

Photo-Induced Polymerization of Methyl Acrylate Vapors on Prewetted Polyamide and Polyester Fibers

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Synopsis

Photo-induced polymerization of methyl acrylate vapors on polyamide and polyester fibers occurred when these fibers were wetted with the polar solvents methanol, N,N-dimethylformamide, or dimethyl sulfoxide (neat or in aqueous solution). Polymer grafting was accompanied by homopolymer formation, with the amount of grafting and ratio of grafting to homopolymerization being dependent on the fiber type, the solvent used to wet the fiber, and the amount of water present in the wetting solution. Overall deposition of polymer was higher on polyamide than on polyester under all wetting conditions. Water present in the wetting agent had a limited effect on polymerization of poly(methyl acrylate) on polyamide, whereas water caused a rapid decrease in polymerization on polyester. The nature of polymer grafting on the fibers under various wetting conditions was examined by scanning electron microscopy and tensile property measurements, and the mode of polymer deposition was outlined in light of our findings.

INTRODUCTION

Photo-induced grafting of acrylic monomers as liquids¹ and vapors^{2,3} on unwetted fiber surfaces has been found to be limited to the fiber surface and to occur only in the presence of photosensitizers at wavelengths of ultraviolet energy below 300 nm. Recently, Ogiwara and co-workers⁴ showed that organic wetting solvents greatly enhanced photo-induced grafting and grafting efficiency of liquid methyl methacrylate on nylon 6 and polyester fiber substrates at wavelengths above 300 nm.

In the course of investigation of photo-initiated grafting of acrylic monomer vapors on water-wetted fiber substrates in the presence of biacetyl using ultraviolet light > 300 nm,⁵ it became apparent that use of water alone as a wetting agent for more hydrophobic fibers was inadequate and led to low irregular grafts on these fibers, whereas aprotic solvents such as N,N-dimethylformamide and dimethyl sulfoxide increased the degree of grafting. Recently, we studied the photo-induced polymerization of methyl acrylate vapors on polyamide (nylon 66) and polyester [poly(ethylene terephthalate)] fibers wetted with the polar solvents methanol, N,N-dimethylformamide, or dimethyl sulfoxide alone or as aqueous solutions to gain a more complete understanding of the role of wetting solvent in the overall photo-induced polymerization on fiber substrates in the absence of sensitizers. No reports appear in the literature concerned with the role of wetting agents and the effect of water on photo-induced grafting of monomer vapors on synthetic fibers such as nylon and polyester.

TABLE I
Effect of Poly(methyl Acrylate) Grafting on Tensile Properties of Nylon

Wetting solution	% Uptake of grafted polymer	Tensile properties		
		Breaking strength, g	% Elongation at break	Energy to break, g-cm
—	—	745 ± 124	51 ± 7	1570 ± 440
H ₂ O	4.3	923 ± 113	45 ± 6	1728 ± 483
MeOH	2.4	961 ± 106	44 ± 6	1756 ± 343
50% MeOH	4.2	1008 ± 179	44 ± 7	1826 ± 699
DMF	1.4	1037 ± 172	43 ± 5	1756 ± 549
50% DMF	3.6	1002 ± 112	49 ± 7	2075 ± 630
DMSO	1.9	988 ± 112	45 ± 7	1821 ± 548
50% DMSO	2.6	901 ± 130	45 ± 4	1678 ± 398

EXPERIMENTAL

Materials and Reagents

The fabrics (Polyester-Dacron Type 54, #754-N and Nylon-spun Type 200, #358) were obtained from Test Fabrics, Inc., and were thoroughly washed at 60°C with aqueous detergent solution, dried, and conditioned at 21°C and 65% R.H. prior to use.

The monomer and solvents were Baker or Eastman reagent-grade chemicals and were used without further purification.

Vapor Phase Grafting Procedure

A 6 × 12 in. sample of conditioned fabric was wet out in neat methanol, N,N-dimethylformamide, dimethyl sulfoxide, or water or aqueous solutions of the above polar solvents (w/w). Excess solution was removed by passing the fabrics through a laboratory pad to obtain a wet pickup of approximately 50%. The sample was stapled to a wire screen and placed in a 3-l. resin kettle and allowed to conform to the outer perpendicular walls of the reactor. The top of the reactor was placed on the kettle and was equipped with a Pyrex cold finger in the center containing a 200-W Hanovia high-pressure mercury arc and with two gas inlets and a gas outlet. The distance of the light source from the wetted samples was fixed at 6 cm. Methyl acrylate vapors were carried into the reactor by passing nitrogen through two bubblers containing neat methyl acrylate in-

TABLE II
Effect of Poly(methyl Acrylate) Grafting on Tensile Properties of Polyester

Wetting solution	% Uptake of grafted polymer	Tensile properties		
		Breaking strength, g	% Elongation at break	Energy to break, g-cm
—	—	881 ± 112	40 ± 5	1149 ± 254
H ₂ O	0.1	796 ± 117	40 ± 2	1051 ± 205
MeOH	0.2	887 ± 173	44 ± 2	1337 ± 301
50% MeOH	0.2	869 ± 166	42 ± 4	1266 ± 359
DMF	1.8	809 ± 103	44 ± 2	1128 ± 171
50% DMF	0.8	772 ± 110	42 ± 2	1029 ± 189
DMSO	0.5	881 ± 143	43 ± 5	1334 ± 386
50% DMSO	0.1	888 ± 120	40 ± 1	1280 ± 262

