Graft Copolymerization of Vinyl Monomers onto Pure Cotton Cellulose Using Mn^{3+} Ions as Initiator

Dedicated to the Memory of the late Professor Ichiro Sakurada

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ABSTRACT: A sample of chemical cotton (pure cellulose) has been grafted with acrylonitrile (AN), methyl methacrylate (MMA) and acrylamide (AAd) using Mn^{3+} ions complexed with pyrophosphate in acid aqueous solution ($\text{pH}=1.7$) at 30°C . The conversion of monomer to polymer and the add-on to the substrate weight have maxima at an Mn^{3+} concentration of about 0.50 mM and at a monomer/substrate ratio of about 2:1. Under optimal conditions the grafting efficiency is about 95% for AN and 65—75% for MMA. For AAd the conversion is low (8—10%) and the grafting efficiency < 50%. These results have been interpreted as due to the low accessibility of the cotton cellulose (high crystallinity) and the known properties of the three monomers. The homopolymer formed of MMA is interpreted as largely due to chain transfer to monomer and that of AAd as mainly due to initiation by Mn^{3+} oxidation of monomer. Alkaline hydrolysis of AN-grafted cotton fibers gives a water retention value of 65—70 g g^{-1} .

KEY WORDS Cotton Cellulose / Graft Copolymerization / Vinyl Monomers / Manganic Ion Initiator / Alkaline Hydrolysis / Water Retention /

A new redox system for initiation of graft copolymerization of vinyl monomers to polysaccharides has been developed in our laboratories and first applied to starch.¹ The initiator is Mn^{3+} ions in complex form in aqueous solution of pH 1.5 to 2 at about 30°C . This initiator is also active with cellulose as substrate.² Both bleached cellulosic fibers from wood (lignin-free) and water-swelling cellulose ethers of low degree of substitution are efficiently grafted with this initiator.³

A review of new graft copolymerizations onto cellulosic fibers using chemical initiation has recently been published.⁴ An extensive monograph on grafting to cellulosic materials

using all known initiation methods appeared at the same time.⁵ The purpose of this paper is to describe grafting experiments with a very pure cotton cellulose as substrate and complexed Mn^{3+} ions in aqueous acid solution as initiator. Based on the results, the mechanism of initiation is discussed in detail, considering our recent studies of metal ion oxidation of model compounds.⁶

EXPERIMENTAL

Materials

Chemical cotton (Grade 359, Type ES 4000, "Wet Stock Loose," from Hercules Corp., U.S.A.), viscosity 4000 s. (ACS method), a

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cotton linters pulp for papermaking and cellulose derivatives, is used in never-dried form (supplied as 35.65% dry weight).

Acrylonitrile (AN) (synthetic grade from Merck) is purified by washing with 5% aqueous alkali and distillation under reduced atmosphere and stored in the dark at 4°C.

Methyl methacrylate (MMA) (synthetic grade from Merck) is shaken with 10% aqueous alkali, washed with distilled water, and dried over magnesium sulfate.

Acrylamide (AAd) (synthetic grade from Merck) is used as received.

The salts ($\text{MnSO}_4 \cdot \text{H}_2\text{O}$, KMnO_4 and $\text{Na}_4\text{P}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$) are of analytical grade (from Merck) and used as received.

Preparation of Initiator

The initiator solution is prepared by mixing the following three solutions in the addition funnel before adding it to the reaction vessel.

I. A solution of 0.320 M MnSO_4 is prepared by dissolving 5.408 g $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ to 100 ml in distilled water. The pH of the solution is adjusted to 6.0 by adding drops of an aqueous NaOH solution and checking with a pH meter (Metrohm, Type 632, Switzerland).

II. A solution of 0.080 M KMnO_4 is prepared by dissolving 1.264 g KMnO_4 to 100 ml in distilled water.

III. A solution of 0.150 M $\text{Na}_4\text{P}_2\text{O}_7$ is prepared by dissolving 16.727 g $\text{Na}_4\text{P}_2\text{O}_7 \cdot 10\text{H}_2\text{O}$ to 250 ml in distilled water. The pH of the solution is adjusted to 6.0 by adding drops of aqueous H_2SO_4 and checking with a pH meter.

