Photoinitiated Polymerization of N-Methylolacrylamide with Crosslinked Cotton Cellulose

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Synopsis

The effects of crosslinking both unswollen and swollen cotton cellulose on the photoinitiated reactions of N-methylolacrylamide (NMA) with cotton are reported. Formaldehyde and dimethylolethyleneurea were used as crosslinking agents. Crosslinked cellulose had a decreased efficiency of photoconversion of NMA to poly(N-methylolacrylamide) (pNMA) with cotton. If the cellulose was crosslinked in the swollen state, increased dosages of ultraviolet radiation gave complete conversion of NMA to pNMA with cotton. Cotton that was crosslinked in the unswollen state probably restricted movement of the aqueous solution of NMA within the fiber and fabric structures and decreased chain propagation within the structures. This restriction resulted in decreased photoconversion of NMA to pNMA with cotton. Transmission and scanning electron microscopy of cotton cellulose that was crosslinked in the swollen state and of cotton cellulose that was crosslinked in the unswollen state showed that swollen cotton was less compacted than unswollen cotton.

INTRODUCTION

Macromolecular reactivity of modified cellulosic fibers has been of considerable interest. Hebeish, Kantouch, and El-Rafie have reported on the effects of crosslinking and chemical modification of cellulose on ceric ion-initiated grafting reactions with vinyl monomers.[1–5] Also, the macromolecular reactivities of the two most used crystalline forms of cellulose, lattice types I and II, with vinyl monomers can be controlled.[6–8] Reactions of ethyl acrylate[6,7] and styrene[8] with cellulose I and II were reported.

The effects of modification of cellulosic fibers on their photoinitiated macromolecular reactivity is of interest in developing photoprocesses. This report deals with the effects of crosslinking of cotton, in both unswollen and swollen states, on the photoinitiated reactions of N-methylolacrylamide with cellulose. Formaldehyde and dimethylolethyleneurea were used as crosslinking agents.

EXPERIMENTAL

Materials

The cotton fabric, a commercial grey printcloth (0.109 kg/m^2, 3.15 threads/mm by 3.15 threads/mm), was desized, alkali scoured, bleached, washed with water, and air dried. Samples of the fabric were equilibrated overnight in air at about 298 K and 45% R.H. to constant weight, as previously described.[9]

N-Methylolacrylamide (NMA), a commercial product in 60% aqueous solution,

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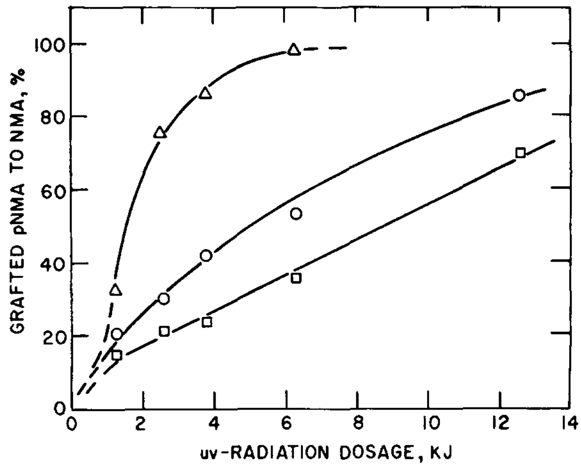


Fig. 1. Effects of formaldehyde crosslinking of cotton in the unswollen state on photoinitiated polymerization of N-methylolacrylamide (NMA) with cotton cellulose. Cellulose padded with aqueous solution that contained NMA (10%) to a wet pickup of about 85–90% by weight; irradiated in a quartz container in an atmosphere of nitrogen with 300 nm light; (△) cotton cellulose; (○) cotton cellulose–HCHO (0.37%); (□) cotton cellulose–HCHO (2.11%).

was obtained without inhibitor and was used as received. Dimethylolethyleneurea (DMEU) and formalin (37% formaldehyde) were also commercial products. Other chemicals used were reagent grade.

