

Photoinitiated Polymerization of Glycidyl Methacrylate with Cotton Cellulose

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Synopsis

Unsensitized, photoinitiated polymerization reactions of glycidyl methacrylate from solutions of water and water-methanol with cotton cellulose fabrics were investigated. When several layers of cotton fabrics were immersed in solutions of glycidyl methacrylate and only the surface layer was exposed to light, polymerization reactions were initiated in this layer and also initiated in inner layers of fabrics, probably by chain transfer reactions. Photoinitiated (350 nm, 24 W, 34 min) polymerizations of glycidyl methacrylate (7.5 vol-%) from water (43 vol-%)-methanol (57 vol-%) with cotton fabrics in one-, three-, and six-layered configurations were: one-layered, 32% polymer; three-layered, 30%, 27%, and 25% polymer; and six-layered, 29%, 25%, 22%, 20%, 14%, and 11% polymer. Electron-microscopic examination of the distribution of poly(glycidyl methacrylate) within the cotton fibrous structure showed that polymer was distributed throughout the cross section of the fiber. At the surface of the fibers, the polymer tended to be more concentrated than within the cross section of the fibers and to encapsulate them. Photoinitiated polymerization reactivities of several vinyl monomers from solution with cotton cellulose fabrics were compared with those of glycidyl methacrylate as follows: methyl methacrylate > glycidyl methacrylate > diacetone acrylamide > 1,3-butylene dimethacrylate > methacrylic acid > acrylonitrile > divinylbenzene.

INTRODUCTION

Development of textile finishing processes based on use of ultraviolet light to initiate free-radical chain reactions can be divided into four classes: graft polymerization reactions of vinyl monomers to modify textile fibers macromolecularly; crosslinking reactions between chemically modified fibers; homopolymerization of vinyl monomers on and within fibrous textile structures; and oxidative depolymerization reactions of the textile fibers. Modifications of the properties of cellulose in the solid state by photoinitiated reactions, including oxidative depolymerization,¹⁻¹⁵ crosslinking,¹⁶⁻²¹ and graft and homopolymerization,^{1,22-47} have been reported. The energy from the incident ultraviolet light is postulated to be absorbed by sensitizer, monomer, and/or polymer,⁴⁸⁻⁵⁶ or by an electron band structure of the excited cellulose molecule.⁵⁷ In the reactions initiated, activated intermediates that involve formation of free radicals occur.^{8,52,58-64} Homopolymer formation on and within fibrous textile structures generally imparts nondurable properties and increases the stiffness of textiles. Oxidative depolymerization reactions of fibers generally lead to a decrease in the tensile properties of the textiles.

This report will deal with unsensitized, photoinitiated polymerization of glycidyl methacrylate and other monomers from solutions with cotton fabrics. The absorption of the energy of ultraviolet light by these unsensitized systems

results in the formation of initiating free radicals on the cellulose fibers, thereby minimizing homopolymer formation.⁴² The effects of wavelength of the incident ultraviolet light and of other experimental factors on polymerization of vinyl monomers on the textiles and distribution of the polymers within their fibrous structures are reported.

EXPERIMENTAL

Materials

Cotton fabric, a commercial grey print cloth (about 3.4 oz/yd², 86 × 76), was desized, alkali scoured, peroxide bleached, washed with water, and air dried. Samples of the fabric were equilibrated overnight in air at about 25°C and 45% R.H. to constant weight. Acrylonitrile, 1,3-butylene dimethacrylate, divinylbenzene, glycidyl methacrylate, methacrylic acid, and methyl methacrylate were obtained from a commercial source and were treated with activated alumina (80–200 mesh Al₂O₃), as previously described.⁶⁵ Diacetone acrylamide, a commercial product with a melting point of 57°C, was used as received. Other chemicals used were reagent grade.

Methods

The ultraviolet light source was a Rayonet Photochemical Reactor manufactured by the Southern New England Ultraviolet Co. The reactor was equipped with a set of 16 tube-type lamps (0.5 in. diameter, 12 in. length) mounted vertically around the inside walls of a cylindrical chamber (10 in. diameter, 15 in. length) and gave a source of radiant energy with about 85–90% of the light in the desired wavelength range, for example, 254, 300, or 350 nm.

