Graft Polymerizations of Acrylonitrile and Methyl Acrylate onto Starch and Cellulose at Different Stirring Speeds

Recent publications by Graczyk and Hornof[1,2] state that stirring speed is an important variable in determining percent conversion of monomer to polymer during graft polymerization reactions with cellulose. These authors examined several monomers (styrene, acrylonitrile, methyl methacrylate, and dimethylaminoethyl methacrylate), and initiator systems included cellulose xanthate–hydrogen peroxide, ferrous ammonium sulfate–hydrogen peroxide, and ceric ammonium nitrate. In one example, when acrylonitrile was graft-polymerized onto cellulose with xanthate–hydrogen peroxide initiation, conversion of monomer to grafted polyacrylonitrile (PAN) dropped from about 45–50% at a stirring speed of 100 rpm to less than 5% when the speed was increased to 350–400 rpm.

As part of a long-standing research program on polysaccharide graft copolymers, we have examined a number of monomers and reaction variables in graft polymerization reactions with starch and cellulose. Since we never considered stirring speed as an important variable, the results of Graczyk and Hornof caused us some concern, even though differences obviously existed between our reaction conditions and theirs. We therefore carried out a series of graft polymerizations onto starch and cellulose at different stirring speeds using two of our most frequently used monomers: acrylonitrile[3] and methyl acrylate.[4-6] Polymerizations were initiated with ceric ammonium nitrate, and reaction conditions were similar to those used by us in earlier studies. These experiments showed no large effects of stirring speed on the graft polymerization reaction, within a range of stirring speeds that one might consider normal for preparative polymerizations.

EXPERIMENTAL

Materials

Globe Pearl corn starch was from CPC International and contained 10% moisture. Cellulose was bleached softwood pulp (Alberta Hi-Brite) from St. Regis Paper Co.; analyses showed 0.06% lignin and 85.8% α-cellulose, the remainder being pentosans. Acrylonitrile (Eastman) and methyl acrylate (Polysciences) were distilled at atmospheric pressure through a 14-in. Vigreux column. Ceric ammonium nitrate (Certified ACS) was from Fisher Scientific Co.

Graft Polymerizations

Graft polymerizations were carried out in a 1-L resin flask equipped with a Teflon paddle stirrer. Stirrer speeds were measured with a photoelectric tachometer (Power Instruments, Inc.).

Starch. Stirred slurries of 20.0 g (dry basis) of starch in 400 mL of water were sparged with a slow stream of nitrogen for 1 h at 25°C. For reactions with gelatinized starch, slurries prepared from either 10.0 g or 20.0 g of starch were nitrogen-sparged for 1 h at 85°C and then cooled to 25°C. Acrylonitrile or methyl acrylate was added, followed after 5 min by ceric ammonium nitrate initiator in an amount equal to 1 mol per 100 glucose units of starch (for 20.0 g of starch, the initiator was prepared by dissolving 0.676 g of ceric ammonium nitrate in 6 mL of $1N$ nitric acid). After addition of monomer and initiator, stirring speed was increased for about 15 s to produce a vortex so that reactants would be rapidly dispersed. Stirring speed was then adjusted to the desired setting, and polymerizations were allowed to proceed for 2 h at 25–30°C. Reaction mixtures were neutralized with sodium hydroxide solution, and pol-

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ymers were isolated by filtration, washed with water and/or ethanol, and dried. Starch-*g*-PAN was extracted several times with dimethylformamide (DMF) at room temperature to remove homopolymer. Homopolymer was removed from starch-*g*-poly(methyl acrylate) (starch-*g*-PMA) by extraction with acetone.

Cellulose. Stirred dispersions of 7.5 g (dry basis) of bleached soft wood pulp in 300 mL of water were sparged with a slow stream of nitrogen for 1 h at 25°C. Methyl acrylate (9.4 g) was added, followed after 5 min by 0.25 g of ceric ammonium nitrate dissolved in 4.5 mL of 1*N* nitric acid. Polymerizations were run at the desired stirring speed for 2 h at 25–30°C. Reaction mixtures were neutralized with sodium hydroxide solution, and polymers were isolated by filtration, washed with water, and allowed to air dry. Homopolymer was removed from cellulose-*g*-PMA by extraction with acetone.

Characterization of Graft Copolymers

Grafted PAN was separated from starch-*g*-PAN by heating 5.00 g of graft copolymer under reflux with 150 mL of 0.5*N* hydrochloric acid for 1.5 h. PAN (containing less than 5% residual carbohydrate, by infrared analysis) was isolated by filtration, washed with water, and dried. Weight % PAN in the graft copolymer (% add-on) was calculated from weight loss due to acid hydrolysis. $\bar{M}_v$ of PAN was calculated from the intrinsic viscosity in DMF.[7]

Grafted PMA was separated from graft copolymers by first oxidizing the polysaccharide component with sodium periodate and then degrading the oxidized carbohydrate with sodium methoxide in methanol.[8] To get good wetting and penetration by the aqueous sodium periodate solution, graft copolymers were first suspended in acetone and then washed with water before reaction. Percent add-on was calculated from weight loss due to polysaccharide degradation.

To determine solubility of grafted PMA, about 1 g of polymer (accurately weighed) was stirred overnight in 200.0 g of acetone and the mixture was centrifuged (30 min at 1500 × *g*). An accurately weighed portion of supernatant was evaporated to dryness, and the weight of polymer was determined after freeze drying from benzene. $\bar{M}_w$ and $\bar{M}_n$ of soluble PMA fractions, were determined by gel permeation chromatography as described earlier,[8] except that a 10^6 μ-Styragel column was used in addition to the 10^5, 10^4, 10^3, and 500 Å columns.

