

Photo-Initiated Vapor-Phase Grafting of Acrylic Monomers onto Fibrous Substrates in the Presence of Biacetyl

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Synopsis

A novel vapor-phase process has been developed for grafting relatively volatile acrylic monomers onto various polymeric substrates, using photo-initiation by near ultraviolet irradiation in the presence of biacetyl vapors. With it, very even graft polymerizations on the substrates, with minimum amounts of homopolymerization, were found. Furthermore, there were essentially no changes in the tensile or aesthetic properties of the treated surfaces. The degree of photografting is dependent upon the chemical composition and porosity of the substrate, the volatility and reactivity of the monomers, prewetting of the substrate with a suitable wetting agent, and the conditions of irradiation used. The effects of various reaction parameters on the photo-induced grafting of methyl acrylate, methyl methacrylate, and acrylonitrile on wool keratin are studied in detail. Increasing biacetyl and monomer flow rates and flow times, irradiation times, and moisture content of the wool all caused progressive increases in the amount of polymer grafted to the wool, up to limiting values dependent on the reaction parameters involved and monomer used. In all instances, the amount of homopolymer found on the fiber was limited and remained essentially constant over the range of conditions studied. A series of acrylic monomers of different volatilities and reactivities including methyl acrylate, methyl methacrylate, butyl acrylate, acrylic acid, acrylamide, acrylonitrile, N,N-dimethylaminoethyl methacrylate, and 2,2,2-trifluoroethyl methacrylate was successfully grafted onto several hydrophilic and hydrophobic textile fibers (wool, cotton, rayon, nylon, acrylics, polyester, and polypropylene) and other polymeric surfaces such as filter paper, cellophane, and acetate film by this process. The wetting agents used included water, methyl and *n*-propyl alcohol, N,N-dimethylformamide, dimethylsulfoxide, benzene, and chlorinated hydrocarbon solvents.

INTRODUCTION

In recent years, great interest has been shown in photo-initiated polymerization processes. Within the field of photopolymerization, sensitized and unsensitized photografting of monomers to various substrates has received wide attention.¹⁻³ In general, such techniques have involved immersion or saturation of the substrate to be grafted with neat monomer or with a monomer solution, and subsequent exposure to irradiation of various types. Such photo-induced grafting, both in the presence and absence of photosensitizers, has been accompanied by extensive homopolymerization and has caused uneven, spotty grafting and general loss of aesthetic properties of the substrate surface. Recently, Howard, Kim, and Peters⁴ have shown that methacrylic acid vapors can be grafted to the surface of nylon film when benzophenone vapors are used as photosensitizer. Little homopolymerization occurred under these grafting conditions, and the resulting grafted film had a lower optical density, a higher initial modulus, and improved moisture regain prop-

erties after conversion to the sodium salt. The irradiation time necessary for 10% to 20% grafting was short (2–10 min); however, the techniques initially used to introduce monomer and benzophenone vapors onto the film required long periods (up to 24 hr). In addition, if longer irradiation periods were used, a drop in polymer grafting accompanied by film degradation was noted with the low-wavelength (254 nm) ultraviolet source used.

Since a number of polymer substrates are adversely affected by low-wavelength ultraviolet irradiation,⁵ a rapid, higher wavelength (>300 nm), sensitized, vapor-phase grafting technique for polymer substrates would be desirable and might lead to an economically viable photografting process. In the course of our research into photografting on fiber surfaces, we have obtained extremely even grafts of up to 20% polymer on pretreated surfaces when near UV light and biacetyl vapors were used to initiate graft polymerization. Such a process provides distinct advantages over radiation⁶ and glow discharge^{6,7} systems using vapor-phase monomers, as inexpensive equipment that operates near atmospheric pressure with minimum radiation shielding is used in the photografting process.

EXPERIMENTAL

Material and Reagents

All fabrics used in this study except wool were obtained from Test Fabrics, Inc. The fabrics were Soxhlet extracted for 8 hr with ether and conditioned at 21°C and 65% relative humidity prior to use. The fabrics were acrylic, Acrilan Type 156, #955; acetate, 2 × 2 ply staple, #152; cotton, 80 × 80 print cloth, #400W; nylon, spun type 200, #358; polyester, Dacron Type 54, #754-W; polypropylene, Herculon Type 40, #967; rayon, Viscose Challis, #266. Wool fabric was obtained from Burlington Industries and was 1X1 plain weave worsted. Paper was #1 Whitman filter paper, and films were 2-mil-thick samples from du Pont. Monomers, wetting agents, and other reagents were Baker, Eastman, or PCR, Inc. chemicals. Monomers were distilled at reduced pressure prior to use, and hydroquinone was added to the distilled monomer prior to introduction into the bubbler system.

Vapor-Phase Grafting Procedure

Two or three 3 × 6 in. fabric or film samples were wet out with wetting solvent (0.1% sodium lauryl sulfate was added when water was used), and excess solution was removed using a laboratory pad to a wet pickup of usually 50%. The samples were then stapled to a wire screen and placed in a 3-liter resin kettle equipped in the center with a Pyrex cold finger containing a 100–450-W Hanova high-pressure mercury arc. Two gas inlets and a gas outlet were located in the top of the reactor.

The distance from the source to the fabric surface under these conditions was 6 cm, as the screen conformed to the perpendicular wall of the reactor. In some experiments, the sample was fastened directly to the irradiation cold finger with Teflon tape giving an effective 2-cm distance between the sample and the source. A stream of nitrogen was bubbled through a 1–2% solution of

TABLE I
 Photografting of Methyl Acrylate to Surfaces

Surface	Wetting agent	Procedure ^a	Exposure conditions			% Uptake grafted polymer
			Lamp power, (W)	Distance, cm	Irradiation time, min	
Cotton	H ₂ O	1% aq. B, 45 min; M, final 30 min (10 cc/sec)	200	6	30	22.1
Cotton	H ₂ O	1% aq. B and M, 30 min, (5 cc/sec)	450	6	15	4.5
Wool	H ₂ O	1% aq. B, 35 min; M, final 20 min (10 cc/sec)	200	6	20	6.5
Wool	H ₂ O	1% aq. B and M, 30 min, (5 cc/sec)	450	6	15	1.7
Nylon	H ₂ O	1% aq. B and M, 50 min (2.5 cc/sec)	200	6	30	13.7
Nylon	MeOH	1% B (MeOH), 15 min; ^b M, 5 min (5 cc/sec)	200	2	20	6.2
Acrylic	H ₂ O	1% aq. B and M, 30 min (5 cc/sec)	450	6	15	3.2
Polyester	DMF	2% B (EtAc), 35 min; M, final 20 min (10 cc/sec)	200	2	20	8.2
Polyester	DMSO	2% B (EtAc), 35 min; M, final 20 min (10 cc/sec)	200	2	20	0.8
Acetate film	MeOH	1% B (MeOH), 15 min; M, 35 min (5 cc/sec)	200	6	30	11.2
Acetate film	H ₂ O	1% aq. B and M, 30 min (5 cc/sec)	450	6	20	8.4
Acetate film	—	2% B (abs. MeOH), 45 min; M, final 30 min (10 cc/sec)	200	6	30	0.0
Cellophane	H ₂ O	1% aq. B and M, 30 min (5 cc/sec)	450	6	15	4.4
Cellophane	H ₂ O	no B, M, 30 min (5 cc/sec)	450	6	15	0.0
Filter paper	H ₂ O	2% aq. B, 15 min; ^b M, 25 min	200	6	20	19.0
Filter paper	H ₂ O	no B, M, 25 min	200	6	20	1.3

^a B = Biacetyl; M = methyl acrylate; aq. = aqueous; MeOH = methanol; EtAc = ethyl acetate.

