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Synthesis and Characterization of Water-Soluble Starch-Acrylamide Graft Copolymers

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ABSTRACT

A series of water-soluble starch-polyacrylamide graft copolymers (ST-g-PAM) were prepared by Ce^{4+}-initiated graft copolymerizations of acrylamide (AM) onto starch (ST) dissolved in water at 30°C. The copolymers were found to contain 3-33% (wt) of ST. The structure of the copolymers, including the average number of grafts per chain and the efficiency of the initiator, was determined by acid-catalyzed degradation of the ST followed by size exclusion chromatography (SEC) analysis of the PAM chains and was found to be consistent with the presence or absence of free ST in the polymerization product prior to hydrolysis. The average number of grafts per starch molecule was found to be three or less, depending on conditions. The initiator efficiency (6-43%) was shown to decrease with increasing $[Ce^{4+}]$ and decreasing [AM], and this was found to be qualitatively in accord with the proposed mechanism of initiation and polymerization. The low efficiency was shown to be due, in part, to the low rate of reaction of Ce^{4+} compared to the polymerization rate. The copolymers were characterized by ultracentrifugation, SEC, and viscometry.

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INTRODUCTION

Water-soluble copolymers of polysaccharides and readily available vinyl monomers are of potential interest for enhanced oil recovery (EOR) from several points of view. The cost of polysaccharides such as starch and cellulose is low compared to that of vinyl polymers currently used in EOR such as polyacrylamide (PAM), so their incorporation in a copolymer may be economically advantageous. This would be particularly true if the combination of the two polymers resulted in an enhancement of properties beyond that predicted from the composition and the physical properties of the two polymer components.

For instance, the intrinsic viscosity of graft copolymers may differ from that expected from the intrinsic viscosities of the component polymers as a result of incompatibility of the two chains [1]. In such a case the reluctance of the two polymer segments to interpenetrate could lead to a larger size and/or dissymmetry of the dissolved graft copolymer. Furthermore, polysaccharide graft copolymers [2] may be less susceptible to mechanical degradation compared to the vinyl polymer [3] as a result of the presence of relatively sturdy polysaccharide segments in the copolymer. This would be particularly plausible if several segments of relatively low molecular weight vinyl polymers were grafted onto the polysaccharide backbone.

These and other considerations have prompted us to investigate in some detail the synthesis of water-soluble starch-polyacrylamide graft copolymers (ST-g-PAM) and their characterization and physical properties [4-6]. Starch was chosen because of its low cost, availability, and reasonable water-solubility. Acrylamide was used as the grafting monomer because of the widespread use of PAM and its acrylic acid copolymers in EOR [7].

EXPERIMENTAL SECTION

Materials

Starch was purchased from Pfaltz and Bauer as water-soluble starch and was vacuum dried (0.025 mm) to constant weight. Acrylamide (Eastman) was crystallized once from benzene and vacuum dried (0.025 mm) to constant weight. $Ce(NH_4)_2(NO_3)_6$ was purchased from G. F. Smith Co. and was used as such. Na_2SO_4, $NaNO_3$, and HNO_3 were used as purchased.

Graft Copolymerizations

Copolymerizations were conducted in flasks of appropriate size under either N_2 or argon. The starch (ST) was dissolved in deionized water above 95°C and cooled. Acrylamide (AM) was added, and inert gas was bubbled through while stirring for 30 min. The volume was adjusted with deoxygenated deionized water. The flask was capped, and ceric ion initiator was added as a known molar solution in 1 $\underline{M}$ HNO_3. The graft copolymerization was conducted at 30.00 ± 0.02°C for the desired period of time and was terminated with hydroquinone. The reaction mixture was diluted with water to a viscosity low enough that the polymer solution precipitated rather than wrapping around the stirrer shaft when it was dropped into acetone. The precipitated polymer was removed, slurried with ~300-500 mL of acetone, filtered, and vacuum dried to constant weight at 0.025 mm.

Hydrolysis of ST-g-PAM Copolymers

The solid copolymer was dissolved in deionized water by slow stirring at room temperature. The solution was adjusted to 0.5 $\underline{N}$ acidity by addition of concentrated hydrochloric acid and dilution to 20.0 mL with deionized water. The container was capped and placed in a bath that was maintained at 70°C for 8 h. Hydrolysis of the ST moiety was monitored by withdrawing aliquots every hour and performance of the iodine test for ST.

After cooling the reaction mixture to room temperature, it was neutralized with $NaHCO_3$. The neutralized solution was dialyzed against deionized water to remove all ions and small molecules using a membrane with a molecular weight cut-off of 2000. The dialyzed solution was used for SEC analysis to determine $\overline{M}_n$ and $\overline{M}_w$ of the grafted PAM chains.

Hydrolysis of ST

The ST was dissolved in deionized water at >95°C by stirring. The sample was hydrolyzed using the same procedure as for ST-g-PAM copolymers, except that dialysis was not used. The SEC chromatogram using a column containing glyceryl-controlled porous glass (GCPG) with pore sizes of 74 and 240 Å exhibited one peak with a retention volume identical to that of the solvent peak when 0.2 $\underline{M}$ Na_2SO_4 was used as the mobile phase. The iodine test was negative.

Hydrolysis of PAM (Acid Conditions)

Hydrolysis of a PAM standard was carried out using the procedure for ST-g-PAM. SEC analysis showed that the PAM subjected to this hydrolysis condition had the same retention volume as the original standard when 0.2 M Na_2SO_4 was used as the mobile phase.

Determination of Intrinsic Viscosities ([η])

Four concentrations of copolymeric products were used to determine [η]. The product was dissolved in 1 M $NaNO_3$ by shaking in an orbital shaker. The average flow time through a Cannon-Fenske viscometer was determined at 30.00 ± 0.02 °C only after the solution had stood at least 21 d after initial mixing. The [η] had been found to decrease with time but became constant after 20 d. The [η] was determined by least-squares treatment of the plot of η_{sp} vs C and extrapolation to zero concentration.

Determination of Ceric Ion

The initiator was a solution of $Ce(NH_4)_2(NO_3)_6$ in 1 M HNO_3. The molarity of this solution was determined by potentiometric titration with a standardized solution of ferrous ammonium sulfate in 1 M H_2SO_4. The Fe^{2+} solution was standardized with a primary standard of $Ce(NH_4)_2(NO_3)_6$ in 1 M H_2SO_4.

