Water-Soluble Copolymers. I. Synthesis of Model Dextran-*g*-Polyacrylamides by Fe(II)/H_2O_2 Initiation and Characterization by Aqueous Size Exclusion Chromatography

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Synopsis

Model graft copolymers were synthesized by grafting acrylamide onto dextran ($\overline{M}_w$ = 500,000) utilizing the Fe(II)/H_2O_2 initiation system. Aqueous size exclusion chromatography (SEC) was used to determine the effects of changing reaction parameters on hydrodynamic dimensions of the resulting graft copolymers. It was also possible to optimize reaction conditions yielding the highest viscosity graft copolymer with the least amount of homopolyacrylamide and unreacted substrate. The molecular structures of the graft copolymers were determined by elemental analysis, SEC, and solution viscometry. Selective hydrolysis of the dextran backbone allowed determination of average molecular weight of acrylamide grafts, number of grafting sites, and average molecular weight of the graft copolymers. Rheological studies indicated viscosity and pseudoplastic behavior were largely related to the graft length of the polyacrylamide side chains.

INTRODUCTION

In recent years, increasing interest has arisen in the possibility of using water-soluble graft copolymers as viscosity modifiers in displacement fluids for enhanced oil recovery (EOR). The many requirements necessary for a candidate polymer to perform adequately in this application have been reviewed.[1] From a practical viewpoint, high solution viscosities (large hydrodynamic volumes) in aqueous solution must be maintained at low concentrations of polymer. Additionally, the polymer in solution must permeate the porous medium to displace the residual oil without degradation or adsorption.

The objectives of this work were to prepare a series of model dextran-*g*-acrylamide copolymers using the Fe(II)/H_2O_2 initiation system and to investigate interrelationships between structure and hydrodynamic volume as measured by aqueous size exclusion chromatography. A further goal was to control the number of grafting sites, grafted chain length, and amount of homopolymer by varying the Fe(II) concentration below a critical value (the equilibrium complexed concentration) associated with the polysaccharide substrate in solution. In this study, dextran, a relatively rigid, water-soluble polymer was chosen because of its availability in well-characterized form. Acrylamide was chosen as the grafting monomer because its resulting polymer (and the partially hydrolyzed version) possesses strong hydrogen bonding capability and is widely utilized in enhanced oil recovery.

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EXPERIMENTAL

Materials

Dextran standards used in SEC calibration were obtained from Pharmacia Chemical Co.; polyacrylamide standards were purchased from Polysciences, Inc. Acrylamide (Am) monomer, reagent grade from Eastman Kodak, was recrystallized three times from acetone prior to use. Ferrous ammonium nitrate, hydrogen peroxide (30%), ceric sulfate, *o*-phenanthroline, and anthrone were obtained from Aldrich and used without further purification. Diazyme L-100 was used as received from Miles Laboratories.

Determination of Concentration of Fe(II) Ion Complexed to Dextran T-500 ($\bar{M}_w$ = 500,000)

The concentration of Fe(II) ion, which could complex to dextran in aqueous solution, was determined by modification of a procedure introduced by Ogiwara and Kubota.[2] To 50 ml aqueous solutions of ferrous ammonium nitrate varying from 0.1 to 5 mmole/liter, was added 0.5 g of dextran T-500. The mixture was stirred for 30 min at 30°C for dissolution and complex formation. The dextran–Fe(II) complex was then precipitated by adding the solution to 1 liter of methanol. The precipitate was filtered and washed three times with a 90/10 (v/v) methanol/water solution. The sample was redissolved in 50 ml of distilled water and then titrated with 2×10^{-4} *N* ceric sulfate using *o*-phenanthroline as indicator. The equilibrium complexed concentration of Fe(II) ion onto dextran (T-500) was determined to be 0.64 mmole/100 g of dextran (Fig. 1).

