

Flame Resistant Cotton by Photoinitiated Graft Copolymerization*

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Synopsis

Photoinitiated, free-radical reaction of cotton fabric with vinyl phosphonate oligomer (molecular weight 500–1000) and N-methylolacrylamide monomer from aqueous solutions to form copolymer gave a textile product that had flame resistance (FF 5-74 test). The initiating free radicals were formed on the cellulose molecule when cotton fabric was exposed to ultraviolet radiation. The effects of wavelengths of ultraviolet radiation (254, 300, and 350 nm), reaction time (0–9 ksec), solids in solution (10%–60%), atmosphere (air, nitrogen, and oxygen), and oligomer-to-monomer concentration (1:0.00 to 1:1.20 mole ratio) on efficiency of monomer and oligomer conversion to copolymer (maximum efficiency 70%–80%) were determined. Evaluation of the flame resistant cotton fabric by transmission electron microscopy showed deposits of copolymer throughout the cross sections of the fibers. However, scanning electron microscopy and energy-dispersive x-ray analysis showed that copolymer and phosphorus tended to be more concentrated between and on the surfaces of the fibers.

INTRODUCTION

The development of processes for applying flame retardant compounds to textile fabrics continues to be of interest. Particularly, processes that would increase the durability of these fabrics to laundering, dry cleaning, and normal usage are needed.¹ Also, flame retardant compounds that are soluble in water and are almost totally chemically bonded to textile fibers during the process would minimize aqueous and nonaqueous washing of the treated fabrics and formation of effluents that contain environmental pollutants.

Free radical-initiated reactions of polysaccharides with vinyl monomers have been reported extensively.² The products of these reactions have a high degree of stability and can have a high degree of conversion of monomer to polyvinyl copolymer. Near-ultraviolet radiation has been used in unsensitized free-radical reactions to initiate copolymerization of vinyl monomers with cellulose.²⁻⁹

This report will deal with unsensitized, photoinitiated polymerization of N-methylolacrylamide and vinyl phosphonate oligomer from aqueous solutions with cotton fabrics to impart flame retardancy. The effects of wavelength of ultraviolet light, oligomer-to-monomer concentration, and other experimental factors on graft copolymer composition, distribution of the copolymer in the fibrous structure, and flame retardancy are reported.

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EXPERIMENTAL

Materials

Cotton fabrics used were commercial grey printcloth (about 0.115 kg/m², 3.31 threads/mm × 3.03 threads/mm). The fabrics were desized, alkali scoured, bleached, washed with water, and air dried. Samples of the fabrics were equilibrated overnight in air at about 298 K and 45% R.H. to constant weight.

A polyunsaturated vinyl phosphonate oligomer (VP) (molecular weight 500–1000; 22–23 wt. % phosphorus) that was made by condensation polymerization of vinyl phosphonate monomer^{10–12} and designated FYROL 76 was obtained from the Stauffer Chemical Company. The oligomer was soluble in water. N-Methylolacrylamide (NMA), a commercial product, was used as received. Other chemicals used were reagent grade.

Methods

The ultraviolet light sources used were Rayonet Photochemical Reactors (RPR) manufactured by the Southern New England Ultraviolet Company. The RPR-100 reactor was equipped with a set of 16 tube-type lamps mounted vertically around the inside walls of a cylindrical chamber (0.25 m diameter and 0.38 m long). The RPR-208 reactor was equipped with a set of eight modules that contained U-shaped tube-type lamps arranged to form a circular chamber (0.33 m diameter and 0.48 m long). The reactors gave sources of radiant energy with about 85%–90% of the light in the desired wavelength range. The reactors generated watts of ultraviolet energy as follows: RPR-100—254 nm (35 W), 300 nm (21 W), 350 nm (24 W); RPR-208—254 nm (120 W), 300 nm (85 W), 350 nm (100 W).