Samples of cotton fabric (3.5 × 10 and 5 × 10 in.) were wrapped around Pyrex tubes with circumferences of about 3.5 and 5 in., respectively, so that during irradiation only one side of the fabric was exposed to ultraviolet light. These samples were then immersed in solutions of monomers in either quartz or Pyrex reactor cylinders. The reactor cylinders with walls about 0.1 in. thick were about 3 in. from the lamps. The thickness of the solution between the walls of the cylinders and the fabrics was less than 0.1 in. The solutions were purged with nitrogen and evacuated to about 25 torr at about 23°C for 2 min. The vacuum on the samples was released with nitrogen; then the samples were irradiated under nitrogen, usually at an initial temperature of about 23°C, with the temperature increasing to about 45°C in the reactor after about 5 min of irradiation. Alternatively, before irradiation, the samples were preheated in a water bath to a temperature of about 50°C; then, during irradiation, the temperature of the samples ranged between 45° and 50°C.

After the desired irradiation time, the fabrics were removed from the Pyrex tubes, extracted at about 25°C with methyl ethyl ketone for about 20 min to remove monomer, thoroughly washed in hot water, and dried in an air oven at about 60°C for 45 min. These samples were equilibrated overnight in air at about 25°C and 45% R.H.

The samples were then Soxhlet extracted with methyl ethyl ketone at 80°C for about 36 hr to remove any homopolymer. They were washed with water,

dried in an air oven at about 60°C for 45 min, and again equilibrated overnight in air at about 25°C and 45% R.H. to constant weight. The increase in weight of these extracted samples, as compared with that of untreated fabric, was recorded as polymer add-on.

Similar experiments were conducted in which three and six layers of cotton fabrics were wrapped around Pyrex tubes, so that during irradiation only the outer layer of fabric (no. 1) was directly exposed to ultraviolet light. The layers were numbered, no. 1 being the outer layer and nos. 2–6 the inner ones. Layer no. 6, therefore, was shielded from direct exposure to ultraviolet light by five layers of fabric.

The distribution of poly(glycidyl methacrylate) within the fibrous cotton–poly(glycidyl methacrylate) structure was determined by electron-microscopic observations of ultrathin sections.⁶⁶ To observe regions of strong interactions between cotton and poly(glycidyl methacrylate) that were probably covalent linkages, as well as the effects of ultraviolet light on the ultrastructure of the fibrous polymer, sections were immersed in 0.5*M* cupriethylenediamine dihydroxide (CED) and then treated as previously described.^{65,67}

RESULTS AND DISCUSSION

The effects of wavelength of ultraviolet light on photoinitiated polymerization of glycidyl methacrylate from stabilizer-free and nitrogen-purged aqueous methanol solutions with cotton cellulose are shown in Table I. The total power consumption in each case was about 400 watts. However, the power of the lamps in ultraviolet wattage output varied and is recorded in Table I. The effects of wavelength on polymer add-on were: 300 nm > 350 nm > 254 nm. Homopolymer formation was less than 2%. For example, at a wavelength of 350 nm, poly(glycidyl methacrylate) homopolymer formation ranged from about 0.5%–1.1% at polymer add-on of about 30%. The effects of wavelength on homopolymer formation were: 300 nm >> 254 nm > 350 nm.

When quartz reactors that absorb a minimum amount of ultraviolet light energy were used, polymer add-on was slightly greater with ultraviolet light (254 and 300 nm) than when Pyrex reactors that absorb some ultraviolet light energy (below 350 nm) were used. Polymer add-on for ultraviolet light (350 nm) was about equal in either quartz or Pyrex reactors. If ultraviolet light (350 nm) that generates the maximum concentration of cellulosic radicals⁵⁷ were to be used

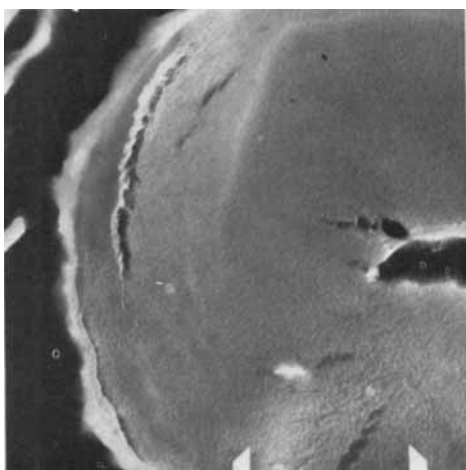
TABLE I
Effect of Wavelength and Type of Reactor on Photoinitiated Copolymerization of Glycidyl Methacrylate with Cotton Cellulose^a

