The Graft Photopolymerization of Acrylates and Methacrylates on Wool in Dimethyl Sulfoxide

HOWARD L. NEEDLES, *Department of Consumer Sciences, University of California, Davis, California 95616*

Synopsis

Irradiation of wool by short-wavelength ultraviolet light in the presence of acrylate or methacrylate esters in dimethyl sulfoxide causes intermediate grafts (2%–10%) of polymer on the surface of the wool. The amount of grafting and homopolymerization and the evenness and regularity of photografted polymer are dependent upon the monomer used. With methyl acrylate, the reaction time, monomer concentration, and introduction of water as cosolvent affect the degree of fiber grafting and the amount and molecular weight of accompanying homopolymer. Polymers grafted onto wool by this technique change the tensile properties and the water desorption characteristics of the wool.

INTRODUCTION

Unsensitized or dye-sensitized photolysis in dimethyl sulfoxide (DMSO) results in free-radical reactions involving the DMSO.[1,2] In the presence of protein,[2] DMSO fragments are substituted into the protein through free-radical attack, and photografting of styrene to gluten protein in DMSO has been observed.[3] The ability of DMSO to undergo photoreactions, coupled with its fiber-swelling properties, make it an excellent reaction solvent for photochemical modification of fibers and photo-induced graft polymerization onto fibers. Recently, I have found that graft photopolymerization of methyl and *n*-butyl acrylates and methacrylates onto wool occurs in DMSO.

EXPERIMENTAL

Wool, Monomers, and Reagents

The source and purification procedure for the wool fabric have been reported previously.[4] The monomers (methyl acrylate, *n*-butyl acrylate, methyl methacrylate, and *n*-butyl methacrylate) and reagents were Baker "analyzed" or Eastman reagents. The monomers were passed over neutral alumina prior to use.

Photopolymerization Procedure

A preweighed 5 × 6 in. piece of wool fabric was mounted around the outside of a Vycor photochemical immersion well, and the well was placed in a

2559

glass photochemical reaction vessel containing a gas inlet and a gas outlet fitted with a condenser. The monomer in 300 ml of DMSO, or DMSO only, was added to the photochemical reactor. A 100-watt Hanovia high-pressure mercury arc was suspended in the center of the water-cooled photochemical immersion well, and the fabric and solution were irradiated for 1 or 2 hr at 25°–30°C under nitrogen. The average distance of the light source from the face of the fabric was 2.0 cm. The intensity of light on the face of the fabric from 220 to 410 nm was 50 milliwatts/cm².

After irradiation, the fabric was removed from the reactor, rinsed with DMSO, hot water, and distilled water, and then dried. The fabrics were extracted in a Soxhlet extractor for 8 hr with benzene to remove any homopolymer, after which they were dried and weighed to determine the amount of polymer grafted to the wool. The DMSO solution remaining in the reactor was poured into cold salt water to precipitate the homopolymer. The homopolymer was washed thoroughly with boiling water and dried. The inherent viscosities of the homopolymers at a concentration of 0.5 g/dl were determined at $30.0 \pm 0.1°C$.

Instrumental Methods and Analyses

The tensile properties of warp yarns from the samples were determined by ASTM procedure D-2256-66T under standard conditions. Differential thermal analyses (DTA) were run on 4-mg samples of fiber under nitrogen at a heating rate of 10°C/min, using a Deltatherm III Thermal Analyzer. Scanning electron microscopy of the samples was done using a Cambridge Stereoscan Mark IIA microscope operated in the secondary mode at 5 kV and at a magnification of 1700–2000. The sample specimens, which were cut from the center of the fabrics, were coated on both sides with gold, cemented to the specimen stub with conductive cement, and recoated with gold. Total sulfur analyses were performed by the Microanalytical Laboratory, University of California, Berkeley.

RESULTS AND DISCUSSION

Graft Polymerizations of Acrylates and Methacrylates on Wool

Acrylate or methacrylate esters ($2.0M$) dissolved in DMSO were irradiated with short-wavelength ultraviolet light in the presence and absence of wool. The extent of homopolymerization and grafting on wool is reported in Table I. The n-butyl esters gave higher grafts on wool both on a weight basis and on a molar basis than did the corresponding methyl esters.

