

This article was downloaded by:

On: 24 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



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 Characterization of Water-Soluble Graft Copolymers from 2, 3-Dihydroxypropylcellulose and Acrylamide

J. -C. Chen^a; Y. -X. Zhang^a; D. Patil^a; G. B. Butler^a; T. E. Hogen-esch^a

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

To cite this Article Chen, J. -C. , Zhang, Y. -X. , Patil, D. , Butler, G. B. and Hogen-esch, T. E.(1988) 'Synthesis and Characterization of Water-Soluble Graft Copolymers from 2, 3-Dihydroxypropylcellulose and Acrylamide', Journal of Macromolecular Science, Part A, 25: 8, 971 – 985

To link to this Article: DOI: 10.1080/00222338808052134

URL: <http://dx.doi.org/10.1080/00222338808052134>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

SYNTHESIS AND CHARACTERIZATION OF WATER-SOLUBLE GRAFT COPOLYMERS FROM 2, 3-DIHYDROXYPROPYLCELLULOSE AND ACRYLAMIDE

J.-C. CHEN, Y.-X. ZHANG, D. PATIL, 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 2,3-dihydroxypropylcellulose-polyacrylamide graft copolymers (DHPC-g-PAM) were prepared by Ce^{4+} ion-initiated graft copolymerization of acrylamide (AM) onto 2,3-dihydroxypropylcellulose (DHPC) dissolved in dilute nitric acid at room temperature under argon. The ratios of the concentration of Ce^{4+} ion to the concentration of DHPC were shown to affect the number and the length of the polyacrylamide grafts. The average number of grafts per chain was determined by acid-catalyzed degradation of the cellulose backbone and was found to be consistent with the presence or absence of free DHPC in the polymerization product prior to hydrolysis. The average number of grafts per DHPC molecule was found to be 2.7 or less depending on the reaction conditions.

*To whom correspondence should be addressed at 205 Loker Hydrocarbon Institute, University of Southern California, Los Angeles, California 90089.

INTRODUCTION

Water-soluble copolymers [1] of polysaccharides [2] and synthetic polymers are of potential interest in the area of enhanced oil recovery (EOR) [3] from several points of view. First, the cost of several common polysaccharides, such as starch or cellulose, is low compared to that of several types of vinyl polymers, such as partially hydrolyzed polyacrylamide, currently being used in EOR applications. Second, the incorporation of a polysaccharide in a copolymer may give rise to increased viscosity as a result of aggregation through the polysaccharide segments of the copolymers or of an enhancement in size or dissymmetry as a result of incompatibility of the polysaccharide and the vinyl polymer segments. Third, the resistance to mechanical degradation may be increased as a result of the presence of the relatively sturdy polysaccharide segments, provided that contribution of such segments to the viscosity is high.

These and other considerations have prompted us to investigate in some detail the synthesis and characterization of water-soluble graft copolymers of 2,3-dihydroxypropylcellulose [4] (DHPC) and polyacrylamide (PAM). DHPC is not only soluble in water, but also possesses a 1,2-diol linkage shown to be susceptible to Ce^{4+} ion-initiated grafting reactions [5]. Therefore, it may be a suitable substrate for homogeneous grafting of water-soluble monomer initiated by ceric ion.

EXPERIMENTAL

All the temperatures are uncorrected and reported in degrees centigrade. Proton nuclear magnetic resonance (NMR) spectra (60 MHz) were recorded on a Varian EM-360L spectrometer. Carbon-13 (25.0 MHz) spectra were obtained on a Jeol JNM-FX-100 instrument in 50% NaSCN/D₂O. Chemical shifts are given in parts per million (ppm) downfield from the methyl protons of sodium 2,2-dimethylsilapentane-5-sulfonate (DSS) or with respect to thiocyanate carbon.

Reagents and Solvents

DHPC was synthesized by the reaction of sodium cellulose in dioxane with 3-chloro-1,2-propanediol or in acetone with glycidol [4]. Acrylamide (Eastman Kodak Co.) was recrystallized from benzene prior to use (mp 84-86°C). Ceric ammonium nitrate was purchased from F. E. Smith and Company and used as received. All the solvents, acids, and salts used for general application were of reagent grade or ACS grade quality.