Graft Copolymerization

The graft copolymerization reactions were conducted in three-necked, round-bottomed flasks equipped with nitrogen inlet tube, stirrer, and addition funnel. First dextran was dissolved in distilled water; then ferrous ammonium nitrate solution was added under nitrogen. After 30 min was allowed for complexation, acrylamide monomer was added with stirring over a 5-min period. The quantities of Fe(II), H_2O_2, Am, and dextran were varied for five reaction series, as shown in Table I. After allowing 4 hr for reaction, the solution was

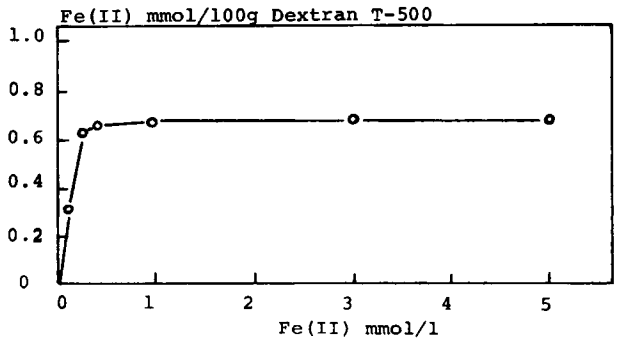

Fig. 1. Determination of 'equilibrium complexed' concentration of Fe(II) on dextran T-500 as a function of added Fe(II).

TABLE I
Effect of Reaction Parameters on Graft Copolymerization of Acrylamide onto Dextran

Reaction ser.	Reaction No.	Reaction Parameters				
		Fe(II), mmole/liter	H_2O_2, mmole/liter	Acrylamide mole/liter	Dextran, mole AGU/liter	Conversion %
I	1	0.064	0.128	0.75	0.062	72.0
	2	0.032	0.064	0.75	0.062	72.5
	3	0.016	0.032	0.75	0.062	73.6
	4	0.128	0.256	0.75	0.062	75.5
	5	0.192	0.384	0.75	0.062	77.1
II	6	0.032	0.032	0.75	0.062	66.0
	7	0.032	0.160	0.75	0.062	55.9
	8	0.032	0.320	0.75	0.062	43.0
III	9	0.128	0.256	0.50	0.062	70.5
	10	0.128	0.256	1.00	0.062	76.6
	11	0.128	0.256	1.50	0.062	77.3
IV	12	0.032	0.064	0.75	0.124	72.8
	13	0.016	0.032	0.75	0.248	83.4
	14	0.008	0.016	0.75	0.372	85.4

diluted to a polymer concentration of about 0.5 g/dl with water. Next 50 ml of this solution was precipitated by addition to 1 liter of methanol. The precipitated polymer was filtered and dried in a dessicator under reduced pressure. The acrylamide conversion was calculated from the following equation:

$$\% \text{ conversion} = \frac{\text{wt polymer} - \text{wt dextran}}{\text{wt Am monomer}} \times 100$$

Aqueous Size Exclusion Chromatography

A Waters Associates high pressure liquid chromatograph ALC 300 with model R401 refractive index detector was used to determine elution volumes. The eluting solvent was distilled and deionized water with 0.05*M* potassium biphthalate. Columns were of stainless steel tubing (0.762 × 60 cm). The columns were maintained at 25°C with pressure of 1050 psi and flow rate of 2 ml/min. A seven-column set was packed with porous glass (Electronucleonics, Inc.) with 3000, 1400, 700, 350, 240, 170 Å pore size. Injected sample size was 0.5 ml at a concentration of 0.2 g/dl.

This column set was calibrated with dextran (Pharmacia) and polyacrylamide (Polysciences) standards according to two calibration methods. The universal calibration curve (Fig. 3) was obtained in aqueous solution of 0.05*M* potassium biphthalate as eluent. In the calibration according to Southern method (Fig. 4), a straight line was obtained for a plot of $ln\ k_d$ vs. $([\eta]\overline{M})^{1/3}$ in which k_d is defined by $(V_e - V_0)/(V_t - V_0)$; V_e is the elution volume and $\overline{M}$ the molecular weight of the given standard. V_0 and V_t represent, respectively, the void volume and the total permeation volume of the column set.[3,4] One advantage of the Southern calibration procedure is that the curve for a given column set is independent of eluting solvent system. The curve obtained for these standards