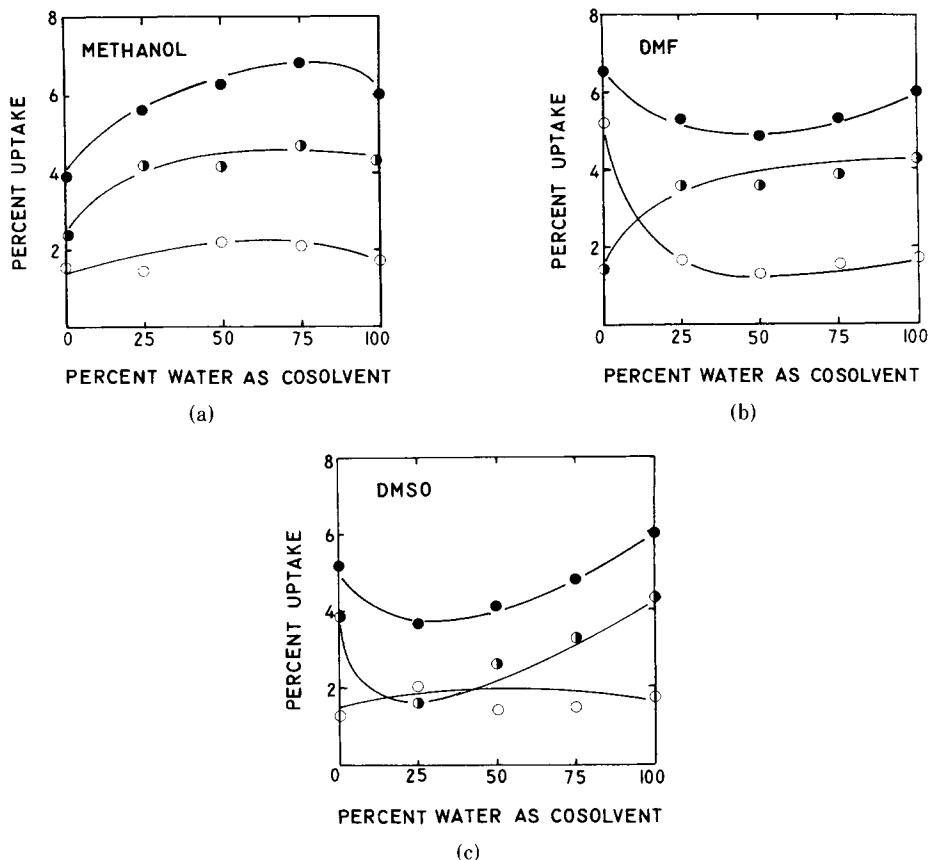


Fig. 1. Effect of wetting solvent and water as cosolvent on photo-induced polymerization of methyl acrylate vapor on nylon: (a) methanol; (b) *N,N*-dimethylformamide (DMF); (c) dimethyl sulfoxide (DMSO). ●-Total polymer uptake; ◐-Grafted polymer uptake; ○-Homopolymer uptake.

hibited with hydroquinone and into the two inlet ports in the reactor at a total rate of 10 cc/sec. After passing the methyl acrylate vapors into the reactor to remove oxygen for 10 min, the mercury arc was started and the samples irradiated for 60 min as methyl acrylate vapors were introduced continuously. After irradiation, the samples were removed from the reactor and washed with hot (60°C) water for 30 min, rinsed with distilled water, dried, and conditioned prior to weighing to determine total polymer uptake. The samples were then extracted for 8 hr with benzene in a Soxhlet extractor to remove homopolymer, and the samples were conditioned and reweighed. The percent uptake of total polymer, grafted polymer, and homopolymer on the fabrics under various wetting conditions are listed in Figures 1 and 2.

Analytical Techniques

Tensile properties of warp yarns from untreated and poly(methyl acrylate)-grafted samples were determined by ASTM procedure D-2256-66T (Tables I and II). Scanning electron microscopy of selected samples was carried out using a Cambridge Stereoscan Mark II operated in the secondary mode at 5 kV and at magnifications of 1920–6250 \times . The sample specimens were cut from the

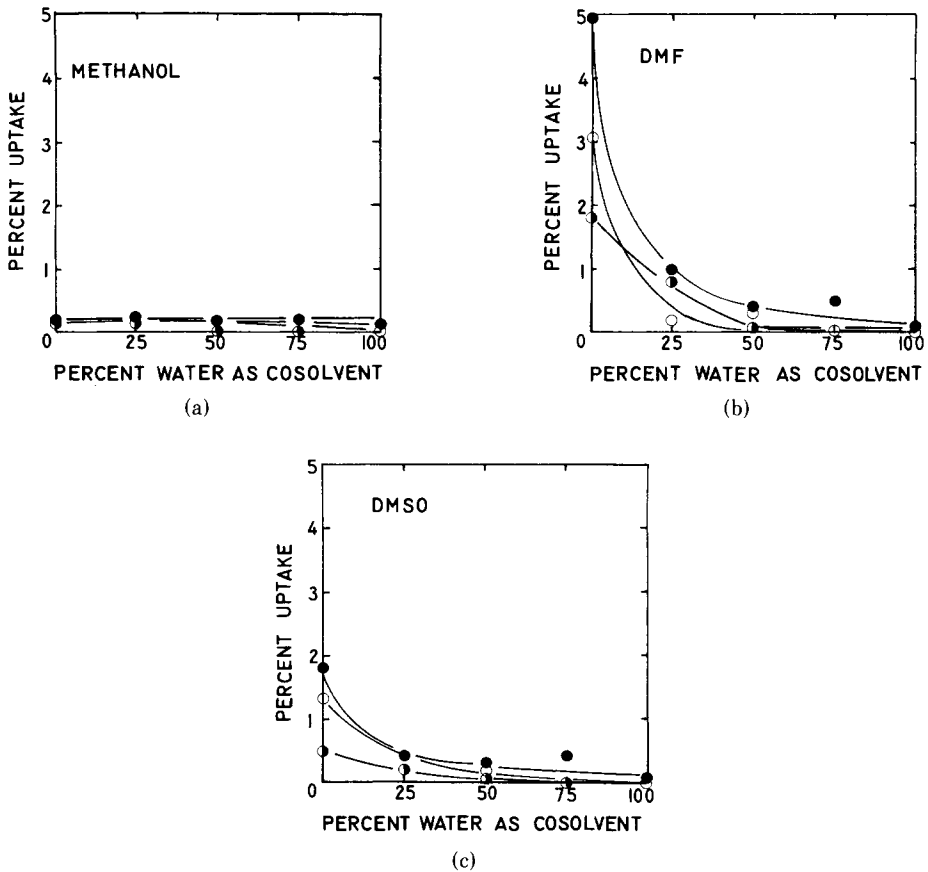


Fig. 2. Effect of wetting solvent and water as cosolvent on photo-induced polymerization of methyl acrylate vapor on polyester: (a) methanol; (b) DMF; (c) DMSO. ● -Total polymer uptake; ●-Grafted polymer uptake; ○-Homopolymer uptake.

center of the fabrics, coated on both sides with gold, cemented to the specimen stub with conductive cement, and recoated with gold.