^b Biacetyl flow was discontinued after initial 15 min flushing, monomer flow followed for 5 min before irradiation was started.

 TABLE II
 The Effect of Wetting Agent on Grafting of Methyl Acrylate to Polypropylene Fabric^a

Wetting agent	% Uptake of grafted polymer
Benzene	0.7
1,2-Dichloroethane	1.7
<i>n</i> -Propanol	0.7
<i>N,N</i> -Dimethylformamide	8.4
Dimethylsulfoxide	7.4
Water	0.0

^a Reaction conditions: biacetyl (1%) in methanol (5 cc/sec), 45 min; monomer (5 cc/sec, final 30 min, irradiated with 200-W Pyrex filtered mercury arc from 6 cm for 30 min.

biacetyl and into the reactor for a given length of time, to carry biacetyl into the reactor and to expel air from the system. Then, nitrogen was bubbled through the hydroquinone-inhibited monomer reservoir with simultaneous or subsequent irradiation for a given length of time. Sometimes biacetyl flow was kept on throughout the entire irradiation time when drying of the substrate by the monomer seemed to be a problem. Superheated steam was sometimes used in place of nitrogen to carry monomers with low vapor pressure (acrylic acid, *n*-butyl acrylate, and acrylamide) into the reactor.

TABLE III
Grafting of 2,2,2-Trifluoroethyl Methacrylate on Fabrics^a

Fabric	Wetting agent ^b	% Uptake of grafted polymer	Spray rating of grafted fabric ^c	Stain release rating ^c
Cotton	H ₂ O	0.4	0 (0)	3.0 (2.2)
Cotton	DMF	4.7	25 (0)	3.0 (2.2)
Rayon	H ₂ O	2.0	0 (0)	2.0 (1.4)
Rayon	DMF	7.6	75 (0)	3.5 (1.4)
Nylon	H ₂ O	1.1	95 (0)	—
Nylon	DMF	0.8	70 (0)	4.0 (3.7)
Polyester	DMF	3.6	—	—
Polypropylene	DMF	3.9	—	—

^a Exposed to 1% aqueous biacetyl (5 cc/sec) and monomer (5 cc/sec) for 45 min, irradiation with 200-W mercury arc from 6-cm distance for final 30 min.

^b H₂O=Water; DMF=N,N-dimethylformamide.

^c Values in parentheses are values for untreated control.

After irradiation, the samples were removed from the reactor and thoroughly washed in hot running tap water for 30 min. They were then rinsed with distilled water and dried and conditioned prior to being weighted to determine polymer uptake. Where the monomer was insoluble in water, the irradiated samples were soaked in a solvent for the monomer and then rinsed with alcohol and finally with distilled water. Homopolymer was extracted from the samples with a solvent for the polymer grafted to remove homopolymer from the fabric. The final weight was taken as that of grafted substrate. Reaction conditions for the photografting experiments, percentage uptake of grafted polymer, and selected properties of the photografted products are listed in Tables I–VI. The effects of various reaction parameters on photografting to methyl acrylate, methyl methacrylate, acrylonitrile, and acrylamide on wool are indicated in Figures 3–11.

Dyeing of Fabrics and Color Measurement Procedures

The 3 × 3 in. fabric samples were dyed with a Renigal Lab-Dyeing Machine. The wetout samples were placed in a basket-type fabric holder, immersed in the dye solution, and agitated at 86 strokes/min. The dyeings were carried out at 80°C for 1 hr at a 200:1 liquor ratio using 3% (owf) basic or acid dye, 5% (owf) sodium sulfate, and 1% acetic acid (owf). After being dyed, the fabric samples were thoroughly washed with 60°C water, rinsed in distilled water, and allowed to dry.

The color of the dyed samples was measured on a Gardner Digital Color Difference Meter, Model XL-10. The color values are expressed as *Rd*, *a*, and *b* color coordinates.

Analytical Methods

Physical tests for the various samples were done by the following ASTM and AATCC standard procedures: water repellency (spray rating), AATCC 22-1967; stain-release rating, AATCC 130-1969; durable press appearance rating, AATCC 124-1969; cantilever stiffness (flexural rigidity), ASTM 1388-64.

TABLE IV
Photografting of Poly(acrylic Acid) to Fabrics

Fabric	Wetting agent	Exposure conditions ^a	% Uptake of grafted polymer	Basic dye	Rd	Color ^b	
						a	b
Cotton	H ₂ O	A	6.9	Blue 4	47.1 (53.5)	-15.9 (-13.0)	-12.0 (-16.0)
Cotton	H ₂ O	B	2.7	Blue 1	8.0 (44.5)	-10.0 (-16.7)	-39.7 (-17.3)
				Violet 14	3.6 (18.4)	30.7 (47.0)	1.1 (-16.5)
				Red 2	8.7 (29.4)	42.6 (40.3)	13.4 (0.9)
				Yellow 2	55.2 (74.6)	-15.0 (-13.8)	46.3 (37.6)
Wool	H ₂ O	B	2.3	Blue 1	3.0 (6.2)	-2.1 (-11.6)	-18.2 (-28.9)
				Violet 14	4.3 (3.3)	11.4 (30.9)	7.3 (0.0)
				Red 2	6.5 (9.0)	45.0 (47.6)	13.8 (11.9)
				Yellow 2	47.4 (58.3)	-16.6 (-8.3)	4.4 (48.7)
Nylon	H ₂ O	A	24.7	Blue 4	5.8 (29.0)	-9.4 (-14.7)	-29.9 (-9.4)
Nylon	H ₂ O	B	2.5	Blue 1	13.9 (45.9)	-19.2 (-17.9)	-37.4 (-10.9)
				Violet 14	6.3 (16.2)	61.0 (59.8)	-20.1 (-28.9)
				Red 2	14.9 (27.1)	56.5 (45.5)	9.6 (-9.4)
				Yellow 2	54.1 (68.0)	-22.1 (-13.2)	40.9 (26.3)
Polyester	H ₂ O	A	1.1	Blue 4	46.7 (63.1)	-12.1 (-3.0)	-12.4 (3.2)
				Blue 26	6.8 (29.3)	8.4 (-6.2)	-33.9 (-16.1)
Polyester	DMF	B	1.2	Violet 14	11.2 (51.6)	41.2 (7.6)	-11.6 (-4.0)
				Red 2	23.6 (57.2)	38.2 (12.6)	0.3 (0.6)
Polypropylene	DMF	B	0.2	Violet 14	26.4 (47.6)	22.6 (10.1)	-13.8 (-2.8)
				Red 2	38.6 (58.0)	20.2 (11.8)	1.0 (3.6)

^a A = Aqueous biacetyl (1%) (5 cc/sec) and steam (5 cc/sec) passed through monomer 25 min, exposed to 200-W lamp from 6 cm for final 20 min. B = Aqueous biacetyl (1%) (5 cc/sec) and monomer (5 cc/sec) for 30 min, exposed to 450-W lamp from 6 cm for final 15 min.

^b The values in parentheses are for control fabrics dyed under the same conditions.