Crosslinked samples of fabric were prepared by reacting cellulose in the unswollen state with formaldehyde by a pad-dry-cure treatment[10] or in the swollen state by a wet treatment in concentrated phosphoric acid solution.[11] DMEU was also used to crosslink fabric by a pad-dry-cure treatment.[12]

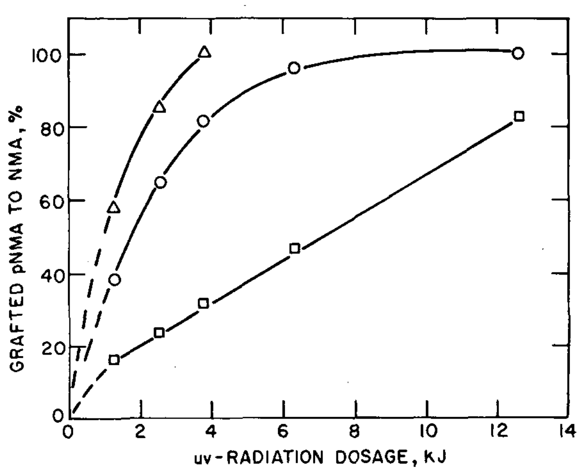


Fig. 2. Effects of formaldehyde crosslinking of cotton in both unswollen and swollen states on photoinitiated polymerization of N-methylolacrylamide (NMA) with cotton cellulose. Cellulose padded with an aqueous solution that contained NMA (10%) to a wet pickup of about 85–90% by weight; irradiated in a quartz container in an atmosphere of nitrogen with 300 nm light: (△) cotton cellulose; (○) cotton cellulose-HCHO (1.27%) swollen; (□) cotton cellulose–HCHO (1.15%) unswollen.

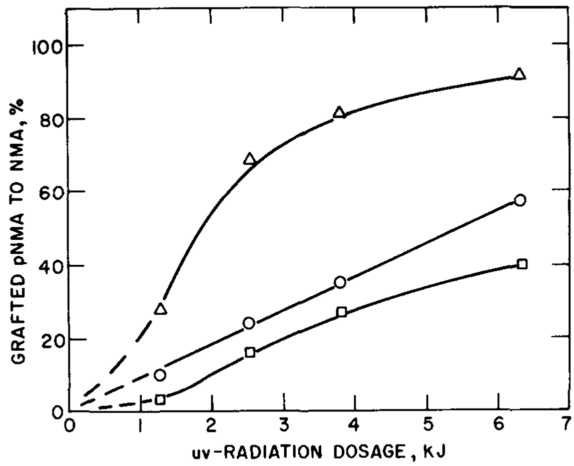


Fig. 3. Effects of dimethylolethyleneurea (DMEU) crosslinking of cotton on photoinitiated polymerization of N-methylolacrylamide (NMA) with cotton cellulose. Cellulose padded with aqueous solution that contained NMA (10%) to a wet pickup of about 85–90% by weight; irradiated in a quartz container in an atmosphere of nitrogen with 300 nm light: (△) cotton cellulose; (○) cotton cellulose–DMEU (0.55% N); (□) cotton cellulose–DMEU (1.75% N).

Methods

The ultraviolet light source was a Rayonet photochemical reactor RPR-100, manufactured by the Southern New England Ultraviolet Company. The reactor was equipped with a set of 16 tube lamps mounted vertically around the inside walls of a cylindrical chamber (0.25 m in diameter and 0.38 m long). The reactor gave a source of radiant energy with about 85–90% of the light in the desired wavelength range. The reactor generated 21 W of ultraviolet energy at 300 nm, previously reported to be the optimum wavelength for photoinitiated polymerization of NMA with cellulose.[9,13]

Samples of fabric about 0.25 by 0.41 m were immersed in an aqueous solution of NMA at 298 K and padded to the desired wet pickup by a two dip–two nip process. These treated samples were wrapped around and fastened to cylinders made of stainless steel hardware cloth. The cylinders were about 0.41 m in circumference and 0.25 m long. These samples were placed in a quartz reactor vessel, the vessel was closed, and the atmosphere was exchanged with nitrogen. The vessel was placed in the reactor and photoirradiated. The ambient temperature of the reactor increased from about 296 to 318 K during the initial 300 sec of photoirradiation. After the desired irradiation time, the fabrics were washed in hot water (340 K) to remove unreacted monomer and allowed to line dry and then equilibrate to constant weight at about 298 K and 45% R.H. The efficiency of conversion of NMA to poly(N-methylolacrylamide) (pNMA) was calculated as (increased nitrogen content of modified fabric)/(nitrogen content in wet pickup).

