Water-Soluble Copolymers. XI. Selectivity in the Graft Copolymerization of Acrylamide/N-(1,1-Dimethyl-3-Oxybutyl)acrylamide Comonomers onto Dextran by Ce(IV)-Induced Initiation

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Synopsis

Characteristic behavior in the graft copolymerization of acrylamide/N-(1,1-dimethyl-3-oxybutyl)acrylamide (AM/DAAM) comonomers onto dextran by Ce(IV)-induced initiation was investigated. From a preliminary study, it was found that ceric ammonium nitrate polymerized AM/DAAM comonomer mixtures and diacetone acrylamide, but not acrylamide alone in the aqueous solution. The effect of grafting conditions on the graft copolymerization product was studied with the aid of aqueous size exclusion chromatography and the anthrone reagent. The selectivity of formation of the graft copolymer over random copolymer was found to increase as the reaction temperature and AM/DAAM ratio increased and as both the Ce(IV)/Dextran molar ratio and HNO₃ concentration decreased. After establishing optimum grafting conditions, graft copolymer samples were prepared, and their aqueous solution behavior studied as functions of structure, temperature, and added salts.

INTRODUCTION

We recently reported conditions for best control of the grafting of acrylamide onto dextran[1] and cografting of acrylamide and sulfonate containing comonomers onto dextran.[2] In this work we report selectivity in the cografting of acrylamide (AM) and N-(1,1-dimethyl-3-oxybutyl)acrylamide (also called diacetone acrylamide, DAAM) onto dextran with the Ce(IV)-induced initiation. Previously we studied the copolymerization of the AM/DAAM pair in aqueous solution.[3]

Since the synthesis and polymerization of this monomer were first reported[4] in 1965, N-(1,1-dimethyl-3-oxybutyl)acrylamide has found a wide variety of commercial applications.[5,6] Homopolymerizations of diacetone acrylamide with various initiation systems including free radical, oxidation–reduction, UV, and beta radiation have been reported[5] along with recent electroinitiation techniques for coatings applications.[7] Franco[8] has reported the effect of different solvents on the copolymerization behavior of diacetone acrylamide.

Graft copolymers of diacetone acrylamide have also been prepared with natural and synthetic polymer backbones. Arthur[9,10] reported photoinitiated graft copolymerizations of diacetone acrylamide and other acrylamide derivatives onto cellulose in the near UV range in an aqueous medium. No reports appear, however, of the chemical grafting methods involving diacetone acrylamide and ceric ion initiation. The aims of this work were to investigate the AM/DAAM cografting reaction with Ce(IV) initiation and

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to study the dilute aqueous solution properties of the resulting graft copolymers.

EXPERIMENTAL

Materials

Dextran T-500 ($\overline{M}_w$ = 500,000 by light scattering) was obtained from Pharmacia Chemical Company. Acrylamide from Eastman Kodak and diacetone acrylamide from Aldrich were recrystallized three times from acetone prior to use. Ceric ammonium nitrate $(NH_4)_2 Ce(NO_3)_6$ from Fisher Chemical and anthrone from Aldrich were used as received. All other reagents were reagent grade and used without further purification.

Graft Copolymerization

Three grafting procedures utilizing Ce(IV)-induced initiation were utilized for the AM/DAAM comonomer study. All three grafting reactions were carried out in a three-necked flask equipped with mechanical stirrer, addition funnel, and N_2 gas outlet as follows: (a) In the conventional Ce(IV) grafting method, dextran T-500 was dissolved in distilled water; the solution was then purged with prepurified N_2 gas. Following the addition of the two monomers, freshly prepared ceric ion initiator solution in HNO_3 was added, and the mixture was stirred for 3 h at a specified temperature. (b) In a modified procedure,[1] the order to reagent addition was changed: dextran/ Ce(IV) + HNO_3/AM–DAAM. After dissolving dextran T-500 under N_2, the Ce(IV)–HNO_3 solution was added, and the mixture was stirred for 10 min at 25°C to allow complex formation. After increasing the reaction temperature to 30°C, AM/DAAM monomers were added; the mixture was stirred for 3 h. (c) In an improved Ce(IV) grafting method,[2] the order of addition of reagents were: dextran/Ce(IV)/AM–DAAM/HNO_3. In this procedure the dextran substrate was treated with an aqueous solution of $(NH_4)_2 Ce(NO_3)_6$ at 35°C for 15 min under N_2 prior to the graft copolymerization reaction. The AM/DAAM monomer pair was added to this partially oxidized dextran which contained active complexed Ce(IV) ions. The grafting reaction was started by adding HNO_3 solution; the mixture was then stirred for 3 h at 40°C.