Felting shrinkage (per cent area shrinkage) was determined by machine washing the wool fabrics for 15 min in 140°F water with 5 lb ballast and 70 g AATCC detergent and repeated for 5 to 15 cycles, measuring the area shrinkage before and after laundering.

Scanning electron micrographs of selected control and polymer-grafted samples were obtained with a Cambridge Stereoscan Mark IIA microscope operated in the secondary mode at 5 kV and at a magnification of 990 to 2050 times (Figs. 1 and 2).

RESULTS AND DISCUSSION

Even grafts of acrylic and methacrylic polymers on the prewetted surfaces of fibrous substrates were achieved through near-ultraviolet irradiation in the presence of gaseous biacetyl and monomers (Tables I-VI). Irradiation of substrate with Pyrex-filtered 100- to 450-W mercury arcs from a 2- to 6-cm distance for 10 to 30 min in an atmosphere of monomer and biacetyl vapors carried by inert gas gave up to 20% uptakes of grafted polymer on substrate surfaces without extensive homopolymer formation. This paper indicates the scope and character of this photografting process through the wide variety of substrates grafted and acrylic-methacrylic monomers used in photografting, the properties of selected photografted fibers (Tables III-VI), and the effect of various reaction parameters on vapor-phase photografting of wool (Figs. 3-11). The degree and evenness of grafting is dependent on the fiber, monomer, and fiber-wetting agent used, the concentration of biacetyl and monomer vapors introduced into the reactor, and the irradiation conditions.

Photografting of Methyl Acrylate to Substrates

Methyl acrylate was photografted to a number of fiber substrates and serves to demonstrate the utility of the reaction (Tables I and II). For most substrates with a degree of affinity for water, water served as a suitable wetting agent to achieve rapid grafting. Other polar wetting agents such as N,N-dimethylformamide and dimethylsulfoxide led to significant grafting of methyl acrylate on hydrophobic fibers such as polyester and polyolefin. The extent of grafting is critically dependent upon the overall conditions of the treatment rather than on the intensity of the irradiation, as indicated by the results with cotton and wool (Table I). Faster flow rates of biacetyl and monomer, with longer irradiation and a smaller lamp, are preferred over slower flow rates together with a higher lamp intensity. The lower degree of grafting on cotton and wool with the 450-W lamp was apparently due to rapid drying of the wet substrates on irradiation. Since wetting of the fabric is critical to achieve high rates and degrees of grafting, such an effect is most readily explained by rapid evaporation of the wetting agent. Cotton also is more readily grafted with methyl acrylate than is wool under these conditions. Nylon was readily grafted with methyl acrylate, using both water and methanol as the wetting agent, and acrylic fiber was readily grafted using water as wetting agent. Although polyester and polyolefin were not grafted using water, certain organic polar solvents that effectively wet these fiber sur-

TABLE V
 Grafting of Other Monomers to Wool Fabric

Monomer	Procedure ^a	% Uptake of grafted polymer	Changes in physical properties ^b
Acrylonitrile	A	11.5	% area shrinkage (5 washes) = 5.0% (7.5%)
<i>n</i> -Butyl acrylate	A	5.6	% area shrinkage (5 washes) = 3.8% (7.5%)
Hexafluoroisopropyl acrylate	B	5.8	Spray rating = 70 (50); stain release rating = 1.5 (1.0)
Methyl methacrylate	C	6.3	% area shrinkage (15 washes) = 14% (22.9%); DP rating (15 washes) = 3.0 (1.7); cantilever stiffness = 163 mg/cm ² (166 mg/cm ²)
Methyl methacrylate	D	12.7	% area shrinkage (15 washes) = 10.6% (22.9%); DP rating (15 washes) = 2.3 (1.7); cantilever stiffness = 201 mg/cm ² (166 mg/cm ²)
Acrylamide	E	2.2	—
90% Aq. acrylamide	F	2.4	—
90% Aq. acrylamide	G	1.6	—

^aA = Aqueous biacetyl (5 cc/sec) and monomer (5 cc/sec) 45 min, then irradiated with 100-W arc for final 30 min from 2 cm. B = Same as A except 3 cc/sec biacetyl and monomer flow rates and 6-cm distance; monomer reservoir was heated at 50–60°C. C = 1% Aqueous biacetyl (10 cc/sec) and monomer (10 cc/sec) 30 min, then irradiated with 200-W arc for 15 min from 6 cm. D = Same as C except 20-min irradiation time. E = 1% Aq. biacetyl (10 cc/sec) was introduced for 15 min and stopped; Solid acrylamide was sublimed at its melting point and carried in by nitrogen at the same rate with simultaneous irradiation with 200-W lamp for 20 min. F = Same as E except 90% aq. acrylamide solution at 30°C was used instead. G = Same as F except no biacetyl solution was used.

 TABLE VI
 Acid Dyeing Properties of Fabrics Photografted with N,N-Dimethylaminoethyl Methacrylate^a

Fabric	% Uptake of grafted polymer	Color ^b					
		Dyed with Acid Blue 67			Dyed with Acid Red 27		
		Rd	a	b	Rd	a	b
Rayon	3.8	21.8 (55.4)	2.8 (−0.6)	−34.4 (−9.0)	21.8 (62.8)	26.4 (7.2)	0.6 (0.1)
Nylon	1.0	4.7 (4.6)	27.4 (28.0)	−96.8 (−96.5)	8.9 (10.4)	56.8 (53.1)	12.3 (11.8)
Polyester	0.1	43.3 (64.4)	−1.0 (0.1)	−1.2 (−18.0)	50.3 (71.2)	17.8 (−0.2)	−1.2 (3.8)
Polypropylene	0.1	34.0 (66.8)	−0.9 (−1.4)	−21.9 (5.1)	40.2 (70.4)	23.0 (−1.2)	0.6 (7.2)

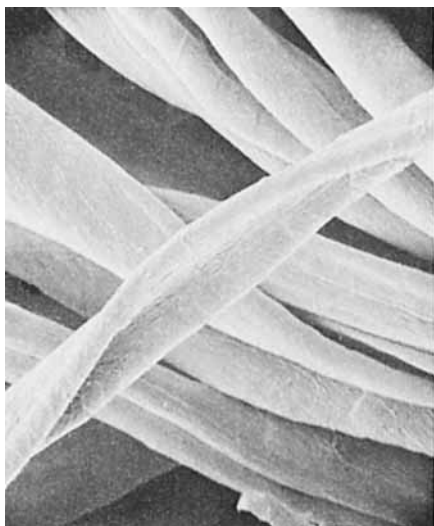
^aAqueous monomer (10%) padded on fabric, then 1% aqueous B for 45 min, irradiated for final 30 min with 200-W Pyrex-filtered mercury arc from 6 cm.

^bColor values for untreated fabrics are found in parentheses.

faces gave satisfactory grafts, even though it was difficult to predict the effect a given polar wetting agent would have. For example, polyester was grafted to an 8.2% polymer uptake using N,N-dimethylformamide as wetting agent, whereas dimethylsulfoxide wetting agent and tetrahydrofuran were ineffective.

Scanning electron micrographs of the grafted fibers (Figs. 1b, d, f, and h) are similar to untreated fibers (1a, c, e, g) in appearance, with little or no poly(methyl acrylate) visible on the fiber surfaces, an indication that polymer deposition occurs within the fiber to a great extent. Only with the grafted filter paper sample (1h) were significant amounts of poly(methyl acrylate) visible on the fiber surface and between fibers. The tensile properties and flexural rigidities of the treated fabrics were usually very nearly the same as those of yarns from untreated fabrics; but, in some instances, the dry and wet tensile properties of the treated fabrics appear somewhat higher than the values for untreated yarns.