Samples of fabric about 0.25 × 0.41 m for RPR-100 and about 0.38 × 0.81 m for RPR-208 were immersed in an aqueous solution of vinyl phosphonate oligomer and N-methylolacrylamide at 298 K and then padded to the desired wet pickup by a two dip–two nip process. These treated samples, either in air-dried

TABLE I
Effects of Wavelength of Ultraviolet Light and Reactor Vessel on Photoinitiated Conversion of Vinyl Phosphonate Oligomer and N-Methylolacrylamide to Copolymer Add-on on Cotton Printcloth^a

Reaction time, ksec	Reactor vessel	Copolymer add-on, %/MJ			
		254 nm ^b	300 nm ^b	300 nm ^c	350 nm ^b
0.3	quartz	1047	1587	2380	1667
0.6	quartz	618	1429	1350	903
1.2	quartz	405	793	793	521
1.8	quartz	302	582	556	417
1.8	Pyrex	121	264	233	393
3.6	quartz	175	370	331	255

^a Atmosphere, nitrogen; mole ratio of vinyl phosphonate oligomer to N-methylolacrylamide, 1:0.80; solids in solution, 40%; wet pickup, 100%. Copolymer add-on shown at three different wavelengths (in nm).

^b Cotton printcloth irradiated dry.

^c Cotton printcloth irradiated wet.

TABLE II
Effects of Atmosphere on Photoinitiated Conversion of Vinyl Phosphonate Oligomer and N-Methylolacrylamide to Copolymer Add-on on Cotton Printcloth^a

Atmosphere	Reaction flush time, sec	Reactor vessel	Reaction time, ksec	Copolymer add-on, %
Air	—	quartz	1.8	9.1
Air	—	quartz	3.6	18
Oxygen	60	quartz	1.8	0.62
Nitrogen	60	quartz	1.8	45
Nitrogen	180	quartz	1.8	44
Nitrogen	180	Pyrex	1.8	34
Nitrogen	180	quartz	3.6	49
Nitrogen	180	Pyrex	3.6	43

^a Ultraviolet light, 300 nm; mole ratio of vinyl phosphonate oligomer to N-methylolacrylamide, 1:0.66; solids in solution, 60%; wet pickup, 100%.

or wet pickup states, were wrapped around and fastened to cylinders that were made of stainless steel hardware cloth. The cylinders were about 0.41 m in circumference and 0.25 m long for the RPR-100 reactor and about 0.81 m in circumference and 0.38 m long for the RPR-208 reactor. These samples were placed in Pyrex or quartz reactor vessels that were then closed, and the atmosphere was exchanged with nitrogen. These vessels were placed in the reactors and photoirradiated. The ambient temperatures of the reactors increased from about 296 to 318 K during the initial 300 sec of photoirradiation. Some samples that

TABLE III
Effects of Concentrations of Vinyl Phosphonate Oligomer and N-Methylolacrylamide in Treating Solutions and of Selected Reaction Conditions on Concentrations of Oligomer and Monomer in the Copolymer on the Fabric

VP:NMA, ^a mole ratio	Solids content, %	Wet pickup, %	Wavelength, nm	Reac- tion time, ksec	Copolymer add-on, %	VP:NMA on fabric, mole ratio
1:0.60	60	100	300	5.1	36	1:0.97
1:0.80	60	97	300	4.2	31	1:1.48
1:1.00	60	99	300	3.3	35	1:1.72
1:1.20	60	99	300	3.0	33	1:2.95
1:0.60	60	104	300	0.6	25	1:1.26
1:0.60	60	104	300	1.2	34	1:0.91
1:0.60	60	104	300	1.8	36	1:1.00
1:0.60	60	100	300	5.1	36	1:0.97
1:0.80	40	96	254	1.8	19	1:1.30
1:0.80	40	96	300	1.8	22	1:1.44
1:0.80	40	96	300 ^b	1.8	22	1:1.91
1:0.80	40	96	350	1.8	18	1:1.28
1:0.60	60	99		control		1:0.75
1:0.60	47	117		control ^c		1:0.64
1:0.80	51	98		control ^d		1:0.84

^a VP, vinyl phosphonate oligomer; NMA, N-methylolacrylamide; mole ratio calculated on basis of nitrogen and phosphorus contents.