In the absence of wool, moderate homopolymerization of the monomers occurred via free-radical initiation. When wool was introduced into the reaction system, homopolymerization decreased, particularly where extensive homopolymerization was observed in the absence of wool. Previous studies[2,3] have indicated that free-radical fragments from DMSO are

TABLE I
Graft Polymerization of Acrylates and Methacrylates on Wool[a]

Monomer[b] (2.0M)	Wool present	Polymer in wool–polymer graft, %	Monomer converted to homopolymer, %	η_{inh} of homopolyner (0.5 g/100 ml)
MA	no	—	6	0.15
MA	yes	2.0	6	0.81
BA	no	—	31	2.65
BA	yes	4.8	16	0.28
MMA	no	—	14	0.26
MMA	yes	2.2	7	0.30
BMA	no	—	47	0.40
BMA	yes	10.1	19	0.26

[a] Irradiation in DMSO for 2 hr.
[b] MA = methyl acrylate; BA = n-butyl acrylate; MMA = methyl methacrylate; BMA = n-butyl methacrylate.

involved in photo-induced free-radical abstraction of hydrogens from soluble proteins and that radical fragments can compete with monomer for free-radical sites formed within the protein. The wool fabric wrapped around the photochemical well selectively absorbs certain wavelengths of ultraviolet light, thereby decreasing the light available to the DMSO–monomer solution. The monomers that gave the highest homopolymerization in the absence of wool also gave the highest grafts of polymer.

In the absence of wool, the n-butyl esters gave higher molecular weight homopolymers than did the methyl esters. When wool was introduced, the methyl esters gave higher molecular weight homopolymers. This particular effect probably resulted from the complex interaction of the reactants during the photoinitiation and photopolymerization process.

The effect of monomer concentration, irradiation time, and water as cosolvent was studied for photopolymerization of methyl acrylate in the presence and absence of wool (Table II). Monomer concentration had lit-

TABLE II
Graft Photopolymerization of Methyl Acrylate on Wool

Monomer concn., M	Ratio DMSO:H₂O	Wool present	Irradiation time, hr	Polymer in wool–polymer graft, %	Monomer converted to homopolymer, %	η_{inh} of homopolymer (0.5 g/100 ml)
1.0	1:0	no	2	—	22	0.36
1.0	1:0	yes	1	0.2	7	0.21
1.0	1:0	yes	2	2.1	31	0.66
1.0	1:1	yes	2	37.5	30	0.43
1.0	0:1	yes	2	64.3	26	0.15
2.0	1:0	no	2	—	6	0.15
2.0	1:0	yes	2	2.0	6	0.81

tle effect on the grafting of methyl acrylate onto wool, but the degree of homopolymerization was much lower at 1.0M monomer than found for 2.0M monomer concentration. Shortening the reaction time to 1 hr at a concentration of 1.0M monomer decreased grafting and reduced homopolymerization and the apparent molecular weight of homopolymer. As water was introduced as cosolvent, the amount of grafting on the wool increased without an increase in homopolymerization. The molecular weight of homopolymer became progressively lower, however. The polymer graft became noticeably uneven at high grafts and was confined to the side of the wool fabric adjacent to the light source.

Tensile Properties and Sulfur Contents of Grafted and Control Wools

The tensile properties and sulfur contents were determined for unirradiated wool, wools irradiated in DMSO in the absence of monomer, and grafted wools (Table III). Yarns from wool irradiated in DMSO were slightly stronger and possessed higher elongations at break and energies to break than unirradiated control wool. In wool irradiated in DMSO under nitrogen, there was no change in sulfur content, whereas in wool irradiated in DMSO under oxygen, there was a slight loss of sulfur. These findings indicate that irradiation of wool in DMSO affected the tensile properties of the wool, but that no substitution of free-radical fragments generated by photochemical scission of DMSO occurred.

TABLE III
Tensile Properties of Grafted and Control Wools

Monomer grafted	Polymer in wool–polymer graft, %	Breaking strength, g	Elongation at Break, %	Energy to break, cm-g	Total[a] sulfur, %
None[b]	—	245 ± 32	32 ± 4	212 ± 59	3.66
None[c]	—	271 ± 16	41 ± 3	273 ± 33	3.63
None[d]	—	286 ± 35	39 ± 3	280 ± 27	3.38
MA	2.0	373 ± 43	38 ± 3	360 ± 43	3.46
BA	4.8	290 ± 18	36 ± 4	250 ± 35	—
MMA	2.2	334 ± 32	38 ± 3	290 ± 44	—
BMA	10.1	325 ± 32	36 ± 3	310 ± 66	3.58

[a] Based on the amount of protein present.
[b] Unirradiated control.
[c] Irradiated under N_2 in DMSO.
[d] Irradiated under O_2 in DMSO.