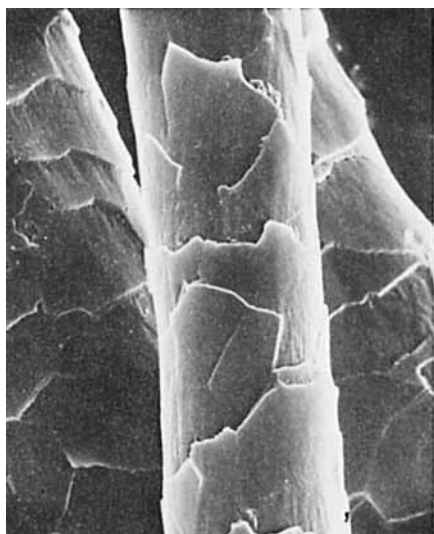
A wide range of fiber substrates can be grafted by this technique, provided



(a)



(b)



(c)



(d)

Fig. 1 (continued)

a suitable polar wetting agent is used, with the degree of fiber grafting being dependent on the particular irradiation conditions used.

The effect of wetting agents on grafting of poly(methyl acrylate) on polypropylene fabric was studied in more detail (Table II and Fig. 2). Polar hydrophilic solvents that do not wet polypropylene (water and *n*-propanol), and hydrocarbon solvents (benzene and 1,2-dichloroethane) gave essentially no, or very limited, polymer grafts on polypropylene, whereas polar solvents such as dimethylsulfoxide and *N,N*-dimethylformamide led to extensive polymer grafting.

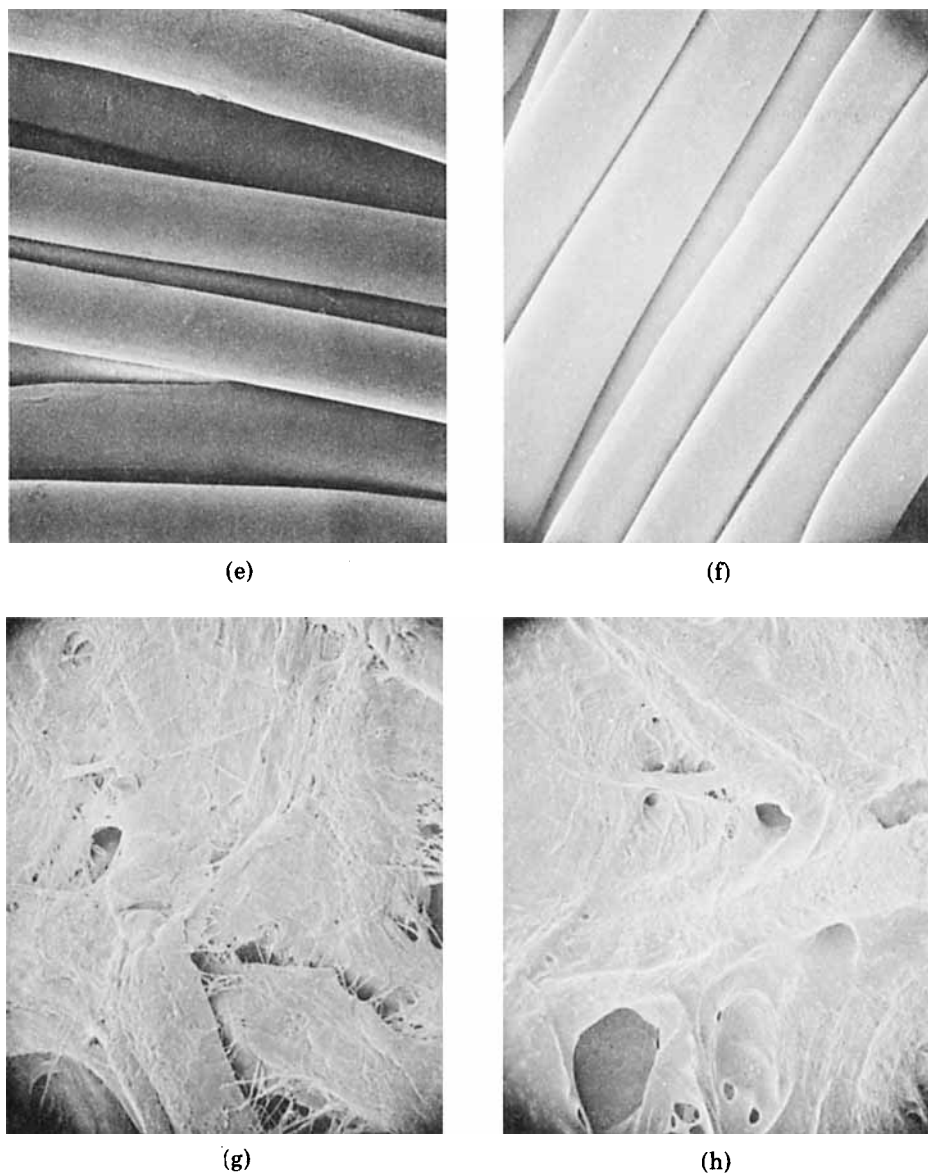


Fig. 1. Scanning electron micrographs of untreated fibers and fibers grafted with (methyl acrylate) vapors in the presence of biacetyl: (1a) untreated cotton, 1200 \times ; (1b) cotton grafted with 22% poly(methyl acrylate), 1150 \times ; (1c) untreated wool, 2000 \times ; (1d) wool grafted with 6.5% poly(methyl acrylate), 1015 \times ; (1e) untreated nylon, 2500 \times ; (1f) nylon grafted with 13.7% poly(methyl acrylate), 1100 \times ; (1g) untreated filter paper, 1015 \times ; (1h) filter paper grafted with 19% poly(methyl acrylate), 1025 \times .

Scanning electron micrographs of these grafted polypropylene fibers were examined to see how the various wetting agents affected the evenness of grafting on polypropylene (Fig. 2). Propanol (2b) caused much more spotty uneven grafts than did benzene (2c) and 1,2-dichloroethylene (2d), and in each case limited interfiber grafting was evident. The differences in the