In all grafting procedures, the product polymer solution was diluted with distilled water after reaction to a 0.5 g/dL concentration before precipitation with acetone. After purification by reprecipitation, the polymer was dried at 40°C under vacuum overnight. The total monomer conversion by weight was calculated from the following equation:

$$\text{conversion } (\%) = \frac{\text{wt graft copolymer } - \text{ wt dextran}}{\text{wt AM/DAAM comonomers}} \times 100$$

Size Exclusion Chromatography

A Waters Associates High Pressure Liquid Chromagraph ALC-300 with a Model R-401 Refractive Index Detector was used for the size exclusion

chromatographic studies. Columns were of stainless steel 60 cm in length and 0.767 cm in diameter. A nine-column set was packed with porous glass (Electro-Neucleonics, Inc.) of nominal pore size 3000 (2), 2000 (2), 1400 (2), 700, 500, 350 Å, respectively. The column set was operated at flow rate of 2 mL/min and a pressure of 1500 psi at 25°C. The eluting solvent was 75/25 (v/v) water/dimethyl formamide mixture. Injected sample size was 2 μL at a polymer concentration of 0.1 g/dL.

Viscosity Measurements

Four-bulb, shear dilution viscometers (Cannon-Ubbelohde) were used for the investigation of dilute aqueous solution properties of graft polymer samples. The shear rate $\dot{\gamma}$ and kinematic viscosity η were calculated from the equations: $\dot{\gamma} = k/t$ and $\eta = c \cdot t$, respectively, in which t represents the efflux time of the polymer solution and k and c represent the shear rate constant and viscometer constant, respectively. All viscosity measurements were conducted after a time interval of 5 days from solution preparation in order to minimize solution aging effects.

RESULTS AND DISCUSSION

Control of the Grafting Reaction

In a preliminary study, we grafted the comonomers DAAM and AM onto dextran utilizing Ce(IV) initiation method (a) detailed in the experimental section. Reaction conditions and conversions are shown in Table I for the copolymerization and homopolymerization of the respective monomers. Under these conditions it was found that AM and DAAM were copolymerized to high yield in the presence of the dextran substrate. Acrylamide did not homopolymerize, in agreement with our previous work, while DAAM was converted to homopolymer although at low yield. Ce(IV) was effective in initiating copolymerization of the 90/10 feed of AM/DAAM. Apparently the DAAM/Ce(IV) complex can disproportionate to produce radicals for homo- or copolymerization. Although graft copolymerization is favored, the reaction mixture from our preliminary experiments contained significant amounts of copolymer; therefore, subsequent experiments examined methods for increasing grafting relative to copolymerization.

The expected sequence of reactions is shown in eq. (1)–(8). The grafting reacton could be favored relative to the solution copolymerization by increasing complexation of Ce(IV) with dextran, D equation (1) relative to DAAM [eq. (3)] and/or by increasing the disproportionation rate of complex C_1 as compared to C_2.
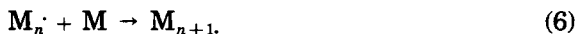
Initiation:

$$Ce(IV) + D \rightleftarrows C_1 \rightarrow D \cdot + Ce(III) \tag{1}$$

$$D \cdot + M \rightarrow D - M \cdot \tag{2}$$

$$Ce(IV) + DAAM \rightleftarrows C_2 \rightarrow DAAM \cdot + Ce(III) \tag{3}$$

TABLE I
Preliminary Study of AM/DAAM Grafting by Ce(IV) Initiation

Sample no.	Polymerization Method	AM/ DAAM ratio	Reaction conditions		Conversion (%)
PP-1	Grafting (a)	90/10	Water = 200 mL 30°C, 3 h, total [M] =	$\dfrac{Ce(IV)}{Dext.} = \dfrac{0.040}{0.004}$ (Mmol)	98.1
PP-2	Grafting (b)	90/10			97.5
PP-3	Grafting (c)	90/10			98.6
PP-4	Copolymerization	90/10	1 mol/L, [HNO] = 0.0025N	$\dfrac{Ce(IV)}{Dext.} = \dfrac{0.200}{0}$ (Mmol)	50.4
PP-5	Homopolymerization	100/0			Zero
PP-6	Homopolymerization	0/100			10.2

$$DAAM\cdot + M \rightarrow DAAM - M\cdot \qquad (4)$$

$$Ce(IV) + AM \rightarrow No\ Rxn \qquad (5)$$

Propagation:

$$M_n\cdot + M \rightarrow M_{n+1}. \qquad (6)$$

Termination:

$$M_m\cdot + M_n\cdot \rightarrow P \qquad (7)$$

$$M_n\cdot\ or\ M_m\cdot + Ce(IV) \rightarrow P + Ce(III) \qquad (8)$$
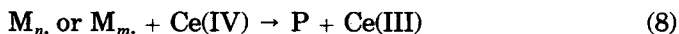
Aqueous Size Exclusion Chromatography Studies

