{dry weight of grafted sample} - \text{dry weight of original sample}}{\text{dry weight of original sample}} \times 100$$

RESULTS AND DISCUSSION

The effect of initiator and monomer concentration and reaction time on the graft yield was investigated to discover the optimal conditions for grafting. Presented below are the results obtained along with appropriate discussion.

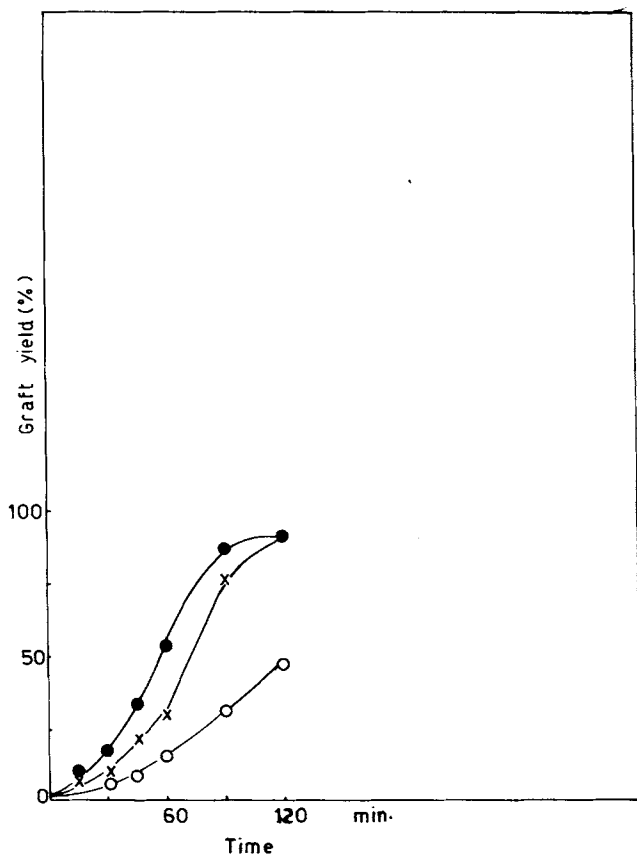


Fig. 1. Effect of benzoyl peroxide concentration on the rate of grafting. Benzoyl peroxide concentration: (O) 0.559 mmole/l.; (X) 1.657 mmole/l.; (●) 2.795 mmole/l.; reaction medium, 10% MVP, temperature 75°C, material-to-liquor ratio, 1:100.

Effect of Initiator Concentration

Figure 1 shows the effect of benzoyl peroxide concentration on the graft yield. As is evident, the graft yield increases with increasing benzoyl peroxide concentration up to 1.657 mmole/l. Further increase in benzoyl peroxide concentration lowers grafting significantly. The initial slow rates of grafting at lower benzoyl peroxide concentration could be attributed to oxygen inhibition, whereas the higher graft yield obtained upon increasing the benzoyl peroxide concentration is direct evidence that the benzoyl peroxide free radical participates in the initiation of the graft. On the other hand, depression of grafting when using higher benzoyl peroxide concentrations provides evidence that benzoyl peroxide radicals may be involved in the termination reaction similar to other initiating system.⁵⁴ However, it is possible that when the concentration of benzoyl peroxide was increased beyond the maximum amount, homopolymerization rate increased, and therefore there was a decrease in the graft yield. Indeed, a tremendous amount of homopolymer formation was observed upon use of higher amounts of benzoyl peroxide.

