Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Synthesis and Solution Properties of Water-Soluble Sulfonated Cellulose-Based Polymers and Their Polyacrylamide Copolymers

Y. -X. Zhang[ab]; Da. A.-H.[ab]; J-C. Chen[a]; G. B. Butler[a]; T. E. Hogen-esch[ab]
[a] Department of Chemistry and Center for Macromolecular Science and Engineering, University of Florida, Gainesville, Florida [b] Department of Chemistry, Loker Hydrocarbon Institute, University of Southern California, Los Angeles, California

To cite this Article Zhang, Y. -X. , A.-H., Da. , Chen, J-C. , Butler, G. B. and Hogen-esch, T. E.(1990) 'Synthesis and Solution Properties of Water-Soluble Sulfonated Cellulose-Based Polymers and Their Polyacrylamide Copolymers', Journal of Macromolecular Science, Part A, 27: 5, 593 — 609

To link to this Article: DOI: 10.1080/00222339009349645

URL: http://dx.doi.org/10.1080/00222339009349645

J. MACROMOL. SCI.—CHEM., A27(5), pp. 593–609 (1990)

SYNTHESIS AND SOLUTION PROPERTIES OF WATER-SOLUBLE SULFONATED CELLULOSE-BASED POLYMERS AND THEIR POLYACRYLAMIDE COPOLYMERS

Y.-X. ZHANG,* A.-H. DA,* J-C. CHEN, G. B. BUTLER, and T. E. HOGEN-ESCH*,†

Department of Chemistry and Center for Macromolecular Science and Engineering
University of Florida
Gainesville, Florida 32611

ABSTRACT

Water-soluble sulfopropylcellulose (SPC) was synthesized by the reaction of 1,3-propane sultone with sodium cellulose in dioxane. The degree of substitution (0.3–1.0) was calculated by elemental analysis. The corresponding water-soluble polyacrylamide graft copolymer was prepared by Ce^{4+} ion-initiated graft copolymerization of acrylmide onto sulfopropylcellulose dissolved in dilute nitric acid solution at room temperature under argon. The graft copolymerization was carried out in 0.2 *M* $NaNO_3$ solution in order to suppress the ionic interaction between the sulfonate ion and ceric ion. The average number of grafts per SPC was found to be 1.1 or less, depending on the reaction conditions.

INTRODUCTION

Over the last decade, increasing interest has arisen in the possibility of using water-soluble graft copolymers as viscosity modifiers in enhanced oil recovery (EOR) and in other applications [1]. Our previous reports dealt with graft copolymers of acrylamide (AM) and nonionic polysaccharides, i.e., starch [2], Schardinger-β-dextrin [3], and 2,3-dihydroxypropylcellulose [4]. The present study, designed to utilize sulfopropylcellulose (SPC) [5] as the substrate for vinyl

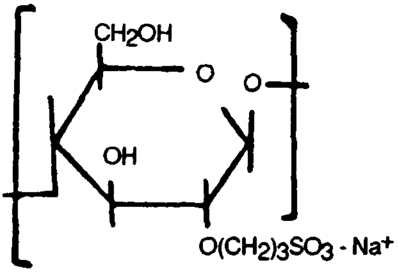
---

*Current address: Department of Chemistry and Loker Hydrocarbon Institute, University of Southern California, Los Angeles, California 90089–1661.

†To whom correspondence should be addressed at his current address.

monomer grafting, was undertaken to provide information on the extent to which the solution properties of SPC and its graft copolymers are affected by the presence of the sulfonate group in the polymer backbone.

Sulfoalkyl ethers of cellulose and starch have been investigated relatively little. SPC was synthesized by the reaction of 1,3-propane sultone with alkali cellulose [5].



Structure of SPC

The sulfonate group bonded to the cellulose backbone imparts characteristic polyelectrolyte behavior in aqueous solution that may be of special interest in EOR [6, 7]. These considerations have prompted us also to investigate in some detail the synthesis and characterization of water-soluble graft copolymers of sulfopropylcellulose and acrylamide (SPC-*g*-PAM).

EXPERIMENTAL

Reagents and Solvents

Acrylamide (Eastman Kodak Co.) was recrystallized from benzene prior to use (mp 84–86°C). Cellulose powder (spruce type) supplied by Fluka and ceric ammonium nitrate (F. E. Smith Co.) were used without further purification. The 1,3-propane sultone (Aldrich) was purified by vacuum distillation (bp 98–99°C/1 mmHg). All of the solvents, acids, and salts used for general application were of reagent grade or ACS grade quality.

Synthesis of Sulfopropylcellulose (SPC)

Into a three-necked round-bottomed flask equipped with condenser, gas inlet/outlet, and mechanical stirrer was charged 2.50 g cellulose powder and 100 mL dioxane under nitrogen or argon. After stirring for 45 min at room temperature, 10 mL of a 12.5% aqueous sodium hydroxide solution was added dropwise during a 15-min period. After heating to 45°C during stirring for 1 h, the required amount of 1,3-propane sultone dissolved in 20 mL dioxane was added dropwise during a 20-min period. The reaction was continued for 6 h at 45°C. The reaction mixture was precipitated by pouring into 300 mL methanol and neutralized with glacial acetic acid. The resulting polymer was filtered, washed several times with CH_3OH/H_2O (9/1 v/v), and dried in a vacuum oven at 50°C for 24 h.