Wavelength, nm	Power, W	Reaction time, min	Polymer add-on, %	
			Quartz reactor	Pyrex reactor
254	35	30	22	18
300	21	30	61	53
350	24	30	32	32
350	24	60	69	72

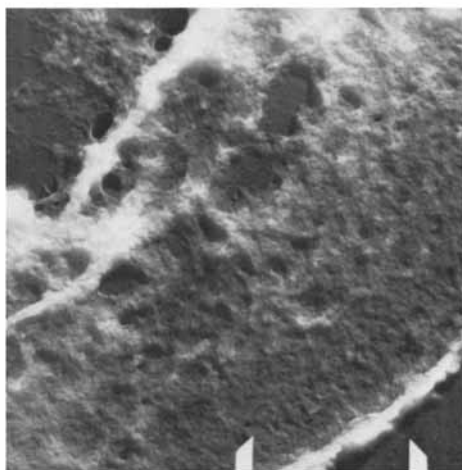
^a *T* = 23–45°C; solvent, 57 vol-% methanol plus 43 vol-% water; monomer concentration, 7.5 vol-%; solution/cellulose, 50 ml/g.

as the initiator, Pyrex reactors could be used to exclude oxygen during the polymerization reaction.

The distribution of poly(glycidyl methacrylate) within the cotton fibrous structure was apparently independent of wavelength of ultraviolet light [see Fig. 1(a) (254 nm), Fig. 2(a) (300 nm), and Fig. 3(a) (350 nm)]. The polymer was distributed throughout the cross sections of the fibers but tended to be more concentrated at their outer surfaces and to encapsulate them. When cross sections of the fibrous polymers were immersed in 0.5*M* CED, their structures were retained. Apparently there was some interaction between cellulose and poly(glycidyl methacrylate) that reduced the solubility of cellulose in CED [see Fig. 1(b) (254 nm), Fig. 2(b) (300 nm), and Fig. 3(b) (350 nm)].

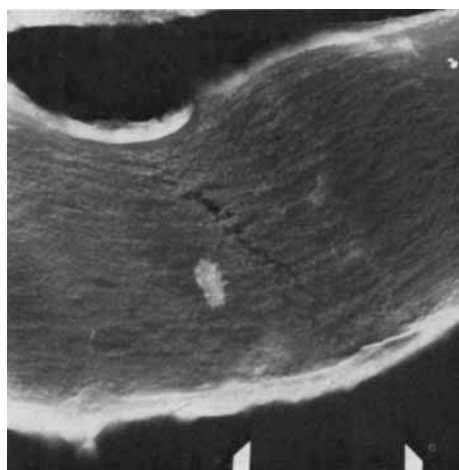


(a)



(b)

Fig. 1. Poly(glycidyl methacrylate)-cotton cellulose copolymer; quartz reactor; 254 nm, 35 W, 30 min; polymer add-on, 22%. For other conditions see footnote to Table I: (a) section as is (27,600 \times); (b) section (a) after CED immersion for 30 min (27,600 \times).



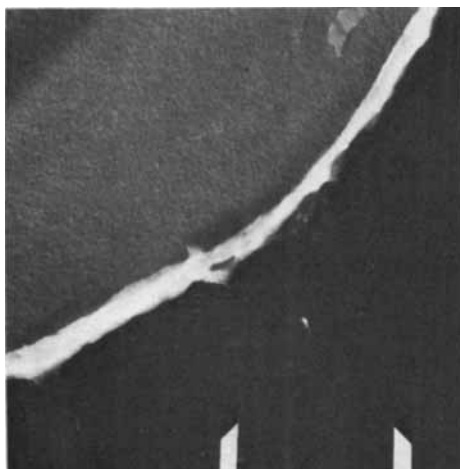
(a)