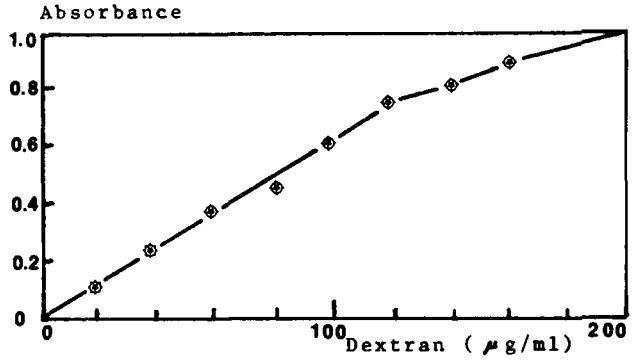

Fig. 2. Calibration curve for determination of dextran content with anthrone reagent.

coincided with that curve previously determined for this column set using sodium poly(styrene sulfonate) with a different eluent.[3]

Determination of Dextran Concentration

Dextran concentration in solution was determined using the anthrone reagent as described by Jermyn.[5] To 1 ml of test sample solution in a 25-ml test tube was added concentrated hydrochloric acid (1 ml). The anthrone reagent was prepared by dissolving 20 mg of anthrone on 100 ml of 80% sulfuric acid at room temperature. The test tube was heated for 12 min in a boiling water bath and then cooled. The solution was stirred for 5 min and the optical density was determined at 630 nm. The concentration of dextran in the sample was determined utilizing the calibration curve obtained with dextran T-500, as shown in Figure 2.

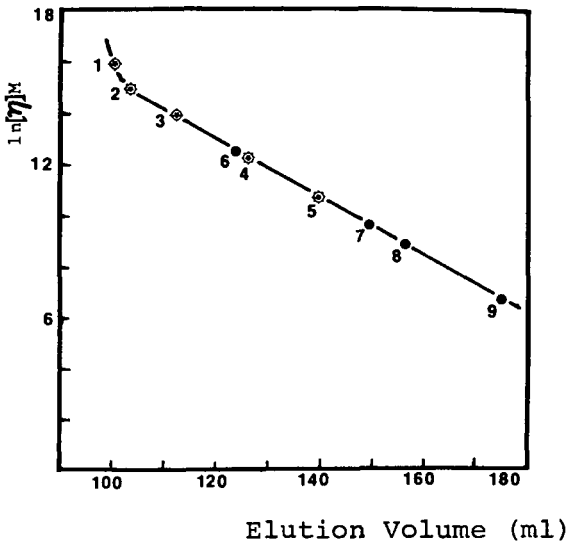

Fig. 3. Universal calibration curve. ⊙, $\overline{M}_w$ of polyacrylamide standards: (1) 20, (2) 15, (3) 5, (4) 2.7, (5) 0.74 × 10^5. ●, $\overline{M}_w$ of dextran standards: (6) 5, (7) 0.7, (8) 0.4, (9) 0.1 × 10^5.

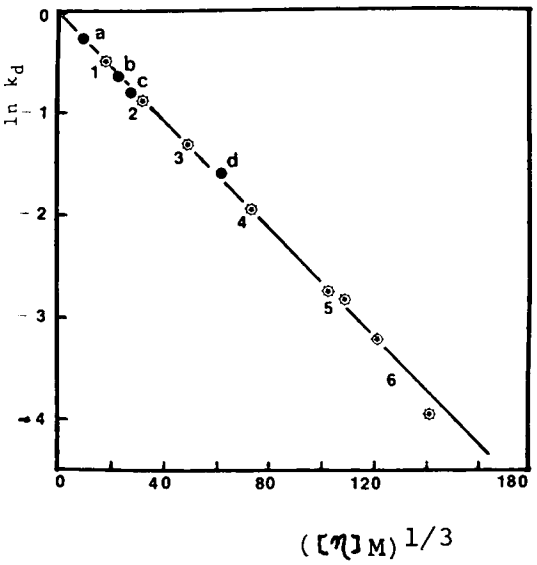

Fig. 4. Southern calibration method. ⊙, $\overline{M}_w$ of sodium poly(styrene sulfonate) standards: (1) 31, (2) 88, (3) 195, (4) 354, (5) 690, (6) 1090 × 10^3. ●, $\overline{M}_w$ of dextran standards: (a) 10, (b) 40, (c) 70, (d) 500 × 10^3.