Synthesis of Sulfopropyl-2,3-dihydroxypropylcellulose (SPDHPC)

The synthesis of SPDHPC is similar to that of sulfopropylcellulose (SPC). After treating the cellulose (MW = 250 000) suspended in 100 mL dioxane with 10 mL of 12.5% sodium hydroxide aqueous solution, a mixture of 1,3-propane sultone and glycidol in dioxane was added dropwise during a 20-min period. The reaction was continued for 6 h at 45°C. The reaction mixture was filtered and washed three times with fresh dioxane. About 50 mL deionized water was added to the solid portion. This mixture was then transferred into a Spectra/Por (MWCO 6000–8000) dialysis tubing and dialyzed against deionized water for 3 days. The water was removed by a rotatory evaporator. The resulting polymer was dried at 50°C under vacuum.

Graft Copolymerization

In a capped round-bottomed flask, argon was bubbled through a 0.2 *M* $NaNO_3$ aqueous solution of the required amounts of SPC and acrylamide for 30 min. Ceric ammonium nitrate was then added in a known concentration in dilute nitric acid (~10^{-3} *M*) solution. The reaction was carried out by shaking in a water bath at 25 ± 0.1°C for 24 h and was then terminated with 1 mL of a 10% aqueous hydroquinone solution. The reaction mixture was dialyzed against deionized water to remove inorganic salts by using Spectra/Por dialysis tubing (MWCO 6000–8000) for 3 days. The polymer solution was then diluted with deionized water to a viscosity low enough that the polymer solution precipitated rather than wrapping around the stirring bar upon addition to acetone. The precipitate was filtered, washed with acetone, and dried under vacuum at 50°C for 24 h.

Hydrolysis of SPC-*g*-PAM copolymers [8]

The graft copolymer (0.25 g) was weighed into a 20-mL beaker, 3.8 mL of 72% sulfuric acid solution was added, and the mixture was stirred throughly for 45 min. The mixture was then diluted to 100 mL, transferred to an autoclave bottle, and heated to 120°C for 1 h. After cooling the reaction mixture to room temperature, it was neutralized with aqueous NaOH solution. The neutralized solution was dialyzed against deionized water to remove all ions and small molecules by using

Spectra/Por dialysis tubing (MWCO 1000) for 3 days. The dialyzed solution was concentrated and added to acetone in order to precipitate the polymer. The resulting polymer was dried under vacuum at 50°C for 24 h.

Hydrolysis of SPC

The SPC was hydrolyzed by using the same procedure as for SPC-*g*-PAM copolymers. The SEC chromatogram showed only one peak with an elution volume identical to that of the solvent peak when 0.2 *M* Na_2SO_4 aqueous solution was used as the mobile phase.

Hydrolysis of PAM

Hydrolysis of a PAM standard was carried out by using the same procedure as for SPC-*g*-PAM. SEC analysis showed that the PAM subjected to these hydrolysis conditions had the same elution volume as the original PAM standard when 0.2 *M* Na_2SO_4 aqueous solution was used as the mobile phase as previously reported [2].

Spectroscopy

All of the temperatures are uncorrected and are reported in degrees centigrade. Carbon-13 (50.3 MHz) spectra were obtained on a Varian XL-200 High Resolution NMR Spectrometer. Chemical shifts are given in parts per million (ppm) downfield from the methyl carbon of sodium 2,2-dimethyl-silapentane-5-sulfonate (DSS) or with respect to thiocyanate carbon (113.0 ppm). Infrared spectra were recorded on a Perkin-Elmer 281 Infrared Spectrophotometer; the observed frequencies are expressed in wavenumbers (cm^{-1}) using the 1610 cm^{-1} line of polystyrene film as a standard.

Aqueous Size-Exclusion Chromatography

A "Waters" SEC system, consisting of model 590 pump and a U6K injector, was used in combination with a Perkin-Elmer LC-25 RI detector and a Krotos Spectroflow 757 variable wavelength UV-VIS detector. The SEC columns, TSK-gel-GMPW and TSK-gel-G1000PW, were purchased from Bio-Rad Lab. The mobile phase (0.2 *M* Na_2SO_4) was filtered through a 0.45-μm millipore membrane under vacuum before use. The linear velocity of the mobile phase was 0.8 mL/min. The polymer concentration in the sample solution was 0.4% by weight or less, and the volume of the sample injection was between 150 and 200 μL. Calibration was made with the use of polydisperse PAM standards which were purchased from American Polymer Standards Co. A personal computer search routine was used to retrieve the true molecular weight calibration curve from the polydisperse standards. The programs used were based on the linear calibration method introduced by Hamielec [9] and later employed by Yau et al. [10].

Viscosity

AT least four concentrations of each polymer sample were measured to determine its intrinsic viscosity. The sample was measured in deionized water or in a 0.2-*M* sodium sulfate aqueous solution at 30 ± 0.1°C. By using a Cannon-Ubbelohde viscometer, the intrinsic viscosity was determined by a least-squares treatment of the plots of η_{sp}/C vs C and In η_r/C vs C and extrapolated to zero concentration. In most cases the intercepts of the two plots are essentially identical (±2%). If the difference of these two values was above 2%, the average value was reported.

A Cannon-Ubbelohde four-bulb shear dilution viscometer was used for dilute solution rheological studies. The kinematic viscosity was obtained by multiplying the efflux time for the polymer solution by the appropriate viscometer constants.