The amount of unreacted ceric ion was determined by adding a measured volume of reaction mixture to a measured volume of standard Fe^{2+} solution. The excess Fe^{2+} was determined by potentiometric titration with a primary standard of $Ce(NH_4)_2(NO_3)_6$ in 1 M H_2SO_4. A platinum indicating electrode was used with a calomel reference electrode. The equivalence point was taken as the volume of titrant, where $\Delta mV/\Delta V$ was a maximum (mV = millivolts, V = mL of added titrant).

Method of Molecular Weight Measurement

A Waters GPC system, consisting of a Model 6000-A pump and a U6k injector, was used in combination with a Perkin-Elmer L-75 variable wavelength UV-Vis detector. The packing material used was glyceryl-controlled porous glass (GCPG) (Electro-Nucleonics, Inc.) with an average particle size of ~50 μm. A combination of four dry-packed, 90-cm columns (700/1400, 2000 + 2 × 3000 Å) was used. A packing of this particle size was necessary because mechanical retention of some of the high-MW polymers was found to occur in a number of high-efficiency columns (particle size ~10 μm). The mobile phase, 0.2 M Na_2SO_4 aqueous solution, was filtered through a 0.22 μ Millipore membrane under vacuum before use. The linear velocity of the mobile phase was 0.086 mL/s. The polymer concentration in the sample solution was 0.3 mg/mL or lower, and the volume of sample injected was 1 mL.

The calibration was made with the use of polydisperse PAM standards (Polyscience, Inc.). A computer search routine was used to retrieve the true MW-calibration curve from the polydisperse standards. The program used, GPCAMW, was written based on the linear calibration method introduced by Hamielec [17] and later modified by Yau et al. [18]. This method involves a best-fit search for an effective calibration line (log M vs V), which is represented by

$$M(V) = D_1 e^{-D_2 V} \qquad (1)$$

where V is the retention volume, and D_1 and D_2 are related to the intercept and slope of the calibration line. This method is valid if the portion of the calibration curve that covers the desired range of separation is linear. If so, $\overline{M}_n$ and $\overline{M}_w$ can then be represented in terms of the retention volume, the slope and intercept of the calibration line, and column dispersion factors.

$$\overline{M}_w = (1 + D_2\tau)\, e^{-[D_2^2\sigma^2/2 + D_2\tau]} \sum_V [F(V)/D_1\, e^{-D_2 V}] \qquad (2)$$

$$\overline{M}_n = \left(\frac{1}{1 - D_2\tau}\right) e^{[D_2^2\sigma^2/2 - D_2\tau]} [\sum_V F(V)/D_1\, e^{-D_2 V}]^{-1} \qquad (3)$$

where σ and τ are parameters which describe the degree of peak broadening and skewness due to column dispersion and extracolumn effects, whereas F(V) (peak height as a function of V) defines the contour of the SEC elution curve.

The assumption of linear calibration was well justified for the following reasons. A calibration in terms of hydrodynamic volume (V_n) using nearly monodisperse polystyrene standards showed a linear calibration range that corresponds to hydrodynamic radii of ~290-1880 Å and covers the separation range. The correlation coefficient of the linear regression was 0.9954. According to the universal calibration concept, there exists a MW-calibration line if a linear V_n calibration has been found and the Mark-Houwink relationship holds for the polymer studied. The column dispersion factors, σ and τ, were determined from the SEC chromatogram of Schardinger-β-dextrin which is monodisperse and has a molar mass of 1134 using the moment method [13].

Method of Size Measurement

The chromatographic conditions used for the size measurement were the same as those described in the previous section, except a Waters R-401 refractive index detector was used in combination with the UV-Vis detector. The duo-detector system was used to determine the absolute concentration of the copolymer at varied retention volumes. The dead volume between two detectors was corrected according to the difference between peak retention volumes indicated by the two detectors. The wavelength of the UV-Vis detector was set at 214 nm, where PAM showed moderate absorption but ST absorption was fairly weak.

The calibration was made using polystyrene standards (Waters Associates and Pressure Chemical, 2000 to 2×10^7 MW) in THF. The polystyrene standards had $\overline{M}_w/\overline{M}_n$ ratios of < 1.1, and the THF was HPLC grade. The use of these standards was necessary because monodisperse water-soluble standards that would cover the desired separation range were not easily available. The universal calibration curve thus obtained would be useful in aqueous SEC only if the pore size of the packing material would not alter in these two solvents. This had been demonstrated earlier for the GCPG columns, as the total permeation and total exclusion volumes were found to be the same in THF and in aqueous Na_2SO_4.

The equivalent hydrodynamic radii, R_η, of copolymers were related to the hydrodynamic volume, $[\eta]M$, by [1]

$$[\eta]M = \frac{10\pi N}{3}(R_\eta^{\ 3}) \qquad (4)$$

where R_η is related to the radius of gyration, $\langle S^2\rangle^{1/2}$, by [19, 20]

$$R_\eta = 0.87\langle S^2\rangle^{1/2} \qquad (5)$$

The band broadening and peak assymetry effects were corrected using the method described by Yau, Kirkland, and Bly [13], and all calculations were carried out with the use of a computer program (GPCS3).

RESULTS

The graft copolymerizations were carried out under argon by dissolution of water-soluble starch (ST) (Pfaltz and Bauer) in deionized water, addition of the desired quantity of acrylamide (AM), followed by addition of $\mathrm{Ce(NH_4{}^+)_2(NO_3)_6}$ in 1.0 M $\mathrm{HNO_3}$. All graft copolymerizations were run at 30°C. After the desired time of polymerization, an aqueous solution of hydroquinone was added to terminate the reaction. Polymer yields were essentially quantitative in most cases (~95%). The results of the polymerizations are shown in Table 1 and Fig. 1.

