1,2-Propanediol–Cellulose–Acrylamide Graft Copolymers

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ABSTRACT: 1,2-Propanediol–cellulose–acrylamide graft copolymers (PCACs) were developed for enhanced oil recovery. They were prepared with acrylamide and 1,2-propanediol (PDO)–cellulose, which was formed through the addition of glycols to cellulose by the Shotten–Baumann reaction between 3-chloro-1,2-propanediol and cellulose. The graft copolymerization was initiated with a redox system between Ce^{4+} and glycols in cellulose. The infrared spectrum of PDO–cellulose had some characteristic absorption bands around 2960 (νC—H) and 1050 cm^{-1} (νC—O) that also appeared for the PDO group and pyranose ring of cellulose, respectively. The rate of Ce^{4+} consumption by PDO–cellulose was investigated through the calculation of the overall kinetic constant from the slopes of $\ln(D - D_R)$ versus time (where D is the absorbance and D_R is the absorbance of the original polysaccharide solution) The results showed that PDO–cellulose had high reactivity and that there were two mechanisms of oxidation by Ce^{4+} with PDO–cellulose. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 92: 3022–3029, 2004

Key words: graft copolymers; hydrophilic polymers; polyamides; polysaccharides; water-soluble polymers

INTRODUCTION

Since the graft polymerization of acrylamide (AM) onto poly(vinyl alcohol) in the presence of Ce^{4+} was reported by Mino and Kaizerman,[1] many attempts have been made to graft-polymerize AM onto polysaccharides.[2–6] Moreover, water-soluble copolymers of polysaccharides and AM are interesting for enhanced oil recovery (EOR) because of their rheological properties.[4] Most reports in the EOR field have concerned water-soluble polysaccharides; few reports have concerned the graft polymerization of AM onto water-insoluble polysaccharides such as cellulose. For economic reasons, cellulose is very important as a polymer for EOR, but it may be difficult to obtain water-soluble copolymers of cellulose and AM because of their molecular design. To solve the problem of cellulose, researchers have added glycols to cellulose molecules by the Shotten–Baumann reaction between cellulose and 3-chloro-1,2-propanediol (CPDO). It has been confirmed by spectroscopy that 1,2-propanediol (PDO)–cellulose has high reactivity with Ce^{4+} because of its *cis*-glycol groups. The molecule of PDO–cellulose has been determined to be huge by gel permeation chromatography (GPC) and might be formed by hydrogen bonding. This PDO–cellulose has been grafted by AM with Ce^{4+}, and the properties of the copolymer have been evaluated with infrared (IR) spectroscopy, GPC, and viscosity measurements. The correlation between the molecular weight of the reactant PDO–cellulose and that of the branch polyacrylamide (PAM) has also been investigated.

EXPERIMENTAL

Chemicals

AM (Eastman Kodak) was purified by two recrystallizations from chloroform before use. Whatman 4 filter paper was used as the source cellulose material. CPDO was obtained from Aldrich Co. Ceric ammonium nitrate (CAN; reagent-grade; G. Frederick Smith Chemical Co.) was dissolved in $1N$ nitric acid, and the stock solution was used to prepare the polymerization solution.

Preparation of PDO–cellulose

Sodium–cellulose was dispersed in acetone. During stirring, CPDO was added to the solution. The mixture was stirred for 8.5 h at 50°C and then stood for 1 night at room temperature. The resultant product was separated from the supernatant liquid and poured into methanol for the removal of the byproduct glycerin. These procedures were repeated twice. The final prod-

uct, pH-adjusted to 7, was washed with methanol and vacuum-dried.

Cellulose was dispersed in *t*-butanol, and then 30% NaOH was added to the dispersion at 20–22°C. During stirring, CPDO was added to the solution. The mixture was stirred for 5 h at 50°C and then stood for 1 night at room temperature. The resultant mixture was separated from the supernatant liquid and poured into 50% *t*-butanol for the removal of the by-product glycerin. These procedures were repeated three times. The final product, pH-adjusted to 7, was washed with 80% methanol and vacuum-dried.