Microscopical analyses[14] were used to determine: the interaction between cellulose and crosslinking agent and pNMA within the fibrous cross section (transmission electron microscopy, TEM) and the surface areas of deposits of pNMA (scanning electron microscopy, SEM). Nitrogen in the fabrics was determined by the Kjeldahl method.[15] Bound formaldehyde was determined after distillation by reaction with chromotropic acid.[16]

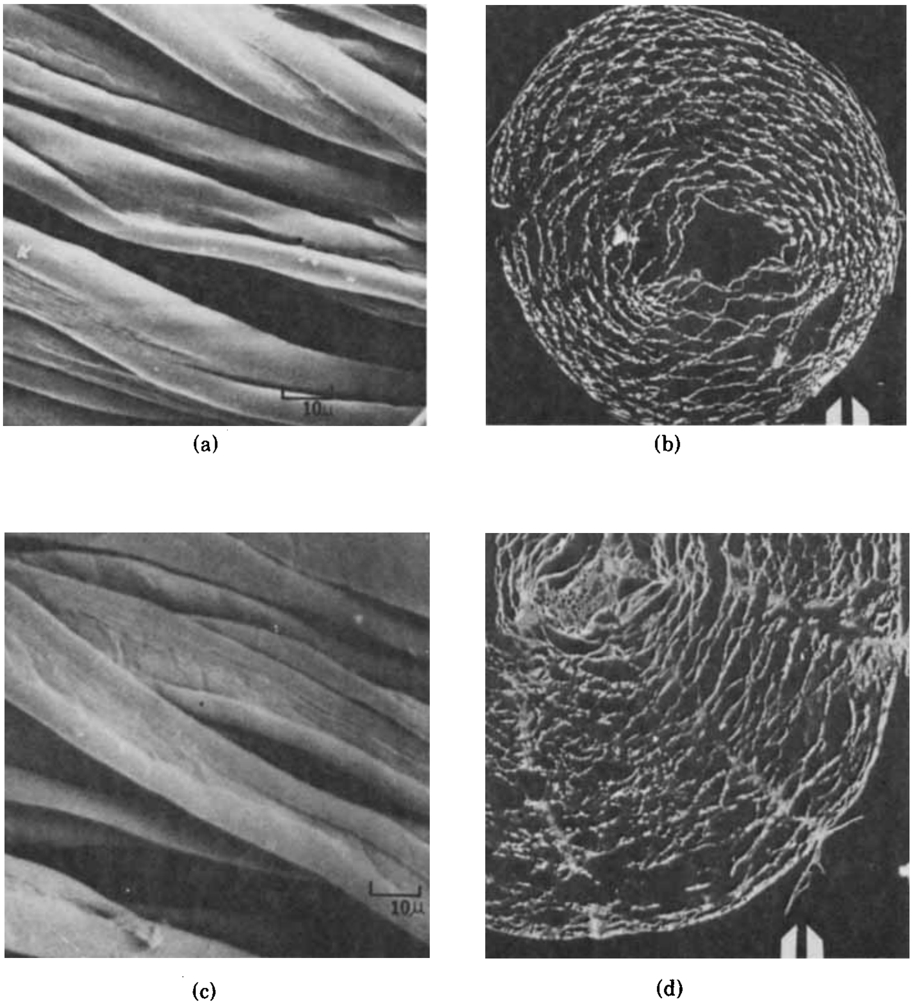
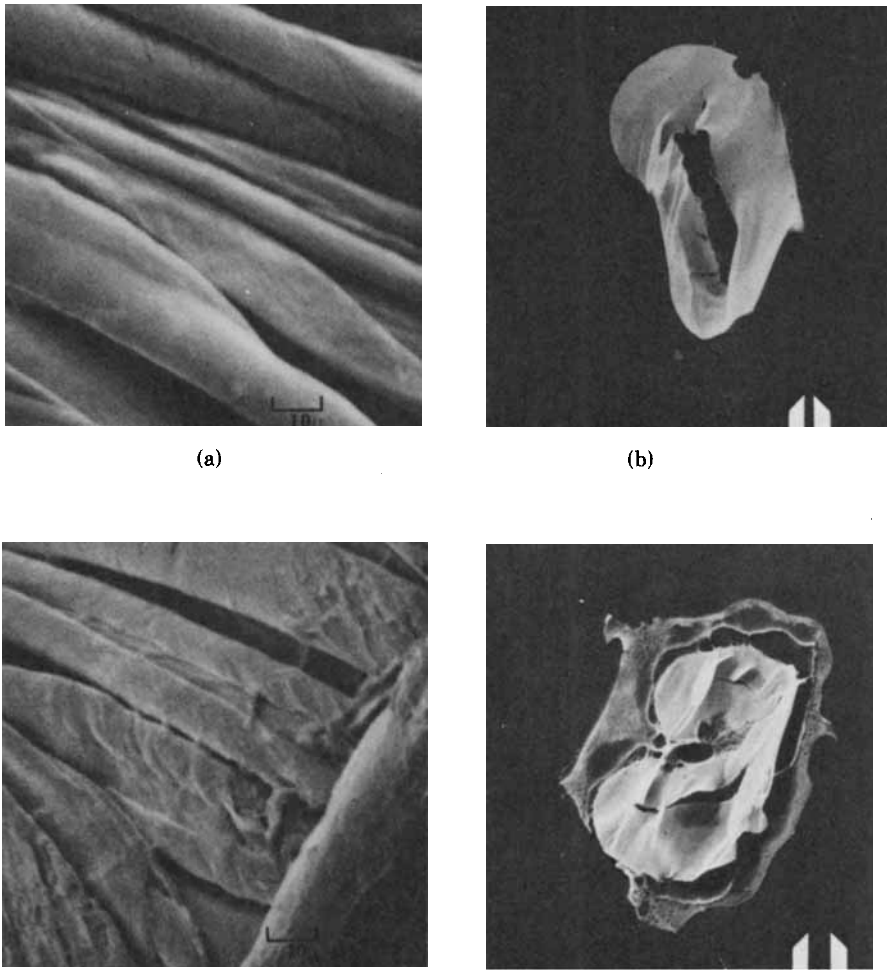