Purification of Graft Copolymer

Graft copolymer samples were purified by repeated fractional precipitation with two different nonsolvents (tetrahydrofuran and methanol) from dilute (0.25 g/dl) solutions. The purification was followed by aqueous size exclusion chromatography (Fig. 10).

Selective Hydrolysis of Dextran Backbone of Graft Copolymers

The purified graft copolymer sample was dissolved in 500 ml of distilled water. Next 1 ml of Diazyme L-100 was added and the pH value was adjusted to 6 with 0.1*N* HNO_3. The solution was allowed to react at 55°C for 24 hr with stirring. The product solution was filtered and precipitated using absolute methanol as a nonsolvent. The resulting polyacrylamide was isolated and dried. The molecular weight was determined from viscosity measurements and aqueous size exclusion chromatography.

Shear Rate Dependent Viscosity

The shear rate dependent viscosity of each graft copolymer was determined using a Cannon–Ubbelohde four-bulb shear dilution viscometer. Measurements were conducted with 0.2 g/dl of purified graft copolymer in distilled water. Shear rate constants (k), for the four bulbs were 124,000, 60,700, 25,300, and 11,400, respectively. Shear rate (γ) was calculated from the equation $\gamma = k/t$, in which t represents the efflux time of the polymer solution. A time interval of four days was allowed from dissolution to measurement, to minimize aging effects.

RESULTS AND DISCUSSION

In order to obtain meaningful correlations between hydrodynamic dimensions and molecular structure for the dextran-grafted acrylamide copolymers prepared by $Fe(II)/H_2O_2$ initiation, two studies were conducted. In the first, reaction conditions were optimized to obtain long grafted chains, little homopolymer, and high conversion. The effect of each change in reaction conditions was followed using aqueous size exclusion chromatography. In the second study, graft copolymers were prepared utilizing the previously mentioned "optimized" conditions and were characterized by elemental analysis, enzyme hydrolysis, viscometry, and size exclusion chromatography. The average number of grafting sites, average molecular weights of the polyacrylamide side chains, and the average molecular weights of the graft copolymers were determined in order to compare the resulting solution properties.

Aqueous Size Exclusion Chromatography

Size exclusion chromatography is an excellent method for examining relative hydrodynamic volumes of graft copolymers and for the effective separation of reaction products, provided proper column and solvent conditions are maintained. No attempts have yet been made to correlate elution volumes with molecular weights directly from the calibration curves; however, hydrodynamic volume changes resulting from changes in reaction conditions can be readily monitored.

For a typical dextran-*g*-polyacrylamide copolymerization under nonoptimized conditions, three peaks may be identified in the chromatogram (Fig. 5). In a typical chromatogram, graft copolymer appeared at $V_e = 93$, homopolyacrylamide at $V_e = 106$, and graft copolymer at $V_e = 126$. These assignments were made by monitoring the eluent for polysaccharide content with the anthrone reagent.[5] The normalized product ratios were calculated by dividing the area under each peak by the total area of the chromatogram.

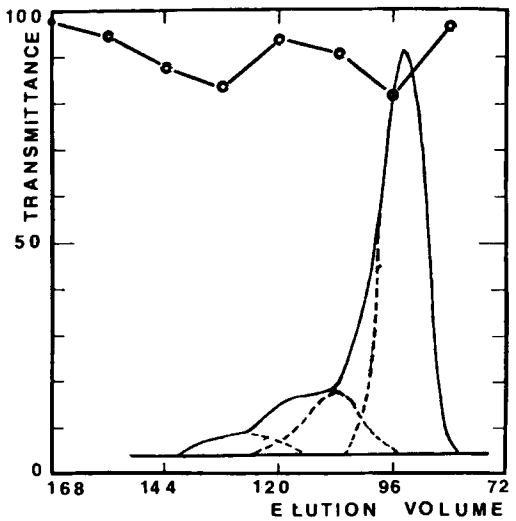

Fig. 5. Representative aqueous size exclusion chromatogram for the graft copolymerization of dextran with acrylamide.