RESULTS AND DISCUSSION

Synthesis, Characterization, and Solution Properties of Sulfopropylcellulose (SPC) and Sulfopropyl-2,3-dihydroxypropyl-cellulose (SPDHPC)

SPC was synthesized by the reaction of sodium cellulose with 1,3-propane sultone in dioxane by using methods similar to those used to prepare DHPC [3]. The effect of the molar ratios of 1,3-propane sultone to the anhydroglucose unit (AGU) and the general reaction conditions described in the Experimental section are shown in Table 1. The effect of SPC concentration on solution viscosity in water is shown in Fig. 1, which clearly shows the characteristic increase in reduced viscosity of polyelectrolytes at low concentration.

The yields and properties of the resulting SPC were clearly affected by the molar ratios of 1,3-propane sultone and sodium hydroxide to the AGU of cellulose. For instance, when the NaOH/AGU molar ratio was changed from 5.0 to 2.0, the polymer yield was increased by about 30% and the water solubility was significantly increased. Decreasing the NaOH concentration may apparently reduce the extent of side reactions involving hydroxide ion and the sultone. It was also found that the sultone/AGU ratio had a pronounced effect upon the isolated yield of SPC. Thus, at a constant NaOH/AGU ratio of 2, increasing the sultone/AGU ratio from 2 to 6 decreased the isolated yield of SPC from 65 to 31%. Some of this decrease may perhaps be attributed to the increased solubility of the SPC in the precipitating solvent (CH_3OH). Curiously, the sulfonate content of SPC was decreased when the sultone/AGU ratio was increased from 3 to 6 (Table 1).

TABLE 1. Conditions and Results for the Synthesis of Sulforopylcellulose[a]

Sample no.	Molar ratio		Yield,[b] %	S,[c] %	DS[d]	SPC(aq)	[η],[e] dL/g
	Sultone/AGU	NaOH/AGU					
SPC-1	2	5	47.4	4.82	0.31	Turbid	—
SPC-2	2	2	65.3	9.33	0.81	Clear	1.42
SPC-4	3	2	50.6	9.64	0.97	Clear	2.20
SPC-3	4	2	42.9	8.91	0.75	Clear	2.16
SPC-5	6	2	31.4	8.46	0.69	Clear	—

[a] Conditions: 2.5 g cellulose, 100 mL dioxane, and 10 mL 12.5% NaOH(aq).

[b] Yield = weight SPC/(weight cellulose + weight sultone) x 100%.

[c] Determined by elemental analysis.

[d] Degree of substitution. The average number of hydroxyl groups substituted per AGU was determined by elemental analysis.

[e] Determined in 0.2 *M* Na_2SO_4 aqueous solution.

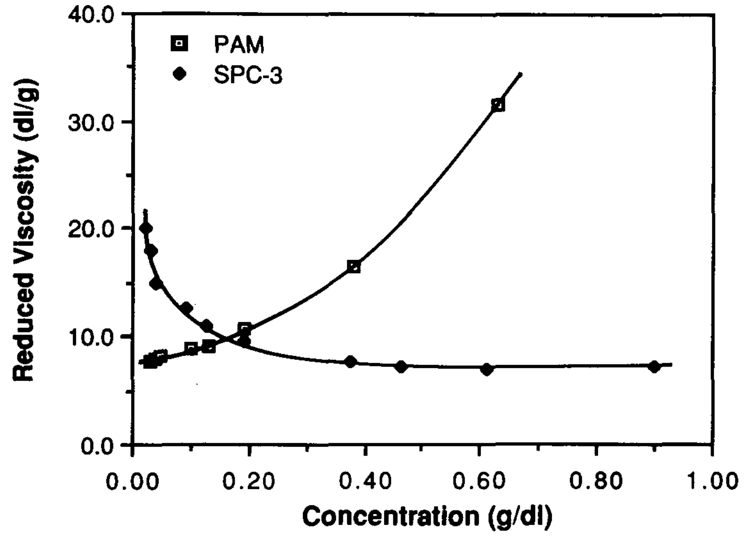


FIG. 1. Influence of polymer concentration on the reduced viscosity of PAM and SPC-3.