Fig. 4. Scanning (SEM) and transmission (TEM) electron microphotographs of untreated and poly(N-methylolacrylamide) (pNMA)-reacted cotton fibers: (a) SEM surface of untreated fiber; (b) TEM layer expansion of untreated fiber; (c) SEM surface of pNMA (1% N)-reacted fiber; (d) TEM layer expansion of pNMA (1% N)-reacted fiber.

RESULTS AND DISCUSSION

The effects of formaldehyde crosslinking of cotton in the unswollen state on photoinitiated polymerization of NMA with cellulose are shown in Figure 1. When the concentration of crosslinks was increased (formaldehyde from 0.37% to 2.11%), efficiency of conversion of NMA to pNMA decreased. The concentration of formaldehyde is directly related to the number of crosslinks formed. It is assumed that formaldehyde not reacted in a crosslinked form with cellulose would be removed during the preparation of the fabrics.[10,11] Also, some of the reacted formaldehyde may be in polyoxymethylene groups; however, the number of these groups would be low.[17] Three additional fabrics with concentrations



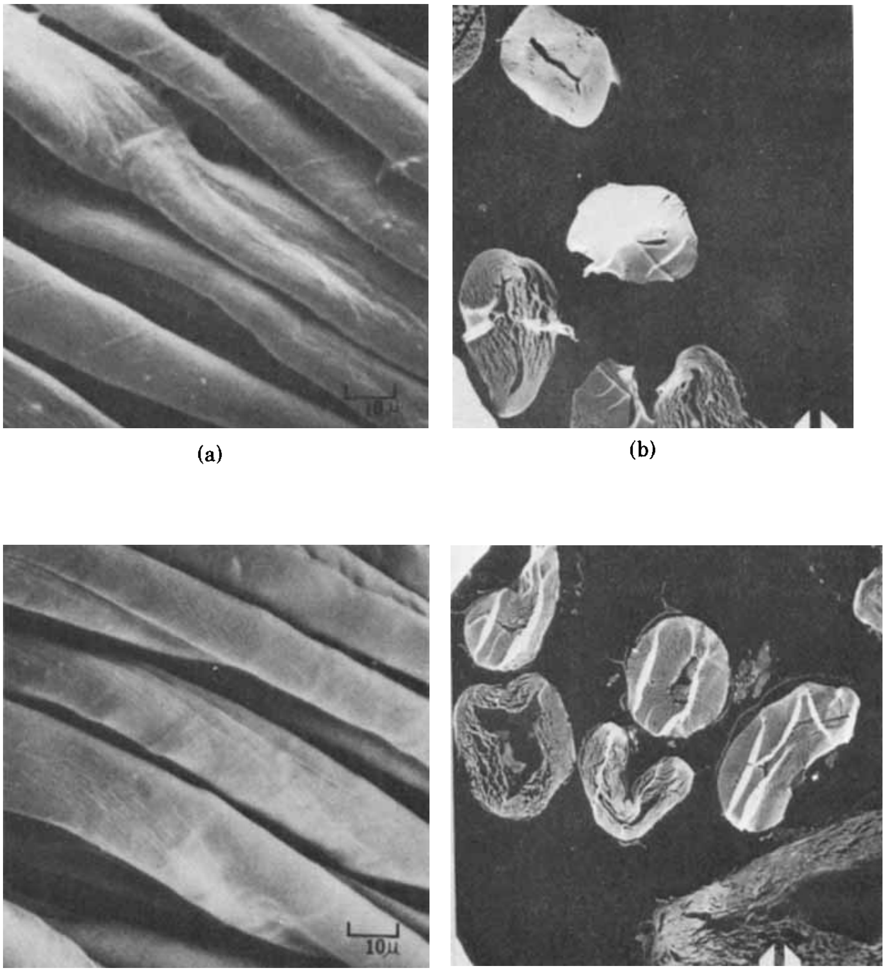
(a) (b) (c) (d)