^b Cotton printcloth irradiated wet.

^c Solution contained 5% dimethyloldihydroxyethyleneurea; 0.5% ZnNO₃.

^d Solution contained fabric softener (Velvetol, 4%) and a wetting agent (Triton-X100, 0.1%).

were fastened on the stainless steel cylinders were placed directly in the RPR-208 reactor, and the atmosphere was exchanged with nitrogen. These samples were then photoirradiated.

After the desired irradiation time, the fabrics were removed from the reactors, washed in hot water to remove unreacted oligomer and monomer, allowed to line dry, and pressed with a cool iron on a wool setting (about 500 K). After equilibration to constant weight at about 298 K and 45% R.H., the increase in weight of the photoirradiated, modified fabric, as compared with the weight of an equivalent sample of unmodified fabric, was recorded as copolymer add-on. The efficiency of conversion of monomer and oligomer to copolymer add-on was calculated as (copolymer add-on)/(solids in wet pickup).

The photoirradiated, modified fabrics were laundered and dried in accordance with AATCC Test Method 124-1969,¹³ as specified in the standards.¹⁴ Flammability measurements were made in accordance with standards.¹⁴ The amounts of phosphorus present in the samples were determined by the reduced molybdate colorimetric method.¹⁵ The amounts of nitrogen present were determined by the Kjeldahl method.¹⁶ Physical properties of the fabrics were determined by ASTM methods for breaking strength,^{17a} tearing strength,^{17b} flex abrasion resistance,^{17c} and conditioned and wet wrinkle recovery.^{17d}

Microscopic analyses¹⁸ were used to determine the interaction between cellulose and vinyl phosphonate oligomer-poly(N-methylolacrylamide) and the location of the oligomer-polymer within the fibrous cross section (transmission electron microscopy); surface areas of deposits of oligomer-polymer (scanning electron microscopy); and phosphorus location within the fibrous cross section (energy-dispersive x-ray analysis).

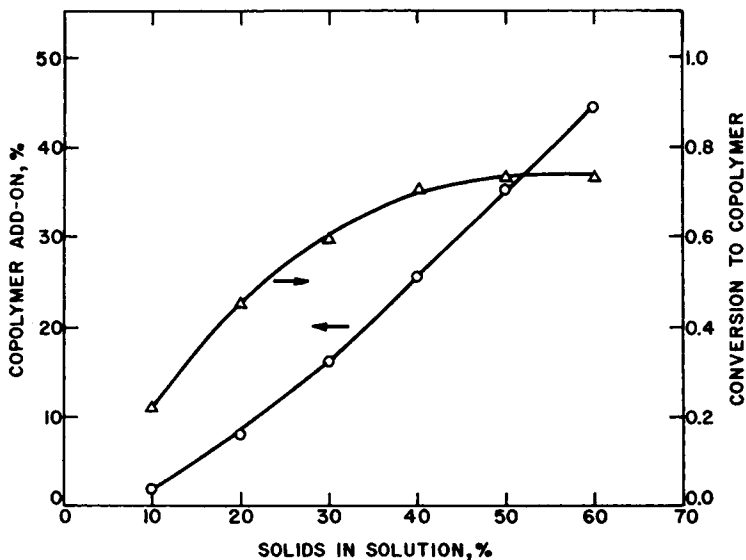
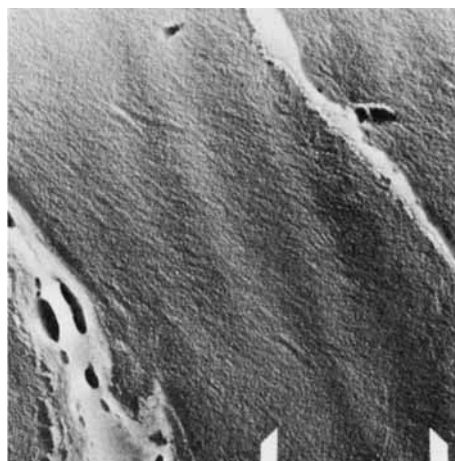
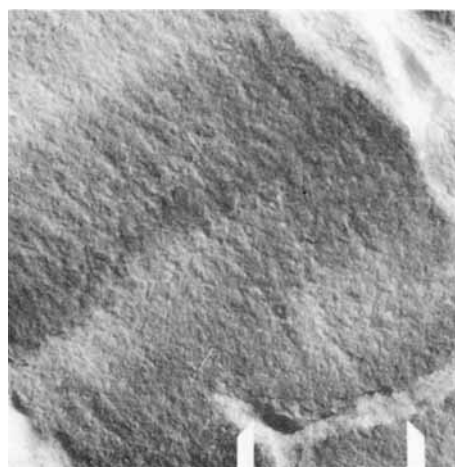