RESULTS AND DISCUSSION

The Effect of Wetting Solvent on Polymerization

The wetting solvent used had a marked effect on grafting and homopolymerization of methyl acrylate vapors on nylon (Fig. 1). With methanol, graft polymerization increased slightly when water was added as cosolvent, Figure 1(a), whereas the homopolymer formation remained fairly constant as water was added as cosolvent. Neat *N,N*-dimethylformamide on nylon resulted in extensive homopolymerization at the expense of grafting, Figure 1(b), and as water was added as cosolvent homopolymerization initially decreased and grafting increased, with the ratio of grafted polymer to homopolymer remaining above 2:1 as the percentage water as cosolvent increased. In neat dimethyl sulfoxide, grafting predominated over homopolymer formation on nylon, but grafting decreased initially and then slowly increased as water was added as cosolvent, Figure 1(c). Homopolymerization remained fairly constant over the entire range as water was added as cosolvent.

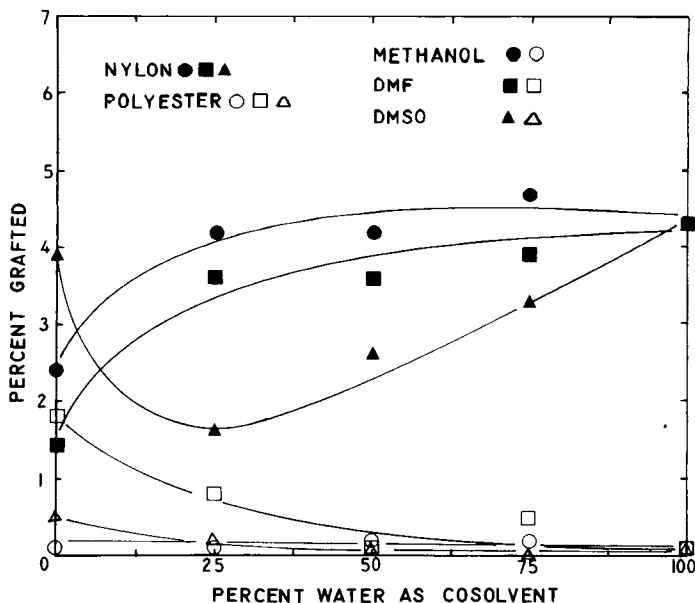
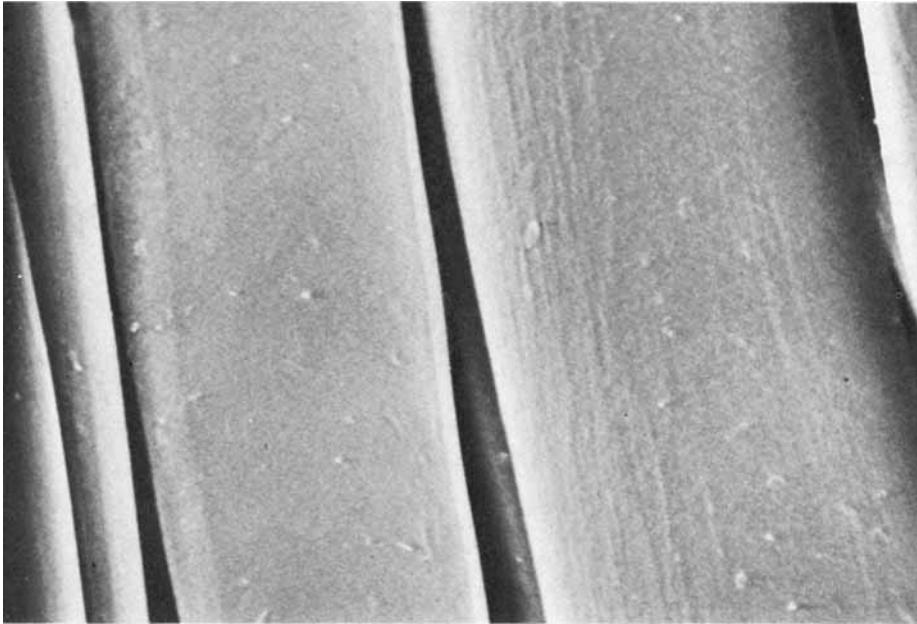


Fig. 3. Effect of wetting solvent and water as a cosolvent on photo-induced grafting of methyl acrylate vapors on nylon (closed symbols) and polyester (open symbols).

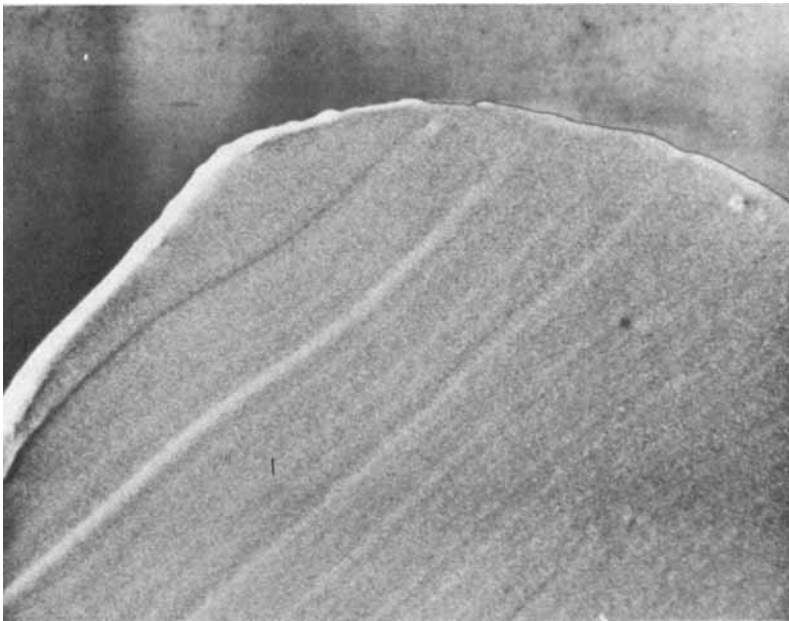
The more hydrophobic polyester wetted with methanol and aqueous methanol gave extremely limited uptakes of poly(methyl acrylate), Figure 2(a). Neat *N,N*-dimethylformamide and dimethyl sulfoxide gave moderate grafting accompanied by extensive homopolymerization, Figures 2(b) and 2(c). As water was added as cosolvent, both grafting and homopolymerization decreased rapidly.