Graft Copolymerization

A simple mechanism for the graft copolymerization of a vinyl monomer, M, onto a polysaccharide, RH, is shown below for the $Fe(II)/H_2O_2$ initiation system. This scheme is similar to the one proposed by Bains[6] and Arthur[7] for heterogeneous grafting onto cellulose.

$$Fe(II) + H_2O_2 \rightleftharpoons Fe(III) + HO^- + HO\cdot \quad (1)$$

$$Fe(II) + HO\cdot \rightleftharpoons Fe(III) + HO^- \quad (2)$$

$$Fe(III) + H_2O_2 \rightleftharpoons Fe(II) + H^+ + HO_2\cdot \quad (3)$$

$$M + HO\cdot \rightleftharpoons HOM\cdot \quad (4a)$$

$$HOM\cdot + nM \rightleftharpoons HO(M)_nM\cdot \quad (4b)$$

$$RH + HO\cdot \rightleftharpoons R\cdot + H_2O \quad (5)$$

$$R\cdot + M \rightleftharpoons RM\cdot \quad (6a)$$

$$RM\cdot + nM \rightleftharpoons R(M)_nM\cdot \quad (6b)$$

$$R(M)_nM\cdot + Fe(III) \rightleftharpoons Fe(II) + H^+ + \text{graft copolymer} \quad (7)$$

$$R(M)_nM\cdot + (\text{radical}) \rightleftharpoons \text{graft copolymer} \quad (8)$$

The concentration of Fe(II) in solution obviously influences the number of HO· radicals formed [eq. (1)], which in turn influences the relative amount of homopolymer [eqs. (4a) and (4b)] and graft copolymer [eqs. (5), (6a), and (6b)] formed. Termination reactions (7) and (8) govern the length of the polyacrylamide side chain.

In order to favor graft copolymer formation over homopolymer formation, the HO· radical should effectively abstract a hydrogen atom from the polysaccharide rather than initiating homopolymerization. This favorable situation can be obtained by keeping the Fe(II) ion in the proximity of the polysaccharide chain during reaction. Therefore, "the concentration" of Fe(II) associated with dextran was determined (Fig. 1). Fe(II) concentrations below the value of 0.64 mmole/100 g dextran T-500 (the "equilibrium complexed concentration") would not be expected to induce significant homopolymerization and would not adversely affect side-chain graft length.

Assuming that each effective transfer reaction would create a grafting site, the number of grafting sites per molecule of dextran was varied systematically. Four series of reactions were conducted (Table I) in which the concentrations of Fe(II), H_2O_2, Am, and dextran were independently varied to examine effects on graft copolymerization.

Effect of Fe(II) Concentration

The effect changes in Fe(II) concentration was studied in reaction series I. Monomer and dextran concentrations were held constant at 0.75 mole/liter and 0.062 mole anhydroglucose (AGU) unit/liter, respectively. The Fe(II) concentration was varied from 0.016 to 0.192 mmole/liter (representing $\frac{1}{4}$ to 3 times the equilibrium complexed concentration). The H_2O_2 concentration was maintained at twice that of Fe(II) for each reaction in this series.

The chromatograms for the graft copolymerization products of this series are shown in Figure 6. The hydrodynamic dimensions of the graft copolymers increased as the amount of the Fe(II) ion decreased. Copolymers I-2 and I-3 eluted at the void volume, indicating the highest hydrodynamic dimensions. It may also be noted (Table II) that increased Fe(II) concentration caused a drastic increase in homopolymer formation [eq. (4)].

The smaller hydrodynamic volumes are explained by an increase in the number of grafting sites and/or a decrease in length of the grafted chains. The latter arises from termination [eq. (7)] favored by a high concentration of Fe(III) generated by the reaction of excess Fe(II) with H_2O_2 [eq. (2), (3)].