The grafted wools had higher tensile strengths and energies to break in certain cases when compared with wool irradiated in DMSO. Wools grafted with poly(methyl acrylate) and poly(n-butyl methacrylate) had higher breaking strengths and energies to break. Wool grafted with poly-(methyl methacrylate) showed a higher breaking strength, while wool

grafted with poly(n-butyl acrylate) showed no change. The elongations at break for the polymer-grafted fibers were all slightly lower than control wool irradiated in DMSO, indicating that interfiber bonding of grafted
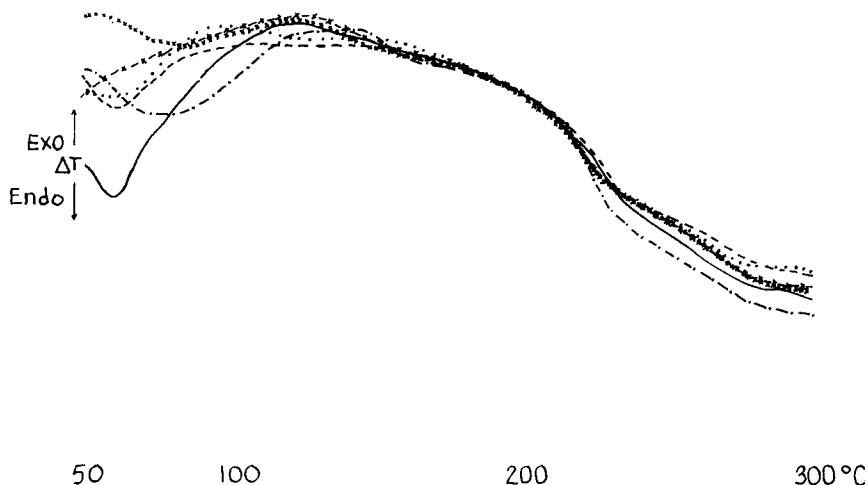

Fig. 1. Differential thermal analysis curves for control and polymer grafted wools: (———) wool control; (—) wool irradiated in DMSO under N_2; (-⸱—⸱-) wool–2.0% poly-(methyl acrylate) graft; (⸱⸱⸱⸱) wool–4.8% poly(n-butyl acrylate) graft; (-x-x-) wool–2.1% poly(methyl methacrylate) graft; (xxxx) wool–10.1% poly(n-butyl methacrylate) graft.

polymer between adjacent fibers affected the tensile properties. The sulfur contents of the grafted fibers were only slightly lower than control fibers.

Differential thermal analysis (DTA) curves for the control wools and grafted wools are presented in Figure 1. Although some small changes in the DTA curves appeared at 100°–150°C and in the wool decomposition region above 200°C, the most significant differences were seen in the region below 100°C. The endothermic transition noted in this region can be attributed to loosely bound water.[5] A smaller water desorption isotherm was noted for wool irradiated in DMSO, and the presence of polymer grafted onto the wool tended to further alter the size and shape of the desorption isotherm.

The nature of the polymer graft and the effect of irradiation in DMSO on the surface of the wool were determined using a scanning electron micro-scope (Fig. 2). Irradiation of wool in DMSO under nitrogen (Fig. 2b) had little effect on the wool; however, similar irradiation under oxygen resulted in significant weathering of the wool surface. Also, striations were ap-parent between scales and scale fragments along the fiber surface (Fig. 2c). The nature of the polymer graft on the surface of the fiber was dependent on the particular polymer grafted to the fiber. With methyl (Fig. 2d) and n-butyl acrylate (Fig. 2e) polymer grafts, the coating of polymer on the