Synthesis and Characterization

Graft Copolymerizations. In a capped round-bottomed flask, argon was bubbled through an aqueous solution of DHPC and acrylamide for 30 min. Ceric ammonium nitrate was then added in a known concentration in dilute nitric acid solution. The reaction was carried out at room temperature ($\sim 23^\circ\text{C}$) for 48 h, and the reaction was terminated with an aqueous hydroquinone solution. The reaction mixture was diluted with water to a viscosity low enough that the polymer solution precipitated rather than wrapped around the stirring bar when it was dropped into acetone. The precipitated polymer was filtered, washed with acetone, and dried under vacuum at 50°C for 24 h.

Hydrolysis of DHPC-g-PAM Copolymers [6]. 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 thoroughly for 45 min. The mixture was then diluted to 100 mL with water, transferred to an autoclave bottle, and heated to 110°C for 1 h. After cooling the reaction mixture to room temperature, it was neutralized with NaOH aqueous solution. The neutralized solution was dialyzed against deionized water to remove all ions and small molecules in a Spectra/por (MWCO 1000) dialysis tubing for 3 d. The dialyzed product was used directly for SEC analysis.

Hydrolysis of DHPC. The DHPC was hydrolyzed by the same procedure as for DHPC-g-PAM copolymers except for the dialysis step. The SEC chromatogram showed only one peak with an elution volume identical to that of the solvent peak when $0.2\text{ M Na}_2\text{SO}_4$ aqueous solution was used as the mobile phase.

Hydrolysis of PAM. Hydrolysis of PAM standard was carried out by the same procedure as for DHPC-g-PAM. SEC analysis showed that the PAM subjected to this hydrolysis condition had the same elution volume as the original PAM standard when $0.2\text{ M Na}_2\text{SO}_4$ aqueous solution was used as the mobile phase as previously reported [1].

Aqueous Size-Exclusion Chromatography. A Waters SEC system, consisting of a Model 590 pump and a U6K injector, was used in combination with a Perkin-Elmer LC-25 RI detector and a Kratos Spectroflow 757 variable wavelength UV-VIS detector. The SEC column, TSK-gel-GMPW ($600 \times 7.5\text{ mm}$, MW range 500-2 million, Toyo Soda) was purchased from Bio-Rad Labs. The mobile phase ($0.2\text{ M Na}_2\text{SO}_4$) was filtered through a $0.45\text{-}\mu\text{m}$ Millipore mem-

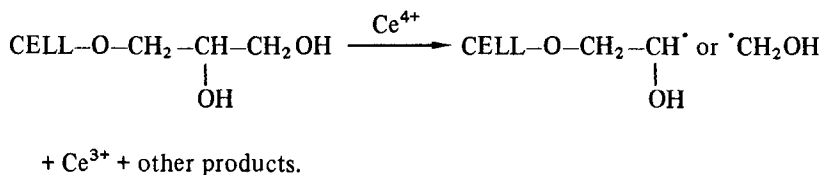
brane under vacuum before use. The velocity of the mobile phase was 0.8 mL/min. The polymer concentration in the sample solution was 0.4 wt% or less, and the volume of sample injection was between 150 and 200 μ L. The calibration was made with the use of polydisperse PAM standards which were purchased from American Polymer Standards Co. A computer search routine was used to retrieve the true MW calibration curve from the polydisperse standards. The programs used, GPC1 and CCP, were written based on the linear calibration method introduced by Hamielec [7] and later modified by Yau et al. [8].

Determination of Intrinsic Viscosity. Four concentrations of each polymer sample were measured to determine its intrinsic viscosity. The sample was in deionized water or in a 0.2 M sodium sulfate aqueous solution. The flow time through a Cannon-Ubbelohde viscometer was determined at $30 \pm 0.01^\circ\text{C}$. The intrinsic viscosity was determined by least-squares treatment of the plots of η_{sp}/c vs c and $\ln \eta_r/c$ vs c and extrapolated to zero concentration. In most cases the intercepts of the two plots were nearly identical ($\pm 2\%$). Otherwise, the average of these two values was reported.