Effect of H_2O_2 Concentration

In reaction series II, the H_2O_2 concentration was varied from one to ten times that of Fe(II) while maintaining Fe(II), Am, and dextran at 0.032 mmole/liter, 0.75 mole/liter, and 0.062 mole AGU/liter, respectively. While the hydrodynamic

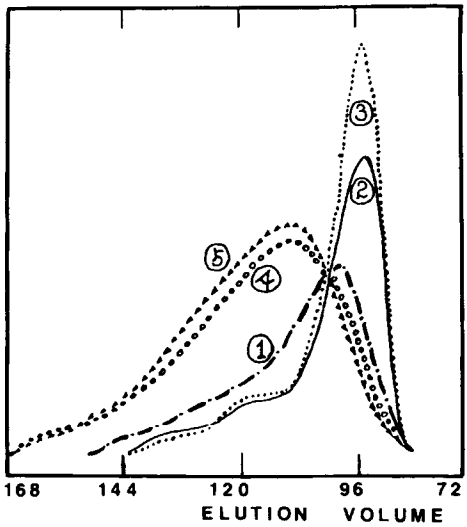

Fig. 6. Effect of Fe(II) concentration on graft copolymerization of dextran with acrylamide (reaction series I of Table I).

TABLE II
Molecular Structure and Product Ratio Data of Graft Copolymers in Reaction Series I

	Reaction ser. I				
Reaction No.	1	2	3	4	5
W_{PAm}	0.65	0.71	0.70	0.60	0.57
MW of PAm graft chain (10^5)	4.5	6.0	12.0	3.5	3.0
MW of graft copolymer (10^6)	1.47	1.79	1.76	1.30	1.20
Average No. of grafting sites	2.11	2.12	1.03	2.22	2.26
	Product Ratio, %				
Unreacted dextran	15	10	12	10	8
Homopolymer	19	13	13	55	57
Graft copolymer	64	77	75	35	35

volumes of the graft copolymers did not change greatly with H_2O_2 concentrations, a broadening of the distribution is noted at higher concentrations (Fig. 7). This may be reasonably attributed to the broad distribution of grafted chain lengths resulting from formation of active sites at different times during the reaction. The Fe(II) initially generated in the presence of higher concentration of H_2O_2 can be converted to Fe(II) using eq. (3). This regenerated Fe(II) would then be active in forming new sites later in the reaction sequence. The data in Table I indicates that highest conversion occurs at a H_2O_2 concentration two times that of Fe(II).

Effect of Acrylamide Concentration

The concentration of acrylamide was varied from 0.5 to 1.5 mole/liter while maintaining the concentrations Fe(II), H_2O_2, and dextran constant for series III as shown in Table I. The hydrodynamic volume (Fig. 8) increased rapidly with increasing monomer concentration. This can be attributed to the increased length of the grafted chain. A practical limit of 1.5 mole/liter is set for the monomer concentration, since problems in stirring arise as a result of sharp increases in viscosity.

Effect of Dextran Concentration

The effect of changes in dextran concentration is shown in reaction series IV in Table I and in Figure 9. The conversion increased with increasing dextran concentration, but aqueous size exclusion chromatography clearly indicated that unreacted substrate was present above 0.062 mole AGU/liter.

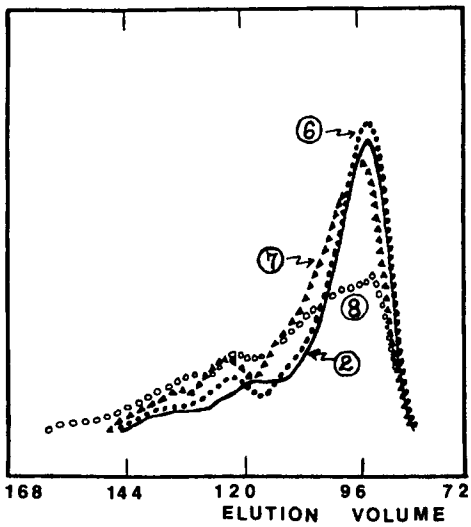

Fig. 7. Effect of H_2O_2 concentration on graft copolymerization of dextran with acrylamide (reaction ser. II of Table I).

