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Graft Copolymerizations of Polysaccharides. II. Acrylamide Grafting to Yellow Dextrin

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ABSTRACT

Graft copolymers of acrylamide and yellow dextrin were prepared using cerium(IV) as initiator. The yellow dextrin had a very broad molecular weight distribution but was fractionated utilizing dialysis and ultrafiltration membranes. Initiator efficiencies were determined using size exclusion chromatography and were found to be between 2.4 and 34%. Initiator efficiency increased with acrylamide concentration at constant cerium(IV) and yellow dextrin concentrations, and decreased with increasing cerium(IV) concentration at constant acrylamide and yellow dextrin concentrations. Plots of acrylamide conversion and intrinsic viscosity vs initial acrylamide concentration at constant yellow dextrin and ceric ion concentrations showed a maximum at about 2.0 M.

INTRODUCTION

This report is one of a series from this laboratory based on our efforts to utilize renewable raw material sources as substrates for modification via grafting of vinyl monomers. The graft copolymers have potential as improved viscosifiers for use in enhanced oil recovery

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(EOR) applications. Among the most readily available materials of this group are such polysaccharides (PS) as starch, cellulose, pectin, dextrin, etc. Previous reports dealing with graft copolymers of PS and vinyl monomers include a variety of graft copolymers of water-soluble starch (ST) and acrylamide (AM) [1], and a series of graft copolymers of AM with Schardinger-β-dextrin (SD) [2]. The major purpose of the latter study was to provide additional information on the efficiency of ceric ion (Ce^{4+}) as an initiator for homogeneous grafting of vinyl monomers to PS substrates. However, because of uncertainties in methods of detection of unreacted PS substrate in this study (the molecular weight of SD is only 1135), it was impossible to obtain accurate initiation efficiencies in this case. The present study, designed to utilize yellow dextrin (YD) as a substrate for vinyl monomer grafting, was undertaken in order to provide reliable information on the efficiency of Ce^{4+} as an initiator for homogeneous grafting of vinyl monomer onto PS substrates.

Yellow dextrin (YD) is reported [3] to be a highly branched polyglucose derived from ST by acid and heat treatment, but unlike ST it contains additional glycosidic linkages at C2, C3, and C6. The YD used in this research was obtained from National Starch and Chemical Co. The material was a yellow powder which contained small amounts of particulates when dissolved in water. These particulates were removed by filtration through a coarse fritted funnel, and the intrinsic viscosity ($[\eta]$) of the filtrate was 0.02 dL/g in 0.2 M Na_2SO_4 at 30°C. The filtrate was treated further before use as outlined below.

EXPERIMENTAL

Materials and Equipment

Acrylamide (AM) (Matheson, Coleman and Bell) was purified by recrystallization from benzene.

Yellow dextrin (YD) (National Starch and Chemical Co.) was purified by dissolution in deionized water at room temperature, followed by successive filtrations through millipore filters. The filtrate from a 0.30-μm filter was dialyzed using either a Spectra/Por hollow fiber bundle with a molecular weight cut off (MWCO) of 5000, a membrane with MWCO of 2000, or a Viva Cell kidney dialysis membrane. In some experiments the dialyzed solution was used as such, and in some experiments the dialyzed solution was fractionated using ultrafiltration (UF) membranes. Number-average molecular weight ($\overline{M}_n$) of the YD was determined by size exclusion chromatography (SEC).

$Ce(NH_4)_2(NO_3)_6$ (F. E. Smith Co.) was dissolved in deoxygenated 1 M HNO_3, stored under argon, and added as a 0.1 M solution in the required amount to the reaction mixture. Graft copolymerizations were carried out under purified N_2 or argon in 50 mL Erlenmeyer flasks closed with serum caps.

Solvents for determination of $[\eta]$ were 0.2 M Na_2SO_4 made with deionized water and $Na_2SO_4 \cdot 10H_2O$ (Mallinckrodt, U.S.P. grade) or $NaNO_3$ (Mallinckrodt, AR grade). Benzene was reagent grade. Acetone was ACS certified.