Considering grafting only, using the wetting solvents alone or as cosolvents with water, the more hydrophilic fiber nylon was more readily grafted than polyester (Fig. 3). Water as cosolvent enhanced grafting on nylon, except for dimethyl sulfoxide where small amounts of water as cosolvent decreased grafting. With polyester, neat *N,N*-dimethylformamide as wetting solvent caused significant grafting and neat dimethyl sulfoxide, more limited grafting. Even low concentrations of water added as cosolvent quickly decreased the amount of polymerization of polyester.

Ultraviolet wavelengths greater than 300 nm were used to initiate polymerization of methyl acrylate vapor on the fibers in this study. Since the wetting solvents and methyl acrylate used in this study do not absorb above 300 nm and the nylon and polyester absorb significant ultraviolet radiation in the region of 300–350 nm,⁶ it was assumed that the wetted fiber substrates are responsible for initiation of polymerization of monomer vapors diffusing onto the fiber surface. Light-induced bond cleavage in the wetted fibers would result in free radicals on the wetted fiber substrate which could initiate graft polymerization or abstract a hydrogen from the wetting solvent or monomer, which in turn would initiate homopolymerization. Wetting and limited swelling of fiber by the solvent would allow monomer to diffuse more readily to free-radical sites on the fiber or solvent radicals within the swollen fiber. Under the conditions of low temperature and limited contact time used in wetting of the fiber substrates, limited swelling of the fiber would be expected,⁷ with the greatest degree of

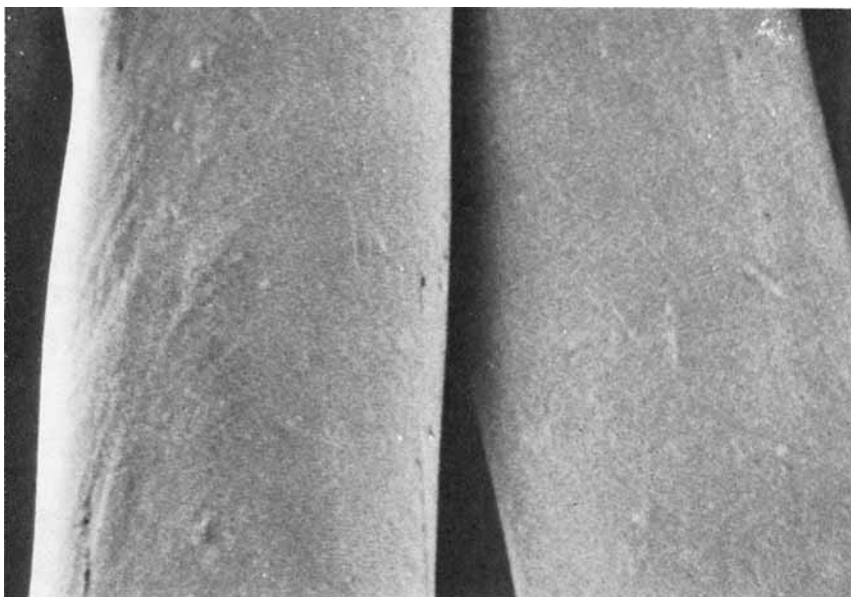


(a)

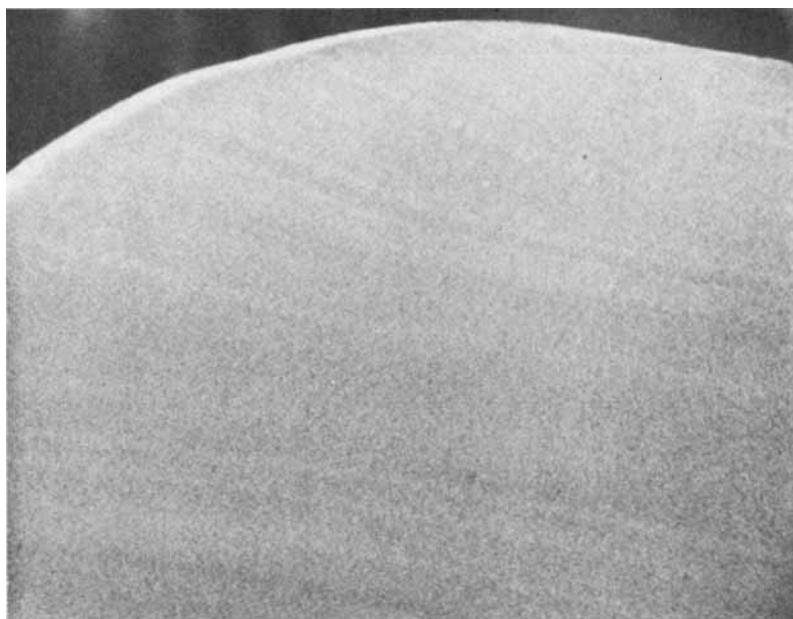


(b)

Fig. 4. Scanning electron micrographs of nylon containing photografted methyl acrylate vapors: (a) untreated control (1920 \times); (b) untreated control in cross section (5900 \times); (c) wetted with water and grafted with 4.3% polymer (1960 \times); (d) wetted with water and grafted with 4.3% polymer in cross section (6100 \times); (e) wetted with 50% aqueous DMF and grafted with 3.6% polymer (1980 \times); (f) wetted with 50% DMF and grafted with 3.6% polymer in cross section (6520 \times); (g) wetted with DMSO and grafted with 1.9% polymer (1975 \times); (h) wetted with DMSO and grafted with 1.9% polymer in cross section (5500 \times).