Figure 1 shows the intrinsic viscosity ($[\eta]$) of the polymerization products as a function of the [AM]/[ST] ratio for various ratios of $[\mathrm{Ce}^{4+}]/[\mathrm{ST}]$. Several trends are clear. First, the $[\eta]$ increases with increasing [AM]/[ST] at constant concentration of Ce^{4+}. Furthermore, the $[\eta]$ at constant [AM]/[ST] increased with decreasing concentration of Ce^{4+}. If the $[\mathrm{Ce}^{4+}]$ was decreased below 10^{-5} M, no polymerization occurred, presumably as a result of reaction of Ce ion with impurities present in the starch (see below). The $[\eta]$ varied from 1.5 to about 16.0 and was found to be reproducible at given ratios of reactants. Both trends are consistent with the occurrence of a graft copolymerization of AM initiated by a polysaccharide radical formed in turn by a reaction of the polysaccharide and ceric ion [8-11]. The occurrence of graft copolymerization was found to be consistent with several observations. First, in the absence of ST and at comparable reaction times, the homopolymerization of AM at the same $[\mathrm{Ce}^{4+}]$ proceeded very slowly, as was found by others [10]. The presence of ST in the isolated polymer was demonstrated by IR and by colorimetric tests, including the well-known blue complex of $\mathrm{I_2}$ and ST. The incorporation of ST into the graft copolymer could also be shown by size exclusion chromatography (SEC). Figure 2 shows an SEC of a graft copolymerization product to which ST has been added after polymerization. The presence of a peak attributable to free ST is clearly visible with a refractive index detector. Similar chromatograms were obtained in cases where the presence of free ST is expected ($[\mathrm{Ce}^{4}\ ]/[\mathrm{ST}] < 2$). Figure 3 shows an SEC of water-soluble ST itself and indicates that at least four components are present, two of which can be expected to overlap with that of the graft copolymer. Although the identity of the four components could not be fully elucidated, SEC proved helpful in ascertaining the nature of these species. Thus, isolation of component 1, followed by reinjection into the column, produced only one peak at a retention volume identical with that of component 1. However, after standing for 21 d, component 1, upon reinjection, produced a chromatogram that was similar to that of the original four-component mixture. Reversible dissociation-aggregation of the ST components apparently occurs to some extent. As result of this complication, no further attempts were made to isolate and use fractions of water-soluble ST for grafting.

TABLE 1. Graft Copolymerization of Water-Soluble Starch (ST) and Acrylamide (AM) Initiated by Ce^{4+} Ion

Experiment no.	$[AM]_i$ (mol/L)	$[ST]_i \times 10^4$ (mol/L)	$[Ce^{4+}]_i \times 10^4$ (mol/L)	$\overline{M}_n \times 10^{-6}$ PAM	$\overline{M}_w \times 10^{-6}$ PAM	$\bar{N}_g$[a]	f[b]	$[\eta]$[c] (dL/g)	Weight fraction styrene in copolymer	$\overline{M}_{nc}$[h] $\times 10^{-6}$
4A'	0.308	2.15	3.15	1.03	2.41	0.092	0.067	4.96	0.104[d]	1.15
4B	1.55	2.11	3.10	0.972	3.07	0.54	0.365	7.78	0.110[d]	1.09
8A	0.513	0.353	0.513	3.39	5.39	0.22	0.152	10.50	0.034[d]	3.51
4C	3.08	2.09	3.10	1.54	3.98	0.64	0.432	7.73	0.082[d]	1.46
12F	1.50	2.10	9.56	0.241	0.671	1.79	0.392	4.35	0.218[e]	0.551
12C	0.903	1.26	5.75	0.756	1.94	0.62	0.137	4.54	0.137	0.876
19A	1.50	1.09	4.95	0.896	2.66	1.09	0.240	6.35	0.109[d]	1.10
9D	0.30	0.418	1.91	0.881	1.90	0.54	0.118	4.29	0.120[d]	1.00
3A	1.21	3.36	24.0	0.199	0.438	1.22	0.170	1.81	0.331[e]	0.363
2-3	0.750	2.09	15.0	0.109	0.571	1.22	0.170	2.20	0.320	0.375
2-2	0.750	2.09	15.0	0.203	0.399	1.20	0.167	3.17	0.330	0.364
19B	1.50	1.08	7.82	1.16	3.05	0.85	0.117	6.98	0.0938	1.28
3C	1.51	2.10	30.2	0.357	0.858	1.33	0.093	3.76	0.202	0.595
6C	0.326	0.148	2.17	1.37	2.93	0.98	0.067	5.05	0.0805	1.49
21C	1.50	0.935	21.3	0.364	0.930	3.10	0.136	2.38	0.0960[e]	1.25
21D	1.50	0.703	16.0	0.627	1.35	2.35	0.103	2.63	0.0755[e]	1.59

21E	1.50	0.560	12.8	0.595	1.68	3.20	0.080	3.60	0.0594[e]	2.02
21H	1.50	0.465	10.7	0.967	2.12	2.34	0.102	3.82	0.0433[e]	2.38
21G	**1.50**	**0.403**	**9.12**	**0.845**	**1.83**	**3.13**	**0.138**	**3.92**	**0.0504[e]**	**2.77**
21F	1.50	0.465	16.0	0.641	1.98	2.78	0.081	1.76	0.0632[e]	1.90
39-1-1	0.521	1.04	10.4	0.524	1.04	0.67	0.067	1.73	0.186[d]	0.644
39-2-1	0.521	1.04	7.93	0.446	0.828	0.78	0.103	2.41	0.212[d]	0.566
39-3-1	0.521	1.04	5.43	0.657	1.54	0.54	0.104	3.39	0.154[d]	0.777
39-4-1	0.521	1.04	2.93	1.25	3.31	0.28	0.101	6.20	0.088[d]	1.37
39-5-1	0.521	1.37	10.4	0.355	0.664	0.76	0.100	1.80	0.253[d]	0.475
39-6-1	0.521	2.00	10.4	0.399	0.716	0.46	0.088	2.41	0.231[d]	0.519
39-7-1	0.521	3.73	10.4	0.409	0.787	0.24	0.087	2.41	0.227[d]	0.529
39-8-1	0.685	1.04	10.4	0.380	0.730	1.21	0.122	2.04	0.207[e]	0.580
39-9-1	1.00	1.04	10.4	0.298	0.536	2.29	0.229	2.82	0.150[e]	0.802
39-10-1	1.86	1.04	10.4	0.975	2.53	1.28	0.128	5.23	0.088[e]	1.37
39-2(2)	0.521	1.04	7.93	0.462	0.741	0.69	0.091	2.35	0.206	0.582
39-8(2)	0.685	1.04	10.4	0.364	0.540	0.61	0.099	1.70	0.248	0.484
39-5(2)	0.521	1.37	10.4	0.435	0.734	0.97	0.081	2.21	0.216	0.555
39-8(3)	0.685	1.04	10.4	0.473	0.984	0.039	0.097	N.D.	0.202	0.593
38-1	0.630	2.08	1.26	2.18	4.16		0.064	7.04	0.0522[d]	2.30
29	1.50	2.10	1.26	N.D.[g]	N.D.[g]		0.435[f]	9.89	0.0597	2.01