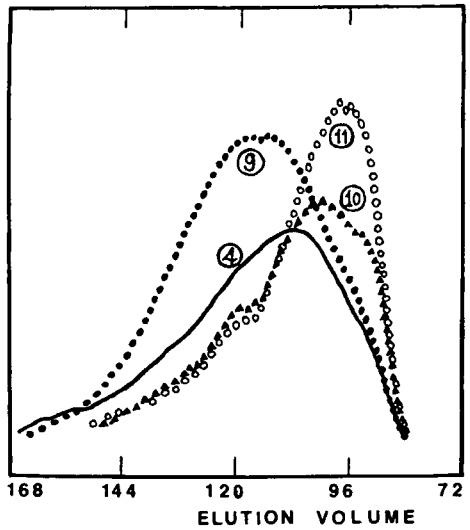

Fig. 8. Effect of acrylamide concentration on graft copolymerization of dextran with acrylamide (reaction series II of Table I).

Optimum Grafting Conditions

From an analysis of the aqueous size exclusion chromatograms, conversion data, and product ratios of graft copolymer to homopolymer, reaction conditions yielding highest hydrodynamic dimensions in grafting of acrylamide onto dextran by the Fe(II)/H_2O_2 system were determined to be 0.016–0.32 mmole/liter Fe(II), 0.032 mmol/liter H_2O_2 and 1.5 mole/liter acrylamide for dextran of $\overline{M}_w$ = 520,000 at a concentration of 0.062 mole AGU/liter.

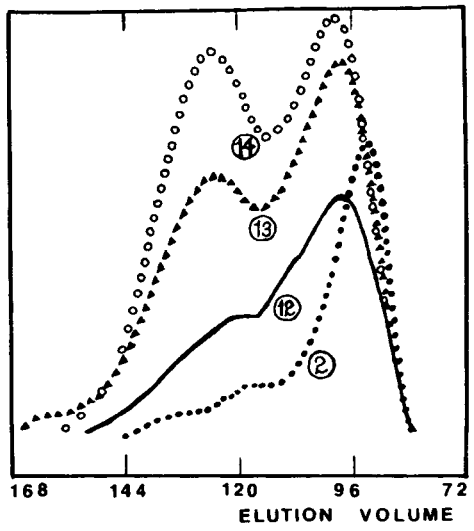

Fig. 9. Effect of dextran concentration on graft copolymerization of dextran with acrylamide (reaction series IV of Table I).

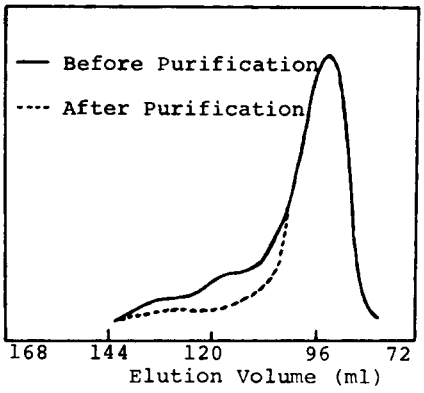

Fig. 10. Graft copolymer purification (reaction No. 2 of Table I) followed by aqueous size exclusion chromatography

Structural Analysis of Graft Copolymers

Experiments were conducted to hydrolyze selectively the carbohydrate backbone of the graft copolymer in order to determine the average number and lengths of the grafted chains. Although several hydrolysis methods have been reported in the literature,[8–13] an enzyme hydrolysis method was chosen because of the absence of imidization reactions. After hydrolysis, the residual polyacrylamide side chains were isolated using methanol as a nonsolvent and the