Intrinsic viscosities were determined in the desired solvent at 30.00 ± 0.02°C using Cannon-Fenske viscometer tubes. Four concentrations, usually between 0.020 and 0.100 g/dL, were used. The $[\eta]$ was calculated from a least squares plot of η_{sp}/c versus c.

Graft Copolymerization and Analysis

A solution of YD of known concentration in deionized water was deoxygenated with purified N_2 or argon. The initiator solution was added to the YD solution, argon was bubbled through for about 15 min, and a deoxygenated aqueous solution of AM was added. The flask was capped under argon or N_2 after addition of the final reactant and placed in a 30°C bath.

After the desired polymerization time, hydroquinone was added to terminate the polymerization, and the reaction mixture was diluted with deionized water. If the copolymer was not to be isolated, the homogeneous diluted reaction mixture was diluted to a desired volume in a volumetric flask and analyzed by SEC and viscometry. When the copolymer was to be isolated, dilution with deionized water was made while stirring until a homogeneous solution was obtained which had a viscosity sufficient to allow for precipitation of the polymer in acetone as a nonsticky fibrous material. The fibrous polymer was added to about 500 mL acetone, allowed to stand at least 15 h, and filtered. The filtered polymer was vacuum dried (0.025 mm or less) at room temperature to constant weight.

Unreacted AM was determined by the weight difference between the copolymer and the charged YD. In the case where the copolymer was not isolated, its concentration was determined by SEC using a set of glycerated porous glass columns which separated the copolymer from unreacted YD and AM (Fig. 1).

Since the conversion of YD is low (17%, Table 1), the probability of having more than one PAM graft per YD is negligible. Assuming that homopolymerization in this and similar systems is negligible, we can write for the initiator efficiency (f):

$$f = [PAM]/[Ce^{4+}] = ([YD]_i - [YD])/[Ce^{4+}]_i \quad (1)$$

TABLE 1. Graft Copolymerization between Acrylamide (AM) and Yellow Dextrin (YD)

Expt No. GYD-	$[AM]_i$[a]	$[YD]_i$ $\times 10^3$[b]	Ceric ion[c] $[Ce^{4+}]_i$ $\times 10^4$	% Conversion, AM	Reaction product $[\eta]$[d] dL/g	Reaction medium volume, mL	% Conversion, YD[e]	Initiator efficiency (f)	$\bar{M}_n$[f] $\times 10^{-6}$
2	1.59	13.78[g]	3.10		3.60[d]	40			2.06[k]
3	0.705	7.143	2.50	49.5	3.80	40		0.21[j]	0.476
4	1.41	7.143	2.50	65.8	6.85	40		0.23[j]	1.16
5	2.11	7.143	2.50	68.0	8.00	40		0.28[j]	1.47
6	2.83	7.143	2.50	56.4	7.50	40		0.34[j]	1.33
7	0.705	7.143	3.75	61.0	3.95	40		0.16[j]	0.505
8	0.705	7.143	7.50	94.0	4.30	40		0.11[j]	0.574
12	0.229	7.143	2.50	9.2	0.47	40		0.30[j]	0.020
14-1	1.00	2.79	20.5	52.0[h]	7.15[i]	20	8.77	0.12[e]	
-5	0.789	2.79	20.5	45.9[h]	5.55[i]	20	8.77	0.12[e]	
-6	0.583	2.79	20.5	29.2[h]	5.22[i]	20	3.51	0.049[e]	
-7	0.375	2.79	20.5	23.6[h]	3.41[i]	20	1.75	0.024[e]	

13-5	0.69	3.51	16.6	5.7		16.3	7.1	0.15^e
-1	0.69	3.49	24.4	62.9		16.4	6.3	0.090^e
-6	0.68	3.43	40.4	90.5		16.7	7.5	0.064^e
-7	0.65	3.31	77.9	30.9		17.3	9.7	0.041^e
-8	0.60	3.06	144	38.0		18.7	12.6	0.026^e
-9	0.56	2.86	202	49.5		20.0	17.8	0.025^e

[a] Crystallized from benzene and vacuum dried.

[b] Runs 2-12, $\overline{M}_n$ (YD) = 1820; Runs 14-1 to 13-9, $\overline{M}_n$ (YD) = 5910.

[c] 0.1 M solution of $Ce(NH_4)_2(NO_3)_6$ in 1 M HNO_3.