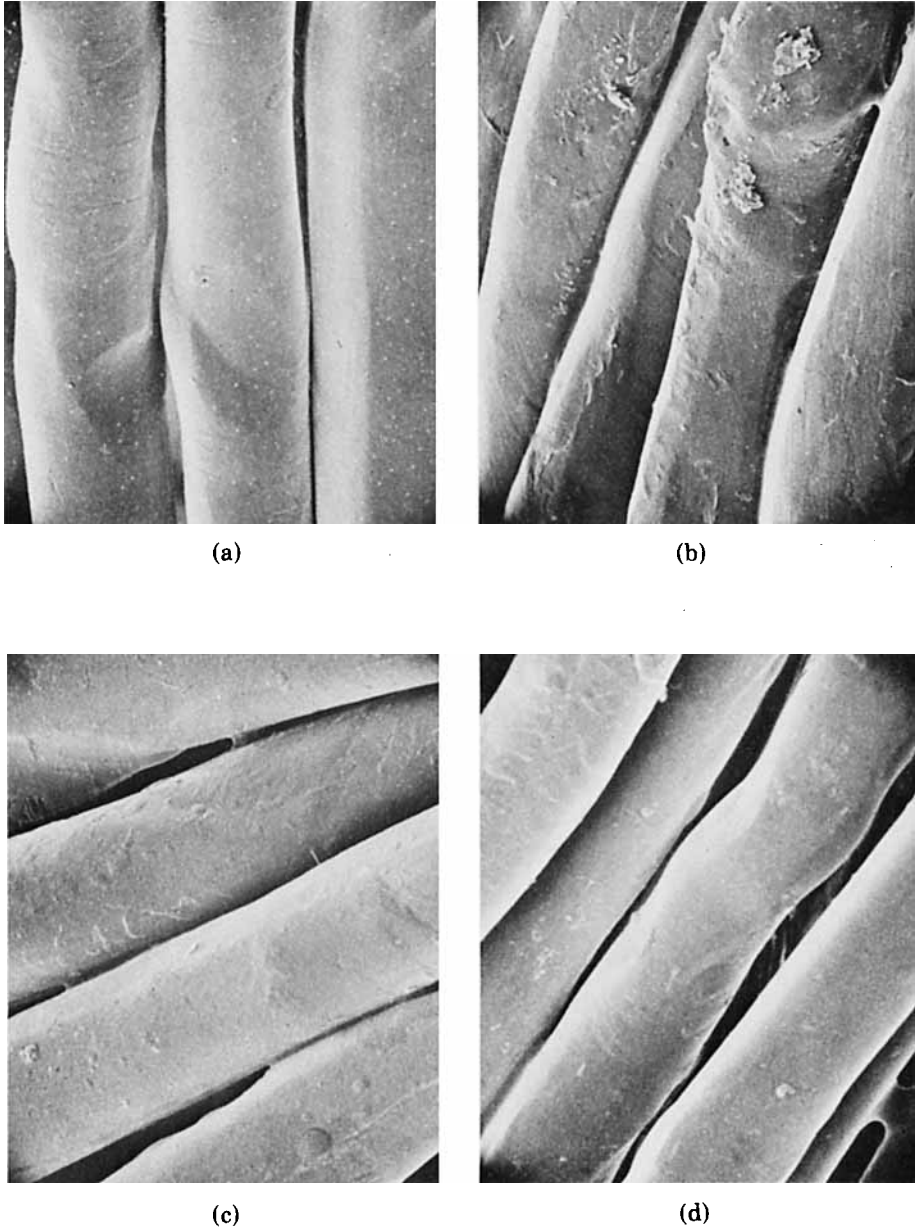


Fig. 2 (continued)

evenness of the graft might be expected, as the wetting agents would have such different wetting characteristics for polypropylene. *N,N*-Dimethylformamide (2e) gave satisfactory grafts on polypropylene, whereas with dimethylsulfoxide (2f) nodes of polymer were grafted to the fiber surface. The degree of evenness of the grafted polymer in general appears to be related to the ability of the solvent to wet and swell the polypropylene fiber.

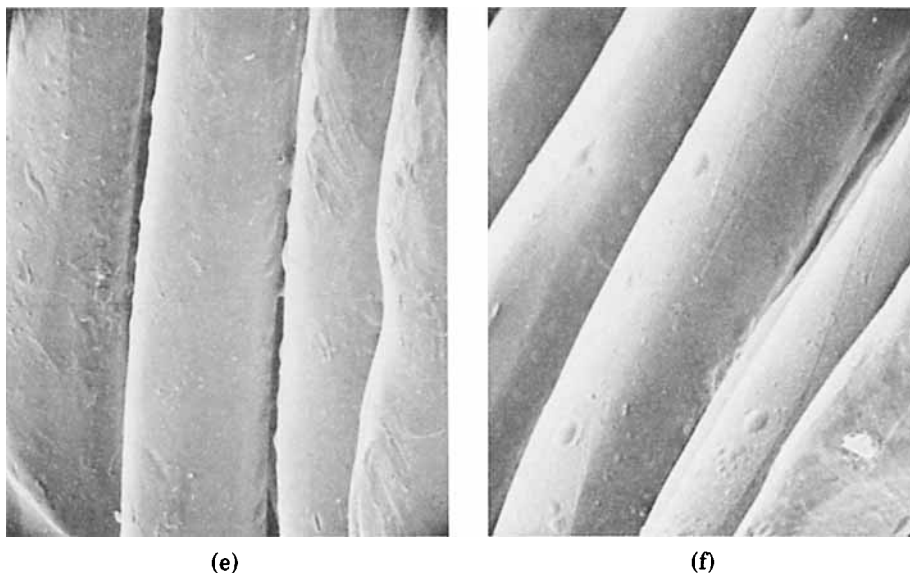


Fig. 2. Scanning electron micrographs showing the effect of wetting agent on vapor phase grafting of methyl acrylate to polypropylene in the presence of biacetyl (as listed in Table II): (2a) untreated control, 1025 \times ; (2b) grafted using *n*-propanol wetting agent, 1050 \times ; (2c) grafted using benzene, 1180 \times ; (2d) grafted using 1,2-dichloroethane, 990 \times ; (2e) grafted using N,N-dimethylformamide, 1000 \times ; (2f) grafted using dimethyl sulfoxide, 1140 \times .

Photografting of 2,2,2-Trifluoroethyl Methacrylate to Fibers

In a related study, the effect of two wetting agents (water and N,N-dimethylformamide) on photografting of the fluorinated monomer 2,2,2-trifluoroethyl methacrylate on a number of fiber types was explored (Table III). In general, N,N-dimethylformamide as wetting solvent resulted in higher grafts of this monomer than did water. An exception was nylon, which gave similar grafts with both wetting agents. Of the two cellulosic fibers studied, rayon gave higher grafts with both wetting agents than did cotton. This was to be expected, as rayon is more readily penetrated and swollen than cotton by these two solvents. It is interesting that in the case of this fluorinated monomer, the choice of the proper wetting agent was more significant than the reactivity of the substrate under the reaction conditions.

The water repellency and stain-release properties of the treated fabrics were markedly improved by the fluoropolymer finish, even at low uptakes. It was apparent that higher uptakes of fluoropolymer on the cellulosic fibers were necessary to achieve a high degree of water repellency compared to nylon, which had high spray ratings with even low fluoropolymer grafts. The stain-release properties of the modified fabrics did not seem to be as sensitive to the amount of polymer grafted on the fabric; but in all instances, improved stain-release properties were found after grafting with this monomer. When scanning electron micrographs of the fabrics photografted with fluoromonomer were compared with those of untreated fabric samples, the polymer of the fiber surface was found to be extremely even in each fabric grafted, with no perceptible difference between grafted fabrics when N,N-dimethyl-

formamide or water was used as wetting agent. No interfiber bonding due to polymer formation was observed on any of the modified fabrics.