(continued)

TABLE 1 (continued)

Experiment no.	$[AM]_i$ (mol/L)	$[ST]_i$ $\times 10^4$ (mol/L)	$[Ce^{4+}]_i$ $\times 10^4$ (mol/L)	$\overline{M}_n$ $\times 10^{-6}$ PAM	$\overline{M}_w$ $\times 10^{-6}$ PAM	$\overline{N}_g$ [a]	f [b]	$[\eta]$ [c] (dL/g)	Weight fraction styrene in copolymer	$\overline{M}_{nc}$ [h] $\times 10^{-6}$
12E	1.50	0.863	0.525	N.D.[g]	N.D.[g]		0.408[f]	15.2	0.0291	4.13
30	1.50	1.14	1.07	N.D.[g]	N.D.[g]		0.309[f]	11.9	0.0407	2.95
28	1.44	0.828	0.80	N.D.[g]	N.D.[g]		0.303[f]	15.9	0.0433	2.77
35	1.50	1.13	1.53	N.D.[g]	N.D.[g]		0.267[f]	13.2	0.0455	2.64
7-3	1.20	2.10	0.80	N.D.[g]	N.D.[g]		0.438[f]	9.46	0.0494	2.43
7-2	1.50	2.10	1.28	N.D.[g]	N.D.[g]		0.435[f]	9.19	0.0588	2.04
6A	1.02	0.706	1.025	N.D.[g]	N.D.[g]		0.215[f]	12.1	0.0379	3.17
6B	0.965	0.437	0.65	N.D.[g]	N.D.[g]		0.266[f]	15.8	0.0331	3.63
12B	0.600	0.837	3.82	N.D.[g]	N.D.[g]		0.089[f]	4.49	0.0938	1.28

[a] $\overline{N}_g = [PAM]/[ST]_i$.

[b] $f = [PAM]/[Ce^{4+}]_i$.

[c] Determined in 1.0 <u>M</u> $NaNO_3$ at 30.00 ± 0.02°C after standing for 21 d.

[d] Unreacted ST was detected by SEC.

[e] No unreacted ST detected by SEC.

[f] Calculated from a plot of f vs $[AM]_i[ST]_i[Ce^{4+}]_i$ that showed a correlation coefficient of 0.95.

[g] Not determined by hydrolysis of copolymer.

[h] $\overline{M}_{nc} = \overline{N}_g(\overline{M}_n) + 1.2 \times 10^5$.

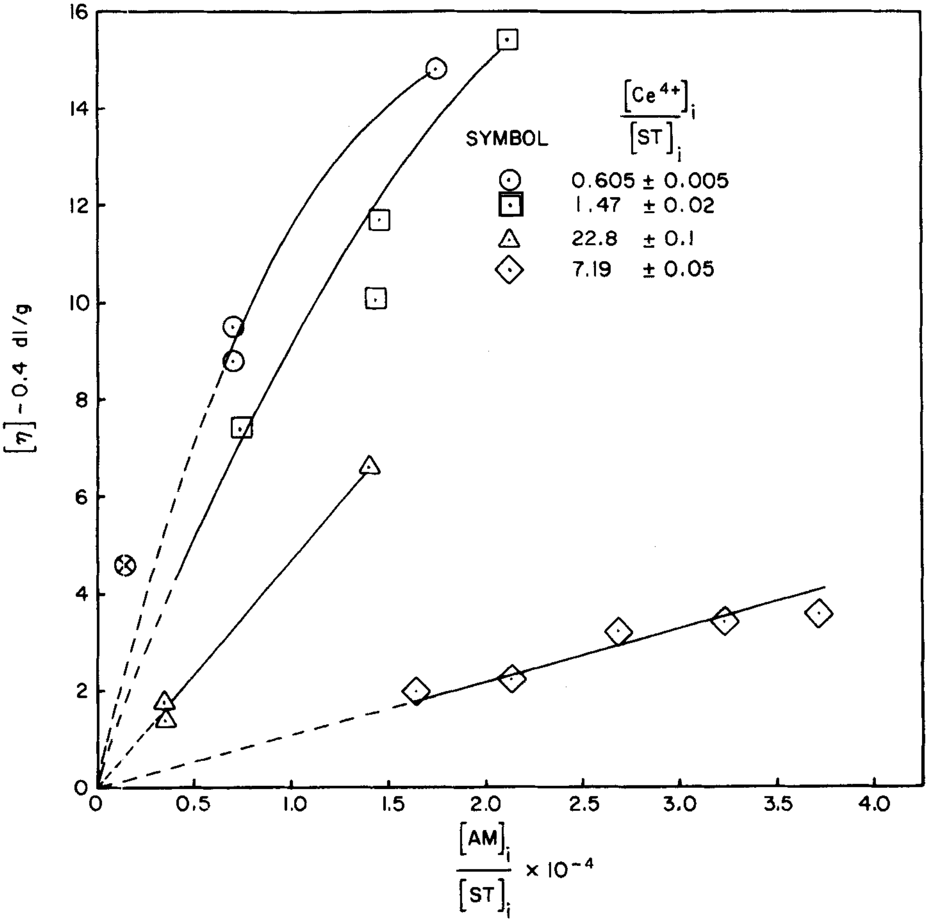

FIG. 1. Intrinsic viscosity of starch-g-polyacrylamide copolymers as a function of the monomer/starch mass ratio at various molar ratios of Ce^{4+} and starch.