The effects of reaction temperature, HNO_3 concentration, monomer ratios, Ce(IV)/dextran ratio, and order of addition of reagents on conversion and the distribution of products were studied utilizing aqueous size exclusion chromatography. Despite the obvious separation problems due to broad molecular weight distributions of the starting dextran and that inherent in radically initiated polymerization, it was possible to monitor products and thus optimize reaction conditions. Proper conditions must be maintained in order to avoid adsorption, to limit polymer solution dimensions, and to maximize the differences in refractive index of the polymer and solvent.[11,12]

Various solvents and solvent mixtures were tested (Table II), and a 75/25 (v/v) mixture of water/dimethyl formamide was found to be most suit-

TABLE II
Test of Solvents for the Chromatographic Study of Dextran-*g*-Poly(AM-co-DAAM) Samples

Solvent, mixture solvent & (polymer sample solution)	Refractive index N^2O	SEC resolution[a] (+, °, −)
H_2O, 0.5M potassium biphthalate (PBP)	1.3346	
(+ 0.2 g/dL pp-12, graft copolymer)	1.3347	−
(+ 0.2 g/dL dextran T-500)	1.3362	+ +
H_2O, 0.05M PBP & 0.05M urea	1.3357	
(+ 0.2 g/dL pp-12, graft copolymer)	1.3355	−
(+ 0.2 g/dL dextran T-500)	1.3356	−
H_2O/CH_3OH, 80/20 (v/v)	1.3371	
(+ 0.2 g/dL pp-12, graft copolymer)	1.3373	°
H_2O/DMSO, 50/50 (v/v)	1.4116	
(+ 0.2 g/dL pp-12, graft copolymer)	1.4117	−
H_2O/dioxane, 80/20 (v/v)	1.353	
(+ 0.2 g/dL pp-12, graft copolymer)	1.3534	+
H_2O/HCHO, 90/10 (v/v)	1.3360	
(+ 0.2 g/dL pp-12, graft copolymer)	1.3362	°
(+ 0.2 g/dL dextran T-500)	1.3365	+ +
H_2O/DMF, 75/25 (v/v)	1.3891	
(+ 0.2 g/dL pp-12, graft copolymer)	1.3896	+ + +
(+ 0.2 g/dL dextran T-500)	1.3897	+ + +

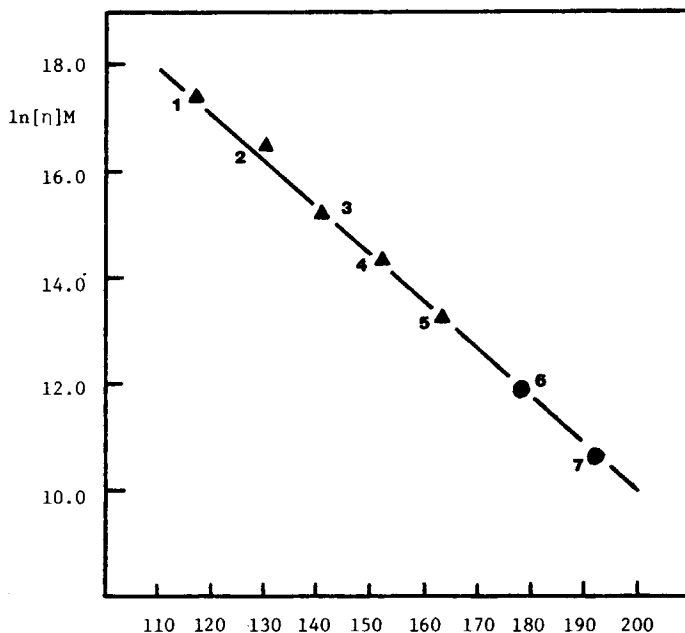[a] + = resolved; ° = some resolution; − = no resolution.

Fig. 1. Universal calibration curve obtained with polyacrylamide and dextran standards in 75/25 (v/v) water/DMF solvent. $\overline{M}_w$ of standard (polyacrylamides): (1) 5.5 × 10⁶; (2) 3.0 × 10⁶; (3) 1.5 × 10⁶; (4) 0.86 × 10⁶; (5) 0.51 × 10⁶ (dextran); (6) 0.50 × 10⁶; (7) 0.25 × 10⁶.

able. Separation was possible with controlled porous glass packing (see Experimental). The column set was calibrated using polyacrylamide and dextran standards (Fig. 1); no attempts, however, were made to predict molecular weights or hydrodynamic volumes for our synthetic polydisperse samples. Rather, fractions of the eluent from aqueous size exclusion chromatography were analyzed utilizing the anthrone reagent which quantitatively interacts with anhydroglucose units. The absorbance of each fraction was then studied spectroscopically at 630 nm and compared to standard dextran solutions[13] to determine composition. Note that unreacted dextran (T-500) elutes at 160 mL in this column set.