RESULTS AND DISCUSSION

Graft polymerizations of acrylonitrile onto granular and gelatinized starch (Table I) yielded starch-*g*-PAN containing about 50–55% PAN, regardless of stirring speed. Stirring speed also had little influence on $\bar{M}_v$ of grafted PAN, even though PAN $\bar{M}_v$ was, as expected,[9] higher when starch was gelatinized before graft polymerization. A small percentage of each polymer is present as ungrafted PAN, and this fraction was removed by extraction with DMF. DMF also dissolves some polysaccharide, especially with gelatinized starch-*g*-PAN, and this is reflected in the higher percentages of DMF solubles found with gelatinized products. In the characterization of graft copolymers, unextracted and DMF-extracted starch-*g*-PAN gave about the same values for % add-on and PAN $\bar{M}_v$ (see reactions 2 and 7). To permit efficient stirring, gelatinized starch reactions 6–8 were run with half the amount of starch and acrylonitrile used for granular starch reactions 1–3. When gelatinized starch was used at the same concentration as granular starch, the high viscosity of the reaction mass prevented the formation of a vortex, even at 560 rpm (reaction 5).

Ceric-initiated graft polymerizations of methyl acrylate onto granular starch and onto cellulose also showed little dependence on stirring speed (Table II). Ungrafted PMA was removed from graft copolymers by extraction with acetone, and $\bar{M}_w$ and $\bar{M}_n$ values for polymer grafts were determined by gel permeation chromatography. Partial insolubility of grafted PMA has been observed by us in earlier work,[4] and molecular weight data refer to the soluble fractions obtained after removal of gel by centrifugation. Lower reactant concentrations were used in cellulose reactions 12–14 to permit efficient stirring of reaction mixtures.

Although it is not apparent why our results differ from those of Graczyk and Hornof, the effect of stirring speed on polysaccharide graft polymerization seems to be highly dependent on reaction conditions, for example, the particular polysaccharide, monomer, and initiating system used. Indeed, a referee has suggested that, with our reaction times, the kinetics of ceric-initiated polymerizations might be rapid enough (with acrylonitrile and methyl acrylate as monomers) to produce high conversions, even under the most adverse stirring conditions.

TABLE I
Graft Polymerization of Acrylonitrile onto Starch[a]

							DMF[e] extraction of product			
							Insoluble			Soluble
No.	Starch (g)	AN[b] (g)	RPM	Conversion[c] (%)	Add-on[d] (%)	PAN $\overline{M}_v$	% of total	Add-on[d] (%)	PAN $\overline{M}_v$	% of total
1	Granular (20)	30	100	85	53	130,000	99	—	—	1
2	Granular (20)	30	250	83	53	110,000	98	51	110,000	2
3	Granular (20)	30	400	85	53	140,000	97	—	—	3
4	Gelatinized (20)	30	100	92	56	760,000	91	—	—	9
5	Gelatinized (20)	30	560	94	56	770,000	96	—	—	4
6	Gelatinized (10)	15	100	85	55	650,000	90	—	—	10
7	Gelatinized (10)	15	250	81	56	620,000	91	52	610,000	9
8	Gelatinized (10)	15	400	77	54	—	83	—	—	17

[a] Reactions run in 400 mL of water with 1 mol of ceric ammonium nitrate per 100 glucose units of starch.
[b] Acrylonitrile.
[c] Total conversion of monomer to polymer.
[d] Wt % polyacrylonitrile (PAN) in the copolymer, as determined by weight loss on acid hydrolysis.
[e] Dimethylformamide.

TABLE II
Graft Polymerization of Methyl Acrylate onto Starch and Cellulose[a]

						Acetone extraction of product					
						Insoluble					Soluble
No.	Polysaccharide (g)	MA[b] (g)	H_2O (mL)	RPM	Conversion[c] (%)	% of total	Add-on[d] (%)	PMA $\overline{M}_w$	PMA $\overline{M}_n$	PMA solubility[e] (%)	% of total
9	Granular starch (20)	30	400	180	88	92	51	1,120,000	340,000	82	8
10	Granular starch (20)	30	400	300	81	90	47	1,360,000	550,000	72	10
11	Granular starch (20)	30	400	450	85	91	51	1,340,000	490,000	82	9
12	Cellulose (7.5)	9.4	300	130	96	90	50	670,000	180,000	100	10
13	Cellulose (7.5)	9.4	300	300	96	92	51	730,000	190,000	100	8
14	Cellulose (7.5)	9.4	300	520	93	89	49	670,000	235,000	93	11

[a] Reactions run with 1 mol of ceric ammonium nitrate per 100 glucose units of polysaccharide.

[b] Methyl acrylate.

[c] Total conversion of monomer to polymer.

[d] Wt % poly(methyl acrylate) (PMA) in the copolymer, as determined by weight loss on periodate-alkali degradation of the polysaccharide.

[e] In acetone.

We do not wish to speculate further on possible reasons for an effect of stirring speed under some reaction conditions or the lack of such an effect under others. The important conclusion to be drawn from this publication is that stirring speed plays a minor role when acrylonitrile and methyl acrylate are graft polymerized under conditions used in all of our previous research, which has been directed toward obtaining maximum conversions of monomer to polymer. There is certainly a need for more research in this area.

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