Fig. 1. Effects of concentrations of vinyl phosphonate oligomer and N-methylolacrylamide monomer in aqueous solution on copolymer add-on and conversion of oligomer and monomer to copolymer. (VP:NMA, 1:0.80 mole ratio in aqueous solution; wet pickup, 85%–100%; 300 nm, 1.8 ksec.)



(a)



(b)

Fig. 2. TEM cotton fiber cross section from printcloth treated with vinyl phosphonate oligomer and N-methylolacrylamide. (VP:NMA, 1:0.60 mole ratio in 60% aqueous solution, wet pickup, 104%; 300 nm, 1.2 ksec; copolymer add-on, 34%, VP:NMA, 1:0.91). Distance between markers equals 1 μm : (a) cross section as is; (b) cross section extracted with 0.5M cupriethylenediamine dihydroxide.

RESULTS

The effects of wavelength of ultraviolet light and type of reactor vessel on photoinitiated conversion of vinyl phosphonate oligomer and N-methylolacrylamide to copolymer add-on on cotton printcloth are shown in Table I. The total power consumption in each case was about 400 watts. The effects of wavelength on copolymer add-on when a quartz reactor that absorbs a minimum amount of ultraviolet energy was used were 300 nm > 350 nm > 254 nm. When a Pyrex reactor that absorbs some ultraviolet energy below 350 nm was used, the copolymer add-on was reduced, and the effects of wavelength on copolymer add-on were 350 nm > 300 nm > 254 nm.

The effects of atmosphere and type of reactor vessel on photoinitiated conversion of vinyl phosphonate oligomer and N-methylolacrylamide to copolymer

TABLE IV
Effects of Machine Wash-and-Dry Cycles on Phosphorus and Nitrogen Contents of Modified Cotton Printcloth^a

VP:NMA, ^b mole ratio	Reaction time, ksec	Copolymer add-on, %	1 wash-and- dry cycle		25 wash-and- dry cycles		50 wash-and- dry cycles	
			P, %	N, %	P, %	N, %	P, %	N, %
1:0.60	5.1	36	3.41	1.42	3.17	1.45	3.00	1.32
1:0.80	4.2	31	2.59	1.57	2.25	1.62	2.40	1.64
1:1.00	3.3	35	2.23	1.63	2.32	1.87	2.30	1.88
1:1.20	3.0	33	1.55	1.87	1.40	2.05	1.56	2.08

^a Ultraviolet light, 300 nm; atmosphere, nitrogen; reactor vessel, none; solids in solution, 60%; wet pickup, 100%.

^b Same as footnote a, Table III.