Photografting of Acrylic Acid to Fabric Surfaces

Because of the low volatility of acrylic acid, two techniques were used to achieve significant grafts of this monomer to fiber surfaces in the vapor phase (Table IV). In exposure condition A, nitrogen at 10 cc/sec was bubbled through a 1% aqueous solution of biacetyl and into the reactor for 15 min. Then superheated steam was passed through the monomer reservoir containing 15 cc of acrylic acid and into the reactor and the sample was irradiated simultaneously using a 200-W lamp for 20 min. The monomer was exhausted during this period. Under condition B, nitrogen was bubbled through the monomer, or its solution, as in previous experiments. As might have been expected, exposure condition A resulted in higher grafts of poly(acrylic acid) on the fabric surface with hydrophilic fibers, but it was essentially no more effective than procedure B on polyester. In addition, the lower grafts by procedure B were more evenly distributed on the fabric surfaces in each case. The poly(acrylic acid)-modified fabrics and control fabrics were dyed with representative basic dyes to determine the effect of the grafted polymer on the dyeing properties of the fabrics. In each instance, the poly(acrylic acid)-modified fabric dyed to a deeper shade than did the untreated control fabric. The depth of shade was dependent on the amount of poly(acrylic acid) grafted to the fiber, and in some cases the shades of the modified and control fabrics differed. The shade depths and shade differences indicated that the acid groups grafted to the modified fibers affected the fiber environment sufficiently to cause both deeper dyeings and shifts in the color of the dyes on modified fibers.

Photografting of Various Monomers to Wool

As previously shown, a wide variety of fabrics can be grafted by such different monomers as methyl acrylate, 2,2,2-trifluoroethyl methacrylate, and acrylic acid by this vapor-phase photografting technique. To demonstrate the utility of this process, we have grafted additional volatile monomers to wool and examined the properties of the resulting modified wools (Table V). A slightly modified process was adopted in the case of acrylamide where sublimation was used to vaporize the compound. Unfortunately, the result was not any more promising than that obtained by the simpler method of bubbling nitrogen gas through an aqueous solution of acrylamide. A number of acrylates and methyl methacrylate were successfully grafted to wool at levels of 5.6% to 12.7%. The modified wools had such improved properties, in comparison to untreated wool, as reduced felting shrinkage and higher durable press, spray, ratings, and stain-release ratings, with only minimal changes in the flexural rigidity of the fabrics. A feature of the vapor-phase grafting process is the improvement of selected fabric properties without significant effect on the aesthetic properties of the fabric.

The effect of several reaction parameters, including variation of wet pickup on wool, biacetyl, and monomer flow times, and flow rates and irradiation

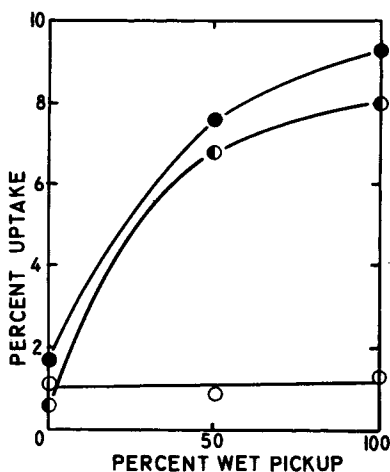


Fig. 3. Effect of water content (wet pickup) on grafting of methyl acrylate to wool. Initial flow of 1% aqueous biacetyl (10 cc/sec) for 15 min, followed by monomer (10 cc/sec) for 20 min with simultaneous irradiation from a 200-W lamp from 6-cm distance: (●) total polymer uptake; (◐) graft uptake; (○) homopolymer.

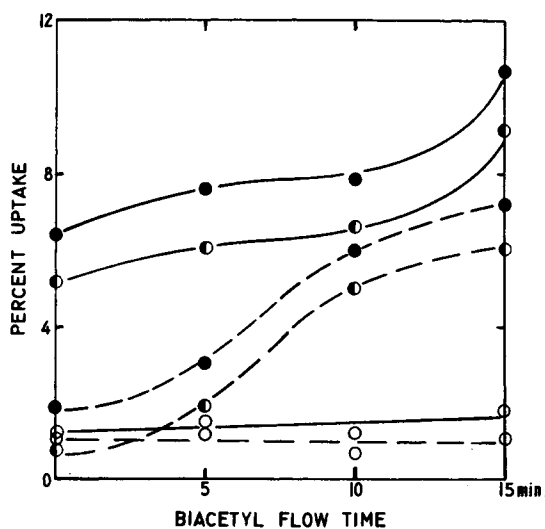


Fig. 4. Effect of biacetyl flow time on grafting of methyl acrylate to wool. Reaction conditions are the same as Fig. 2, except biacetyl flow time varied from 0 to 15 min without compensating water vapor flow time for biacetyl (—) or with compensating water vapor flow up to 15 min replacing biacetyl flow (- - - - -). Wet pickup of wool held at 50%.

times on vapor-phase grafting of methyl acrylate on wool was studied (Figs. 3–11). Selected data for methyl methacrylate and acrylonitrile grafting are also included.

The wet pickup of water on the wool had a critical effect on grafting of methyl acrylate vapor. At no wet pickup, only limited grafting and homopolymer formation was observed; but at wet pickups, extensive grafting with essentially no increase in homopolymerization was observed. Grafting reached

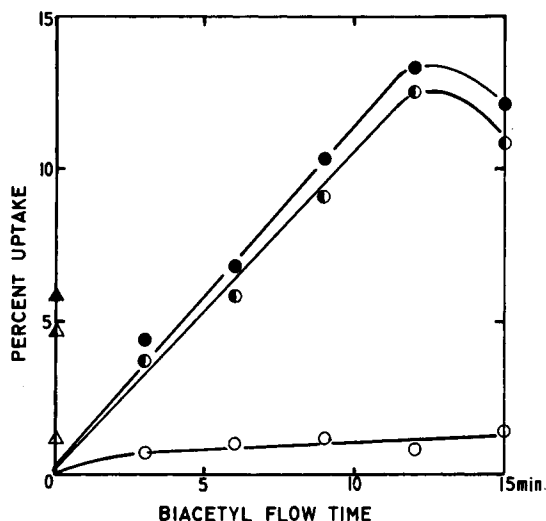


Fig. 5. Effect of biacetyl flow time on grafting of methyl methacrylate to wool. Reaction conditions are the same as found in Fig. 4, with no water compensation for biacetyl flow time.

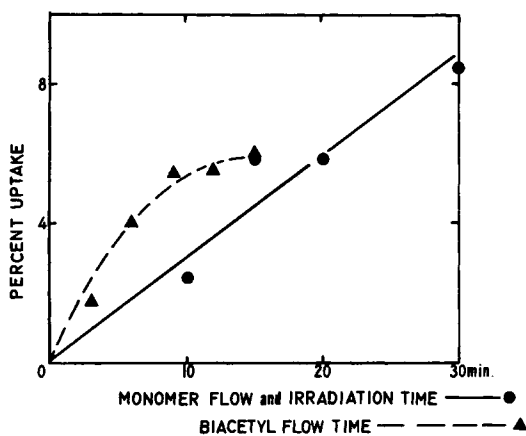


Fig. 6. Effect of biacetyl flow time (\blacktriangle) and monomer-irradiation time (\bullet) on grafting of acrylonitrile to wool. Reaction conditions are the same as found in Figs. 4 and 5, except irradiation was carried out with 100-W lamp from 2-cm distance. (Values for grafted polymer only since homopolymer formation was negligible in this case.)

a limiting value of approximately 10% uptake and a graft polymer-homopolymer ratio of 9:1 at 100% wet pickup (Fig. 3). These data indicate that wetting of the fiber is critical for significant grafting on the fiber surface.