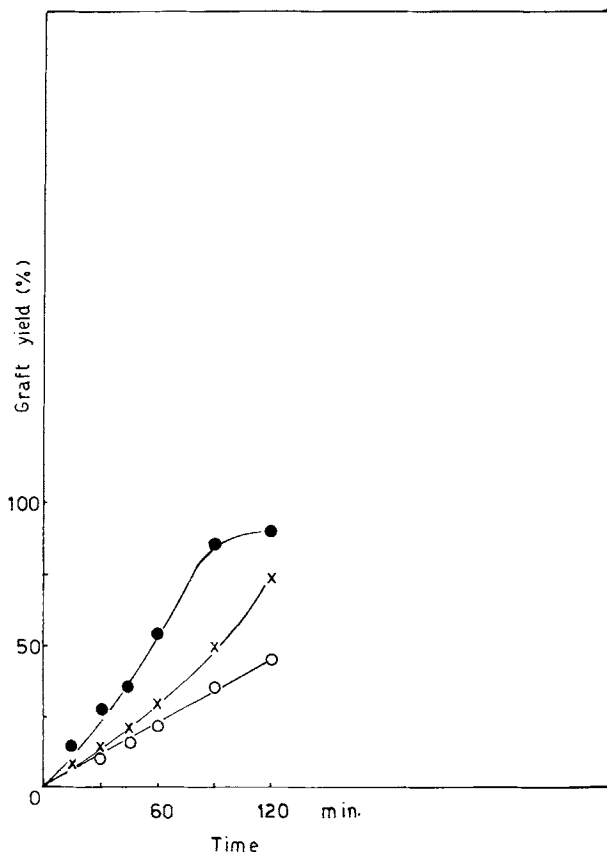


Fig. 2. Graft yield as a function of MVP concentration. MVP concentration: (O) 4%; (X) 6%; (●) 10%; benzoyl peroxide concentration, 1.675 mmole/l.; temperature, 75°C, material-to-liquor ratio, 1:100.

Effect of Monomer Concentration

The effect of MVP concentration on the graft yield was evaluated in a series of polymerizations in which three monomer concentrations, viz., 4%, 6%, and 10%, were used. Results are shown in Figure 2. It is clear that increasing the monomer concentration from 4% to 6% causes an outstanding enhancement in the graft yield, particularly when the grafting reaction is allowed to proceed for longer periods. The same holds true for 10% monomer concentration, but the polymerization levels off with time.

Effects of Temperature

Figure 3 shows that increasing the polymerization temperature from 65°C to 75°C enhances the rate of grafting significantly. Further enhancement in the grafting rate could be achieved by raising the temperature to 85°C. Raising the polymerization temperature would be expected to cause (a) creation of more active species, i.e., free radicals, in the reaction medium due to faster decomposition rate of benzoyl peroxide; (b) enhancement of the swellability of the blend; (c) increasing the anisotropic swelling of the wool component in the blend with

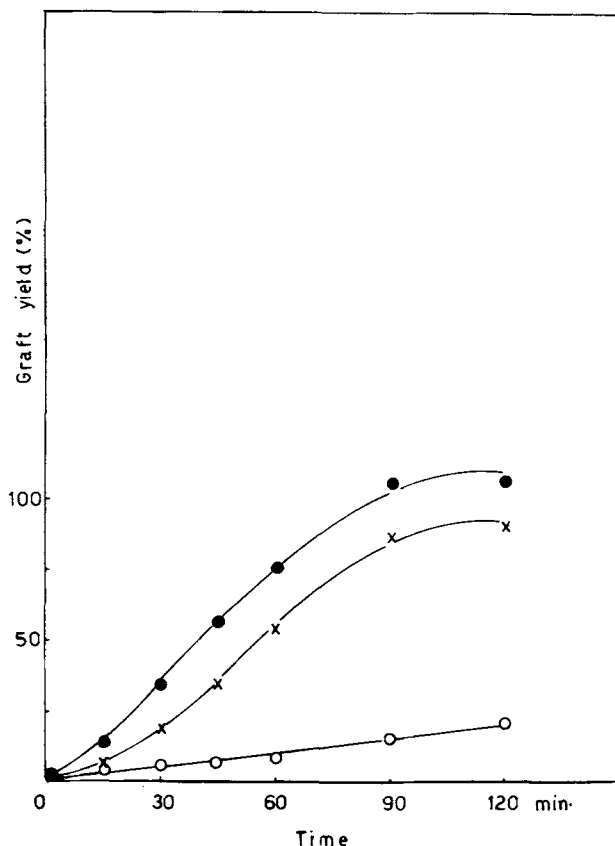


Fig. 3. Effect of temperature on grafting: (O) 65°C; (X) 75°C; (●) 85°C. MVP concentration 10%, benzoyl peroxide concentration, 1.657 mmole/l.; material-to-liquor ratio, 1:100.

resulting scission of the side linkages to bring about additional free radicals on the wool backbone; (d) increased mobility of the monomer molecules; (e) higher rate of monomer diffusion from the reaction medium to the blend; (f) possible reaction between the growing homopolymer chain with the substrate and/or the substrate macroradicals; (g) enhancement in the rate of initiation and propagation of the graft. The net effect of these factors is certainly increased grafting.