Fig. 5. Scanning (SEM) and transmission (TEM) electron microphotographs of cotton fibers crosslinked in the unswollen state by formaldehyde and reacted with poly(N-methylolacrylamide) (pNMA): (a) SEM surface of formaldehyde (1.69%)-crosslinked fiber; (b) TEM layer expansion of fiber from (a); (c) SEM surface of fiber from (a) reacted with pNMA (1.05% N); (d) TEM layer expansion of fiber from (c).

of formaldehyde between these limits were also photolyzed, and the results confirmed these findings.

The effects of formaldehyde crosslinking of cotton, in both swollen and unswollen states, on photoinitiated polymerization of NMA with cellulose are shown in Figure 2. Cotton that was crosslinked in the swollen state was more reactive than cotton that was crosslinked in the unswollen state. When the dosage of ultraviolet radiation was increased to more than 6 kJ, conversion of NMA to pNMA with swollen, crosslinked cotton was about 100%.

The effects of DMEU crosslinking of cotton on photoinitiated polymerization



(a) (b)

(c) (d)

Fig. 6. Scanning (SEM) and transmission (TEM) electron microphotographs of cotton fibers crosslinked in the swollen state by formaldehyde and reacted with poly(N-methylolacrylamide) (pNMA): (a) SEM surface of formaldehyde (1.44%)-crosslinked fiber; (b) TEM layer expansion of fiber from (a); (c) SEM surface of fiber from (a) reacted with pNMA (1.12% N); (d) TEM layer expansion of fiber from (c).

of NMA with cellulose are shown in Figure 3. As the number of calculated crosslinks per anhydroglucose unit[12] increased from 0.005 for DMEU (0.55% N, 0.69% HCHO) to 0.046 for DMEU (1.75% N, 2.68% HCHO), efficiency of conversion of NMA to pNMA decreased. Two additional fabrics with concentrations of DMEU between these limits were also photolyzed, and the results confirmed these findings.

Crosslinking of cotton cellulose decreased the efficiency of photoconversion of NMA to pNMA with cotton. However, if the cotton was crosslinked in the swollen state, an increased dosage of ultraviolet radiation gave complete conversion of NMA to pNMA with cotton. Cotton that was crosslinked in the unswollen state restricted movement of the aqueous solution of NMA within the morphological structure. Therefore, chain polymerization reactions of NMA photoinitiated in the surfaces of cotton fabrics had decreased propagation within the fabric structure.[18] This decrease resulted in decreased photoconversion of NMA to pNMA with cotton.

Reaction of cotton fibers with pNMA (1% N) did not alter the appearance of the surface of the fibers, Figures 4(a) and 4(c), and layer expansion of the fiber cross sections, Figures 4(b) and 4(d). Both untreated and pNMA (1% N) reacted fibers were soluble in 0.5*M* cupriethylenediamine dihydroxide (CED). However, pNMA was an insoluble residue.

Crosslinking cotton fibers in the unswollen state by the pad-dry-cure treatment with formaldehyde (1.69%) and reacting these fibers with pNMA (1.05% N) did alter their surfaces, Figures 5(a) and 5(c), and layer expansions, Figures 5(b) and 5(d). Heavy deposits of pNMA were on the surface, Figure 5(c), and in the outer layers, Figure 5(d), of the fibers. Both the crosslinked and the crosslinked pNMA-reacted fibers were insoluble in 0.5*M* CED.

Crosslinking swollen cotton fibers in concentrated phosphoric acid solution with formaldehyde (1.44%) and reacting these fibers with pNMA (1.12% N) did not alter their surfaces, Figures 6(a) and 6(c). However, these reactions did alter their layer expansions, Figures 6(b) and 6(d). The variable degrees of layer expansions of reacted fibers indicate that different fibers within the fabric were swollen to different degrees during the crosslinking reaction. Both the crosslinked and crosslinked pNMA-reacted fibers were insoluble in 0.5*M* CED.

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