The reaction volume is kept constant at 500 ml in all experiments. A mixture of 1.25 ml of solution I and 1.25 ml of solution II gives an Mn^{3+} concentration of 1.00 mM in the reaction vessel (500 ml). Addition of 7.50 ml of solution III gives a concentration of 2.00 mM $\text{Na}_4\text{P}_2\text{O}_7$ in the reaction vessel, i.e., $\text{Mn}^{3+}/\text{P}_2\text{O}_7^{4-}$ of 1:2 molar ratio for the complex formation.

Graft Copolymerization

The experiments are carried out in 500 ml reaction solution in a 1 liter glass reactor, equipped with mechanical stirrer, condensor, thermometer, two addition funnels and gas inlet tubes for nitrogen bubbling.

Chemical cotton (dry weight 10.0 g) is slurried with a precalculated amount of distilled water (around 420 ml) in the reaction vessel. An oxygen-free stream of nitrogen gas is bubbled through the pulp slurry under stirring for 30 min and 25 ml of 1.60 M H_2SO_4 is added. The reaction vessel is immersed in a water bath maintained at 30°C. The initiator solutions of MnSO_4 , KMnO_4 , and $\text{Na}_4\text{P}_2\text{O}_7$ are added and mixed in an addition funnel¹ in amounts to give the desired concentration of complexed Mn^{3+} ions in the reaction vessel. The required amount of monomer (AN and MMA as such and AAd as an aqueous solution) is added to addition funnel.² The oxygen-free nitrogen stream is bubbled slowly through the initiator solution, the monomer and the acidified cotton slurry for 30 min. The initiator solution is added to the reaction solution which gives it a clear pink color. After another 30 min of N_2 bubbling, the monomer is added to the reaction solution. After 3 h at 30°C and slow N_2 bubbling, the grafting reaction is stopped by letting air into the reaction vessel. The grafted cotton, which retains its white color in the reaction solution of a slightly pink shade, is washed with distilled water several times and dried at room temperature over night to a dry weight of about 45%.

Homopolymer Content in Grafted Samples

A cotton sample grafted with AN of 4.00 g (dry basis) is extracted with 250 ml dimethylformamide (DMF) for 48 h at room temperature and then filtered and washed with DMF. The collected DMF solution is concentrated to about 80 ml by distillation under reduced pressure and poured into 500 ml methanol. The precipitated AN-polymer is separated by filtration, washed several times with meth-

anol and dried at 60°C to constant weight.

In the case of grafting with MMA, the homopolymer is extracted with 250 ml acetone.

In the case of grafting with acrylamide, the homopolymer which is water-soluble, is separated by filtration of the reaction solution, washed with water, concentrated by distillation under reduced pressure and precipitated by pouring into acetone.

Molecular Mass of MMA Homopolymer

The molecular mass (M) of the extracted MMA homopolymer is measured in an Ubbelohde viscometer in acetone solution, starting at a concentration of 0.30 g/100 ml. The M -values are calculated using the Mark-Houwink-Sakurada equation⁷:

$$[\eta] = 5.5 \times 10^{-5} \times M^{0.73}$$

Alkaline Hydrolysis of AN-Grafted Cotton

The AN-grafted cotton samples (2 g) are hydrolyzed in 1% aqueous NaOH solution (200 ml) at 100°C for 1.5 h.³ After hydrolysis the swollen samples are precipitated by pouring into 600 ml methanol, washed with methanol and ethanol, dried in air and weighed. The alkaline hydrolysis is known to give a total conversion of the nitrile groups in PAN chains to amide and carboxyl groups, which enhances the water-swelling of the grafted samples.⁸

Water Retention of Grafted and Hydrolyzed Samples

The water retention of the grafted and hydrolyzed samples (never-dried) is measured by a centrifugation method.⁸ A weighed sample (0.04 g dry weight) in a centrifuge tube is swelled in distilled water (10.0 ml) for 20 min and then centrifuged at 3000 revolutions per min (about 900 G) for 30 min. The excess water is poured off and the amount of water retained in the gel determined by weighing. The amount of water retained per gram of dry graft copolymer, is expressed as water re-

tention value (WRV) in g g^{-1} .