The weight-average molecular weight ($\overline{M}_w$) of ST was found to be 1.20×10^5 by SEC. Sedimentation velocity measurements, carried out by analytical ultracentrifugation, gave a $\overline{M}_w$ of $\sim 0.8 \times 10^5$. The SEC value was used in subsequent calculations. The presence of ST in the isolated copolymers could be detected by IR, and ranged from ~3 to 33% (Table 1).

The presence or absence of free ST in these graft copolymerizations would be expected to be determined by the initiator efficiency (f), i.e., the fraction of Ce ion resulting in the formation of vinyl

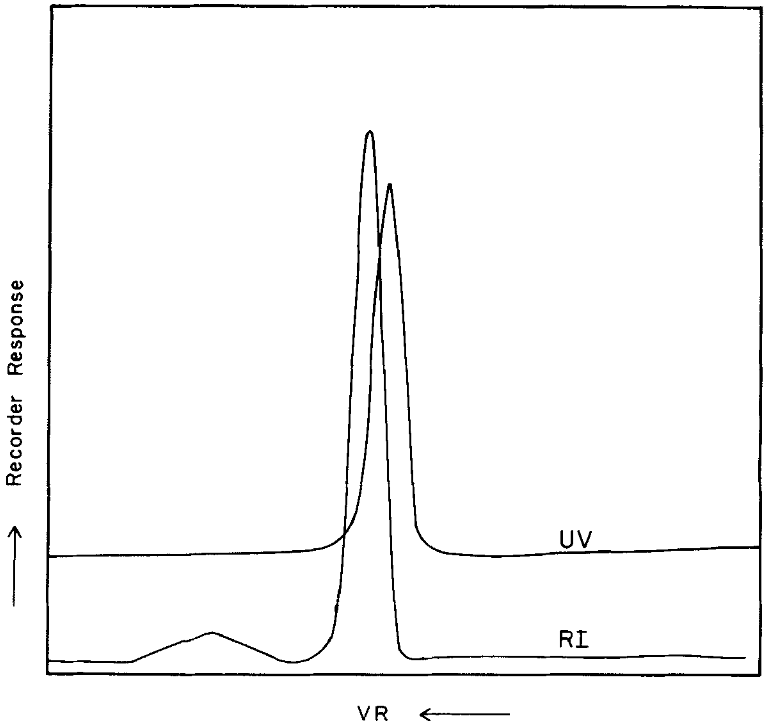

FIG. 2. UV detector and refractometer SEC responses of a starch-g-polyacrylamide copolymer containing unreacted starch. Columns: CPG 74/240, 700/1400, 3125, and 3125 Å. Moving phase: 0.2 M Na_2SO_4.

polymer. We have attempted to determine this parameter by acid-catalyzed hydrolysis of the ST backbone, followed by SEC analysis of the vinyl polymer fragments (Experimental Section). The acid hydrolysis (0.5 N HCl, 70°C, 8 h) of ST is rapid and was shown to lead only to mono- and oligosaccharides by SEC that showed only the presence of an oligosaccharide component with a retention volume approximately the same as that of Schardinger-β-dextrin. The absence of a polysaccharide could also be demonstrated by the absence of complex formation upon addition of I_2. The oligosaccharides could be readily removed by dialysis with a 2000-MW cut-off membrane. Under these hydrolysis conditions, partial hydrolysis of PAM is expected to occur. However, when using a 0.2 M Na_2SO_4 mobile phase, no difference in retention volume of a PAM standard before or after acid hydrolysis could be detected. Treatment of a PAM standard under more stringent conditions (10 N HCl, 30°C, 2 h, or 0.5 N HCl, 70°C, 36 h, followed by 80°C for 1 h) showed changes in retention volume and the appearance of addi-

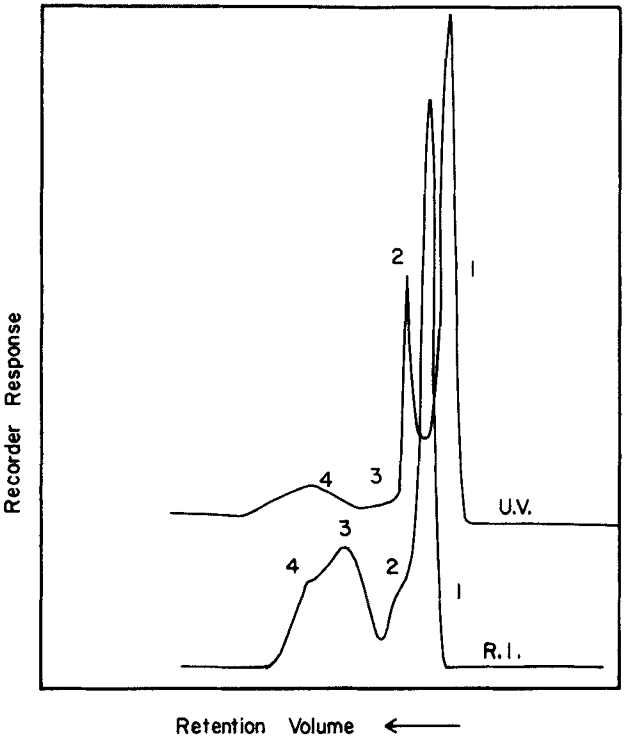

FIG. 3. SEC chromatogram of oxidized starch (Pfalz and Bauer). Columns: GPG 74/240, 700/1400, 3125, and 3125 Å. Moving phase: 0.2 M Na_2SO_4.