Based on the results of Figure 3, the apparent activation energy was calculated. For this purpose, we used an Arrhenius equation by plotting $\log R_p$ versus $1/T$ (Fig. 4). The apparent energy of activation calculated from the slope of the line is about 5.5 kcal/mole, which is of the same order as that obtained for the usual redox polymerization.^{64,65}

Effect of Reaction Time

The effect of reaction time on the graft yield may be realized from Figures 1, 2, and 3. Increase in reaction time is accompanied by a significant enhancement in the graft yield. However, at higher temperatures, the enhancement in the latter caused by the initial periods of the reaction is much greater than that

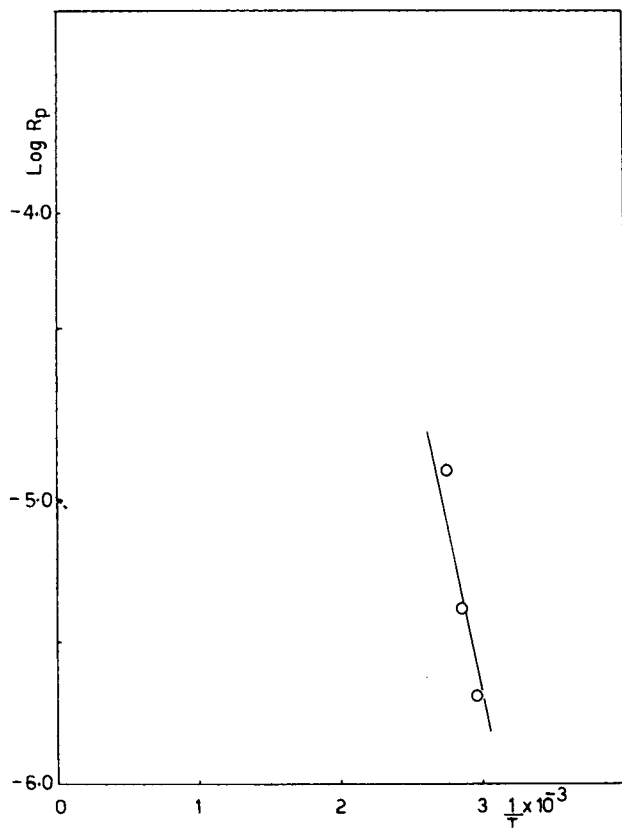


Fig. 4. Logarithm of initial rate of graft polymerization R_p of MVP vs $1/T$: MVP concentration, 10%; benzoyl peroxide concentration, 1.657 mmole/l.; material-to-liquor ratio, 1:100.

brought about by prolonging duration during the later stages of polymerization. That is, the grafting reaction proceeds initially at a fast rate and decreases with time to a slower rate. This could be associated with depletion in monomer and initiator concentrations as well as reduction in the available active centers on the substrate (blend) backbone as the reaction proceeds.

Tentative Mechanism for Initiation of Grafting

In the foregoing section, it has been shown that considerable graft formation occurred on polyester/wool blended fabric when MVP was polymerized in the presence of this blend. That grafting took place on both components of the blend is clearly shown in Figure 5, where fibers and fabrics of 100% polyester and 100% wool proved to be amenable for grafting. However, wool is much more susceptible to grafting than polyester. This is rather expected, since wool contains many possible centers for free-radical formation such as thiol, amine, hydroxyl, etc. Beside this, wool acquires an open structure and good swelling properties which facilitates diffusion of both monomer and initiator. In contrast, polyester is highly crystalline, markedly hydrophobic and contains only few types of centers for free-radical formation.