Definitions

The graft copolymers are characterized according to Fanta's definitions⁹:

$$\text{Conversion (\%)} = \frac{\text{Polymer formed}}{\text{Monomer charged}} \times 100$$

$$\text{Add-on (\%)} = \frac{\text{Synthetic polymer}}{\text{Graft copolymer}} \times 100$$

$$\text{Grafting ratio (\%)} = \frac{\text{Grafted polymer}}{\text{Weight of substrate}} \times 100$$

Grafting efficiency (%)

$$= \frac{\text{Grafted polymer}}{\text{Polymer formed}} \times 100$$

The amount of homopolymer formed (%) is (100 – Grafting efficiency in %).

RESULTS

Grafting with Acrylonitrile

The grafting of acrylonitrile onto chemical cotton is carried out with different concentrations of initiator and various amounts of monomer (Table I). The grafting experiments are fairly well reproducible (*cf.* Experimental No. 1.3 and 1.4). The initiator concentration has a strong influence on the results. The conversion of monomer to polymer and the add-on has a maximum at about 0.50 mM Mn^{3+} ions and decreases strongly at higher Mn^{3+} conc. (Figure 1). This is interpreted as due to the low accessibility of chemical cotton, *i.e.*, few reactive sites, and will be further interpreted in the discussion. With increasing ratio of monomer to substrate, conversion and add-on have a maximum at a weight ratio of about 2:1 of AN to cotton (Figure 2). The homopolymer content is low in all experiments which means that the grafting reaction is highly specific for the substrate. Addition of monomer first and then initiator (Experimental No. 1.8 and 1.9) gives much lower conversion and add-on than addition of

Table I. Acrylonitrile (AN) grafted onto chemical cotton

Experimental No.	AN g	Concn. of initiator		Conversion %	Homopolymer %	Add-on %	Grafting ratio %	Grafting efficiency %	WRV of Hydr. copolymer g g ⁻¹
		mM							
		Mn ³⁺	Na ₄ P ₂ O ₇						
1.1	10.0	2.00	4.00	14.60	6.66	12.74	13.63	93.36	—
1.2	10.0	1.00	2.60	36.30	6.03	26.63	34.11	93.97	64.2
1.3	10.0	0.50	1.30	59.00	5.24	37.11	55.91	94.76	65.6
1.4	10.0	0.50	1.00	65.40	2.69	39.54	63.64	97.31	—
1.5	10.0	0.25	0.65	51.50	4.73	33.40	49.04	95.22	—
1.6	20.0	0.50	1.30	75.90	1.28	60.29	74.93	98.72	71.3
1.7	26.6	0.50	1.30	49.03	2.11	56.60	47.99	97.89	—
1.8	10.0	0.50	1.30	36.30	6.26	26.63	34.03	93.75	—
1.9	10.0	1.00	2.60	10.40	12.69	9.42	9.08	87.31	—

^a Reaction conditions: Chemical cotton, 10.0 g (dry basis); H₂SO₄, 80.0 mM; reaction volume, 500 ml; reaction time, 3 h; temp, 30°C. In experimental No. 1.1—1.7 the initiator is added to the N₂-bubbled reaction solution first and then the monomer is added. In experimental No. 1.8 and 1.9, the monomer is added first and then the initiator.

Figure 1. Add-on (—○—) and total conversion of monomer to polymer (--- × ---) in grafting of acrylonitrile onto chemical cotton. Reaction conditions: concentration of cotton, 20.0 g l⁻¹; acrylonitrile, 20.0 g l⁻¹; [Na₄P₂O₇], 2.0 mM/mM Mn³⁺; [H₂SO₄], 80 mM l⁻¹. Reaction time, 3 h; temp, 30°C. Monomer was added to slurry of cotton in acidified water and initiator. (cf. Table I).

Figure 2. Add-on (—○—) and total conversion of monomer to polymer (--- × ---) in grafting of acrylonitrile onto cotton. Reaction conditions; concentration of cotton in reaction solution, 20.0 g l⁻¹; [Mn³⁺], 0.5 mM l⁻¹; Na₄P₂O₇, 1.3 mM l⁻¹; [H₂SO₄], 80 mM l⁻¹. Reaction time, 3 h; temp, 30°C.

the initiator before the monomer. In earlier experiments,³ the molecular mass of PAN grafted chains onto cellulose fiber substrates is

known to be 50000 to 100000.