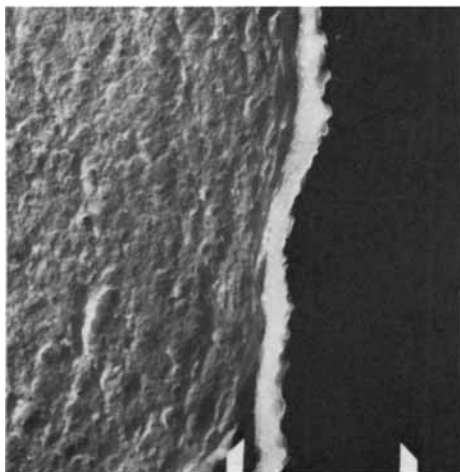
(b)

Fig. 2. Poly(glycidyl methacrylate)-cotton cellulose copolymer; quartz reactor; 300 nm, 21 W, 30 min; polymer add-on, 61%. See footnote Table I: (a) section as is (27,600 \times); (b) section (a) after CED immersion for 30 min (27,600 \times).

The effects of oxygen and monomer stabilizer on photoinitiated polymerization of glycidyl methacrylate from aqueous methanol solutions with cotton cellulose are shown in Table II. The presence of oxygen in both air and monomer solution and of monomer stabilizer reduced polymer add-on; compare reaction no. 1 with no. 7 for a given exposure to ultraviolet light (350 nm, 12 W-hr). Oxygen dissolved in the monomer solution was apparently the most critical factor in reducing polymer add-on under the experimental conditions used; compare reaction no. 2 with nos. 3-6. It has been reported that when cotton cellulose is exposed to ultraviolet light, macrocellulosic free radicals are formed⁸ and that these radicals serve as initiating sites for the polymerization of vinyl monomers with cellulose.⁴² Oxygen dissolved in the monomer solution probably reacts with



(a)



(b)

Fig. 3. Poly(glycidyl methacrylate)-cotton cellulose copolymer; quartz reactor; 350 nm, 24 W, 30 min; polymer add-on 32%. See footnote Table I: (a) section as is (27,600 \times); (b) section (a) after CED immersion for 30 min (27,600 \times).

the chain propagating radical that originates on polymerization of the vinyl monomer and terminates the reaction, thereby decreasing polymer add-on.

The effects of monomer concentration on photoinitiated polymerization of glycidyl methacrylate from aqueous methanol solutions with cotton cellulose are shown in Figure 4. Polymer add-on was directly related to monomer concentration. As the ratio of monomer solution to cotton cellulose increased, there was a slight reduction in polymer add-on at a given monomer concentration.

The effects of solvent composition on photoinitiated polymerization of glycidyl methacrylate from aqueous methanol solutions with cotton cellulose are shown in Figure 5. Polymer add-on was directly related to water content of the aqueous methanol to about 50 vol-% water. At water contents above 50 vol-%, the monomer solution separated into two phases, and polymer add-on decreased.

TABLE II
Effect of Monomer Stabilizer and Oxygen on Photoinitiated Copolymerization of Glycidyl Methacrylate with Cotton Cellulose^a

Experimental condition before reaction ^b	Reaction number	Polymer add-on, %						
		1	2	3	4	5	6	7
Monomer, stabilizer, removed		+	-	+	+	+	-	-
Solution, purged with nitrogen		+	+	+	-	-	-	-
Vacuum (25 torr), applied to solution and released with nitrogen		+	+	-	+	-	+	-
		32	27	21	15	8.0	3.6	2.4

^a Quartz reactor: $T = 23-45^{\circ}\text{C}$, 350 nm, 30 min, 24 W; solvent, 57 vol-% methanol plus 43 vol-% water; monomer concentration, 7.5 vol-%; solution/cellulose, 50 ml/g.

^b +, Experimental action taken; -, no action taken.