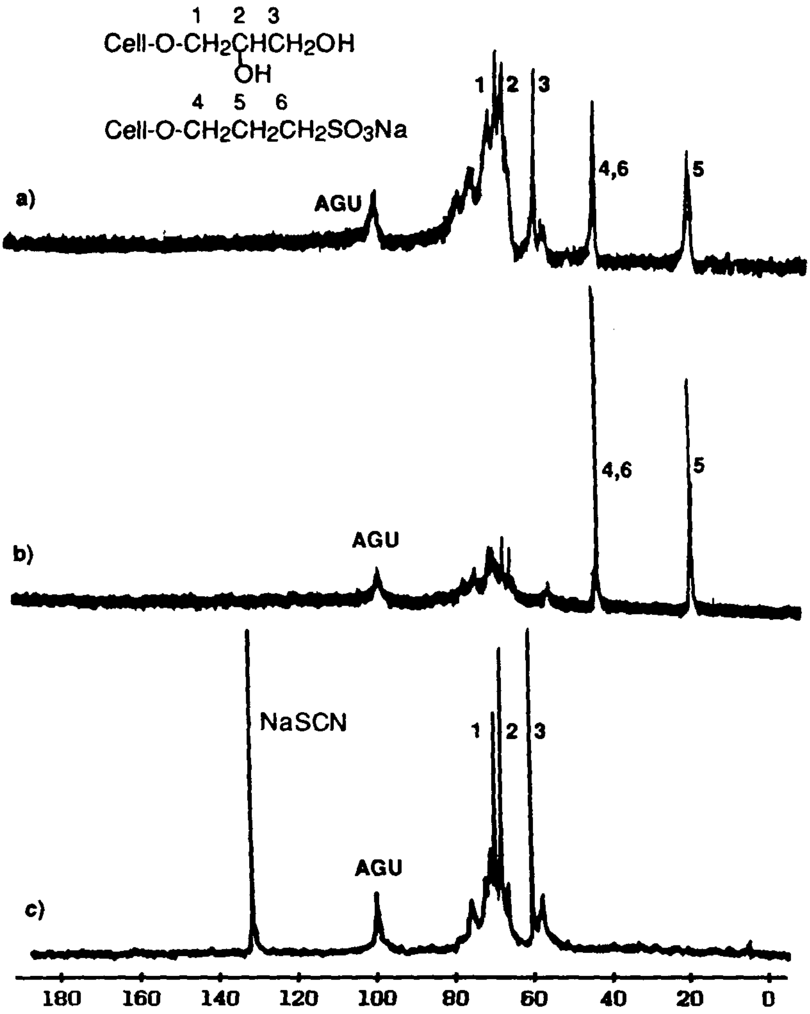


FIG. 2. ^{13}C-NMR spectra: a) SPDHPC in D_2O; b) SPC in D_2O; c) DHPC in 50% NaSCN aqueous solution.

Similar results were obtained for the preparation of DHPC from Na cellulose and glycidol or 3-chloro-1,2-propanediol [4].

The conditions and results for the synthesis of sulfopropyl-2,3-dihydroxypropylcellulose are summarized in Table 2. The yield of the polymer was affected by the NaOH/AGU molar ratio, the yield and S content being highest at a ratio of 2.4 (Table 1). This is again consistent with the occurrence of competing reactions of hydroxide ion with the sultone and/or with the glycidol. At lower NaOH concentration it would appear that the concentration of Na cellulose is lower, resulting in a lower extent of reaction, especially of glycidol. The resulting modified cellulose was shown to contain both sulfopropyl and 2,3-dihydroxypropyl groups by inspection of the C-13 NMR spectra shown in Fig. 2. The reduced viscosity–concentration profile of SPDHPC is shown in Fig. 3. It is obvious that its behavior is very different from that of SPC and DHPC. Especially at concentrations above 0.6 g/dL, the reduced viscosity of SPDHPC was increased dramatically compared to that of SPC. The differences in reduced viscosity of SPDHPC on the one hand and DHPC and SPC on the other are probably not caused by differences in the molecular weights of the polysaccharides since the cellulose source was the same in all three cases. Likewise, the degree of substitution by sulfonate on the backbone was similar. The differences in the reduced viscosity versus concentration profiles of SPC and DHPC on the one hand and SPDHPC on the other are not well understood and will be the subject of further studies.

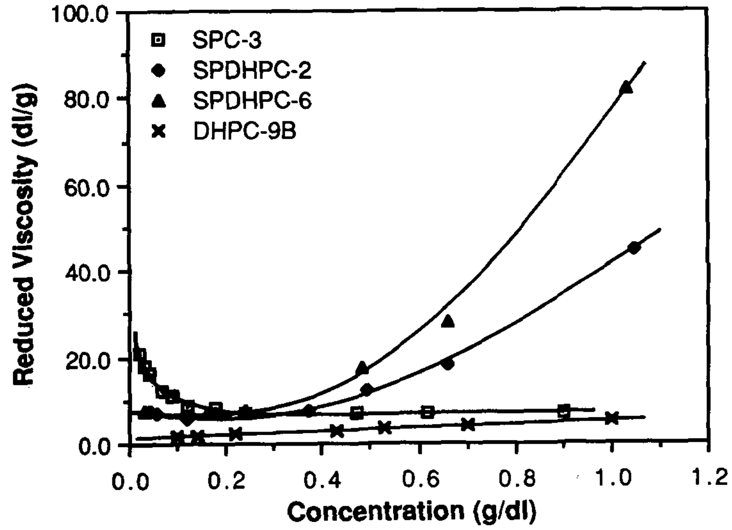


FIG. 3. Effect of polymer concentration on the reduced viscosity of SPDHPC, SPC, and DHPC.

TABLE 2. Conditions Employed for the Synthesis of Sulfopropyl-2,3-dihydroxypropylcellulose (SPDHPC)[a]

Code	Molar ratio			Yield,	S,[b]		
no.	Sultone/AGU	Glycidol/AGU	NaOH/AGU	g	%	*DS*[c]	SPDHPC(aq)
SPDHPC-2	3	4	4.0	4.33	5.61	0.72	Clear
SPDHPC-3	3	4	2.4	6.13	7.14	1.02	Clear
SPDHPC-4	3	4	1.6	4.31	6.32	0.85	Clear
SPDHPC-5	2	8	2.4	6.20	5.46	0.70	Turbid
SPDHPC-6	3	8	2.4	6.63	5.74	0.75	Clear

[a] Conditions: To 2.5 g cellulose in 100 mL dioxane was added 10 mL of 12.5% aqueous NaOH and sultone and glycidol as indicated.