[d] Determined in 0.2 M Na_2SO_4 at 30°C after at least 21 days standing.

[e] Calculated from SEC data.

[f] $\overline{M}_n$ of PAM with same $[\eta]$ as copolymer.

[g] Filtered (0.3 μm) undialyzed solution.

[h] Calculated from SEC peak weight for polymer.

[i] PAM concentrations determined by SEC.

[j] Calculated from conversion of monomer and $\overline{M}_n$ determined from viscometry using the relationship: $[\eta] = 6.8 \times 10^{-4}\ \overline{M}_n^{0.66}$ (see Ref. 4).

[k] Determined by SEC.

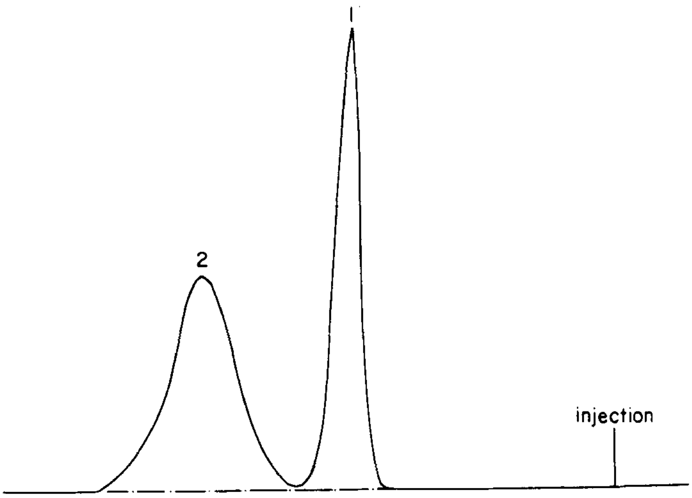

FIG. 1. A typical SEC chromatogram showing separation of unreacted YD from the copolymer. Peak 1: Copolymer (UV at 214 nm/RI = 23.6). Peak 2: Unreacted YD (UV at 214 nm/RI = 2.3). Columns: Glyceryl CPG 75 and 240 Å. Mobile phase: 0.2 M Na_2SO_4 aqueous solution.

in which $[Ce^{4+}]_i$ and $[YD]_i$ are the initial concentrations of Ce^{4+} and YD, respectively, and [YD] refers to the concentration of unreacted YD as determined by SEC of YD using a standard YD solution as a calibration standard. In some cases, f was determined by viscometric determination of the molecular weight and the monomer conversion [4]. Thus, assuming only one YD fragment per copolymer, the molecular weight is given by

$$\overline{M}_n = \frac{C[AM]_i(71)}{[YD]_i - [YD]} + \overline{M}_n(YD) \qquad (2)$$

where C is the fraction of converted monomer. Since the molecular weight of YD is small compared to that of the copolymer, the initiator efficiency is then determined from

$$[YD]_i - [YD] = \frac{C[AM]_i(71)}{\overline{M}_n} \qquad (2a)$$

and Eq. (1).

RESULTS AND DISCUSSION

The graft copolymerizations were carried out under conditions designed to probe separately the effects of the concentrations of YD, AM, and Ce^{4+} on the yield and intrinsic viscosity of the graft copolymer as well as the initiation efficiency of the Ce^{4+} initiator. The results are shown in Table 1 and in the figures. In Runs 3 through 6 and 14-1, -5, -6, and -7, the concentrations of Ce^{4+} and YD were kept constant while varying $[AM]_i$. The results show that the initiator efficiency (f) increases with increasing $[AM]_i$. The yield and intrinsic viscosity have a somewhat more complex pattern, showing a maximum in the conversion vs $[AM]_i$ and $[\eta]$ vs $[AM]_i$ plots (Figs. 2 and 3). Figure 4 shows a decrease of the initiation efficiency with increasing $[Ce^{4+}]$ at constant [YD] and $[AM]_i$, but the data in Table 1 (Runs 13-1, 5, 6, 7, and 8) also indicate that the conversion of YD increases with increasing $[Ce^{4+}]$.