RESULTS AND DISCUSSION

Proof of Grafting

Due to its high mobility relative to that of the cellulose matrix, the diol linkage of the 2,3-dihydroxypropyl group could be regarded as more reactive than that of the AGU. Upon decomposition of the ceric ion 1,2-diol complex [5], two possible radicals are generated, of which only the macroradical can give rise to the formation of graft copolymers:



Whether AM homopolymerizes concurrently with the graft copolymerization is difficult to prove [1]. Upon preparation of DHPC, some portions of water-soluble DHPC were obtained. Under the conditions used for the preparation of water-soluble DHPC-g-PAM polymers, this water-insoluble DHPC was copolymerized with acrylamide by Ce^{4+} initiation. Sixty percent of the result-

TABLE 1. Effect of Conditions of Hydrolysis on the Composition of Hydrolyzed PAM and DHPC-g-PAM

Sample	Hydrolytic method	Chemical analysis		
		C, %	H, %	N, %
PAM standard	No treatment	47.74	7.84	17.04
PAM standard	3 <i>N</i> HCl, reflux, 1 d	34.05	4.49	0.04
DHPC-g-PAM	3 <i>N</i> HCl, reflux, 1 d	34.23	4.51	0
DHPC-g-PAM	9 <i>N</i> HCl, 70°C, 5 h	37.38	5.34	4.91
DHPC-g-PAM	72% H ₂ SO ₄ , 4 h ^a	41.98	6.68	12.08

^aDiluted, 110°C, 1 h (autoclaved).

ing polymer was shown to contain polyacrylamide and to be water insoluble. Since homopolyacrylamide is quite water-soluble, this insoluble part should be graft copolymer. The remaining water-soluble polymer was fractionated by solution precipitation into two portions, both of which were shown to contain polysaccharide fragments by the anthrone test [9] as well as PAM. Therefore, it could be reasonably concluded that graft copolymerization is the major reaction under the conditions studied.

Characterization of Graft Copolymers by SEC and ¹³C NMR

In order to characterize the MW distribution of the grafted PAM chains, an adequate hydrolytic method is required so that the cellulose backbone is completely degraded to oligosaccharides. Several hydrolysis reactions were evaluated, and the results are shown in Table 1.

Based on the elemental analysis, 72% sulfuric acid does not cause extensive hydrolysis of the PAM chains and is preferred over the hydrochloric acid treatment. Therefore, this method was used to degrade the cellulose backbone. The ungrafted DHPC was hydrolyzed by the same method to test whether cellulose was effectively degraded to oligosaccharides. This was apparently the case since the SEC chromatogram showed only one peak with an elution volume identical to that of the solvent peak when 0.2 *M* Na₂SO₄ aqueous solution was used as eluent. SEC analysis of a PAM standard before and after hydrolysis in 72% H₂SO₄ showed the same elution volumes in 0.2 *M* Na₂SO₄. Therefore, under these conditions, the grafted PAM could be characterized by SEC.