tional SEC peaks, presumably as a result of imide formation [12]. Hydrolysis of ST-g-PAM copolymers (GS-21F) with 0.5 N HCl at 70°C for 8 h resulted in a product in which no ST could be detected by IR or by the I_2 test. As a result, SEC analysis of the acid hydrolysis products of the graft copolymers provided important data on the number and degree of polymerization of the grafted chains. The $\overline{M}_n$ and $\overline{M}_w$ of the grafted PAM homopolymers were determined by a modified GPCV-3 method [13]. As a result, the gross structure of these graft copolymers and the initiator efficiency in these systems could be determined. Inspection of Table 1 shows that the initiator efficiency varies from ~6 to 43%, depending on conditions. As a result, the number of grafts per ST molecule (N_g) is considerably lower than previously estimated [4, 5] (ranging from 1-3), and many of these copolymers thus appear to resemble block copolymers. It is worth pointing out that no free ST could be detected by SEC under conditions where the molar concentration of PAM chains exceeded that of the ST. Conversely, free ST was usually detected when the molar ratio of [PAM]/[ST] was < 1. Values of $N_g > 3$ were difficult to obtain due to a decrease in initiator efficiency with increasing $[Ce^{4+}]$ (Table 1) (see below). Initiator efficiency was also shown to increase with increasing monomer concentration (Table 1, Runs 4A, 4B, and 4C) and decreasing concentration of Ce^{4+} at constant [AM] and [ST] (Table 1, Runs 19A and 19B, 12F and 3C, 21H and 21F). At relatively high monomer concentration, the efficiency seems to be mostly determined by the $[Ce^{4+}]_i/[ST]_i$ molar ratio rather than by the concentrations of Ce^{4+} and ST (Runs 21C-H). At lower AM concentrations, however, the effects of the $[Ce^{4+}]_i/[ST]_i$ molar ratio are less clear (Runs 39-2-1, -3-1 and, -4-1, and 39-5-1, -6-1, and -7-1) (see Discussion).

Determination of Ce^{4+}

In order to obtain a better understanding of the factors responsible for these trends, the concentration of Ce ion during the graft copolymerization was monitored. The $[Ce^{4+}]$ was thus determined at various reaction times by addition of a known excess of standardized Fe^{2+} solution and backtitrated with a Ce^{4+} solution of known concentration [14] (see Experimental). Figure 4 indicates that, except for an initial short period, the decrease in $[Ce^{4+}]$ generally follows first-order kinetics through about one-half life at constant AM and ST concentrations. The first-order rate constant was $1.4\ (\pm\ 0.4) \times 10^{-5}\ s^{-1}$. Interestingly, only ~50% of the Ce^{4+} had reacted under these conditions after ~10 h. Under our polymerization conditions, most or all of the monomer had reacted in the first several hours. It therefore appears that the low initiator efficiency is due, at least in part, to the low rate of initiation with Ce^{4+}.

Characterization

The graft copolymers generally contain a relatively large weight fraction of PAM (Table 1). Furthermore, the number of PAM grafts per ST molecule is low. For N_g values <2, these copolymers would therefore be essentially AB or ABA block copolymers containing large blocks of PAM. Figure 5 shows a logarithmic plot of $[\eta]$ vs $\overline{M}_n$ of the copolymers calculated from the $\overline{M}_n$ of the PAM grafts, the MW of the ST, and from the grafting number, N_g. Although the data points are scattered, the copolymers characterized by N_g values <2 and $\cong 3$ fall

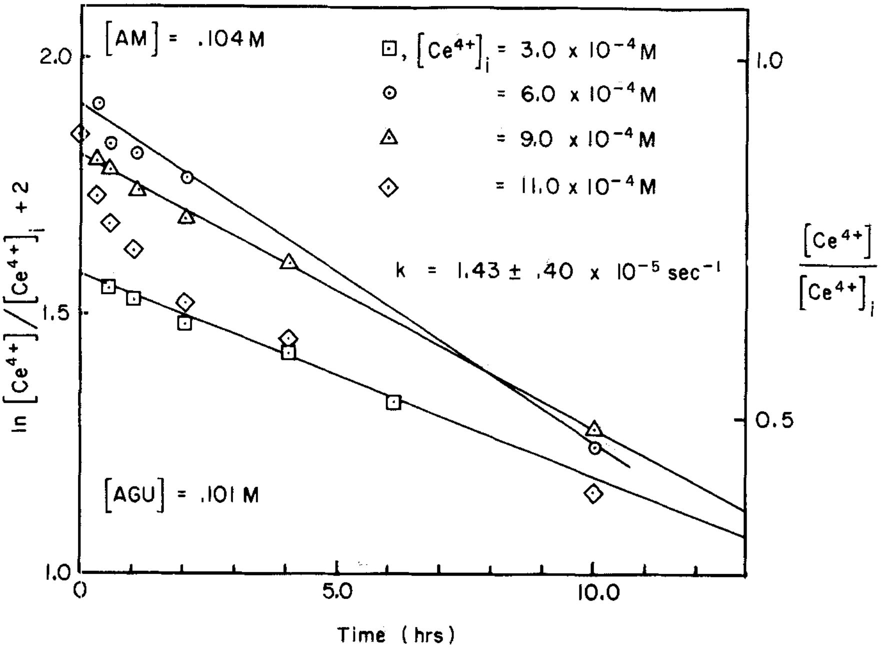

FIG. 4. First-order plot of the decrease of ln $[Ce^{4+}]$ in 1.0 M HNO_3 solutions of starch and acrylamide.

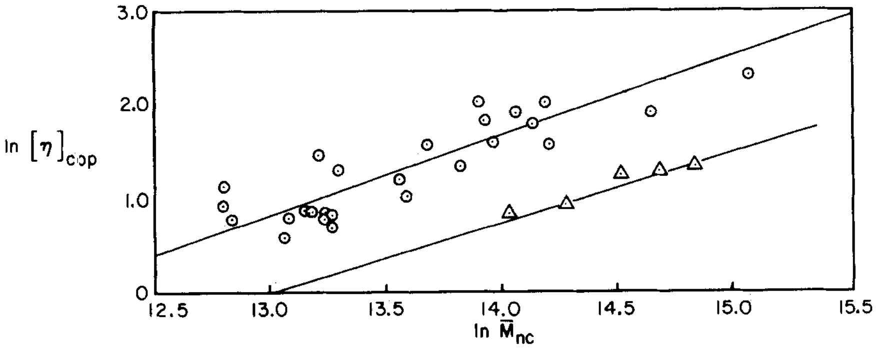

FIG. 5. Intrinsic viscosity as a function of the number-average molecular weight of St-g-PAM copolymers for different grafting numbers N_g ([PAM]/[ST]). (○): $N_g \leq 2$. (△) $N_g \approx 3$.