TABLE V
Effects of Vinyl Phosphonate Oligomer and N-Methylolacrylamide Photoinitiated Polymerization on Some Textile Properties of Cotton Printcloth^a

VP:NMA, ^b mole ratio	Reaction time, ksec	Copolymer add-on, %	Breaking strength, N	Tearing strength, N	Flex abrasion, cycles	Wrinkle recovery angle, rad (W + F)		Stiffness, mNm
						Conditioned	Wet	
control	—	0	156	7.9	693	3.56	3.42	0.0192
1:0.60	6.3	38	111	2.4	89	4.66	4.45	0.112 (0.0305 ^d)
1:0.80	3.6	30	129	3.5	138	4.26	3.96	0.0814 (0.0531 ^d)
1:0.80 ^c	4.3	26	111	3.8	435	4.50	4.54	0.0701
1:1.00	4.4	30	125	2.8	96	4.08	4.31	0.180 (0.0407 ^d)
1:1.20	3.0	34	142	3.5	146	3.77	4.54	0.114 (0.0509 ^d)

^a Ultraviolet light, 300 nm; atmosphere, nitrogen; reactor vessel, none; solids in solution, 23%–51%; wet pickup, 100%.

^b Same as footnote a, Table III.

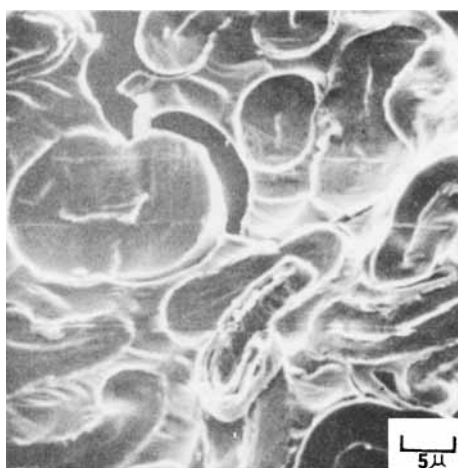
^c Oligomer-monomer solution contained a fabric softener (Velvetol, 4%) and a wetting agent (Triton-X100, 0.1%).

^d Measured after 50 machine wash-and-dry cycles.

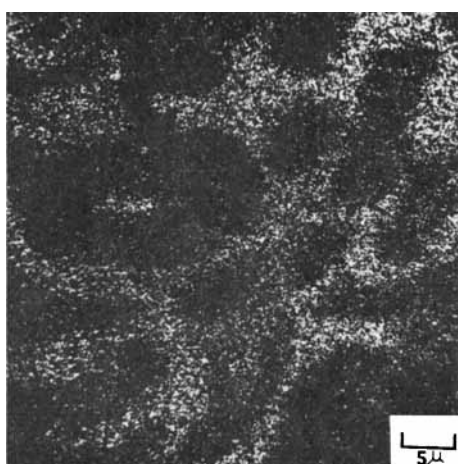
add-on on cotton printcloth are shown in Table II. In an atmosphere of air or oxygen, the conversion of oligomer and monomer to copolymer was reduced; however, in the photoreactor used, flushing the reactor with nitrogen before irradiation increased the copolymer add-on.

The effects of the concentrations of vinyl phosphonate oligomer and N-methylolacrylamide monomer in aqueous solution (mole ratio of VP to NMA 1:0.80) on copolymer add-on and conversion of oligomer and monomer to copolymer are shown in Figure 1. There were small variations in wet pickups on the fabric samples. The copolymer add-on increased with increase of solids in solution. The conversion of oligomer and monomer to copolymer reached a maximum efficiency at about 0.70 to 0.80, that is, 70% to 80%.