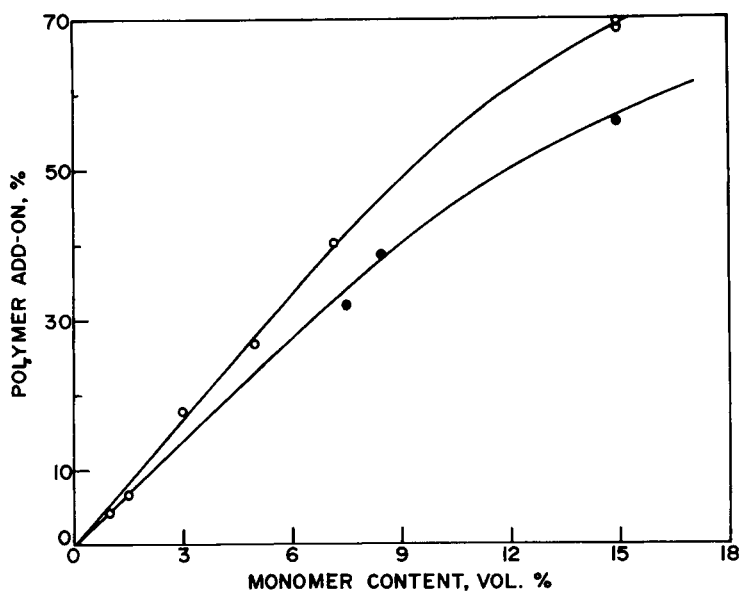


Fig. 4. Effects of monomer concentration on photoinitiated copolymerization of glycidyl methacrylate with cotton cellulose; quartz reactor; $T = 23-45^{\circ}\text{C}$; 350 nm, 24 W, 34 min; solvent, 57 vol-% methanol plus 43 vol-% water: (●) solution/cellulose, 50 ml/g; (○) solution/cellulose, 24 ml/g.

The effects of reaction time and temperature on photoinitiated polymerization of glycidyl methacrylate from aqueous methanol solutions with cotton cellulose are shown in Figure 6. Polymer add-on was directly related to reaction time and temperature.

The effects of multilayered fabrics on photoinitiated polymerization of glycidyl methacrylate from aqueous methanol with cotton cellulose in which only the external layer of fabric was irradiated directly by ultraviolet light are shown in Table III. Polymer add-on in one-, three-, and six-layered fabric configurations was about the same in the external layer on exposure to ultraviolet light (350 nm, about 14 W-hr). There was a decrease in polymer add-on in the fabric layers that were not directly exposed to ultraviolet light. Photoinitiated polymerization of glycidyl methacrylate with fabrics that were not directly exposed to ultraviolet light probably occurred by chain transfer reactions. The ratio of monomer so-

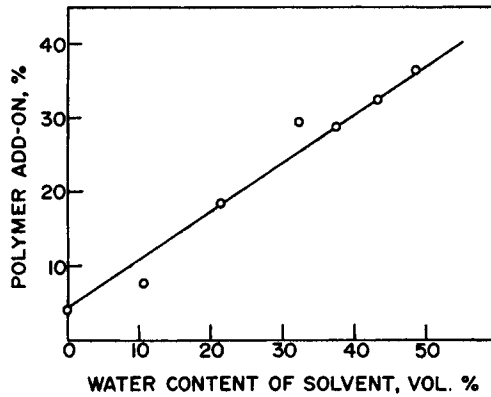


Fig. 5. Effects of water content of solvent on photoinitiated copolymerization of glycidyl methacrylate with cotton cellulose; quartz reactor; $T = 23\text{--}45^\circ\text{C}$; 350 nm, 24 W, 30 min; solvent, methanol plus water; monomer concentration, 7.5 vol-%; solution/cellulose, 50 ml/g.