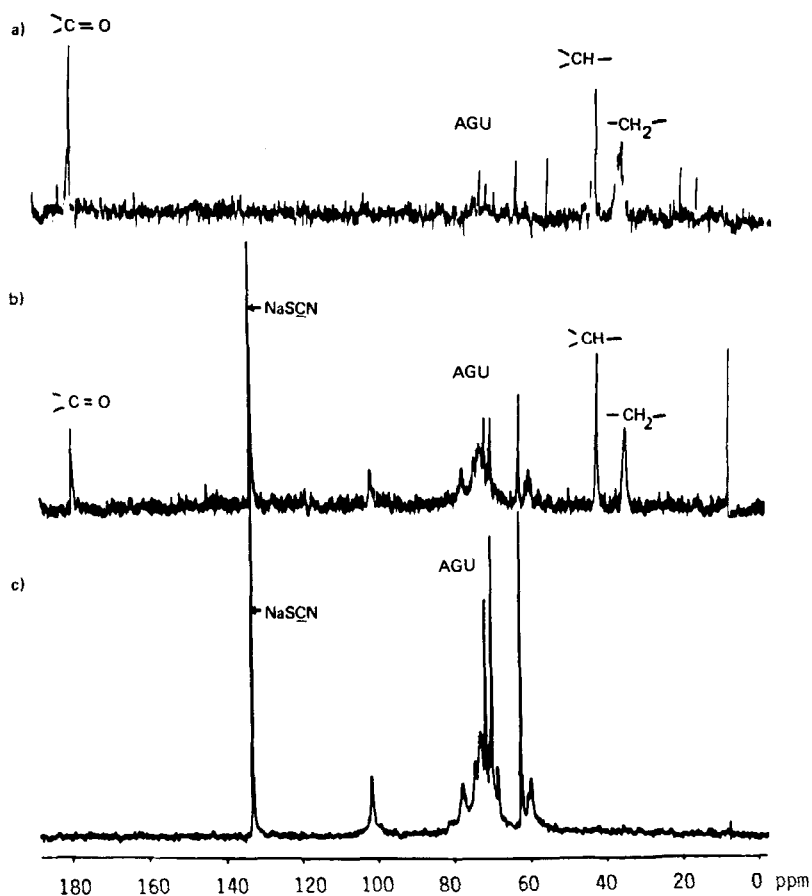


FIG. 1. ^1H Decoupled ^{13}C -NMR spectra: a) Hydrolyzed DHPC-g-PAM in D_2O ; b) DHPC-g-PAM in 50% NaSCN aqueous solution; c) DHPC in 50% NaSCN aqueous solution.

The ^{13}C -NMR spectra of DHPC, DHPC-g-PAM, and hydrolyzed DHPC-g-PAM are shown in Fig. 1. The intensity of the absorptions in the chemical shift range of the AGU of the hydrolyzed graft copolymer is much lower than that of original graft copolymer. This result supported that the cellulose backbone was largely hydrolyzed to oligosaccharides that most likely remain attached to the PAM chains.

TABLE 2. Effect of Nitric Acid Concentration on the Graft Copolymerization of DHPC and Acrylamide^a

Experiment no.	[AM] ₀ , mol/L	[AGU] ₀ , mol/L	[Ce ⁴⁺] ₀ , mmol/L	[HNO ₃], mmol/L	Conversion, ^b %	[η], ^c dL/g
CS-39	0.47	0.034	0.3	3.0	91.9	2.90
CS-58	0.47	0.034	0.3	30.0	27.2	1.76
CS-59	0.47	0.034	0.3	300.0	6.5	2.18

^aDHPC—spruce, $\bar{M}_n = 3.31 \times 10^4$, $\bar{M}_w = 2.51 \times 10^5$.

^bConversion = (wt graft copolymer - wt DHPC)/(wt acrylamide).

^cIntrinsic viscosity was determined in deionized water at 30°C.

Effects of Reaction Parameters on the Graft Copolymer [11]

a) Nitric Acid. The dependence of grafting on the concentration of nitric acid is shown in Table 2. It is seen that at higher acid concentration, lower conversions were obtained. This could be attributed perhaps to a reduction in the extent of Ce⁴⁺-DHPC complex formation as well as an increase in the termination rate [10]. Based on these results, the concentration of nitric acid was kept at 3.0 mmol/L in most cases.

b) Ceric Ion. As shown in Table 3, most reactions were carried out under similar conditions, except that the concentration of ceric ion was changed systematically. It is clear that the intrinsic viscosity at constant [AM]/[DHPC] ratio increases with decreasing [Ce⁴⁺] in most cases, except when [Ce⁴⁺] was below 0.1 mmol/L. The intrinsic viscosity also increased with increasing [AM]/[DHPC] ratio at constant concentration of ceric ion. The average number of grafts per DHPC molecule was 2.7 or less, depending on the reaction conditions. When this number is less than 1, the resulting polymer should contain some unreacted DHPC. This was supported by SEC analysis. Thus, the hydrolyzed DHPC-*g*-PAM copolymers were shown to have a lower elution volume than the DHPC-*g*-PAM copolymers.

In some cases the intrinsic viscosities of the resulting DHPC-*g*-PAM polymers were lower than those of their parent polymers. This could be due to the acid-catalyzed cleavage of the DHPC backbone. The number of grafts/DHPC (N_g) is obtained by dividing the concentration of PAM by that of DHPC.

