

Photopolymerization of Hydroxypropyl Acrylate and Tetraethylene Glycol Dimethacrylate Initiated by Uranyl Ion

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Synopsis

Uranyl nitrate, acetate, sulfate, and dibutyl phosphate were used in solution for the photoinitiation of homopolymerization and copolymerization of hydroxypropyl acrylate and tetraethylene glycol dimethacrylate. Solvents used included water, water-ethylene glycol mixtures, and dimethylformamide. Polymer yields in excess of 90% can readily be obtained by exposing solutions containing 0.014M UO_2^{2+} to light from a tungsten bulb for 1 hr. The rigidity of the polymers varied directly, the affinity for water inversely, with the concentration of tetraethylene glycol dimethacrylate in the monomer mixture. Poly(hydroxypropyl acrylate) contained 52% water and poly(tetraethylene glycol dimethacrylate) 34% water, at equilibrium.

Hydrophilic homopolymers and copolymers from glycol and polyglycol esters of acrylic and methacrylic acids have been prepared by Wichterle,¹ Wichterle and Lím,² Wichterle, Bartl, and Rosenberg,³ and Refojo and Yasuda.⁴ The polymerizations were usually initiated with persulfate or benzoyl peroxide.

The uranyl ion is a frequently used initiator for room-temperature photo-induced polymerizations of vinyl compounds.⁶⁻²³ Economical photopolymerization processes might well be developed with uranium that has been depleted of ^{235}U . In our work reported here uranyl salts were tested as photoinitiators of the homopolymerization and copolymerization of hydroxypropyl acrylate (H) and tetraethylene glycol dimethacrylate (T) monomers. The monomers were obtained from Monomer-Polymer Laboratories, The Borden Chemical Co., Philadelphia, Pennsylvania. Uranyl nitrate hexahydrate (UNH) was used most often as the initiator, but the acetate, sulfate, and dibutyl phosphate compounds were also used. The uranyl dibutyl phosphate was made in earlier work.²⁴

The polymerization was shown to be photo-induced with uranyl ion as initiator by tests in the presence and in the absence of light. Monomer H solution (1:1 by volume with dimethylformamide), 0.01M in UO_2^{2+} , did not react in 20 hr. in the dark but polymerized in a few minutes in light. Photopolymerization without uranyl ion initiation occurred only with monomer T and much more slowly than when UO_2^{2+} was present.

Solutions to be exposed to light from a tungsten bulb were prepared by

TABLE I
Water Content of Water-Soaked Polymers from Hydroxypropyl Acrylate and Tetra-ethylene Glycol Dimethacrylate Mixtures Photopolymerized with 0.014M Uranyl Ion as Initiator^a

Monomer compn., %	Irrad. time, hr.	Polym. yield, %	Water cont., ^b %
All H	1	89	50.8
"	24	94	52.4
"	24 ^c		53.0
95 H-5 T	1	92	45.1
80 H-20 T	1	94	35.9
"	1	90	35.9
All T	0.5	91	34.2
"	1	100	33.5
"	1 ^d	97	31.9
"	1 ^e	96	34.2
"	24	98	34.2
"	24 ^d	99	33.0
"	72 ^e	96	34.5

^a All monomer solutions were dissolved in an equal volume of dimethylformamide 0.028M in uranyl nitrate except those indicated by footnotes c, d, and e.

^b Polymer was soaked in water at 19–22°C. for 8–19 days, blotted, and dried *in vacuo* at 76–100°C.; water content, wt.-% based on weight of wet (blotted) polymer.

^c Monomer was dissolved in an equal volume of water containing 0.028 moles of uranyl sulfate per liter.

^d Monomer was dissolved in an equal volume of dimethylformamide solution containing 0.028 moles of uranyl dibutyl phosphate per liter.

^e Monomer was dissolved in an equal volume of dimethylformamide solution containing 0.028 moles of uranyl acetate per liter.

dissolving a monomer solution of known composition in an equal volume of solvent, usually dimethylformamide but sometimes water or water-ethylene glycol, containing a known concentration of uranyl ion as initiator. The initiator solutions were freshly prepared just before each polymerization experiment. Weighed monomer solutions (100% H, H containing 5 and 20 wt.-% T as crosslinking agent, and 100% T) were dissolved in an equal volume of solvent containing various amounts of uranyl ion. The weights were again recorded so that the fractional weight of monomers would be known for determination of polymer yield. The solutions were then drawn up into tared 4 mm. Pyrex tubes to a height of 15–16 cm., after which rubber tubes at the top were closed off with hemostats.