Effect of Reaction Temperature

The reaction temperature for cografting, method (a), of AM/DAAM monomers onto dextran was varied from 30°C to 60°C while keeping other grafting conditions constant (Table III). The total monomer conversion increased

TABLE III
Effect of Reaction Temperature on AM/DAAM Cografting onto Dextran

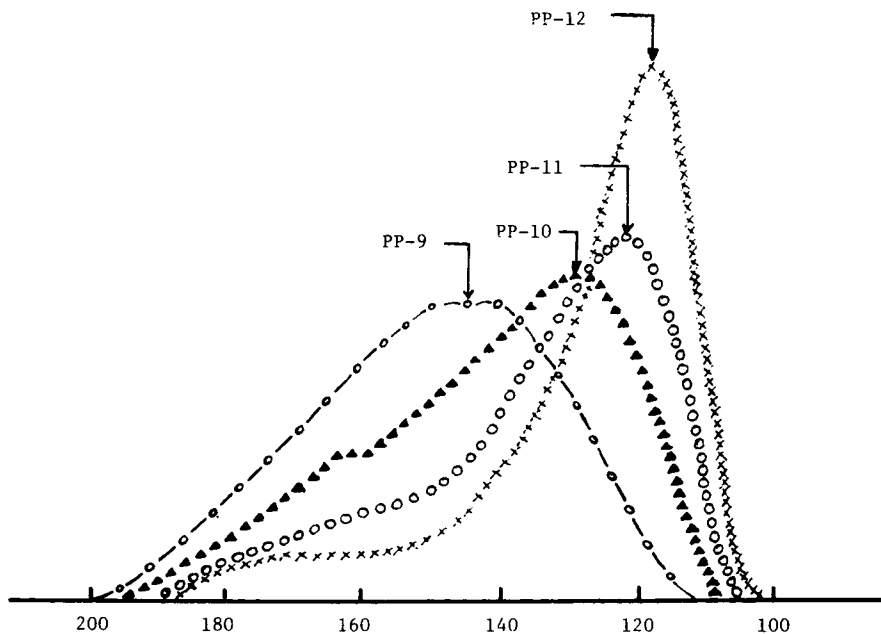| Reaction no.	Reaction conditions	Reaction temperature (°C)	Conversion (%)
PP-9	Conventional Ce (IV), grafting	30	53.4
PP-10	method (a), Ce(IV)/D = 20, AM/	40	67.4
PP-11	DAAM = 90/10, [M] = 0.8	50	76.5
PP-12	mol/L, [HNO₃] = 0.01N, 3 h	60	77.3

Fig. 2. Chromatograms of AM/DAAM cografting at different reaction temperatures under conditions given in Table III.

from 53.4% at 30°C to 76.5% at 50°C but then increased only slightly to 77.3% at 60°C.

The chromatograms (Fig. 2) and the anthrone tests of collected fractions indicate graft copolymers at smaller elution volumes and random copolymers at higher elution volumes. As the temperature was increased, selectivity toward the grafting reaction increased. Additionally, molecular size of the grafts increased as evidenced by a movement toward the total void volume of the column set. No unreacted dextran was detected.

Effect of the HNO₃ Concentration

The concentration of nitric acid during graft copolymerization, method (a), has a profound effect on both conversion (Table IV) and product distribution (Fig. 3) from size exclusion chromatography and eluent analysis using the anthrone reagent. Below concentrations of $0.005N$ HNO₃, grafting

TABLE IV
Effect of HNO₃ Concentration on AM/DAAM Cografting onto Dextran

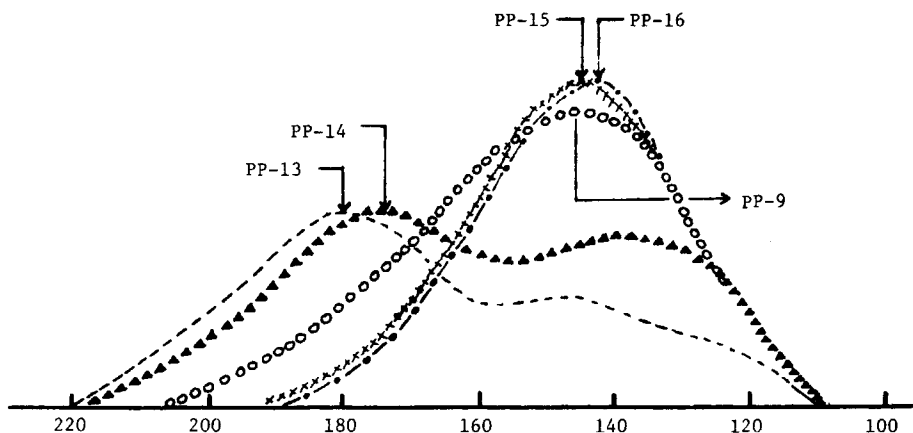| Reaction no.	Reaction conditions	[HNO₃] (N)	Conversion (%)
PP-13		0.100	5.6
PP-14	Conventional Ce(IV), grafting method (a)	0.050	17.2
PP-9	Ce(IV)/D = 20, AM/DAAM = 90/10,	0.010	53.4
PP-15	[M] — 0.8 mol/L, temp 30°C, 3h	0.005	70.9
PP-16		0.0025	85.3