[b] Determined by elemental analysis.

[c] Degree of substitution. The average number of hydroxyl groups substituted per AGU was determined by sulfur elemental analysis. *DS* of glycidol was determined by C-13 NMR [4].

Grafting onto SPC

It was found that when ceric ion was added to an solution of SPC, significant precipitation of SPC occurred. This precipitation might be due to complex formation between the sulfonate ion and the ceric ion. Inorganic salt ($NaNO_3$ or Na_2SO_4) was added to the aqueous solution to suppress this ionic interaction. The influence of the presence of the inorganic salts on the graft copolymerization of SPC and AM is shown in Table 3. In the absence of SPC, AM could be homopolymerized by ceric ion to a polymer of very high molecular weight in 0.2 *M* Na_2SO_4 aqueous solution. No homopolyacrylamide was isolated in 0.2 *M* $NaNO_3$ aqueous solution. Thus, the homopolymerization of AM could be effectively prevented in 0.2 *M* $NaNO_3$ aqueous solution, and this is consistent with the occurrence of graft copolymerization in the presence of SPC. From a comparison of Figs. 4 and 5, it is clear that the solution viscosities of SPC-*g*-PAM are lower than those of a mixture of SPC and PAM homopolymers of about the same molecular weight and composition as in the graft copolymer. Furthermore, the presence of oligosaccharide chains on the PAM chains of the hydrolyzed SPC-*g*-PAM copolymers is demonstrated by ^{13}C NMR (see below). These data appear to be consistent with the occurrence of graft copolymerization.

Effects of Reaction Parameters on the Graft Copolymer

The effects of various reaction parameters on the graft copolymerization of SPC with AM were investigated in detail and are summarized in Tables 4 and 5. The dependence of the reaction time on graft copolymerization is shown in Table 4. The conversion, average molecular weight of PAM, and intrinsic viscosity all increase with reaction time. The effect of raising the temperature is slight except for a modest decline in intrinsic viscosity above 30°C and in the MW of grafted

TABLE 3. The Influence of Inorganic Salts on the Ce^{4+} Ion-Initiated Graft Copolymerization of SPC and Acrylamide (AM)[a]

Code no.	SPC, g	Added salt (0.2 *M*)	Yield, g	Conversion, %
9–1	0	Na_2SO_4	0.33	41
9–2	0.2	Na_2SO_4	0.84	84
9–3	0	—	0	0
9–4	0	$NaNO_3$	0	0
9–5	0.2	$NaNO_3$	0.81	81

[a] Conditions: weight AM = 0.8 g, $[Ce^{4+}] = 1 \times 10^{-3}$ *M*, $[HNO_3] = 3.2 \times 10^{-3}$ *M*.

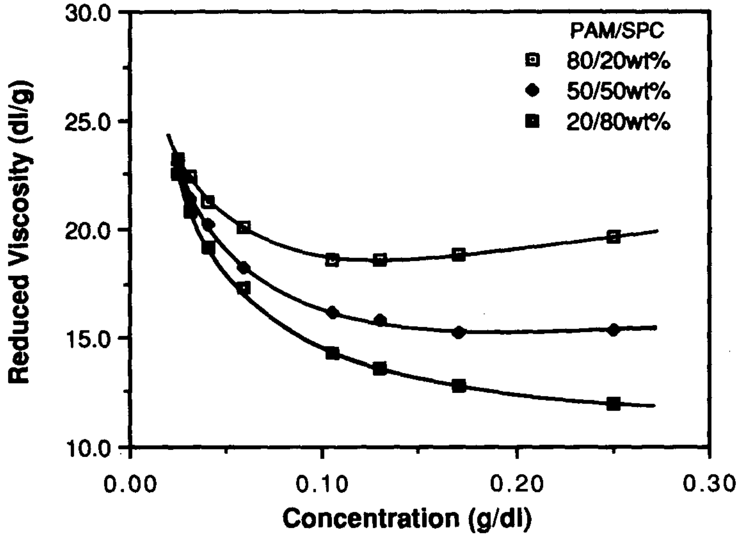


FIG. 4. Effect of polymer concentration of 1:4, 1:1, and 4:1 mixtures of SPC and PAM on the reduced viscosity.

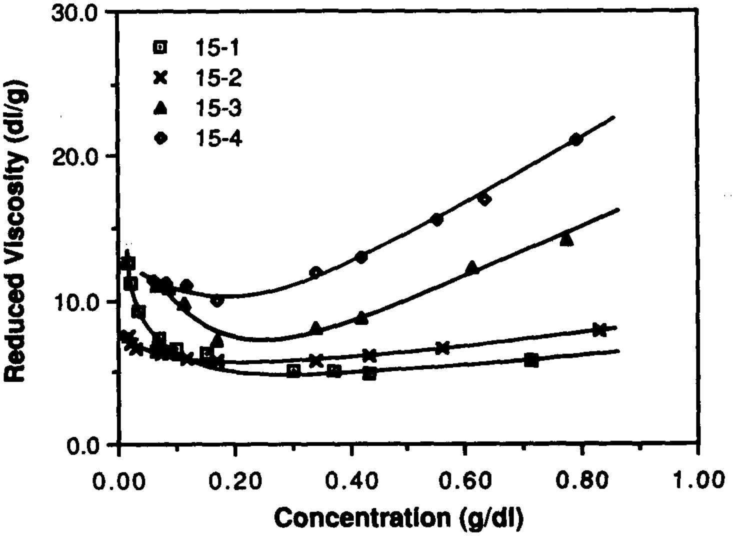


FIG. 5. Dependence of reduced viscosity on the concentration of SPC-*g*-PAM graft copolymers.