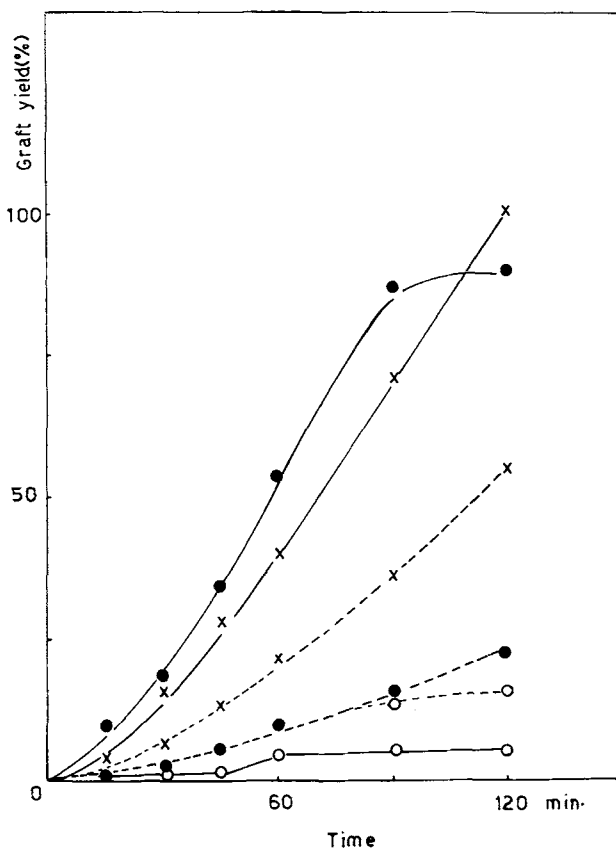
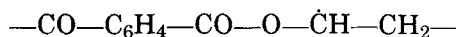


Fig. 5. Grafting onto various substrates: (○) wool/polyester fabric; (●) manual blend of wool and polyester fibers; (X) wool fabric; (X) wool fibers; (○) polyester fabric; (○) polyester fiber; MVP concentration, 10%; benzoyl peroxide, 1.657 mmole/l.; temperature, 75°C; material-to-liquor ratio, 1:100.

Hence, introduction of free radicals into wool may be accomplished by (a) direct hydrogen abstraction from the wool molecules by the primary free-radical species ($C_6H_5COO\cdot$) brought about by decomposition of benzoyl peroxide or by the secondary free-radical species ($C_6H_5\cdot$) caused by decomposition of the primary radical species, and (b) homolytic scission of the disulfide bonds through anisotropic swelling of wool at higher temperature used and/or under the influence of the initiator employed. Addition of the wool radical to the double bond of the monomer results in a covalent bond between wool and monomer, with creation of a free radical on this monomer which is capable of propagating a chain by subsequent addition of monomer molecules.

In case of polyesters, active centers seem to be created by either direct hydrogen abstraction or by oxidizing the polymer to hydroperoxide at several points along the chain in a random manner. The hydroperoxide decomposes into the active form at high temperature to produce ultimately macroradicals one of which may be represented as



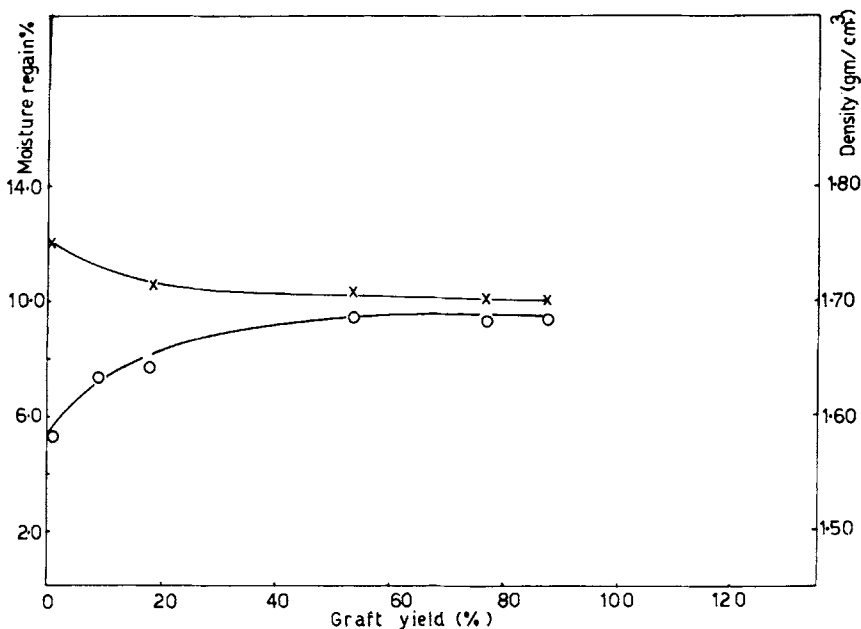


Fig. 6. Influence of graft yield on density and moisture regain % of polyester/wool blended fabric: (O) density; (X) moisture regain %.