Fig. 3. Chromatograms of the AM/DAAM cografting mixture obtained at different HNO concentrations under conditions outlined in Table IV.

is highly favored over random copolymerization. Apparently the relative rates of formation or disproportionation of complexes C_1 and C_2 [eqs. (1) and (3), respectively] are affected by HNO_3 concentration, although this observation was not studied further.

Effect of Ce(IV)/Dextran Molar Ratios

The effect of the Ce(IV)/dextran ratio [method (a), $\overline{M}_w$ of dextran 500,000] on grafting conversion (Table VI) and the resulting chromatograms (Fig. 4) was studied. The total monomer conversion increased as the Ce(IV)/dextran ratio was increased. Previously we had shown that under these same conditions for grafting of acrylamide alone, a maximum in conversion had been reached at a ratio of 20; above values of 50 in those experiments, a dramatic reduction in conversion was observed. Additionally, termination by reaction with "free" Ce(IV) was shown to substantially reduce molecular weight and grafting efficiency as well as broaden molecular weight distribution.

From SEC and the anthrone test (Fig. 4), it is evident that large amounts of ungrafted random copolymer of AM and DAAM are present in the reaction mixture. Bimodal distributions are attributed largely to graft copolymer near the total void volume and random copolymer at higher elution volumes. This conventional grafting procedure obviously gives broad distributions of grafted and ungrafted chains.

TABLE V
Effect of Monomer Feed Ratio on AM/DAAM Cografting onto Dextran

Reaction no.	Reaction conditions	AM/DAAM (molar ratio)	Conversion (%)
PP-20		95/5	40.7
PP-9	Conventional Ce(IV), grafting method	10/10	53.4
PP-17	(a), Ce(IV)/D = 20, [M] = 0.8 mol/	80/20	56.9
PP-19	L, [HNO₃] = 0.01N, temp 30°C, 3 h	70/30	61.2
PP-18		60/40	68.2

TABLE VI
Effect of Ce(IV)/D Molar Ratio on AM/DAAM Cografting onto Dextran

Reaction no.	Reaction conditions	Ce(IV)/D (molar ratio)	Conversion (%)
PP-21	Conventional Ce(IV), grafting method (a), AM/DAAM = 90/10, [M] = 0.8 mol/L, [HNO₃] = 0.01N, temp 30°C, 3 h	5	46.7
PP-22		10	46.8
PP-9		20	53.4
PP-23		50	54.9
PP-24		100	64.2

Selection of Optimal Grafting Conditions

The above cografting studies with conventional Ce(IV) initiation, method (a), and previous studies in our laboratories on Ce(IV)-initiated grafting of acrylamide onto dextran[1] led us to select controllable grafting procedures, methods (b) and (c). First, the self-initiation capacity of the DAAM monomer [eqs. (3) and (4)] can be controlled by decreasing the HNO_3 concentration as well as the Ce(IV)/dextran ratio and by increasing the reaction temperature.

Previous studies[1] had also shown that the order of addition of reagents in the grafting reaction could affect controllability of structure. Best control of structure resulted from addition of the Ce(IV) to the dextran substrate prior to addition of HNO_3 and monomer, method (b). However, some preoxidation of dextran, method (c), is helpful in favoring formation of complex C_1, eq. (1), over the DAAM/Ce(IV) complex C_2.