fiber surface was uneven and irregular, with small nodes of polymer appearing randomly on the surface.   Higher concentrations of polymer along scale edges and lifted scale edges were noted.   Wools grafted with poly(methyl methacrylate) (Fig. 2f) and poly(n-butyl methacrylate) (Fig. 2g) were regular and even, but also had some nodes of grafted polymer along the fiber.   The wool containing poly(n-butyl methacrylate) had some cracking in the polymer grafted to the fiber surface.
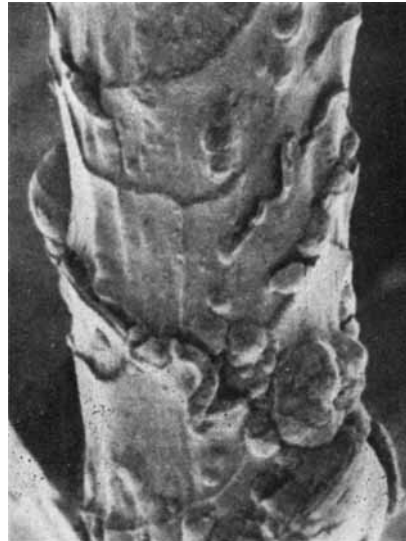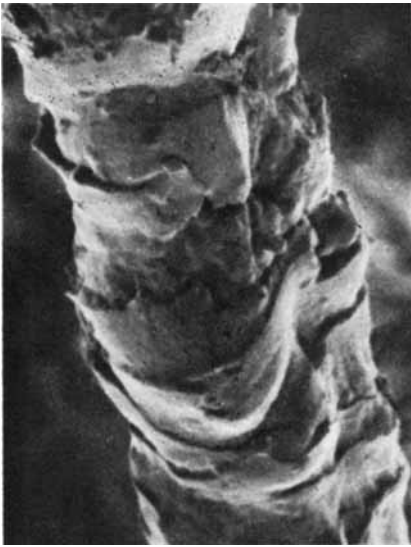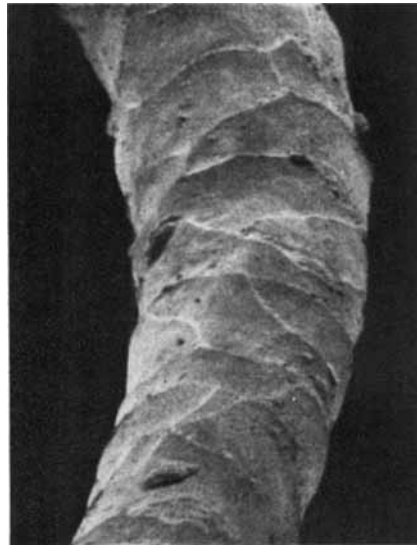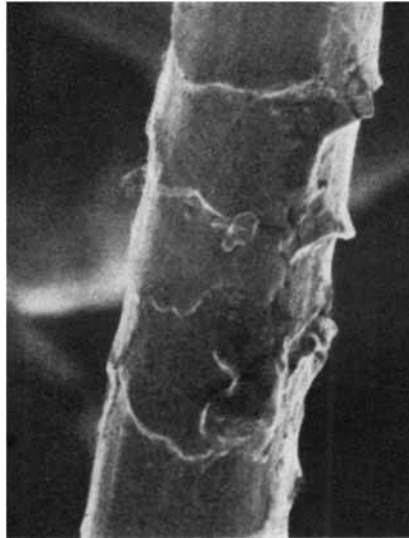

(a)
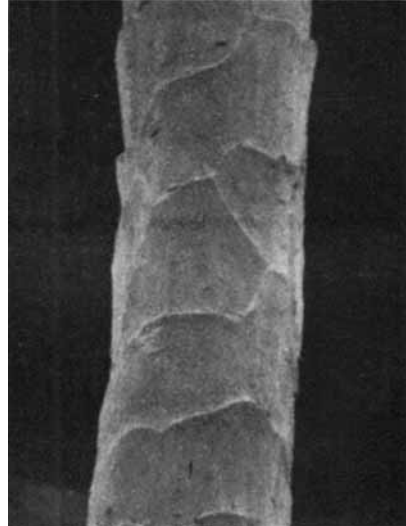
(b)

(c)

(d)

Fig. 2 (continued)

(e)

(f)

(g)

Fig. 2. Surface of control and grafted wools by scanning electron microscopy: (a) wool control; (b) wool irradiated in DMSO underN₂; (c) wool irradiated in DMSO under O₂; (d) wool–2.0% poly(methyl acrylate) graft; (e) wool–4.8% poly(n-butyl acrylate) graft; (f) wool–2.1% poly(methyl methacrylate) graft; (g) wool–10.1% poly-(n-butyl methacrylate) graft.

References

1. G. O. Schenck and C. H. Krauch, *Chem. Ber.*, **96**, 517 (1963).
2. K. Eskins and M. Friedman, *Amer. Chem. Soc., Polymer Preprints*, **9**, 461 (1968).
3. K. Eskins and M. Friedman, *J. Macromol. Sci.-Chem.*, **A4**(4), 947 (1970).
4. H. L. Needles, *Text. Res. J.*, **35**, 298 (1965).
5. E. Menefee and G. Yee, *Text. Res. J.*, **35**, 801 (1965).