Initiator Efficiency

The increase of initiator efficiency (f) with increasing $[AM]_i$ and decreasing $[Ce^{4+}]_i$ (Figs. 2 and 5) is of interest and consistent with

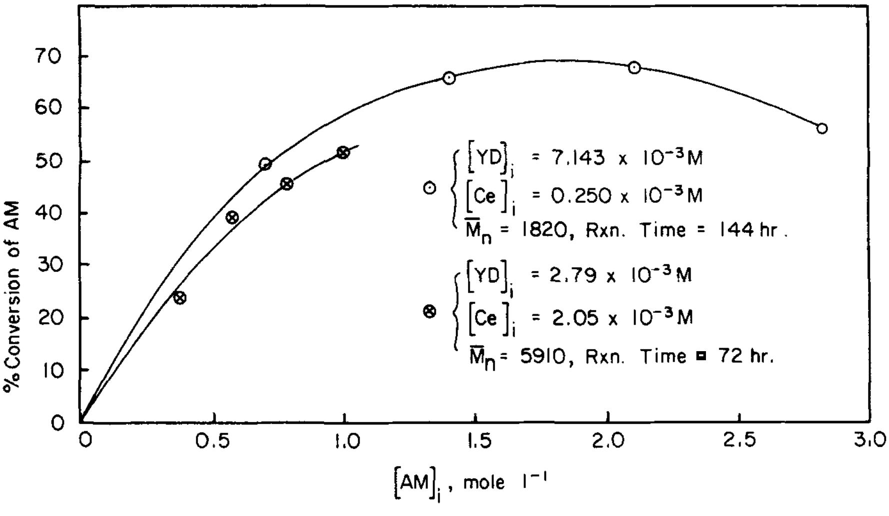

FIG. 2. Effect of initial concentration of acrylamide on acrylamide conversion at constant ceric ion and yellow dextrin concentrations.

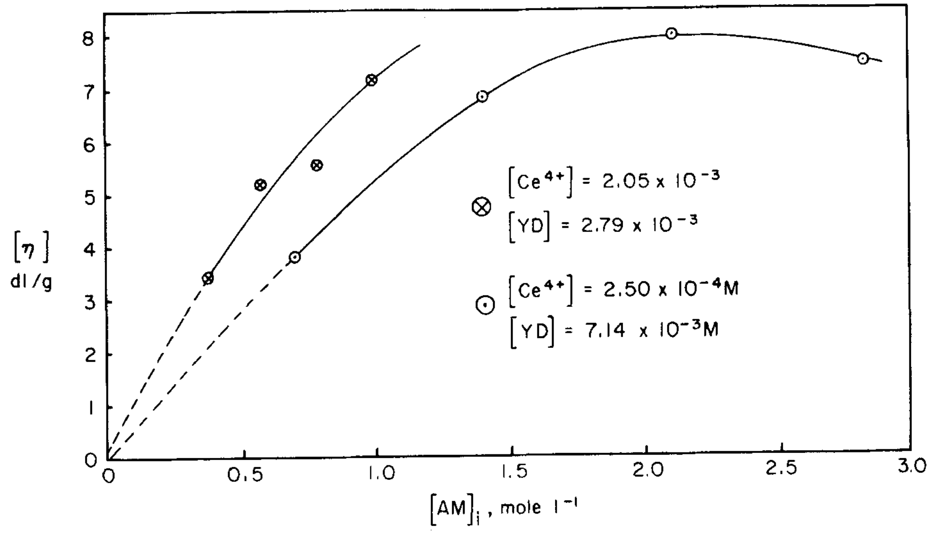

FIG. 3. Effect of initial concentration of acrylamide on intrinsic viscosity at constant initial concentrations of cerium(IV) and yellow dextrin.