The biacetyl flow time was varied to determine how the amount (i.e., concentration) of biacetyl flowing into the system affected grafting and homopolymer formation (Figs. 4, 5, and 6). The experiment, using methyl acrylate monomer, was done in two ways (Fig. 4). In one, the biacetyl was allowed to flow in for 0 to 15 min prior to introduction of monomers and irradiation with light. In the other, water vapor was substituted for biacetyl for the time period during the 15-min period that biacetyl was not allowed to flow. An in-

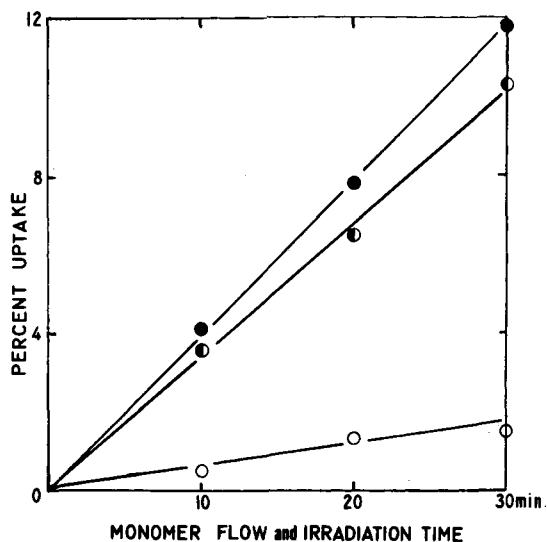


Fig. 7. Effect of simultaneous monomer flow and irradiation time on grafting of methyl acrylate on wool. Reaction conditions are the same as Fig. 3, except biacetyl flow time is 15 min in each case, the wet pickup of the wool is held at 50%, and the monomer flow-irradiation time is varied.

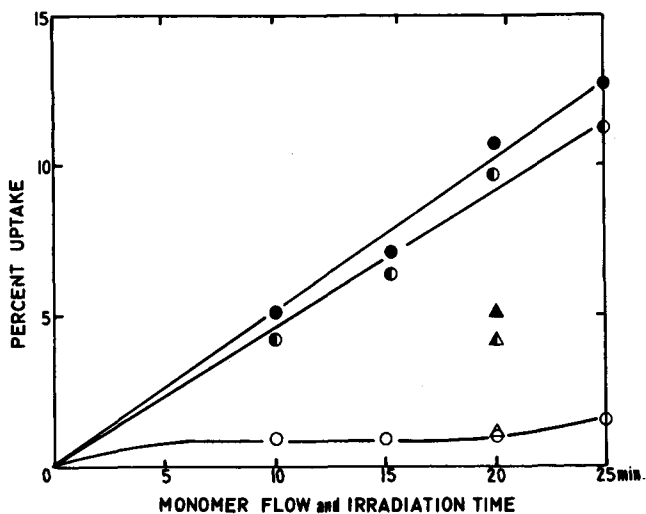


Fig. 8. Effect of monomer flow-irradiation time on grafting of methyl methacrylate to wool. Reaction conditions are the same as found in Fig. 4; ($\blacktriangle \blacktriangle \blacktriangle$) values for unsensitized grafting under the same conditions.

teresting finding concerned the effect of water vapor only passed into the reactor for 15 min. Such treatment caused significant grafting on the wool, compared to biacetyl-induced grafting of monomer without such treatment. Also, the degree of grafting resulting from the water vapor treatment was about the same as sensitized grafting for a similar period. It appears, therefore, that the water vapor pretreatment of wet-out wool can enhance unsensitized grafting on wool to the same degree that biacetyl sensitizer can under

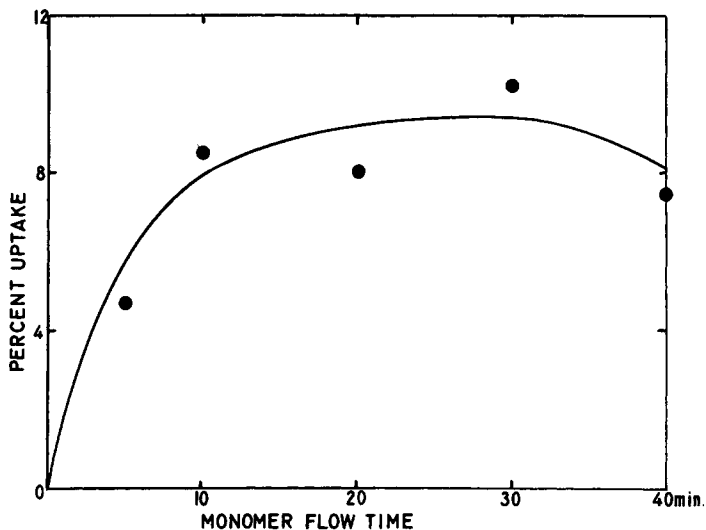


Fig. 9. Effect of monomer flow time followed by irradiation on the grafting of methyl acrylate to wool. Initially a flow of aqueous 1% biacetyl (10 cc/sec) is introduced for 15 min, then monomer vapor is introduced for 5 to 40 min followed by 20 min irradiation with a 200-W mercury arc lamp from 6-cm distance. The wet pickup of wool is 50%. (Values for grafted polymer only.)

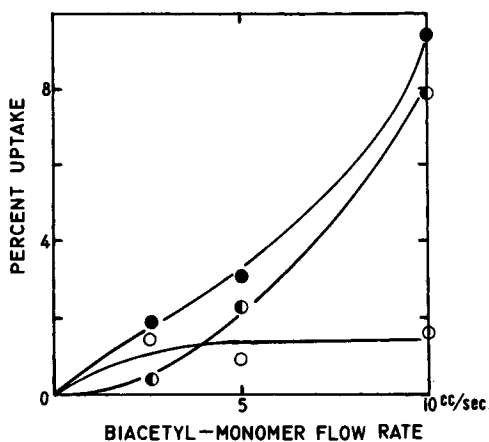


Fig. 10. Effect of biacetyl and monomer flow rates on grafting of methyl acrylate on wool. Initially vapor from a 1% aqueous biacetyl solution was introduced for 15 min, then monomer vapor was introduced for 20 min with simultaneous irradiation with a 200-W mercury arc from 6-cm distance. The flow rate of sensitizer and monomer were varied between 0 and 10 cc/sec and the wet pickup was held at 50%.

this particular condition. Williams and Stannett⁸ found that under high swelling conditions and long contact times with water, a high degree of grafting could be achieved with the wool-ethyl acrylate system without the use of any of the normal means of initiating graft copolymerization. This result was explained in terms of the greater ability of the monomer to diffuse into highly swollen wool at a rate sufficient to keep the active centers supplied for growth before termination took place. Our results have substantiated their

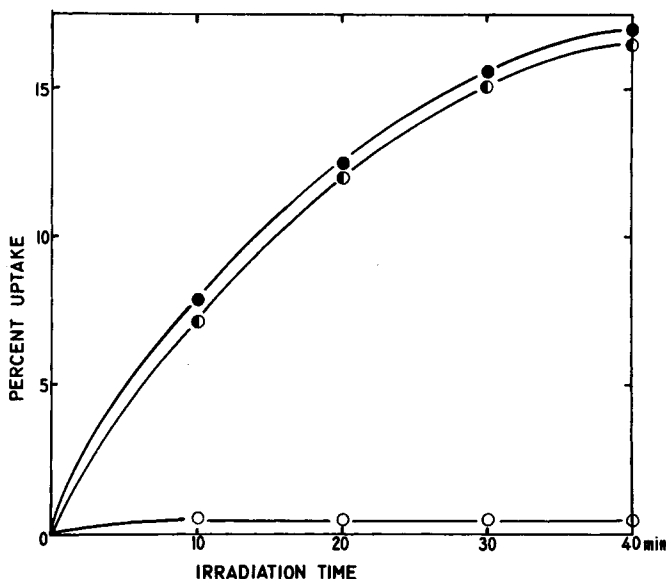


Fig. 11. Effect of irradiation time on grafting of acrylamide to wool; 10% aqueous acrylamide was padded onto wool to a 75% wet pickup initially, then the treated fabric was irradiated with a 100-W mercury arc in the presence of biacetyl vapor (5 cc/sec) for varied periods of time from 6 cm.

observation. Furthermore, besides wool, it seems that porous fibers, such as those of cotton and rayon, should be readily grafted under highly swollen conditions.