Separate experiments with incomplete removal of oxygen (short periods of N₂ bubbl-

Table II. Methyl methacrylate (MMA) grafted onto chemical cotton (CC)

Experimental No.	MMA g	Conversion %	Homopolymer %	Add-on %	Grafting ratio %	Grafting efficiency %	Molar mass of MMA homopolymer
2.1	10.0	49.50	33.88	33.11	32.73	56.12	—
2.2	20.0	67.65	29.93	57.50	94.80	70.07	3.01×10^6
2.3	30.0	37.07	19.77	52.65	89.88	80.83	2.68×10^6

^a Reaction conditions: CC, 10.0 g (dry basis); Mn^{3+} 0.50 mM; $\text{Na}_4\text{P}_2\text{O}_7$, 1.30 mM; H_2SO_4 , 80.0 mM; reaction volume, 500 ml; time, 3 h; temp, 30°C.

ing) have given low conversion and poorly reproducible results. The water retention values (WRV) for the hydrolyzed graft copolymers are of the order 60–70 which is much lower than the corresponding values for hydrolyzed starch copolymers (up to 800, *cf.* ref 8).

Grafting with Methyl Methacrylate

Methyl methacrylate (MMA) is efficiently grafted to chemical cotton (Table II) using the optimal initiator concentration from AN grafting ($\text{Mn}^{3+}/\text{Na}_4\text{P}_2\text{O}_7 = 0.50/1.30$ mM). A monomer/substrate ratio of 2:1 gives the highest conversion and add-on also for MMA (Figure 3). The grafting efficiency for MMA increases with increasing monomer/substrate ratio, but it never reaches the high values obtained for AN (>95%). The very high average molecular mass for the homopolymer of MMA is typical for PMMA synthesized with free radical mechanism (Table II). It is mainly due to the low termination rate in free radical polymerization of MMA. The ratio of propagation rate/termination rate is about 400 for MMA and about 30 for AN.

Grafting with Acrylamide (AAd)

When acrylamide is grafted onto chemical cotton, the conversion of monomer to polymer is low (7–10%) and the amount of homopolymer formed is high (45–78%). This means a quite low grafting efficiency in comparison with AN and MMA (Table III).

Figure 3. Add-on (—○—) and conversion of monomer to polymer (---x---) in grafting of methyl methacrylate onto chemical cotton. Reaction conditions: concentration of cotton in reaction solution, 20.0 g l⁻¹; $[\text{Mn}^{3+}]$, 0.50 mM l⁻¹; $[\text{Na}_4\text{P}_2\text{O}_7]$, 1.3 mM l⁻¹; $[\text{H}_2\text{SO}_4]$ 80 mM l⁻¹. Reaction time, 3 h; temp, 30°C.

The water retention value (WRV) is also rather low (about 20 g g⁻¹), which is unexpected. PAAAd is a hydrophilic and water soluble polymer. The different grafting properties of the three studied monomers (AN, MMA and AAd) is clearly shown in Figure 4. The results refer to the same experimental conditions for the three monomers: $\text{Mn}^{3+}/\text{Na}_4\text{P}_2\text{O}_7$ ratio 1:2 (or 1:2.6) monomer/substrate ratio 1:1, 2:1, and 3:1, temp 30°C and time 3 h. All three monomers show a maximum in

Table III. Acrylamide (AAd) grafted to chemical cotton (CC)

Experimental No.	AAd	Concn. of initiator		Conversion %	Homopolymer %	Add-on %	Grafting ratio %	Grafting efficiency %	WRV %
	g	mM							
		Mn ³⁺	Na ₄ P ₂ O ₇						
3.1	10.0	0.50	1.30	9.43	53.34	4.21	4.40	46.66	22.5
3.2	20.0	0.50	1.30	9.42	45.86	9.25	10.20	54.14	19.6
3.3	30.0	0.50	1.30	7.52	71.64	6.01	2.13	28.36	—
3.4	20.0	1.00	2.60	9.26	62.23	6.54	7.00	37.78	—
3.5	20.0	0.50	1.30	10.24	78.03	4.30	4.50	21.98	—

^a Reaction conditions: Chemical cotton, 10.0 g (dry basis); H₂SO₄, 80 mM; reaction volume, 3 h; temp, 30°C. The initiator solution is added to the cotton slurry. Monomer is added 30 min later. In experimental No. 3.5 the initiator solution is added to the cotton slurry after the monomer (reaction time, 6 h).