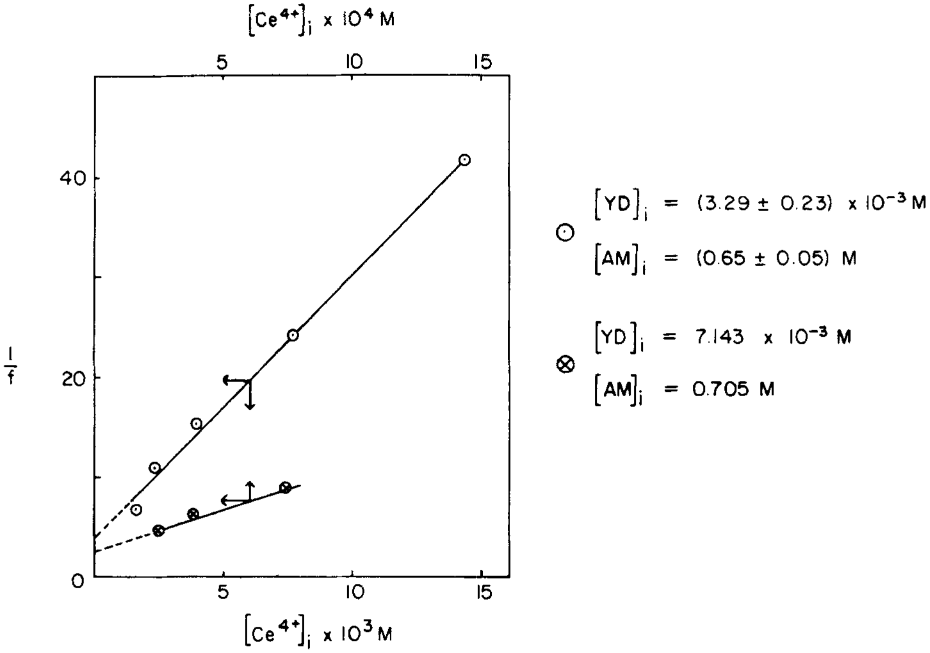

FIG. 4. Dependence of the reciprocal of the initiator efficiency upon $[Ce^{4+}]_i$ in the graft copolymerization of YD and AM.

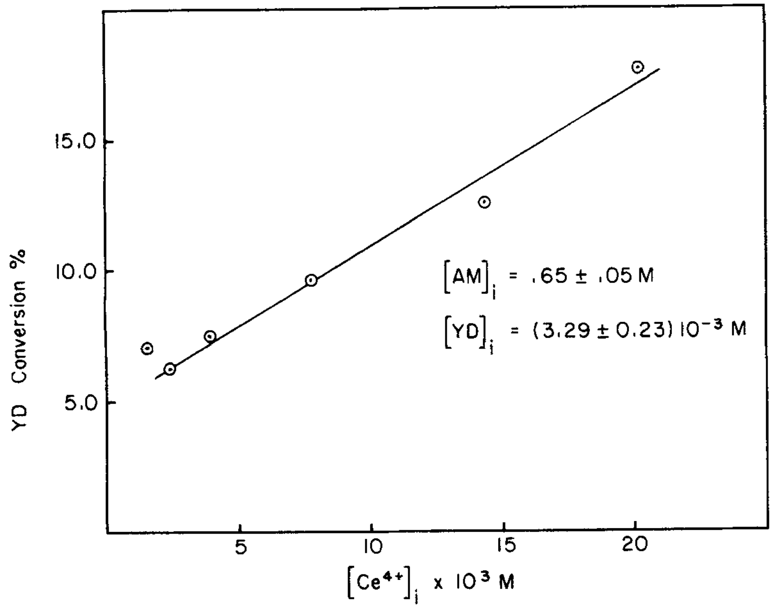

FIG. 5. YD conversion as a function of $[Ce^{4+}]_i$ at constant $[AM]_i$ and $[YD]_i$.

$$Ce^{4+} + YD \overset{K_e}{\rightleftharpoons} [Ce, YD]^{4+} \xrightarrow{k_1} YD^{\cdot} + Ce^{3+} + H^{+} \tag{3a}$$

$$YD^{\cdot} + AM \xrightarrow{k_i} YD\text{-}AM^{\cdot} \tag{3b}$$

$$YD\text{-}AM^{\cdot} + nAM \xrightarrow{k_p} YD\text{-}(AM)_n\text{-}AM^{\cdot} \tag{3c}$$

$$YD^{\cdot} + T \xrightarrow{k_t} YD \tag{3d}$$

which is a mechanism proposed by Johnson and Pottinger [5] and modified by the inclusion of a termination step (3d) in which the YD radical is scavenged with a reaction impurity or Ce^{4+} or both. It could also signify a bimolecular YD· coupling reaction. Thus, the initiation efficiency does appear to depend on the relative rates of Reactions (3b) and (3d). A higher concentration of AM, therefore, would be expected to increase initiation efficiency (f), and this is observed. The nature of the termination reaction is not entirely clear at present. However, the pronounced decrease of f with increasing