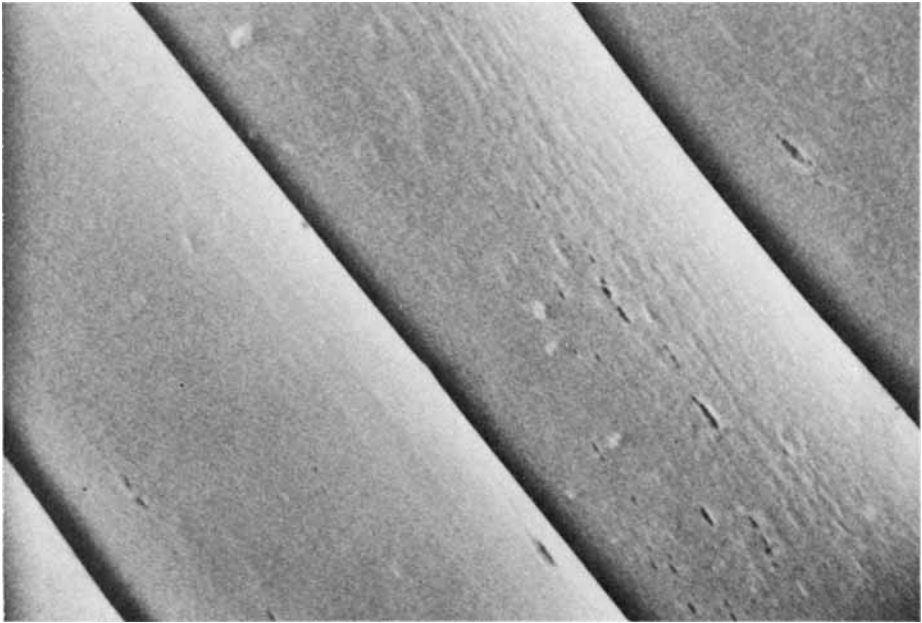
(c)



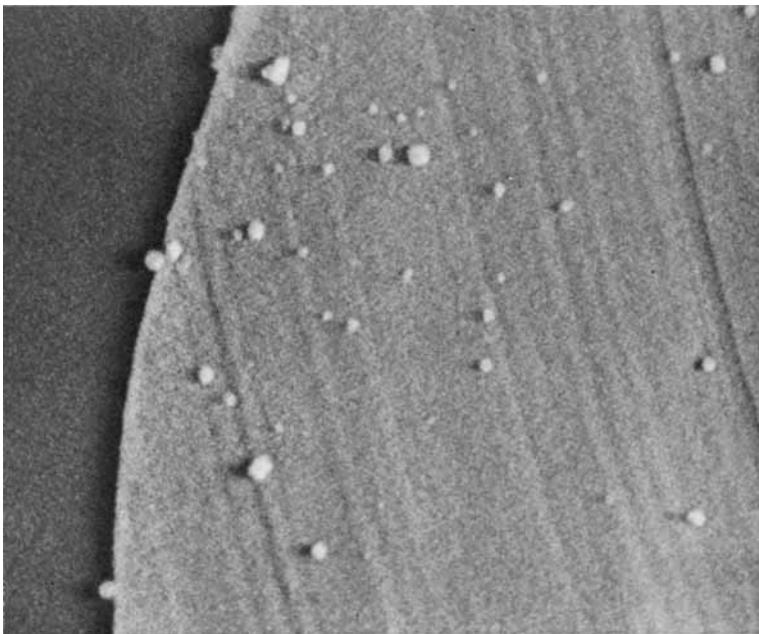
(d)

Fig. 4. (Continued from previous page.)

solvent penetration and swelling occurring on nylon. Solvents that tend to penetrate the fiber would be expected to increase the overall polymerization of methyl acrylate vapors diffusing into the fiber, but the relative population of radicals on the fiber substrate and on the solvent or monomer would affect the relative amount of grafting and homopolymerization. Also termination of growing fiber-monomer radicals would be expected to contribute to homopolymerization.



(e)

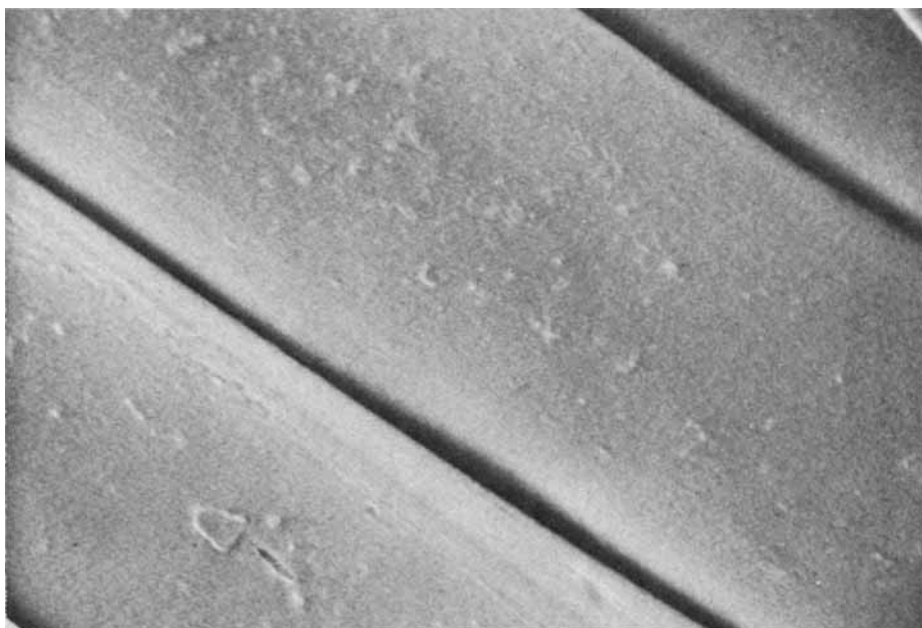


(f)