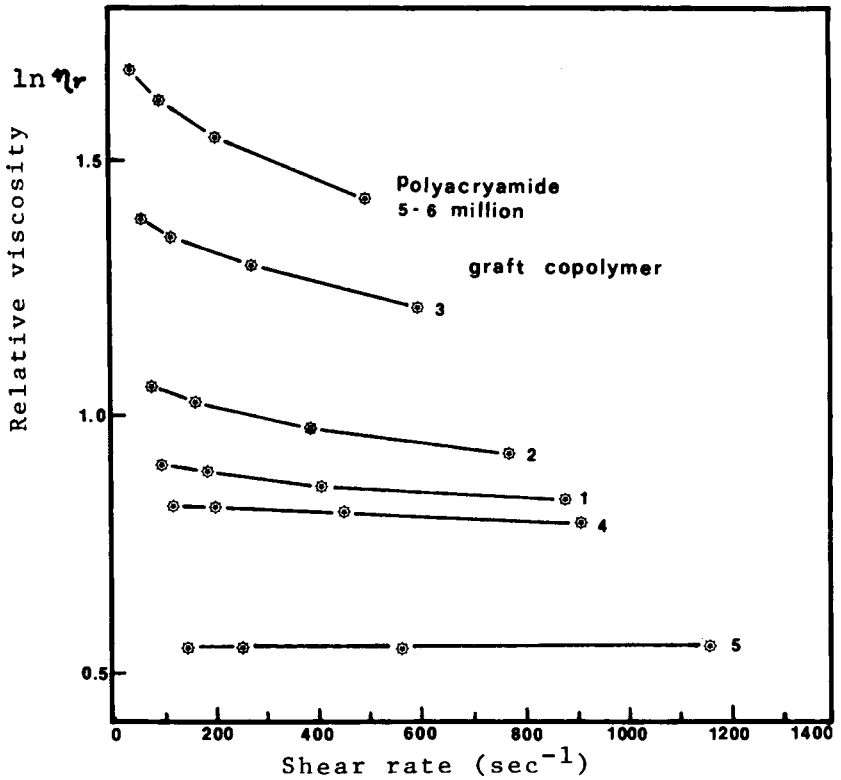

Fig. 11. Relative viscosities of graft copolymers (P1–5) as function of shear rate at 0.1 g/dl in water at 25°C.

weight-average molecular weights were determined from viscosity measurements using the following equation[14]:

$$[\eta] = 6.31 \times 10^{-5} \cdot \overline{M}_w{}^{0.8}$$

The average molecular weight of graft copolymer was calculated from eq. (9).[15]

$$\frac{\overline{M}_w \text{ of graft copolymer}}{\overline{M}_w \text{ of dextran backbone}} = \frac{1}{1 - W_{\text{PAm}}} \tag{9}$$

W_{PAm} represents the weight fraction of polyacrylamide portion of the graft copolymer. This value was calculated from elemental analysis data (Galbraith Laboratories) of the purified graft copolymer sample.

The number of grafting sites was calculated from eq. (10).[15]

$$\text{Average number of grafting sites} = \frac{(\overline{M}_w \text{ of graft copolymer}) \times W_{\text{PAm}}}{\overline{M}_w \text{ of PAm graft chain}} \tag{10}$$

Table II lists values of W_{PAm}, number of grafting sites, and weight-average molecular weights for the graft copolymers prepared in series I and II.

As the concentration of Fe(II) increased, the average molecular weight of the polyacrylamide grafted chains decreased. This is in agreement with the findings of Morin, et al.[16] for the Fe(II)/H_2O_2 initiated grafting of styrene onto cellulose.

The number of grafting sites changed from 1.03 to 2.12 when the concentration of Fe(II) was changed from 0.016 to 0.064 mmole/liter (the equilibrium complexed concentration). Interestingly, large increases of Fe(II) concentration above this value did not drastically increase the number of grafting sites. Apparently, Fe(II) above this concentration only increases homopolymer formation and decreases the molecular weight of the polyacrylamide side chains. Formation of active sites [eq. (5)] from regeneration [eq. (3)] of Fe(II) apparently is minimal for these homogeneous grafting conditions unless large amounts of H_2O_2 are added. These results are in accordance with the suggestion[17,18] of Ogiwara and co-workers that the number of grafted chains is determined early in the reaction when oxidation of Fe(II) is fastest.

Rheological Behavior

The dextran-*g*-polyacrylamides in this study exhibit pseudoplastic behavior at molecular weights greater than 1.5 million Daltons at concentrations of 0.2 g/dl. The natural logarithm of the relative viscosity is plotted as a function of shear rate in Figure 11 for graft copolymers prepared from reaction series I (Table II). Sample concentrations were 0.2 g/dl in distilled water. The relative viscosities and pseudoplasticity of this series reflect the effect of the length of the polyacrylamide side chain rather than that of the total molecular weight of the graft copolymer (Table II). It is also evident that graft copolymer I-3 with one long chain graft shows higher relative viscosity and a greater dependency on shear rate at this concentration than does sample I-2 with two equivalent grafted chains, although the samples have nearly the same total molecular weight.

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