$[Ce^{4+}]_i$ (Fig. 4) suggests that electron transfer to Ce^{4+} may be involved. This would have to be confirmed by further experiments. The increase of YD "conversion," i.e., the incorporation of YD in the copolymer with increasing $[Ce^{4+}]_i$, is consistent with the involvment of Ce^{4+} in the termination reaction. Thus, according to Eq. (1), the rate of formation of the $YD^\bullet$ is proportional to $[Ce^{4+}]$, but the rate of depletion of $YD^\bullet$ does not increase linearly with $[Ce^{4+}]$. Following Eq. (3), we can write (assuming termination by Ce^{4+} and the occurrence of steady-state conditions)

$$\frac{d[YD^\bullet]}{dt} = 0 = k[Ce^{4+}][YD] - (k_i[AM] + k_t[Ce^{4+}])[Yd^\bullet]$$

where $k = k_i K_e$, provided that the equilibrium is fast compared to the decomposition of the equilibrium, so that

$$[YD^\bullet] = \frac{k[Ce^{4+}][YD]}{k_i[AM] + k_t[Ce^{4+}]} \qquad (4)$$

The partitioning between initiation and termination reactions could then be described by a parameter f' that equals the ratio of the rates of initiation and $YD^\bullet$ generation,

$$f' = \frac{k_i[AM][YD^\bullet]}{k[Ce^{4+}][YD]} = \frac{k_i[AM]}{k_i[AM] + k_t[Ce^{4+}]} \qquad (5)$$

so that 1/f' is expected to vary linearly with $[Ce^{4+}]$ and with 1/[AM]. The overall initiation efficiency, f, is expected to be related to f', although probably not in a simple manner given the complexity of the system. Nevertheless, 1/f' varies approximately linearly with $[Ce^{4+}]_i$, so that the $YD^\bullet$ scavenging reaction by Ce^{4+} appears consistent with our results. However, 1/f does not appear to vary linearly with $1/[AM]_i$. It is thus possible that other scavenging reactions are involved, and confirmation of the mode of $YD^\bullet$ scavenging would have to be confirmed by further experiments. Figure 5 shows the dependence of YD conversion at constant [YD] and [AM] upon $[Ce^{4+}]$ as measured by SEC. The approximately linear relationship is not unexpected on the basis of the mechanism (Eq. 3a). Thus, the rate of formation of Yd radicals is expected to increase linearly with $[Ce^{4+}]$.

Monomer Conversion and Intrinsic Viscosity

Figures 2 and 3 show that both intrinsic viscosity and conversion increase with increasing $[AM]_i$ but pass through a maximum. The increase in the 0.4 to 2.0 M range can be readily attributed to the higher degree of polymerization expected when the monomer concentration is increased. The decrease beyond 2.0 M both in $[\eta]$ and conversion is puzzling, however. It may be related to the very high viscosity of the reaction medium limiting monomer diffusion or to impurities in the monomer. Further work on this question is in progress.

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REFERENCES

[1] H. Pledger Jr., J. J. Meister, T. E. Hogen-Esch, and G. B. Butler, Society of Petroleum Engineers Paper SPE 8422, 54th Annual Fall Tech. Conf., Las Vegas, 1979.
[2] H. Pledger Jr., T. S. Young, T. E. Hogen-Esch, and G. B. Butler, "Graft Copolymerizations of Polysaccharides. I. Acrylamide Grafting to Schardinger-β-Dextrin," Manuscript in Preparation.
[3] R. L. Davidson (ed.), Handbook of Water-Soluble Gums and Resins, McGraw-Hill, New York, pp. 22-34.
[4] E. Collinson, F. S. Dainton, and G. S. McNaughton, Trans. Faraday Soc., 53, 489 (1957).
[5] C. R. Pottinger and D. C. Johnson, J. Polym. Sci., Part A-1, 8, 301 (1970).

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