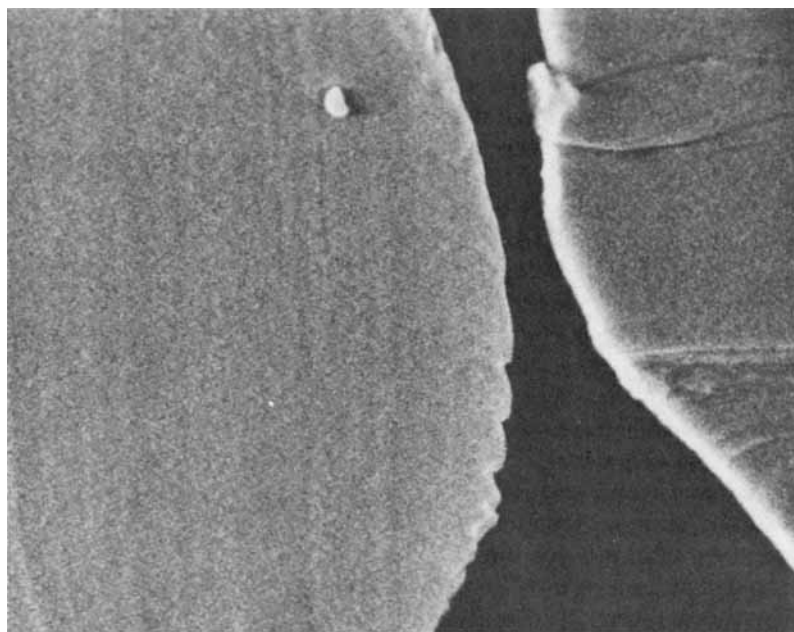
Fig. 4. (Continued from previous page.)

Tensile Properties of the Grafted Fibers

The tensile properties of the grafted nylon and polyester fibers were characterized (Tables I and II). Yarns from nylon grafted with poly(methyl acrylate) using various wetting solvents showed increased breaking strength and energy to break values along with decreased elongations at break (Table I).



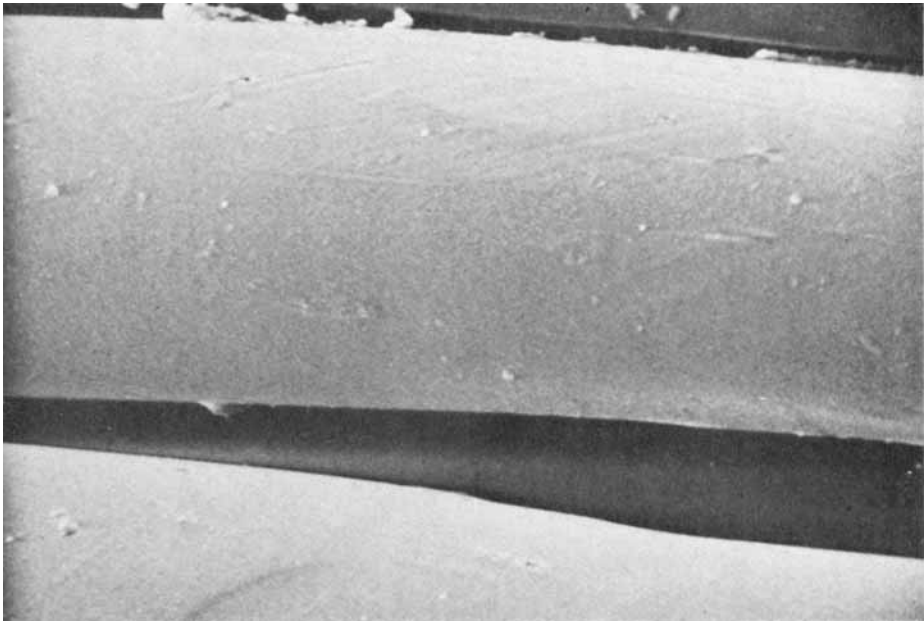
(g)



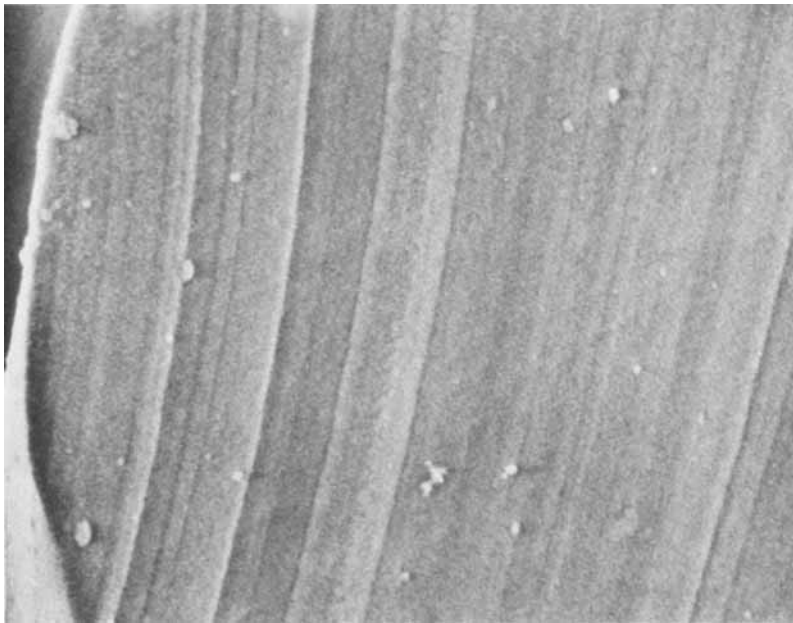
(h)

Fig. 4. (Continued from previous page.)