The effects of concentrations of vinyl phosphonate oligomer and N-methylolacrylamide monomer in treating solutions on the mole ratio of VP and NMA in the copolymer on the fabric are shown in Table III. When the VP-to-NMA



(a)



(b)

Fig. 3. EDX map showing location of phosphorus in cotton fiber cross sections (see Fig. 2(a) for preparation of sample): (a) fiber cross sections; (b) phosphorus location in Fig. 3(a).

mole ratio in solution ranged from 1:0.60 to 1:1.20 and the treated fabric samples were irradiated to yield approximately the same copolymer add-on, the VP-to-NMA mole ratio in the copolymer ranged from 1:0.97 to 1:2.95. The effects of copolymer add-on when the VP-to-NMA mole ratio in solution was 1:0.60 show that a lower copolymer add-on (25%) the NMA content of the copolymer was greater than at higher copolymer add-ons. When the VP-to-NMA mole ratio in solution was 1:0.80 and the treated fabrics were irradiated after drying, the effects of wavelength on the VP-to-NMA mole ratio in the copolymer were 254 nm, 1:1.30; 300 nm, 1:1.44; and 350 nm, 1:1.28. When treated fabric was irradiated wet at 300 nm, the VP-to-NMA mole ratio in the copolymer was 1:1.91. As shown in the treated, unirradiated control samples, the concentrations of NMA in the padded-on wet pickups were greater than in the treating solutions.

The durabilities of the VP and NMA copolymers on the irradiated, treated fabrics are shown in Table IV. The treated fabrics were irradiated to yield approximately the same copolymer add-on. The effects of wash-and-dry cycles on the phosphorus and nitrogen contents of the modified cotton printcloths are shown. The retention of phosphorus and nitrogen in the modified cotton printcloths through 50 wash-and-dry cycles indicates the durability of the treatment.

The effects of VP and NMA photoinitiated polymerization on some textile properties of cotton printcloth are shown in Table V. The breaking and tearing strength, flex abrasion, wrinkle recovery, and stiffness of the treated fabrics are compared with those of control fabric. Conventional flame retardant treatments of cotton fabrics usually cause similar changes in textile properties of fabrics.¹ The stiffness of the treated fabrics was increased over that of the control but was reduced after machine washing and drying. However, after 50 machine wash-and-dry cycles, their stiffness was greater than that of the control fabric. Compared with the control, all of the treated fabrics had harsh textile hands.

The effects of wash-and-dry cycles on flame resistance of VP-NMA-modified cotton printcloths are shown in Table VI. Samples were selected with about the same copolymer add-ons but with different ratios of VP to NMA in treating solutions. See Table III for details of preparation of these samples and Table IV for their phosphorus and nitrogen contents. Three of the samples passed the flammability test¹⁴ after 50 machine wash-and-dry cycles. The fourth sample, which had a much higher concentration of NMA than VP in the co-

TABLE VI
Effects of Machine Wash-and-Dry Cycles on Flame Retardance of Modified Cotton Printcloth^a

VP:NMA, ^b mole ratio	Reaction time, ksec	Copolymer add-on, %	1 ^d	Char length, mm ^c		
				10	25	50
1:0.60	5.1	36	61	69	61	66
1:0.80	4.2	31	64	58	69	79
1:1.00	3.3	35	66	74	69	61
1:1.20	3.0	33	66	69	99	107(4) BEL(1)

^a Same as footnote a, Table IV.

^b Same as footnote a, Table III.

^c FF 5-74 flammability test; char lengths less than about 175 mm pass; BEL, burned entire length, about 254 mm.

^d Number of wash-and-dry cycles.

polymer (VP:NMA 1:2.95 mole ratio), passed the test four times and failed one time.

Microscopic analyses¹⁸ of VP-NMA-modified cotton printcloth fabric that has flame retardance are shown in Figures 2 and 3. Copolymers of VP and NMA were deposited throughout the fibrous cross section, Figure 2(a), and were resistant to dissolution of 0.5M cupriethylenediamine dihydroxide, Figure 2(b), as shown by transmission electron microscopy. Heavy deposits of phosphorus occurred between the fibers, with some phosphorus within the fibrous cross section (Fig. 3), as shown by energy-dispersive x-ray analysis. Scanning electron microscopy of VP-NMA-modified fibrous cross sections also showed heavy copolymer deposition between the fibers.

Names of companies or commercial products are given solely for the purpose of providing specific information; their mention does not imply recommendation or endorsement by the U.S. Department of Agriculture over others not mentioned.

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