The reaction conditions and conversion data for a series of graft copolymers prepared by method (c) are shown in Table VII. The total monomer conversions were above 86% for all compositions of AM/DAAM prepared at Ce(IV)/dextran molar ratios of 10–50. The lower conversion of 66.7% at Ce(IV)/dextran of 5 is likely due to Ce(IV) consumption during oxidation of dextran. The aqueous size exclusion chromatographic study and anthrone reagent analysis showed no significant amounts of random copolymers of DAAM with AM in samples PP-33–PP-38. However, samples PP-39 and PP-40, prepared from high Ce(IV)/dextran ratios, exhibited high proportions of ungrafted random copolymers.
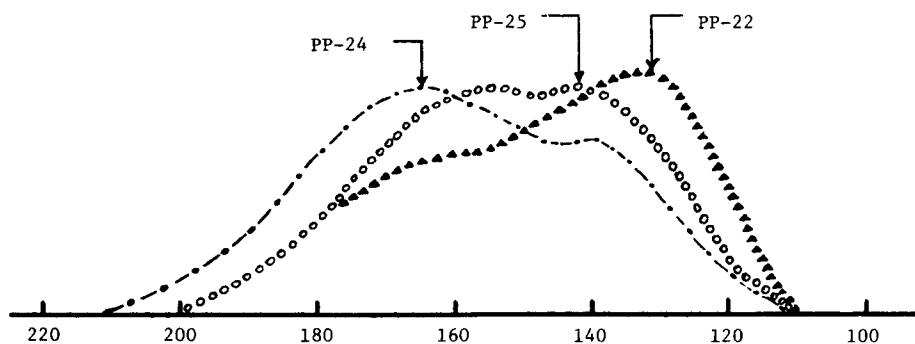

Fig. 4. Chromatograms of AM/DAAM cografting obtained at different Ce(IV)/D molar ratios under conditions outlined in Table VI.

TABLE VII
Reaction Conditions[a] and Conversion Data for the Model Graft Copolymer Samples

Reaction no.	Reaction conditions		Conversion (%)
PP-33	Ce(IV)/D = 10, [M] = 0.5 mol/L, [HNO₃] = 0.0025N, temp 40°C, 3 h	AM/DAAM = 100/0	87.3
PP-34		95/5	83.3
PP-35		90/10	84.5
PP-36		80/20	86.2
PP-37		70/30	89.2
PP-38	[M] = 0.5 mol/L, AM/DAAM = 90/10, [HNO₃] = 0.0025N, Temp 40°C, 3h	Ce(IV)/D = 5	66.7
PP-39		20	84.5
PP-40		50	86.6

[a] Improved Ce(IV) grafting procedure (method c) was used with pretreatment of dextran substrate [by $(NH_4)_2Ce(NO_3)_6$, 15 min, 35°C] under N_2.

Graft Copolymer Structure and Solution Viscosity

The relationship between graft copolymer structure and dilute aqueous solution behavior is important for establishing potential applications of water-soluble graft copolymers. The structural data of model dextran-g-poly(AM-co-DAAM) samples synthesized by the optimized Ce(IV) grafting method are shown in Table VII.

The graft copolymer composition is expressed in terms of mole fractions of three components (F_{AG}, F_{AM}, F_{DAAM}); the respective mole fraction of anhydroglucose units in the dextran backbone and those of acrylamide and diacetone acrylamide in the side chains. Normalized moles were calculated from elemental analysis data for each graft copolymer sample utilizing eqs. (9)–(11). Mole fractions F_{AG}, F_{AM}, and F_{DAAM} were then calculated (Table VIII):

$$6(AG) + 3(AM) + 9(DAAM) = (\%C)/12.01 \tag{9}$$

$$(AM) + (DAAM) = (\%N)/14.01 \tag{10}$$

$$5(AG) + (AM) + 2(DAAM) = (\%O)/16.00 \tag{11}$$

The weight fraction of side chains in the graft copolymer, W_g, was calculated using data obtained from eqs. (9)–(11):

$$W_g = \frac{71.08\,(AM) + 169.23\,(DAAM)}{162.14\,(AG) + 71.08\,(AM) + 169.23\,(DAAM)} \tag{12}$$

The total molecular weight of graft copolymer, $\overline{M}_{w,g}$, was obtained from eq. (13) using the W_g value of each graft copolymer sample:

$$\frac{\text{MW graft copolymer } (\overline{M}_{w,g})}{\text{MW dextran } (\overline{M}_w = 500{,}000)} = \frac{1}{1 - W_g} \tag{13}$$

The molecular weight and W_g values of the control graft copolymer, PP-33,

TABLE VIII
Structural Data of Model Graft Copolymer Samples

Sample no.	Elemental analysis				Graft copolymer composition				$\overline{M}_{wg}$ ($\times 10^{-6}$)
	C	H	N	O	F_{AG}	F_{AM}	F_{DAAM}	W_g	
PP-34	48.67	7.37	13.36	30.33	0.162	0.826	0.012	0.696	1.65
PP-35	50.12	7.44	12.72	27.08	0.130	0.769	0.101	0.773	2.20
PP-36	51.85	8.12	11.81	26.20	0.128	0.692	0.180	0.793	2.41
PP-37	52.63	7.61	10.44	25.39	0.140	0.587	0.273	0.795	2.44
PP-38	48.56	7.25	11.73	32.36	0.217	0.760	0.023	0.621	1.32
PP-39	49.57	7.35	12.37	27.10	0.138	0.759	0.103	0.762	2.10
PP-40	48.65	7.10	12.14	25.82	0.128	0.756	0.116	0.781	2.28

were calculated to be 1.52×10^6 and 0.671×10^6, respectively, using a similar calculation procedure.[1]