Figure 4. Grafting efficiency in graft copolymerization of cotton with acrylonitrile (○), methyl methacrylate (▽), and acrylamide (□).

Figure 5. Grafting ratio in cotton-polyacrylonitrile (○), -poly(methyl methacrylate) (▽), and -polyacrylamide (□) graft copolymers.

grafting ratio for the monomer/substrate ratio 2:1 (Figure 5).

DISCUSSION

The three monomers (AN, MMA, AAd) react very differently in the grafting process as

shown from the grafting efficiency values at increasing monomer/substrate ratios (Figure 5). This is to some extent due to known properties of the monomers. The MMA has a low termination rate and gives, therefore, very long grafted chains. The lower grafting efficiency of MMA (65–75%) compared with AN is more difficult to interpret. With starch as substrate, the grafting efficiency of MMA is 85–90% (ref 1). Homopolymer formation is a side reaction. The initiation of MMA homopolymer may be due to some low molecular

impurity, original or formed in the Mn^{3+} reaction with the substrate. The same number of free PMMA chains (of high molecular mass) will on a weight basis be a larger amount than the same number of PAN chains, *i.e.*, lower grafting efficiency for MMA than for AN.

The mechanism of grafting initiation with Mn^{3+} ions has been studied using UV and ESR spectroscopy.⁶ The Mn^{3+} ions are oxidizing aldehyde groups (eq 1) and vicinal diol groups (eq 2) by one-electron reactions:

Both alkoxy (1) and alkhydroxy (2) radicals can initiate polymerization by addition of a sufficiently reactive monomer, *e.g.*, acrylic and methacrylic esters. Vinyl acetate is not grafted by Mn^{3+} initiation due to its low reactivity. Cyclic 1,2-diols are reacting fast ac-

cording to eq 2, *e.g.*, 1,2-cyclohexane-diol and monosaccharides with several vicinal diol groups like D-ribose.⁶

The acrylamide monomer in aqueous solution of low pH would be enolized by addition of water and react in this form:

The chemical cotton is a very pure cellulose substrate of high crystalline order, *i.e.*, low accessibility. In the initiation reaction, it is expected to give rather few active sites for grafting. If mainly vicinal diols react with

Mn^{3+} (eq 2), the alkhydroxy radical can be further oxidized to an aldehyde group (eq 4).

This would mean a consumption of grafting sites by an excess of Mn^{3+} ions charged, *i.e.*, a decrease in conversion of monomer to polymer, which agrees with the experimental results for grafting of AN to cotton cellulose (Table I and Figure 1).

In the grafting experiments at optimal concentration of Mn^{3+} initiator, there is an excess of initiator. Assume 10.0 g of cotton substrate is grafted with 20.0 g AN monomer using 0.50 mM Mn^{3+} as initiator. With a conversion of 76% AN a grafted chain length of about 2000 mers (molar mass 100000) according to earlier measurements,³ 0.152 mmol PAN chains are formed. The amount of Mn^{3+} charged is 0.250 mmol, *i.e.*, only about 60% is used for initiation of grafted chains. In grafting with MMA the conversion is lower (68%) and the grafted chains much longer (molar mass about 3.0×10^6). This means that only about 2% of the Mn^{3+} ions are initiating grafted chains, *i.e.*, a very large excess of Mn^{3+} ions.

CONCLUSIONS

In grafting chemical cotton with acrylic monomers using Mn^{3+} ions as pyrophosphate complex in acid aqueous solution as initiator the conversion of monomer to polymer and the grafting efficiency has a maximum at an

Mn^{3+} concentration *ca.* 0.5 mM and a monomer/substrate ratio of about 2:1. The grafting efficiency and the grafting ratio are also related to the monomer used and decrease in the order: acrylonitrile > methyl methacrylate > acrylamide. Only acrylamide seems to form homopolymer by a direct reaction of the Mn^{3+} ions with the monomer.

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