TABLE 2. Instinsic Viscosities of ST-g-PAM Copolymers and PAM Homopolymers of Approximately Equal Molecular Weight

	3C	29	28	6B	4B	4A
Starch content (%)	20.0	19.5	13.3	7.9	18.4	51.1
$[\mathrm{Ce}^{4+}]_i/[\mathrm{St}]_i$	.05	.61	.48	1.47	1.47	1.49
$[\eta]$ Copolymer	3.9	9.8	16.2	12.5	9.2	3.5
$\overline{M}_w \times 10^{-6}$[a]	.73	3.08	7.81	5.85	2.64	0.87
$\overline{R}_g$ (Å)	409	899	1261	1050	728	364
$[\eta]$ PAM[b]	2.8	7.1	13.2	10.9	6.5	3.1
% Increase in copolymer	41.3	37.1	22.6	14.5	42.5	12.8

[a] Measured by sedimentation transport [15].
[b] Calculated from $[\eta] = 3.73 \times 10^{-4} \overline{M}_w^{0.66}$ [23].

on approximately parallel lines. The $[\eta]$ of the latter group of copolymers are smaller by a factor of ~2.5. Such behavior is in qualitative accord with that expected for linear and branched polymers [15]. Since the molecular weight of the ST fragment is quite small compared to that of the PAM blocks, the polymers with $N_g \cong 3$ may actually resemble three-arm star polymers.

Comparison of the $[\eta]$ of the ST-g-PAM and PAM homopolymers of equal molecular weight is of special interest. For instance, a substantial increase in $[\eta]$ of the copolymer over the PAM homopolymer would be of substantial practical and theoretical interest (see Introduction). Table 2 shows pertinent results for several graft copolymers. The $[\eta]$ of homopolymers of the same molecular weight was calculated from the molecular weights of the copolymers determined by sedimentation of velocity (see below) and the Mark-Houwink relationship for PAM homopolymer [23]. The data show an increase in the $[\eta]$ for the copolymers in all cases ranging from 12.8 to 42.5%.

Although encouraging, it remains to be seen whether the increases are genuine. Systematic errors in the molecular weights determined by ultracentrifugation and uncertainties in the effects of molecular weight distribution on sedimentation and $[\eta]$ render these results somewhat tentative. Moreover, since the molecular weight of the ST is low, the effects on the hydrodynamic volume of the copolymer are most likely rather small. It sould be possible to observe more definitive effects with graft copolymers that contain both a larger fraction of polysaccharide and a higher molecular weight polysaccharide fragment. Experiments along these lines are in progress.

Determination of Molecular Weight and Size

Molecular weights (MW) of selected ST-g-PAM polymers were determined by the sedimentation transport method in 0.20 M KCl solutions using the Flory-Mandelkern equation [16]. The measured sedimentation velocities, together with the $[\eta]$, provided a MW which approximates a viscosity-average molecular weight and a corresponding average molecular size (Table 3) [21].

SEC was used to determine 1) the hydrodynamic size of ST-g-PAM copolymers and 2) the MW of PAM segments obtained by acid-catalyzed hydrolysis of the graft copolymer. The determination of hydrodynamic sizes of graft copolymers was made with the use of the universal calibration method. The M_n and M_w of PAM segments were determined from a MW-calibration curve which was obtained with the use of polydisperse PAM standards.

Since macromolecules are separated by their hydrodynamic sizes in SEC analysis, the principal information obtained is on the size distribution, from which a weight-average size may be rigorously calculated. According to the universal calibration concept, this statement will be true for a variety of polymers under proper experimental conditions. Thus, SEC should be sufficient to yield the weight-average molecular size for these graft copolymers. However, this is the only information obtainable from SEC for the copolymers that are heterogeneous in structure. A well-defined $\overline{M}_w$ and MW distribution for heterogeneous copolymers cannot be obtained from SEC alone, because copolymers of the same MW but different compositions may have different hydrodynamic sizes.

Nevertheless, SEC can be useful in the determination of MW of one of the components in the copolymer if this component can be separated from the others. As discussed earlier, acid-catalyzed hydrolysis was found to lead to degradation of the ST backbone into oligosaccharides that were very small compared to PAM segments. These oligosaccharide fragments were so small that the probability of finding more than one PAM graft on one of these fragments was essentially zero. It was thus reasonable to consider the PAM segments to be homo-PAM. With this assumption it was possible to determine MW distribution of PAM grafts by SEC using PAM MW standards.

Comparison of the data (Table 3) shows differences between the molecular weights and sizes obtained by ultracentrifugation (UC) and SEC. These differences are not unexpected since the UC data refer to viscosity-average molecular weight [21] and are not directly comparable with the number- and weight-average molecular weights calculated from the SEC results obtained from the hydrolyzed copolymers. As a result, the UC and SEC results are expected to vary widely depending on the width of the MW distribution. Other potential complicating factors include the formation of aggregates under centrifugation

TABLE 3. Molecular Weight and Size of ST-g-PAM Copolymers by Sedimentation Velocity (SV) and SEC

Sample	[η] (dL/g)	$\overline{M}_{SV}$ (× 10^6)	$\overline{M}_{n,SEC}$[d] (× 10^6)	$\overline{M}_{w,SEC}$[d]	R_{SV} (Å)	R_{SEC} (Å)
GS-3C	3.76	.73	.59	1.26	356	
GS-4A	4.96	.87	1.15	2.53	364	
GS-4B	7.8	2.64	1.09	3.19	728	965
GS-6A	12.1	6.91	3.17[e]	-	1051	
GS-6B	15.8	5.85	3.63[e]	-	1050	1156
GS-29	9.9	3.08	2.01[e]	-	760	
GS-28	15.9	6.92 (4.83)[b]	2.77[e]	-	1069	1139
ST		.08				
PAM (2 × 10^6)		1.72 (2.26)[c]				
PAM[a]		6.88[c]			1128	

[a] Obtained from Polysciences, Inc.; specified MW $\cong 5 \times 10^6$.

[b] Obtained by sedimentation equilibrium.

[c] Obtained from the empirical equation $S = 8.17 \times 10^{-15}\ M^{.31}$ relating the sedimentation of PAM to MW [24].