TABLE 4. Effects of Reaction Time, Reaction Temperature, and Concentration of $NaNO_3$ on the AM Graft Copolymerization of SPC[a]

Run	Parameter	Conversion,[b] %	PAM(hydrolyzed) $\bar{M}_n \times 10^{-6}$	$\bar{M}_w \times 10^{-6}$	N_g[c]	f,[d] %	[η],[e] dL/g
I) Reaction Time (h)[a]							
14–4	2	47.2	0.077	0.39	0.49	0.7	1.75
14–1	4	56.0	0.18	0.86	0.28	0.4	1.89
14–2	8	70.1	0.17	1.09	0.41	0.6	2.07
14–5	16	71.4	0.17	1.58	0.42	0.6	2.21
14–6	24	72.3	0.29	1.98	0.25	0.3	2.43
II) T (°C)[a]							
18–1	25	76.3	0.29	1.98	0.25	0.4	2.43
18–2	30	77.0	0.21	2.20	0.38	0.5	3.43
18–3	40	83.0	0.20	2.37	0.44	0.6	2.35
18–4	50	77.0	0.20	1.44	0.40	0.6	2.18
III) [$NaNO_3$] (mol/L)[a]							
13–1	0.1	72.5	0.10	0.41	0.73	1.0	1.74
13–2	0.2	76.0	0.15	0.86	0.52	0.7	1.94
13–3	0.5	79.0	0.12	0.83	0.68	1.0	1.43
13–4	1.0	63.8	0.06	0.20	1.01	1.5	1.31

[a] Reaction was carried out under the following conditions: [AUG] = 0.039 mol/L; $[AM]_0$ = 0.56 mol/L; $[Ce^{4+}]_0$ = 0.5 mmol/L; $[HNO_3]_0$ = 3.2 mmol/L; reaction time = 24 h; 25°C; and [$NaNO_3$] = 0.2 *M* unless otherwise indicated.

[b] Conversion = weight graft copolymer/(weight acrylamide + weight SPC).

[c] The average number of grafts per SPC molecule: $N_g = [PAM]/[SPC]_0$.

[d] Initiator efficiency: $f = [PAM]/[Ce^{4+}] \times 100\%$.

[e] Intrinsic viscosity of the graft copolymer was measured in 0.2 *M* Na_2SO_4 aqueous solution.

TABLE 5. Effects of Concentrations of Nitric Acid, Ceric Ion, Cellulose Substrate, and Acrylamide Monomer on the Graft Copolymerization of SPC and AM

Run	Parameter	Conversion,[b] %	PAM (hydrolyzed)		N_g[c]	f,[d] %	[η],[e] dL/g
			$\bar{M}_n \times 10^{-6}$	$\bar{M}_w \times 10^{-6}$			
I) [HNO_3] (mmol/L)[a]							
16–1	0.64	66.7	0.13	1.42	0.50	0.7	—
16–2	3.2	76.3	0.29	1.98	0.27	0.4	2.43
16–3	16.0	64.5	0.20	3.69	0.31	0.4	3.22
16–4	80.0	13.7	0.048	1.19	—	—	0.90
II) [Ce^{4+}] (mmol/L)[a]							
10–3	2.7	63.0	0.053	0.22	1.12	1.6	1.19
10–1	1.0	68.2	0.15	0.86	0.44	0.6	1.94
10–2	0.75	81.0	0.16	1.37	0.53	0.8	2.14
10–4	0.50	76.3	0.21	1.59	0.37	0.5	2.31
10–5	0.27	81.0	0.38	2.00	0.22	0.3	2.95
10–6	0.10	56.4	0.69	4.50	0.07	0.1	4.89
III) [AGU] (mol/L)[a]							
17–1	0.020	77.6	0.17	1.82	0.47	.07	—
17–2	0.039	76.3	0.29	1.98	0.27	0.4	2.43
17–3	0.078	69.4	0.16	2.11	0.43	0.6	2.41
17–4	0.117	70.3	0.14	1.11	0.50	0.7	2.29
IV) [AM] (mol/L)[a]							
15–1	0.28	65.3	0.078	0.36	0.34	0.5	1.58
15–2	0.56	76.3	0.29	1.98	0.27	0.4	2.65
15–3	0.84	73.0	0.26	2.35	0.44	0.6	3.63
15–4	1.12	71.4	0.20	2.83	0.75	1.1	4.59

[a-e]See the footnotes in Table 4.