These significant changes in tensile properties at only 1.4–4.3% uptakes of grafted poly(methyl acrylate) suggest that polymerization occurred within the fiber matrix giving a stronger but less extensible fiber. Polyester grafted with 0.1%–1.8% poly(methyl acrylate) exhibited only limited changes in tensile properties (Table II). No distinct trends could be seen with grafted polyester,

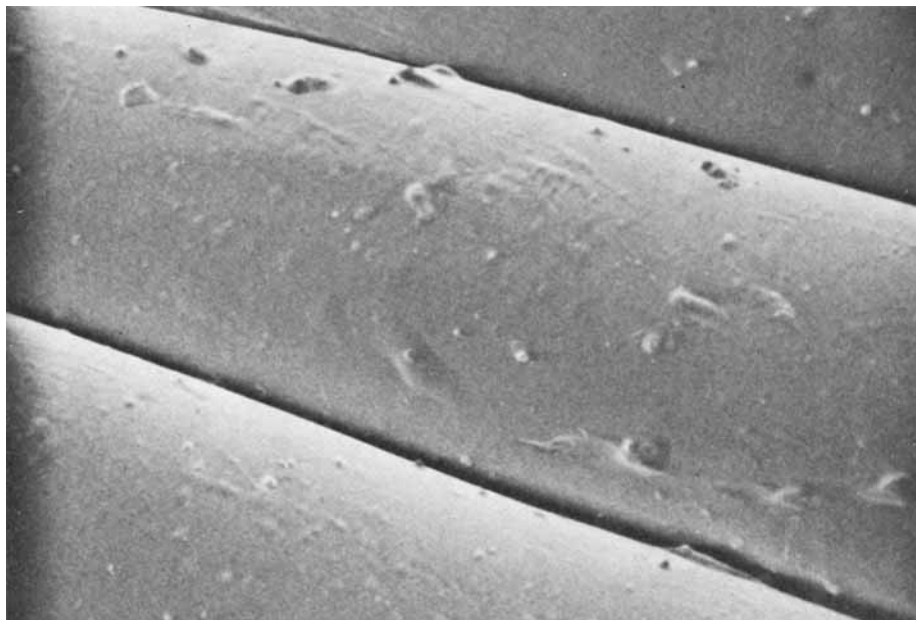


(a)



(b)

Fig. 5. Scanning electron micrographs of polyester photografted with methyl acrylate vapors: (a) untreated control (1900 \times); (b) untreated control in cross section (5500 \times).

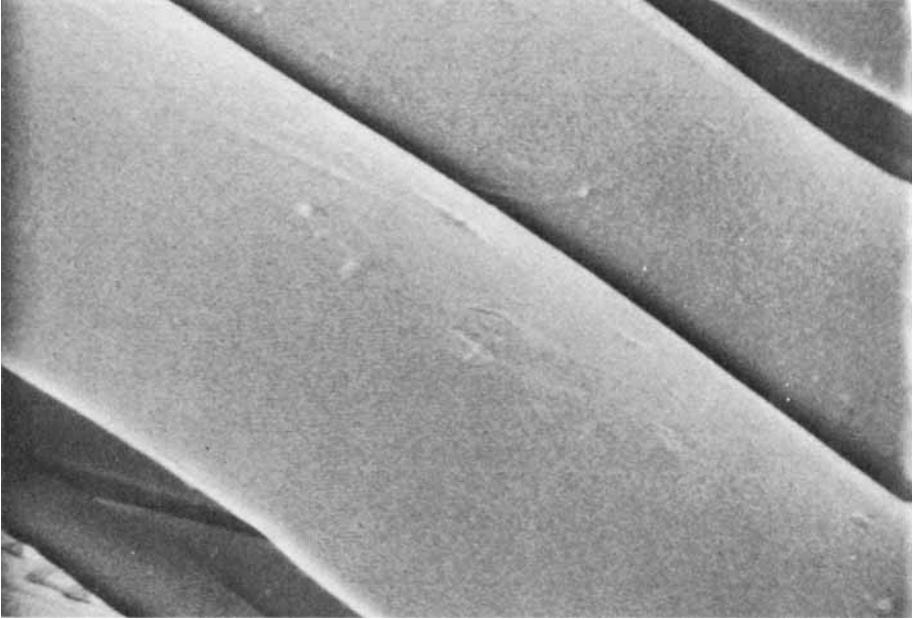


(c)

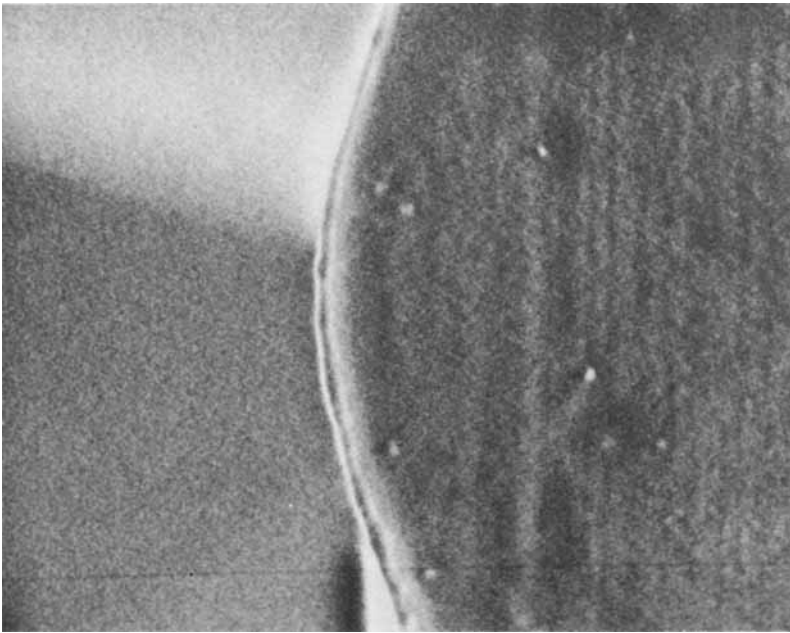


(d)

Fig. 5. (c) Wetted with 50% aqueous methanol and grafted with 0. polymer (2000 \times); (d) wetted with 50% aqueous methanol and grafted with 0.2% polymer in cross section (5500 \times).