TABLE 3. Effect of Ceric Ion Concentration on

Experiment no.	[AM] ₀ , mol/L	[Ce ⁴⁺] ₀ , mmol/L	PAM (hydrolyzed)	
			$\bar{M}_n \times 10^{-6}$	$\bar{M}_w \times 10^{-6}$
DHPC-50- μ m cellulose, $\bar{M}_n = 2.45 \times 10^4$, $\bar{M}_w = 5.75 \times 10^4$				
CS-10	0.45	5.0	0.055	0.084
CS-11	0.45	2.0	0.120	0.194
CS-12	0.45	1.0	0.360	0.537
CS-13	0.45	0.5	0.395	1.063
CS-14	0.45	0.2	0.380	2.232
CS-15	0.45	0.1	0.397	1.584
CS-16	0.94	5.0		
CS-5	0.94	3.0		
CS-17	0.94	1.0		
CS-18	0.94	0.5		
CS-19	0.94	0.1		
DHPC-spruce, $\bar{M}_n = 3.31 \times 10^4$, $\bar{M}_w = 2.51 \times 10^5$				
CS-32	0.94	5.0	0.049	0.226
CS-33	0.94	3.0	0.061	0.482
CS-34	0.94	1.0	0.116	1.109
CS-35	0.94	0.5	0.719	2.471
CS-36	0.94	0.3	1.287	5.957
CS-37	0.94	0.1	1.937	6.541
DHPC-cotton linter, $\bar{M}_n = 6.80 \times 10^4$, $\bar{M}_w = 2.44 \times 10^5$				
CS-20	0.94	5.0		
CS-21	0.94	3.0		

Graft Copolymerization of DHPC and Acrylamide^a

N_g^b	$f,^c \%$	Conversion, ^d %	DHPC- <i>g</i> -PAM, ^e $\bar{M}_n \times 10^{-5}$	$[\eta]_g,^f$ dL/g	Gel, ^g wt%
0.89	11.7	100.0	0.73	1.06	
0.38	12.6	93.7	0.70	1.24	
0.08	5.4	60.7	0.53	1.35	
0.10	13.8	84.7	0.64	1.56	
0.03	11.8	27.8	0.36	1.68	
0.03	17.7	21.8	0.36	1.47	
		100.0		1.32	
		98.5		1.46	
		85.9		2.18	
		100.0		2.97	
		12.5		2.28	
2.70	27.3	99.4	1.65	1.80	
2.17	36.6	99.4	1.66	2.11	
1.24	57.5	99.4	1.77	2.98	
0.18	18.2	97.9	1.62	3.23	
0.10	16.1	93.4	1.62	3.61	
0.04	19.2	64.7	1.10	4.60	
		100.0		2.10	7.7
		91.9		2.48	13.5

(continued)

TABLE 3 (continued)

Experiment no.	[AM] ₀ , mol/L	[Ce ⁴⁺] ₀ , mmol/L	PAM (hydrolyzed)	
			$\bar{M}_n \times 10^{-6}$	$\bar{M}_w \times 10^{-6}$
DHPC-cotton linter, $\bar{M}_n = 6.80 \times 10^4$, $\bar{M}_w = 2.44 \times 10^5$ (continued)				
CS-22	0.94	1.0		
CS-23	0.94	0.5		
CS-24	0.94	0.3		
CS-25	0.94	0.1		
DHPC-cotton wool, $\bar{M}_n = 2.68 \times 10^5$, $\bar{M}_w = 9.78 \times 10^5$				
CS-26	0.94	5.0		
CS-27	0.94	3.0		
CS-28	0.94	1.0		
CS-29	0.94	0.5		
CS-30	0.94	0.3		
CS-31	0.94	0.1		

^aReaction conditions: [AGU]₀ = 0.1 mol/L; [HNO₃] = 3 mmol/L.

^bAverage number of grafts per DHPC molecule, $N_g = [\text{PAM}]/[\text{DHPC}]_0$.

^cInitiator efficiency, $f = [\text{PAM}]/[\text{Ce}^{4+}]_0$.

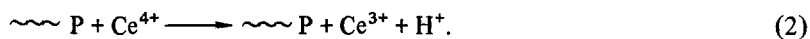
^dConversion = (wt graft copolymer - wt DHPC)/(wt acrylamide).

^eNumber-average molecular weight of graft copolymer, $\bar{M}_n = \bar{M}_n(\text{PAM}) \times N_g + \bar{M}_n(\text{DHPC})$.