PAM. From Table 4 it can be seen that better conversions were obtained when the grafting reaction was carried in 0.2 or 0.5 *M* $NaNO_3$ aqueous solution, perhaps as a result of the better homogeneity of the reaction mixture under these conditions. The dependence of copolymer yield on the concentration of nitric acid is shown in Table 5. It is seen that at higher concentrations of nitric acid, lower conversions were obtained. This was observed previously [7, 11] and was attributed to a greater rate of termination of the growing radical by the ceric ion. Based on these results, the concentration of nitric acid was kept at 3.2 mmol/L in most cases. As shown in Table 5, most reactions were carried out under similar conditions except that the concentration of ceric ion, AGU, and AM was changed systematically. It is obvious that the hydrodynamic volume of the graft copolymer increased with decreasing ceric ion concentration, as was observed previously [11]. The highest apparent weight-average molecular weight of the PAM graft determined by SEC was about 4.5 million. The average number of grafts per cellulose substrate was found to be 1.1 or less, depending on the concentration of ceric ion. The low values of N_g reflect the very low efficiency of the grafting process. The low N_g values are consistent with termination of the grafted chains by coupling [7, 11]. In order to increase the number of grafts per SPC chain, increasing the ceric ion concentration was necessary. However, by increasing the concentration of the ceric ion, the possible competing terminating reaction between ceric ion and the PAM macroradical is also increased, resulting in lower conversion as well as lower molecular weight of the graft PAM chains [7, 11]. From Table 5 it is clear that the intrinsic viscosity and the average molecular weight of the grafted chains increases with increasing acrylamide concentration, in agreement with earlier work on the corresponding graft copolymerization of AM onto starch, DHPC, and dextran [1, 12]. Intrinsic viscosities (in 0.2 *M* Na_2SO_4) of the SPC-*g*-PAM were found to have values of 4.9 dL/g or less.

Characterization of Graft Copolymers by Size-Exclusion Chromatography (SEC) and ^{13}C-NMR

In order to characterize the molecular weight distribution of the PAM grafts, a hydrolytic method is required to completely degrade the SPC backbone to oligosaccharides. It was shown previously that the hydrolysis of cellulose in the presence of 72% H_2SO_4 does not result in extensive hydrolysis of the polyacrylamide chains and that the molecular weight of this partially hydrolyzed polyacrylamide may be readily determined by SEC analysis in 0.2 *M* Na_2SO_4 aqueous solution [4]. Therefore, this method was utilized to degrade the SPC-*g*-PAM. The ungrafted sulfopropylcellulose was hydrolyzed by the same method in order to test whether the degradation of the polysaccharide backbone to oligosaccharides was completed. This was apparently the case since the SEC chromatogram in 0.2 *M*

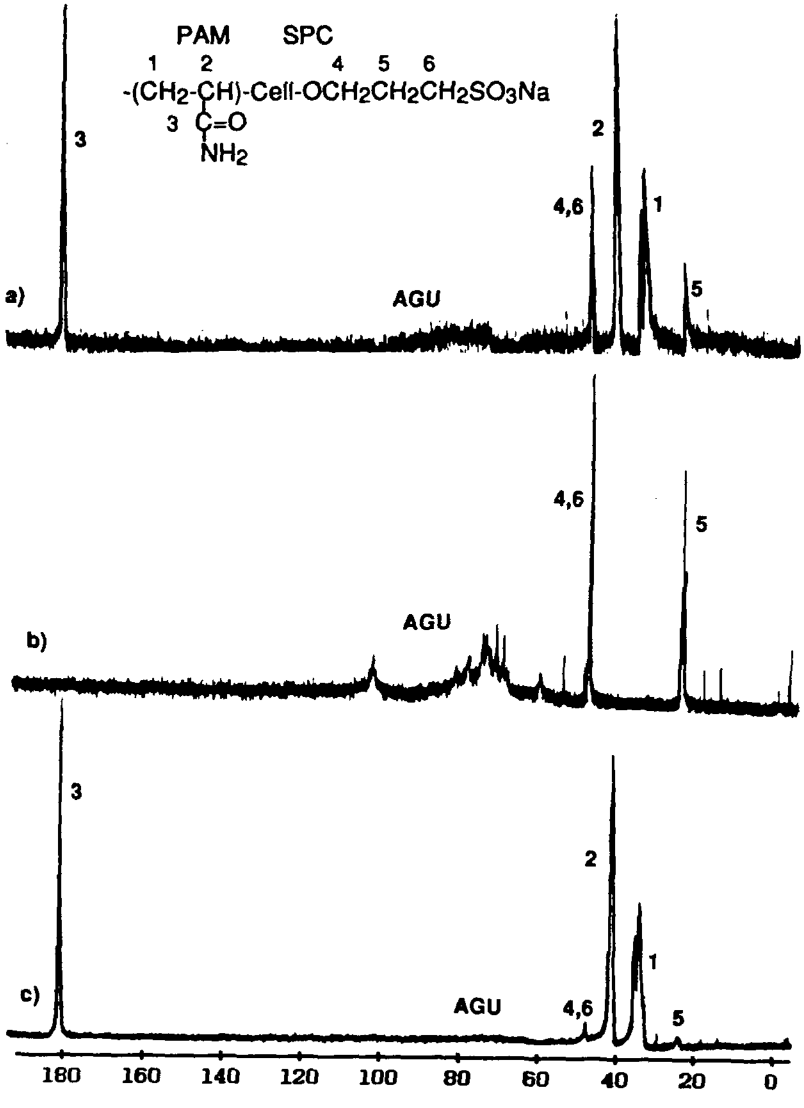


FIG. 6. ^{13}C-NMR spectra: a) SPC-*g*-AM in D_2O; b) SPC in D_2O; c) hydrolyzed SPC-*g*-AM in D_2O.