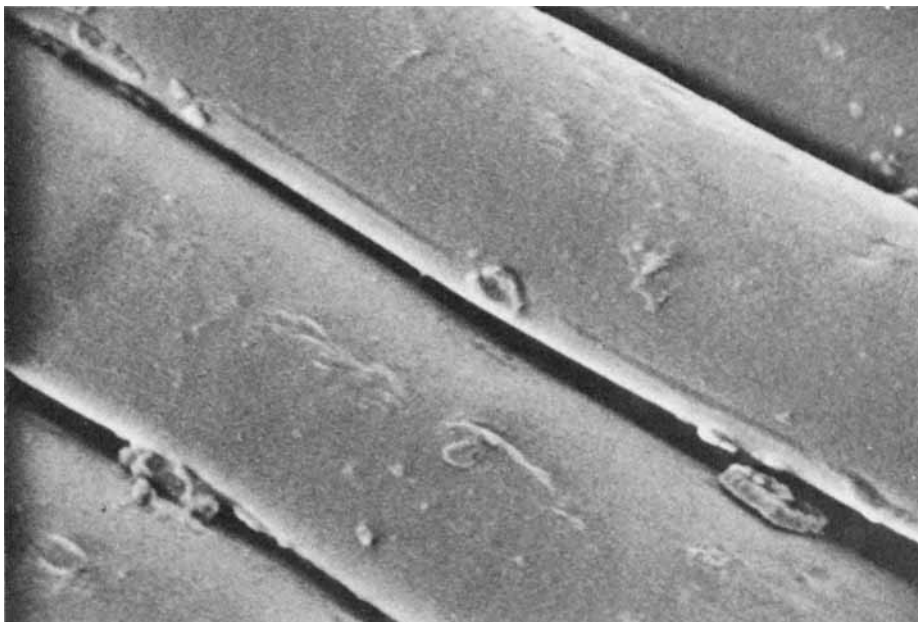


(e)

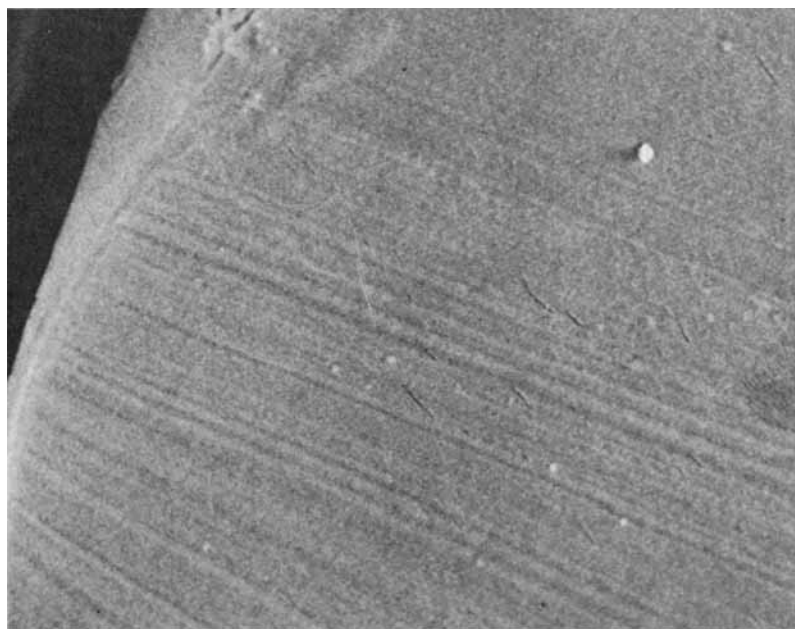


(f)

Fig. 5. (e) Wetted with DMF and grafted with 1.8% polymer (1950 \times); (f) wetted with DMF and grafted with 1.8% polymer in cross section (6050 \times).



(g)



(h)

Fig. 5. (g) Wetted with D₂O and grafted with 0.5% polymer (2000 \times); (h) wetted with DMSO and grafted with 0.5% polymer in cross section (5300 \times).

suggesting that at the low level of grafting, changes in tensile properties were confined to the surface of the polyester thereby having a minimal effect on the tensile properties.

Scanning Electron Micrographs of the Grafted Fibers

Longitudinal and cross-sectional scanning electron micrographs of selected grafted and untreated fibers were prepared to ascertain the location of poly(methyl acrylate) grafted to the fibers (Figs. 4 and 5). Nylon grafted with 4.3% polymer using water as wetting agent, Figures 4(c) and (d), was not significantly different than control nylon, Figures 4(a) and 4(b), suggesting that the poly(methyl acrylate) was fairly evenly distributed in the fiber matrix. Nylon grafted with 3.6% poly(methyl acrylate) using 50% aqueous N,N-dimethylformamide had small cracks along the fiber axis, Figure 4(e), and the fiber cross section, Figure 4(f), showed no particular differences compared to untreated nylon. Nylon wetted with dimethyl sulfoxide and grafted with 1.9% polymer had some surface irregularities, Figure 4(g), suggesting the presence of nodes of irregular polymer grafted to the fiber surface. The cross section of the fiber, Figure 4(h), also showed an irregular surface on the fiber. At the known graft uptakes of poly(methyl acrylate) on nylon, it appears that the polymer was evenly distributed on the grafted nylons in most cases but that some surface polymer was evident when wetting solvents such as dimethyl sulfoxide were used. Surface damage also occurred in some cases.

Polyester grafted with only 0.2% polymer from 50% aqueous methanol showed significant irregular polymer distributed on the fiber surface, Figure 5(c), compared to untreated polyester, and cross sections, Figures 5(b) and (d), were not particularly different. Polyester wetted with N,N-dimethylformamide and grafted with 1.8% poly(methyl acrylate) showed no change in longitudinal view, Figure 5(e), but the cross-sectional view showed a surface layer of polymer on the fiber and some possible changes in the fiber matrix. Polyester wetted in dimethyl sulfoxide and grafted with 0.5% polymer possessed highly irregular polymer nodes on the fiber surface, Figure 5(g), and the cross section indicated the presence of such a irregular piece attached to the fiber, Figure 5(h).

In summary, the wetting solvents permitted greater penetration of methyl acrylate vapor into nylon than polyester and therefore a higher concentration and more even distribution of polymer on nylon than found for polyester in which the grafting was localized near the fiber surface. The large changes in tensile properties for grafted nylon fibers compared with grafted polyester fibers are consistent with this concept.

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