These radical sites permit attachment of monomer molecules which may grow into short chains.

It should be emphasized that results of the graft yield for 100% fibers and fabrics of wool and polyester and the manual blend of both fibers would not give a means to show to what extent each component contributes to the graft yield on the polyester/wool blended fabric (Fig. 5), since the substrates used have different histories as well as different constructions with respect to fabrics. But the data justify the aim which they were designed for. That is, wool and polyester can be graft copolymerized with MVP by benzoyl peroxide under the conditions used in this investigation.

Properties of the Grafted Blend

Polyester/wool fabrics of varying graft add-on of MVP were prepared and evaluated for moisture regain, density, and dyeability.

Moisture Regain. Moisture regain of the grafted fabrics was determined by allowing the samples to attain equilibrium moisture at 25°C and 65% relative humidity. Figure 6 shows the moisture regain versus graft yield. At a graft yield of ca. 20%, the moisture regain decreases from 12% to 10.5%. Increasing the graft yield up to 90% causes only little further decrease in the moisture regain. The decrease in moisture regain is unequivocally due to the introduction of hydrophobic poly(methylvinylpyridine) into the substrate. Beside blocking some of the water sorptive sites, particularly in the wool component, the polymer produces a hydrophobic environment inside the blend. The point that increasing the graft yield does not have a significant effect on moisture regain suggest either (a) that the graft yield represents few polymer chains with high molecular weight

TABLE I
Dye Exhaustion by Polyester/Wool Blended Fabric
During Dyeing with Acid Dye Kiton Fast Red BL (CiBA)

Graft yield, %	% Exhaustion after								
	0 min	5 min	10 min	15 min	20 min	30 min	40 min	50 min	60 min
0	0	22.3	45.5	58.3	70.9	77.5	89.1	93.1	96.4
8.1	0	62.5	71.6	81.1	89.5	94.6	100	100	100
15.2	0	65.2	73.5	81.8	90.9	95.5	100	100	100
21.5	0	67.4	74.8	83.3	92.3	96.4	100	100	100
45.7	0	70.2	76.3	84.7	93.1	96.8	100	100	100
57.7	0	73.8	77.8	86.2	94.2	99.0	100	100	100

or (b) that grafting of higher levels brings about the opening of the substrate to an extent that outweighs the shift toward hydrophobic nature.

Density. The density of the samples was determined by a density gradient column. The liquids used to prepare the gradient column were xylene (density = 0.886) and carbon tetrachloride (density = 1.595). Figure 6 shows the effect of grafting on the density of the blended fabrics. Obviously, the density of the fabric increases with increasing the graft yield up to ca. 50%. Therefore, increasing the graft yield has no significant effect on the density. The increase in density could be associated with location of the graft polymer within the noncrystalline regions of the fiber, thus filling the voids present in the amorphous regions.

Dyeability. The grafted blended fabrics were dyed with the acid dye Kiton Fast Red B1(CIBA), C.I.17045, at 100°C using a material-to-liquor ratio of 1:100. The dyeing bath was prepared so as to give 5% shade in the presence of acetic acid (3%) and Glauber salt (3%). Dyeing was carried out for different lengths of time varying from 5 to 60 min. It was observed that the depth of shade of the grafted and the untreated fabrics increases with increasing duration of dyeing. However, the grafted fabrics showed higher depth of shade than the untreated fabric, though the depth of shade was independent of the magnitude of grafting. The loss in concentration of the dye bath was determined colorimetrically, and the amount of the dye on the fiber was calculated. The results are shown in Table I. The results agree with the observation of increasing depth of shade with increasing duration of dyeing as well as the point that the grafted samples acquire higher depth of shade than the untreated fabric.

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