Na_2SO_4 showed only one peak with an elution volume identical to that of the solvent peak.

The ^{13}C-NMR spectra of SPC, SPC-*g*-PAM, and hydrolyzed SPC-*g*-PAM are shown in Fig. 6. The intensity of the absorption in the chemical shift range of the anhydroglucose unit (AGU) and the sulfopropyl group of the hydrolyzed graft copolymer is much lower than that of the original graft copolymer. This result indicates that the cellulose backbone was largely hydrolyzed to oligosaccharides which most likely remain attached to the polyacrylamide chains. The presence of oligosaccharides on the polyacrylamide chains is consistent with the presence of grafted chains (see above).

Solution Properties of SPC-*g*-PAM

The reduced viscosity–concentration profile of SPC-*g*-PAM is shown in Fig. 5. As expected, the polyelectrolyte character of the graft copolymer is generally more pronounced as the SPC content of the graft copolymer increases, SPC itself, of course, having the most pronounced polyelectrolyte character. From a comparison with Fig. 1 it is apparent that the presence of the PAM chains in the graft copolymer plays a very important role in the graft-copolymer solution properties. As expected at higher PAM content, the polyelectrolyte character of the graft copolymer is much less pronounced.

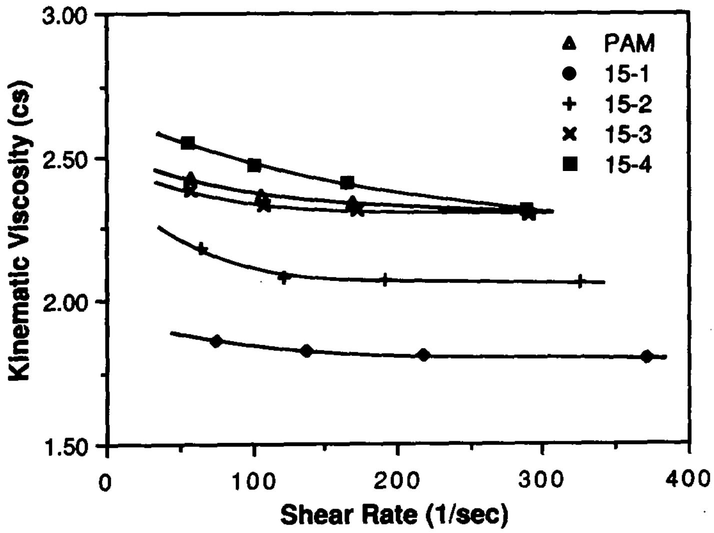


FIG. 7. Influence of shear rate on the kinematic viscosity of SPC-*g*-PAM, SPC, and PAM at 0.20 g/dL.

The influence of the shear rate on the kinematic viscosity of the SPC-*g*-PAM is shown in Fig. 7. A Cannon-Ubbelohde four-bulb dilution viscometer was used for measuring this parameter of the polymer solution (0.2 g/dL) at 30°C. As expected, it is seen that the shear rate dependence of the viscosity increases with higher molecular weight of the graft copolymer [13].

ACKNOWLEDGMENTS

Support for this work by the U.S. Department of Energy, Office of Basic Energy Sciences, under Grant DF-AS05-83ER45031, is gratefully acknowledged.

REFERENCES

[1] J. Doane et al., *J Appl. Polym. Sci., 23*, 635 (1979).

[2] H. Pledger Jr., T. S. Young, G. S. Wu, G. B. Butler, and T. E. Hogen-Esch, *J. Macromol. Sci.—Chem., A22*(4), 415 (1985).

[3] H. Pledger Jr., G. S. Wu, T. S. Young, T. E. Hogen-Esch, and G. B. Butler, *Ibid., A22*(9), 1297 (1985).

[4] (a) J. C. Chen, Y. X. Zhang, D. Patil, T. E. Hogen-Esch, and G. B. Butler, *Ibid., A25*(8), 955 (1988). (b) Y. X. Zhang, J. C. Chen, D. Patil, G. B. Butler, and T. E. Hogen-Esch, *Ibid., A25*(8), 971 (1988).

[5] G. Natus and E. J. Goethals, *Ibid., A2*(3), 488 (1968).

[6] M. T. Szabo, *J. Pet. Technol., 31*, 553 (1979).

[7] C. L. McCormick and G. S. Chen, *J. Polym. Sci., Polym. Chem. Ed., 20*, 817 (1984).

[8] G. A. Adams, in *Methods in Carbohydrate Chemistry*, Vol. 5 (R. J. Whistler, ed.), Academic, New York, 1965.

[9] S. T. Balke, A. E. Hamielec, B. P. LeClair, and S. L. Pearce, *Ind. Eng. Chem., Prod. Res. Dev., 8*, 54 (1969).

[10] W. W. Yau, H. J. Stoklosa, C. R. Ginnard, and D. D. Bly, 12th Middle Atlantic Regional ACS Meeting, April 1978, PO 13.

[11] D. J. McDowall, B. S. Gupta, and V. T. Stannett, *Prog. Polym. Sci., 10*, 1 (1984).

[12] C. L. McCormick and L. S. Park, *J. Polym. Sci., Polym. Chem. Ed., 19*, 2229 (1981); *22*, 49 (1984).

[13] W. R. Krigbaum and P. J. Flory, *J. Polym. Sci., 11*, 37 (1953).

Received June 5, 1989