^fIntrinsic viscosity was determined in 0.2 M Na₂SO₄ aqueous solution at 30°C.

^gGel formed during the graft copolymerization.

In order to increase N_g (Table 3), increasing the ceric ion concentration is necessary. However, by increasing the ceric ion concentration, the possible competing terminating reaction between ceric ion and the macroradical is also increased [10]:



N_g^b	$f,^c \%$	Conversion, ^d %	DHPC- <i>g</i> -PAM, ^e $\bar{M}_n \times 10^{-5}$	$[\eta]_g,^f$ dL/g	Gel, ^g wt%
		87.4		3.75	10.5
		90.4		4.28	13.5
		97.9		5.40	18.8
		82.9		3.20	29.6
		96.4		2.66	18.0
		93.4		2.70	8.5
		97.9		3.27	18.8
		85.9		4.61	9.6
		85.9		5.18	23.5
		78.4		3.57	1.6

The number-average molecular weight of the graft copolymer may be estimated by multiplying the number of grafts by the molecular weight of the associated polyacrylamide side chains and adding the number-average molecular weight of DHPC.

c) *Acrylamide*. From Table 4 it is clear that the intrinsic viscosity, conversion, and the molecular weight of the grafted PAM chains increases with

TABLE 4. Effect of Acrylamide Concentration on

Experiment no.	[AM] ₀ , mol/L	[Ce ⁴⁺] ₀ , mmol/L	PAM (hydrolyzed)	
			$\bar{M}_n \times 10^{-6}$	$\bar{M}_w \times 10^{-6}$
DHPC—spruce, $\bar{M}_n = 3.31 \times 10^4$, $\bar{M}_w = 2.51 \times 10^5$				
CS-40	0.31	0.3	1.084	1.588
CS-41	0.63	0.3	1.517	3.251
CS-42	0.94	0.3	2.308	6.004
CS-43	1.25	0.3	3.015	7.782
DHPC—cotton wool, $\bar{M}_n = 2.68 \times 10^5$, $\bar{M}_w = 9.78 \times 10^5$				
CS-54	0.31	0.3		
CS-55	0.63	0.3		
CS-56	0.94	0.3		
CS-57	1.25	0.3		

^aReaction conditions: [AGU]₀ = 0.034 mol/L; [HNO₃] = 3 mmol/L.

^bAverage number of grafts per DHPC molecule, $N_g = [\text{PAM}]/[\text{DHPC}]_0$.

^cInitiator efficiency, $f = [\text{PAM}]/[\text{Ce}^{4+}]_0$.

^dConversion = (wt graft copolymer - wt DHPC)/(wt acrylamide).

^eNumber-average molecular weight of graft copolymer, $\bar{M}_n = \bar{M}_n(\text{PAM}) \times N_g + \bar{M}_n(\text{DHPC})$.

^fIntrinsic viscosity in 0.2 M Na₂SO₄ aqueous solution at 30°C.

^gGel formed during the graft copolymerization.

increasing acrylamide concentration. At higher acrylamide concentrations, intrinsic viscosities of up to 14.6 dL/g were obtained. However, in the case of DHPC prepared from cotton wool, some water-insoluble gel was formed. The reason for this is as yet unclear.

d) Reaction Time. The dependence of graft copolymerization on reaction time is shown in Table 5. No graft copolymer could be isolated during the first half hour. This might be attributed to a free-radical induction period

Graft Copolymerization of DHPC and Acrylamide^a

N_g^b	$f,^c \%$	Conversion, ^d %	DHPC- <i>g</i> -PAM, ^e $\bar{M}_n \times 10^{-5}$	$[\eta]_g,^f$ dL/g	Gel, ^g wt%
0.07	4.0	58.9	1.09	2.33	
0.17	9.8	99.9	2.91	3.75	
0.17	9.5	98.6	4.26	4.61	
0.17	9.7	98.4	5.46	6.44	
		82.9		3.50	
		98.4		6.68	
		98.6		10.06	42.5
		99.5		14.55	28.7

of the Ce^{4+} -DHPC complex. The molecular weight of the grafted PAM and the intrinsic viscosity of the resulting copolymers were not found to depend strongly on the reaction time.

e) DHPC Type. DHPC based on cotton wool possesses the highest molecular weight and highest intrinsic viscosity; its PAM copolymer was also shown to have the highest intrinsic viscosity (Table 4). Therefore, it could be reasonably concluded that the intrinsic viscosity of the resulting copolymer will increase with increasing molecular weight of the DHPC substrate.