The dilute aqueous solution viscosity of model graft copolymers strongly depends upon the grafting conditions. The effect of the AM/DAAM feed ratio on the solution viscosity is shown in Figure 5. The viscosity of the graft copolymers increased as the content of DAAM monomer increased while the other reaction parameters were kept constant. It was also noted that all graft copolymers with AM/DAAM units in their side chains exhibited higher viscosities than graft copolymer with acrylamide side chains. Total molecular weights (Table VIII) varied from 1.65×10^6 to 2.28×10^6. As the Ce(IV)/dextran molar ratio decreased, the viscosity of the resulting graft copolymer increased (Fig. 6). This result indicates that the graft copolymer with a few long chains show higher viscosity than many short ones. This general tendency was previously confirmed with graft copolymer samples with acrylamide side chains and their hydrolyzed versions.[1,2] Despite the lack of solubility of poly(DAAM) in water, the DAAM units in the graft copolymer apparently act in a way to extend molecular dimensions, thus, increasing viscosity.
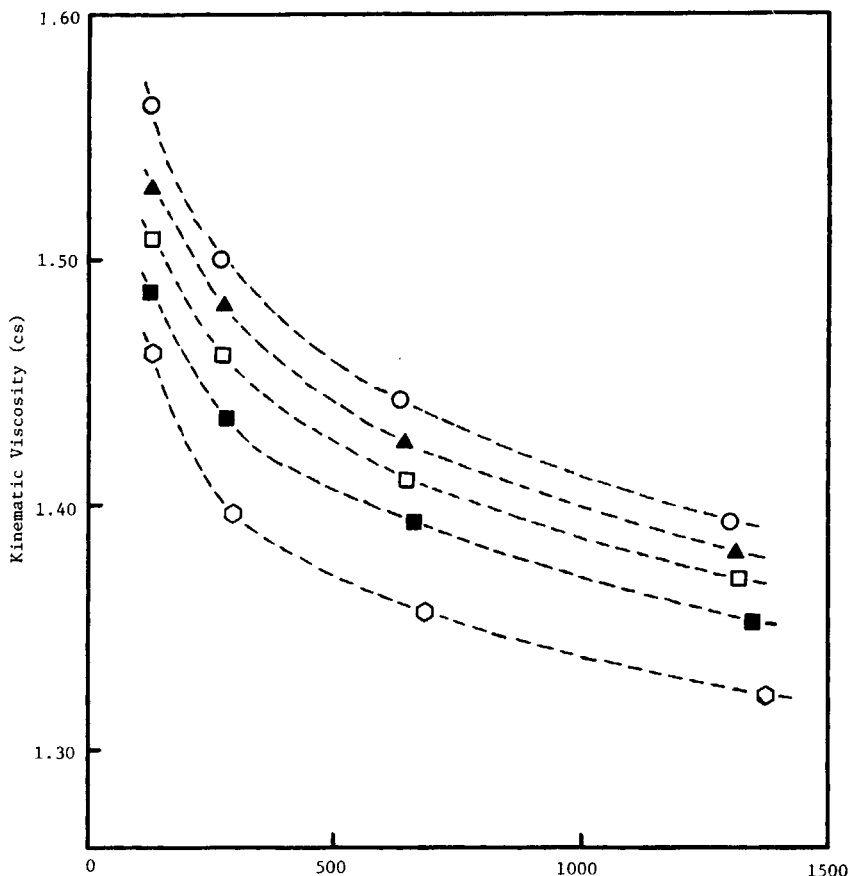

Fig. 5. Effect of the AM/DAAM feed ratio on the viscosity of resulting graft copolymer samples: (○) PP-37, 70/30; (▲) PP-36, 80/20; (□) PP-35, 90/10; (■) PP-34, 95/5; (⬡) PP-33, 100/0.
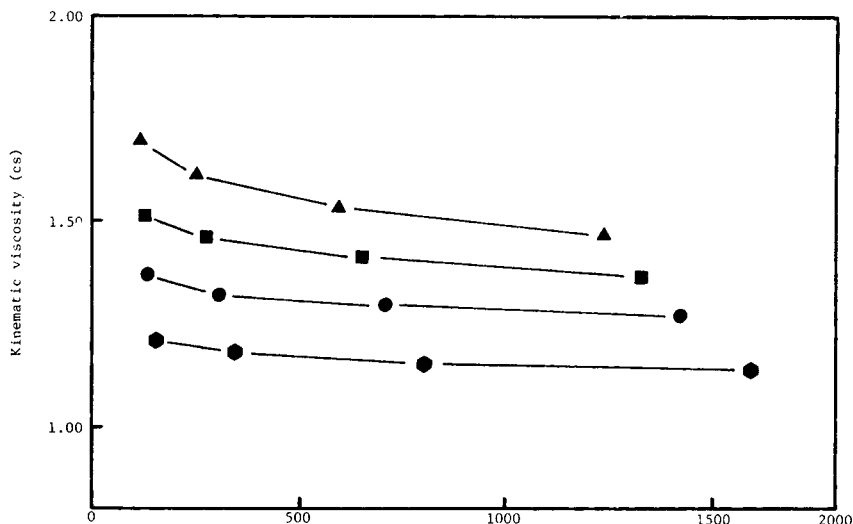
Fig. 6. Effect of Ce(IV)/dextran molar ratios on the viscosity of resulting graft copolymers. Ce(IV)/D (mol/mol): (▲) PP-38 (5); (■) PP-35 (10); (●) PP-39 (20); (⬢) PP-40 (50).