[d] Calculated as $N_g(\overline{M}_{PAM}) + .12 \times 10^6$, where N_g is the determined number of grafts per ST molecule. $N_g = 1$ was used for all values < 1.

[e] Calculated from the interpolated efficiency, f, the $[Ce^{4+}]_i$ and $[AM]_i$, and the monomer conversion. See Table 1, footnote f.

conditions, contamination of the UC sample by unreacted ST, errors in extrapolating the UC data to infinite dilution, and unjustified assumptions associated with the use of the Flory-Mandelkern equation.

DISCUSSION

The presence of a ST-g-PAM copolymer in these reactions is clear. This is demonstrated by IR data and other data showing the presence of the polysaccharide in the copolymer and the absence of free ST in solutions of the polymer, and is also supported by the very slow initiation in the absence of ST. Similar results were obtained by Ce^{4+} determinations that showed a much slower decrease of Ce^{4+} in the absence of ST. Nevertheless, the presence of some PAM homopolymer in the product cannot be excluded. Such a presence would be difficult to demonstrate, since the homo and graft copolymers would be expected to have very similar properties because of the relatively small proportion of ST in the copolymer.

The data on initiation efficiency are of considerable interest. First, they demonstrate that it is the reaction of Ce^{4+} with ST that is a limiting factor in the grafting reaction. The decomposition reaction of the Ce^{4+} complex is apparently slow in competing with the much faster rate of polymerization of AM. As a result, at high Ce^{4+} concentrations, the monomer would be rapidly depleted from the mixture, resulting in relatively low initiation efficiencies. The effect of monomer concentration is very pronounced in several instances. This appears to be in accord with the mechanism proposed for grafting of AM initiated by Ce^{4+} [9, 22]. This mechanism (Eqs. 6-13) involves a rapid reversible complexation of Ce^{4+} with the substrate, followed by a slow decomposition to produce the radical and Ce^{3+}.

$$S + Ce^{4+} \overset{K_e}{\rightleftharpoons} [S,Ce]^{4+} \longrightarrow \qquad (6)$$

$$[S,Ce]^{4} \xrightarrow{k_1} S^\circ + H^+ + Ce^{3+} \quad \text{(radical formation)} \qquad (7)$$

$$\left.\begin{aligned} &S^\circ + AM \xrightarrow{k_1} S\,AM^\circ && (8)\\ &S\,AM^\circ + {}_nAM \xrightarrow{k_p} S[AM]_nAM^\circ && (9)\end{aligned}\right\}\ \text{(propagation)}$$

$$\left.\begin{aligned} &2S^\circ \longrightarrow S_2 && (10)\\ &2S[AM]_nAM^\circ \longrightarrow (S[AM]_{n+1})_2 && (11)\\ &S[AM]_nAM^\circ + S^\circ \longrightarrow S[AM]_{n+1}S && (12)\end{aligned}\right\}\ \text{(termination by combination)}$$

$$S^\circ + Ce^{4+} \xrightarrow[k_t]{H_2O} R^+ + Ce^{3+} \qquad \text{(termination by electron transfer)} \qquad (13)$$

Reaction with monomer (AM) (Eqs. 8 and 9) produces the polymer radicals that may terminate by combination (Eqs. 10-12) or by electron transfer to Ce^4 (Eq. 13).

Barring the occurrence of extensive radical recombination of the substrate radical or polymer radicals, the initiation efficiency (f) would be expected to depend primarily on the relative rates of Eqs. (8) and (13). Assuming steady-state conditions, we can write

$$d[S^\circ]/dt = 0 = k_1K[Ce^{4+}][S] - (k_i[AM] + k_t[Ce^{4+}])[S^\circ]$$

so that

$$[S^\circ] = \frac{k_1K[Ce^{4+}][S]}{k_1[AM] + k_t[Ce^{4+}]} \qquad (14)$$

The partitioning between initiation and termination reactions would then depend on a time-dependent parameter, f', that is proportional to the ratio of the rates of initiation and S° generation:

$$f' = \frac{k_i[S^\circ][AM]}{k_1K[Ce^{4+}][S]} = \frac{k_i[AM]}{k_i[AM] + k_t[Ce^{4+}]} \qquad (15)$$

so that 1/f' is expected to increase linearly with $[Ce^{4+}]$ and with 1/[AM]. The complexity of the system would appear to preclude a similar evaluation of the initiation efficiency, f. However, consistent with Eq. (15), the initiation efficiency increases with increasing $[AM]_i$ and decreasing $[Ce^{4+}]_i$.

Due to the very slow decomposition of the ceric ion complex and the relatively rapid propagation reaction, a large fraction of the $[Ce^{4+}]$ is not used in these initiation reactions. Nevertheless, at low $[Ce^{4+}]_i$ and high $[AM]_i$, f approaches 45%. Most of the AM monomer is depleted within the first few hours of the polymerization. Within that time span, only a relatively small fraction of Ce^{4+} ion is converted (20-50%). For high efficiency reactions (low $[Ce^{4+}]$ and high [AM]), therefore, this appears to be the principal factor limiting the initiation efficiency. This also indicates that termination by recombination under these conditions is not a major pathway, since this would further reduce the number of PAM chains, and therefore f, by a factor of 2. At higher concentrations of Ce^{4+} ion, the efficiencies are considerably lower. This lower efficiency could be caused by three factors. First, the more rapid generation of radicals tends to deplete the AM from the reaction mixture faster, so that the polymerization is complete at lower Ce^{4+} conversion. Second, the larger concentration of polymer radicals may be expected to result in more recombination reactions so that fewer, but longer, PAM chains are formed upon hydrolysis leading to lower f. Finally, at higher $[Ce^{4+}]$, the polysaccharide substrate radical should undergo a faster electron transfer to Ce^{4+}, thus leading to a lower concentration of substrate radicals (Eq. 13). The relative contribution of these pathways is not clear at present.

The observed rapid initial decrease of $[Ce^{4+}]$ upon addition of Ce^{4+} to the ST monomer solution (Fig. 4) is of considerable interest. This decrease was shown to be due to the presence of ST and could be linked to impurities in the ST sample or to the reaction of Ce^{4+} with the reducing endgroups. Further experiments designed to explore this question are currently in progress.

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