TABLE 5. Effect of Reaction Time on Graft Copolymerization of DHPC and Acrylamide^a

Experiment no.	Reaction time, h	Conversion, ^b %	$[\eta]$, ^c dL/g	PAM (hydrolyzed)	
				$\bar{M}_n \times 10^5$	$\bar{M}_w \times 10^5$
CS-60	0.5	~0	2.20		
CS-64	1.0	33.0	2.43		
CS-66	2.0	35.2	2.22	1.24	4.55
CS-67	4.0	42.0	2.16		
CS-65	8.0	46.4	2.20	1.44	4.53
CS-63	16.0	50.9	2.25		
CS-61	24.0	57.6	2.29	1.81	6.10
CS-40	48.0	58.9	2.33		

^aReaction conditions: $[AM]_0 = 0.31$ mol/L, $[AGU]_0 = 0.034$ mol/L, $[Ce^{4+}]_0 = 0.3$ mmol/L, $[HNO_3] = 3.0$ mmol/L.

^bConversion = (wt graft copolymer - wt DHPC)/(wt acrylamide).

^cIntrinsic viscosity in deionized water at 30°C.

Effect of Boric Acid Addition

DHPC was shown to possess the ability to form a reversible crosslinked complex with boric acid [4]. Although DHPC-*g*-PAM graft copolymer also contains a 1,2-diol linkage, its solution viscosity did not increase at all on treating with boric acid under the basic condition. This might be attributed to interference in the complex formation by the grafted PAM chains. However, the degree of complex formation of DHPC was shown to be unaffected by the presence of PAM homopolymer. It is more plausible that the concentration of DHPC in the graft copolymer is below the critical concentration, C^* , of DHPC needed for gel formation [4].

ACKNOWLEDGMENT

Support for this work by the U.S. Department of Energy, Office of Basic Energy Sciences, under Grant DE-ASO5-83ER45031, is gratefully acknowledged.

REFERENCES

- [1] H. Pledger Jr., T. S. Young, G. S. Wu, G. B. Butler, and T. E. Hogenesch, *J. Macromol. Sci.-Chem.*, *A22*(4), 415 (1985), and references therein.
- [2] R. L. Davidson (ed.), *Handbook of Water-Soluble Gums and Resins*, McGraw-Hill, New York, 1980.
- [3] D. C. Williams, J. H. Rogers, and T. J. West, in *Polymer Sciences and Technology*, Vol. 2 (N. M. Bikales, ed.), Plenum, New York, 1973.
- [4] Y.-X. Zhang, J. C. Chen, D. R. Patil, G. B. Butler, and T. E. Hogenesch, *J. Macromol. Sci.-Chem.*, *A25*(8), 955 (1988).
- [5] G. Mino and S. Kaizerman, *J. Polym. Sci.*, *31*, 242 (1958).
- [6] G. A. Adams, in *Methods in Carbohydrate Chemistry*, Vol. 5 (R. J. Whistler, ed.), Academic, New York, 1965.
- [7] S. T. Balke, A. E. Hamielec, B. P. LeClair, and S. L. Pearce, *Ind. Eng. Chem., Prod. Res. Dev.*, *8*, 54 (1969).
- [8] W. W. Yau, H. J. Stoklosa, C. R. Ginnard, and D. D. Bly, 12th Middle Atlantic Regional ACS Meeting, April 1978, PO 13.
- [9] R. Dreywood, *Ind. Eng. Chem., Anal. Ed.*, *18*, 499 (1946).
- [10] D. J. McDowall, B. S. Gupta, and V. T. Stannett, *Prog. Polym. Sci.*, *10*, 1 (1984).
- [11] C. L. McCormick, K. C. Lin, and L. S. Park, *J. Macromol. Sci.-Chem.*, *A16*(8), 1441 (1981); *J. Polym. Sci., Polym. Chem. Ed.*, *19*, 2229 (1981).

Received September 10, 1987

Revision received December 11, 1987