Light was furnished by a 150 w. tungsten filament bulb 15 cm. away from the mid-height of the liquid. Exposure time varied from as little as 0.5 hr., with 0.014M UO_2^{2+} , to as long as 8 days, with 0.00014M UO_2^{2+} .

Reaction was rapid at 0.014M UO_2^{2+} . At this concentration the T polymerized fastest to form a clear hard gel in 15 min.

Both polymer yield and amount of water contained in polymer that had been soaked in water were obtained by weight measurements. After the light irradiation treatment the tube was reweighed, and the contents were

TABLE II
Photopolymer Yield at Various Uranyl Ion Concentrations and Water Content of Water-Soaked Polymers

UNH concn., ^b moles/l.	Irrad. time, hr.	Polym. yield, %			Water cont., ^a %				
		H	H, T ^c	H, T ^d	H	H, T ^c	H, T ^d		
0.014	0.5	89.4	91.6	89.8, 93.6	91	50.8	45.1	35.9, 35.9	34.2
"	1	93.8			100	52.4			33.5
"	24	31.5	50.9	59.0	98				34.2
0.0014	3	80.8	89.0	86.2	89.5	52.4	45.2	34.6	30.9
"	24				67		45.8	36.1	
0.00014	14	0	0	52.0					31.0
"	20	36				51.4			
"	192								

^a Weight per cent of blotted polymer.

^b In irradiated solution of equal volumes of dimethylformamide and monomer solution.

^c H/T ratio, 95:5.

^d H/T ratio, 80:20.

removed. The cylinder of homopolymer from T in dimethylformamide and any other cylinders from monomer in water or water-ethylene glycol could be easily forced by pressure from a rubber bulb into the water wash container. The polymers from H and H-T solutions in dimethylformamide could be removed only by breaking the glass tube. Some fractures formed in the more rigid, crosslinked polymer cylinders, but these had no effect on the determination of polymer yield and apparently none on the water content at equilibrium.

Solvent was removed by soaking the polymer in distilled water, changed daily, for several days. From the weight of a segment of the cylinder, rolled on Whatman #50 filter paper, to blot the surface water, it appeared that the dimethylformamide was completely removed, and the polymer was at equilibrium with the water within 3 days. Assays were made after a minimum of 8 days' water soaking at 19–22°C. The polymers were blotted and weighed in stoppered weighing tubes. Drying to constant weight was done in an Abderhalden dryer at a pressure of 2 mm. Hg. The time required was 4–6 hr. at 100°C. and up to 16 hr. at 76°C. Polymer yield was obtained from the ratio of dried polymer weight to that of the starting monomer. Water content was based on the weight of the water-saturated polymer.

In Table I is shown the influence of crosslinking compound T in the polymer on the water content of the swollen material. The water content decreased from 52% in H polymer saturated with water at 22°C. to 36% with 20% crosslinker in the starting monomer solution. T homopolymer contained essentially the same amount of water (34%). Our values agree favorably with those of Refojo and Yasuda⁴ in the crosslinking range common to both investigations.

Polymer yields were high in all cases in which the photoinitiator ion (UO_2^{2+}) concentration in the irradiated solution was 0.014*M*. The lowest yield was 89% when H was exposed to light for 1 hr. The T polymers from exposures of 1 hr. and longer averaged 98% in yield. Under the conditions shown in Table I no difference in yield or in behavior toward water was found when the anion was varied.

Photopolymerization characteristics as a function of uranyl ion concentration are shown in Table II. The major effect of decreasing the concentration by one-tenth and one one-hundredth was to increase the time for polymerization and to lower the yield. At 0.00014*M* UNH 8 days were required for a 36% yield of H homopolymer, compared to 32% yield in 3 hr. with 0.0014*M* UNH and 89.4% yield in 1 hr. with 0.014*M* UNH. Regardless of yield, however, the water content was essentially the same for polymers derived from the same starting monomer composition but at different initiator strengths.

The appearance of the polymers depended on the solvent for the monomers. Polymers formed in dimethylformamide were clear; those formed in water or water-ethylene glycol were an opaque white. T homopolymer turned white on immersion in water. The clear homopolymers and co-

polymers stayed clear in water, except when the temperature rose; the polymers were expelling water, and they cleared again at equilibrium. All polymers were clear when dried.

As the percentage of T crosslinker was increased, the polymers became more rigid. H homopolymer saturated with water was very pliable and sticky. H polymers crosslinked with T were less pliable and were easily broken. T homopolymer was stiff and harder to break. Drying toughened the polymers.

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