Increasing biacetyl flow time increased the percentage of methyl methacrylate and acrylonitrile grafted on wool (Figs. 5 and 6). There was significant leveling off of the grafting at biacetyl flow times above 10 min, as found with methyl acrylate when no water compensation was used (Fig. 4). This leveling off of grafting indicates that, after a given period of time, saturation of the system by biacetyl occurs, at which time further introduction of biacetyl is much less effective.

Examination of scanning electron micrographs in the absence of biacetyl vapors of photografted fabrics indicated more uneven deposition of monomer on the fiber surface. On the other hand, the presence of biacetyl leads to more even grafting, indicating that the mode of grafting differs in the two cases. In later studies, we found that biacetyl is critical for grafting on other fiber types than wool.

The monomer flow and irradiation times were varied in tandem to determine their combined effect on the percentage grafting of methyl acrylate, methyl methacrylate, and acrylonitrile on wool. The total uptake, graft uptake, and homopolymerization increased essentially linearly with increasing monomer flow-irradiation times (Figs. 6, 7, and 8). The degree of grafting increased much more rapidly than did homopolymer formation, and thus the ratio of grafting to homopolymerization became larger with increasing monomer flow-irradiation times. These data indicate that the amount of polymer grafted is linearly dependent on the light supplied to the fabric surface over the period studied, as long as a constant concentration of monomer vapor is

available with the grafting system. In a related study, monomer vapor was introduced into the reactor for a given period. The fabric was then irradiated for 20 min, with no further monomer being introduced into the system (Fig. 9). Increases in the monomer flow time up to 20 min resulted in increased polymer formation on the fabric surface, with the degree of grafting leveling off, and possibly decreasing, after long periods of introduction of monomer. At long flow times, the monomer vapor flow caused evaporation of moisture and biacetyl from the wool fabric, and thereby slightly decreased the degree of grafting.

The rates of flow for both biacetyl and monomer were increased from 0 to 10 cc/sec while the flow times were held constant, to determine the effect on the degree of grafting and homopolymer formation with methyl acrylate (Fig. 10). Increasing flow rates delivered progressively greater concentrations of biacetyl and methyl acrylate monomer to the wetted fabric surface and caused exponential increases in grafting without additional homopolymerization, over the range studied. The leveling off of homopolymerization with increasing flow rate indicates that grafting is favored by high biacetyl monomer flow rates. These data, coupled with our earlier study of the effect of flow times on grafting, indicate that increasing concentrations of biacetyl and monomer lead to increased grafting, with little additional homopolymerization, up to a limiting value determined by the saturation concentrations of biacetyl and monomer in the reactor system.

Modified Photo-initiated Grafting of Low Vapor Pressure Monomers onto Surfaces

Vapor-phase grafting is limited to those monomers that have sufficient vapor pressure at room temperature and atmosphere pressure to be carried into the photochemical reaction chamber. As a result, derivatives of acrylic and methacrylic monomers of low vapor pressure are necessarily excluded from the vapor-phase grafting process unless the grafting procedure was modified. One approach is to pad solutions of monomer of low volatility onto the fabric surface and then irradiate the sample in the presence of biacetyl vapor. Such a technique met with moderate success and led to grafting of several different monomers to fibers, e.g., the photografting of N,N-dimethylaminoethyl methacrylate on various fabrics (Table VI). Low to moderate uptakes of polymer were grafted to the surface by this technique. Although the grafting efficiency was low in consideration of the amount of monomers applied to the fabrics, the uptake of grafted polymer was sufficient to improve markedly the acid-dyeing properties of the fabric in all cases studied. Also, when a monomer of low vapor pressure, such as acrylamide, is padded onto wool, it is possible to achieve grafting without significant homopolymer formation (Fig. 11). The polyacrylamide grafted to the surface increases with irradiation time without significant homopolymerization, over the irradiation times studied; but the increase in grafting is nonlinear and levels off with time. This might be expected, as the concentration of acrylamide decreases as polymerization occurs, thus causing the rate of grafting to slow. This is in contrast to vapor-phase grafting, in which the concentration of monomer in the system is constantly replenished.

CONCLUSIONS

In light of the findings above, the following can be concluded. Prewetting of the surface is a critical feature of the photo-initiated vapor-phase grafting reaction. The degree of grafting on the surface increases with the degree of wetting and wet-pickup of the fabric, up to a limiting value. Liquids that tend to wet and swell the fiber surface increase the amount of grafting. Use of a wetting solvent with an affinity for the biacetyl vapors and possible monomer vapors favors grafting. Since vapor-phase grafting and accompanying homopolymerization occur at or under the fabric surface, and since the degree of grafting is dependent on both the biacetyl and monomer flow times and rates, the wetted fiber is intimately involved in the grafting process, with the concentrations of biacetyl and monomer on or slightly penetrated into the surface affecting both the rate and degree of grafting. The generally linear dependence of the degree of grafting on irradiation time when monomer is present in a constant concentration indicates the critical importance and constant effect of light quanta falling on the surface that is being grafted. The low degree of homopolymer formation that occurs with the vapor-phase graft process attests to the efficiency of the photo-initiation system with regards to grafting. Initiation of grafting occurs through facile hydrogen abstraction from the fabric surface, and the termination mechanisms in operation do not lead to extensive initiation of homopolymerization. Although formation of homopolymer entrapped within the fiber cannot be excluded as a possibility in this process, several factors tend to minimize the input of such a mechanism. The excited biacetyl would be more likely expected to favor abstraction of accessible hydrogens from polymer backbones within the fiber than abstraction of hydrogens from monomer dissolved within the solvent wetting the fiber. Furthermore, since it does not appear critical that the monomer be soluble in the solvent wetting the fabric, free-radical abstraction of hydrogen from entrapped monomer seems less likely than free-radical addition of monomer diffusing to the surface of fibers where substrate radicals are present.

Biacetyl diffuses onto the prewetted fiber initially. Then, as monomer vapors are introduced and the surface is irradiated with ultraviolet-visible light, the excited biacetyl dissociates to yield acetyl radicals or decays to its more stable triple state through intersystem crossing. These radical species abstract accessible hydrogens from the substrate or near the surface of the fiber substrate, which in turn react with monomer in the proximity or possibly within the solvent wetting the substrate. Growing polymer chains are terminated in a manner whereby only limited initiation of homopolymerization occurs.

The biacetyl-sensitized vapor-phase grafting technique provides a novel and rapid method for even deposition of polymers on substrates at atmospheric pressure and temperature conditions, using a simple photoreactor system. Due to its simplicity, this technique possesses distinct advantages over high energy and glow discharge processes. It requires less elaborate and less expensive instrumentation, and atmospheric pressure is used within the reaction chamber.

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