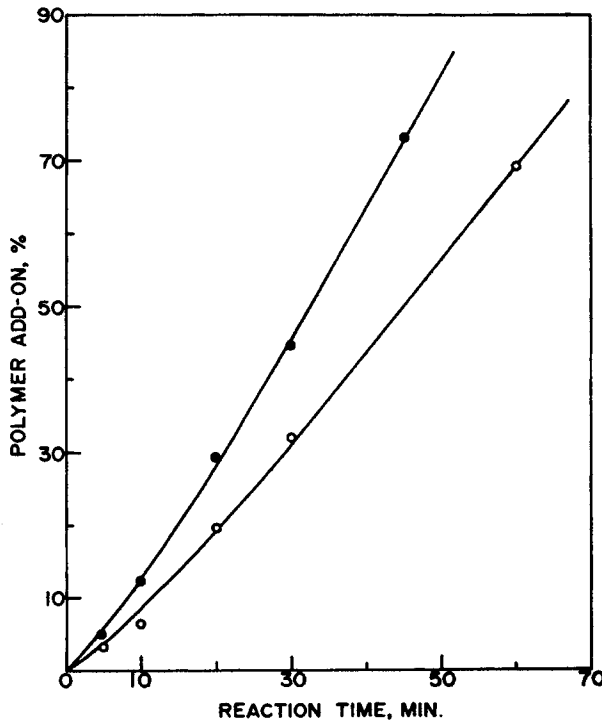


Fig. 6. Effects of reaction time on photoinitiated copolymerization of glycidyl methacrylate with cotton cellulose; quartz reactor; 350 nm, 24 W, solvent, 57 vol-% methanol plus 43 vol-% water; monomer concentration, 7.5 vol-%; solution/cellulose, 50 ml/g; T : (○) $23\text{--}45^\circ\text{C}$; (●) $45\text{--}50^\circ\text{C}$.

lution to cotton cellulose (see Table III, footnotes c-e) varied and probably slightly influenced polymer add-on (compare with results in Fig. 4). However, in order to maintain the same physical configuration and dimensions so that ultraviolet light wattage per unit area was constant, the ratio of monomer solution to cotton cellulose decreased with increased number of layers of fabric.

Photoinitiated polymerization reactivities of selected monomers from aqueous

TABLE III
Effect on Multilayered Fabrics on Photoinitiated Copolymerization of Glycidyl Methacrylate with Cotton Cellulose^a

Fabric layer no. ^b	Polymer add-on, %		
	Number of fabric layers 1 ^c	3 ^d	6 ^e
1	32	30	29
2	—	27	25
3	—	25	22
4	—	—	20
5	—	—	14
6	—	—	11

^a Quartz reactor: $T = 23-45^{\circ}\text{C}$, 350 nm, 34 min, 24 W; solvent, 57 vol-% methanol plus 43 vol-% water; monomer concentration, 7.5 vol-%.

^b Only external fabric layer no. 1 irradiated directly by near-ultraviolet light.

^c Solution/cellulose = 50 ml/g.

^d Solution/cellulose = 17 ml/g.

^e Solution/cellulose = 8 ml/g.

methanolic solutions with cotton cellulose are compared with glycidyl methacrylate in Table IV. Water was added to methanolic monomer solutions in a maximum amount, so that solutions of only one phase were obtained. The optimum compositions of the aqueous methanolic solutions of the different monomers for photoinitiated polymerization with cotton cellulose were determined, as reported for glycidyl methacrylate. Maximum polymer add-on, derived from each monomer by photoinitiated polymerization, occurred on cellulose at these compositions of solutions. When acrylonitrile and divinylbenzene were used, N,N-dimethylformamide was added to effect solution and to obtain only one phase. Monomers copolymerized from aqueous methanol solutions with cotton cellulose were more reactive than those copolymerized from solutions that contained N,N-dimethylformamide. Under the experimental conditions used, methyl methacrylate was the most reactive monomer.

Trade names are given as part of the exact experimental conditions. Mention of a trademark or proprietary product does not constitute a guarantee or warranty of the product by the U. S. Department of Agriculture and does not imply its approval to the exclusion of other products that may also be suitable.

TABLE IV
Comparison of Photoinitiated Copolymerization of Selected Monomers with Cotton Cellulose^a

Monomer ^b	Solvent system			Monomer concentration, vol-%	Reaction time, min	Polymer add-on, %
	Water, vol-%	Methanol, vol-%	DMF, ^c vol-%			
MMA	47	53	—	7.5	30	38
GMA	43	57	—	7.5	30	32
DAA	50	50	—	7.5	30	21
BDMA	33	67	—	7.5	60	18
MAA	50	50	—	15	30	9.2
AN	78	8	14	7.5	60	5.8
DVB	—	67	33	14	60	0.8

^a Quartz reactor: $T = 23-45^{\circ}\text{C}$, 350 nm, 24 W; solution/cellulose, 50 ml/g.

^b MMA, Methyl methacrylate; GMA, glycidyl methacrylate; DAA, diacetone acrylamide; BDMA, 1,3-dibutylene dimethacrylate; MAA, methacrylic acid; AN, acrylonitrile; DVB, divinylbenzene.

^c DMF, N,N-dimethylformamide.

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