The effect of temperature was studied with the two graft copolymer samples, PP-33 and PP-37, which were synthesized from AM/DAAM feed ratio of 100/0 and 70/30, respectively. In Figure 7 are shown the Arrhenius plots of kinematic viscosity versus reciprocal temperature according to eq. (14) under constant shear rate conditions. The incorporation of the DAAM unit in the side chains of graft copolymer adversely affects the temperature sensitivity of solution viscosity, i.e., the more DAAM units in the graft copolymer, the greater the solution viscosity loss with increasing temperature.

$$\ln \eta = \ln A + (E/R)(1/T) \tag{14}$$

In contrast to random copolymers of AM with DAAM previously synthesized,[2] viscosity increases in NaCl and CaCl$_2$ solutions were less than 5%. This is likely due to the adverse effects of branching on chain ordering in dilute solution.

CONCLUSIONS

Graft copolymers can be prepared with controlled structures from co-grafting of AM/DAAM comonomers onto dextran ($\overline{M}_w = 500,000$) utilizing a modified Ce(IV)-induced initiation system. The competing random co-polymerization, also initiated by Ce(IV), can be nearly eliminated by increasing the reaction temperature to 40°C, decreasing HNO$_3$ concentration to 0.0025N, maintaining a Ce(IV)/dextran ratio below 20, keeping the AM/DAAM ratio above 70/30, and allowing precomplexing of the Ce(IV) to dextran prior to addition of comonomers and nitric acid. Dilute solution viscosities were studied as a function of copolymer composition in the molecular weight range from 1.65 to 2.28 × 10^6. Higher viscosities in water were found as the DAAM content in the side chain increased. Viscosity
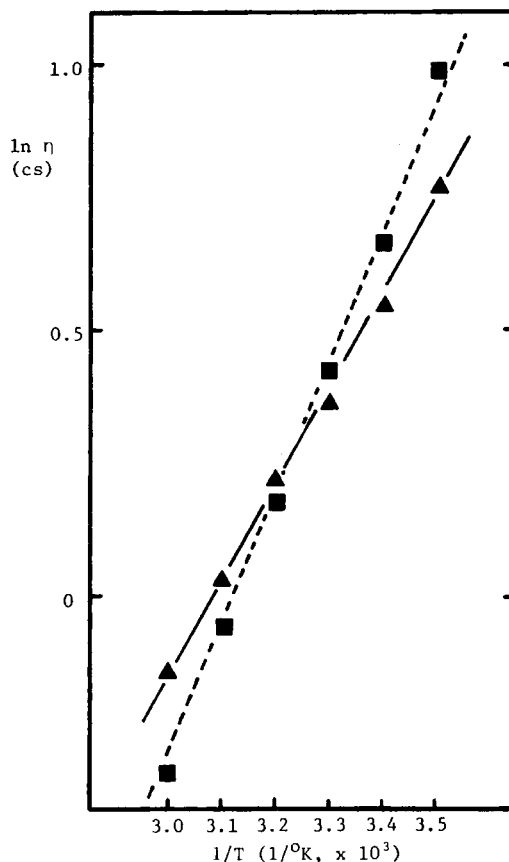
Fig. 7.   Arrhenius type plot of solution viscosity for graft copolymer sample (■) PP-37 and (▲) PP-33.

decreased with increasing temperature for these graft copolymers more rapidly when compared to previously prepared model dextran-*g*-poly(acrylamides). The addition of NaCl and $CaCl_2$ slightly increased viscosity (up to 5%) but to a lesser degree than that observed for previously reported random DAAM/AM copolymers. The increase in viscosity of the AM/DAAM dextran-grafted copolymers as compared to grafted AM copolymers, is likely due to a chain stiffening effect along the grafted chains. This effect is highest for a few long-chain grafts than for a larger number of short-chain grafts.

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