Determination of the rate of CE^{4+} consumption

The reaction rates were determined from the light absorbance of the reaction solution with a PerkinElmer Coleman 124 spectrophotometer. The composition of the solution was as follows: $10^{-3}M$ Ce^{4+}, 1% polymer, and $0.01N$ HNO_3. The absorbance was measured at 25°C in a 0.5 cm $\times$ 1 cm cell. The reactant solutions were purged with nitrogen gas before the mixing. The wavelength at which the absorbance was followed was chosen to give a reasonably large initial absorbance; the wavelength used for this experiment was 425 nm.[7]

Size exclusion chromatograms of PDO–cellulose

A Water Associates model 440 high-pressure liquid chromatograph with a model 590 absorbance detector was used to obtain the chromatograms. A 250-mL sample (0.04/dL PDO–cellulose, $4 \times 10^{-5}M$ Ce^{4+}, and $0.0002N$ HNO_3) was injected through an injection loop into two-column sets packed with porous glass (7.4 and 68.8 nm; Electro-Nucloonics Inc.). The flow rate was kept at 3 mL/min. A $0.2M$ Na_2SO_4 solution was used as the elution solvent. The chromatograms were detected by 214-nm ultraviolet (UV).

Measurement of the near-infrared (near-IR) spectra of aqueous PDO–cellulose solutions

Near-IR investigations were carried out with a PerkinElmer model 330 spectrophotometer for aqueous 0.04–5.6% PDO–cellulose solutions of three different concentrations.

Polymerization procedure

PDO–cellulose was dissolved in water, and then AM was added. During the stirring, the air in the reaction vessel was replaced with nitrogen gas. HNO_3 ($0.1N$) and CAN were added to the solution, and the mixture was stirred for 6 h at 25°C. The reaction solution was held still for 10 h. Then, an aqueous solution of hydroquinone (1%) and water were added to terminate the reaction. The resultant mixture was poured into acetone to form a precipitate. The resulting polymer was dissolved in water at pH 7.0 and reprecipitated from acetone twice. The final resultant product was washed with methanol, filtered, and vacuum-dried at 50°C for 1 night.

Measurement of the IR absorption

IR measurements of the copolymer, PDO–cellulose, and cellulose were carried out with the KBr powder method with a PerkinElmer model 21 spectrophotometer.

Size exclusion chromatograms of 1,2-propanediol–cellulose–acrylamide graft copolymers (PCACs)

A Water Associates model 440 high-pressure liquid chromatograph with a model 590 absorbance detector and a model R-401 refractometer was used to obtain chromatograms. A sample (0.04 g/dL, 200 mL) was injected through an injection loop into column sets consisting of four columns packed with porous glass (two had a pore size of 300 nm, one had a pore size of 70/140 nm, and one had a pore size of 7.5/24 nm). The pressure was maintained at less than 2000 psi and at a flow rate of 2 mL/min. A $0.2M$ Na_2SO_4 solution was used as the elution solvent.

Method of isolating the branch PAM from the graft composition and the measurement of its degree of polymerization

The hydrolysis of the cellulose substrate was required for the analysis of the copolymer product for the molecular weight determinations of the grafted PAM chain. The hydrolysis conditions used were the same as those used by Pledger et al.[8] A sample (1 g) was dissolved in deionized water at room temperature. The solution was adjusted to 20 mL with $0.5N$ HCl. The reaction was carried out at 70°C for 8 h, and the hydrolysis of PDO–cellulose was monitored with an anthrone reagent.[9] After it cooled to room temperature and was neutralized with $NaHCO_3$, the reaction solution was dialyzed in deionized water with a membrane with a molecular weight cutoff of 2000, and it was then freeze-dried. The weight-average molecular weight (M_w) of the grafted PAM chain was calculated with the intrinsic viscosity ($[\eta]$) measured in water at 25°C:[10]

$$[\eta] = 6.31 \times 10^{-5}(M_w)^{0.80}$$

THEORY

Polysaccharides are oxidized by a Ce^{4+} ion/alcohol redox system by way of an intermediate complex:

$$R + Ce^{4+} \xrightarrow{K} \text{Complex} \xrightarrow{k} R^{\cdot} + Ce^{3+} \tag{1}$$

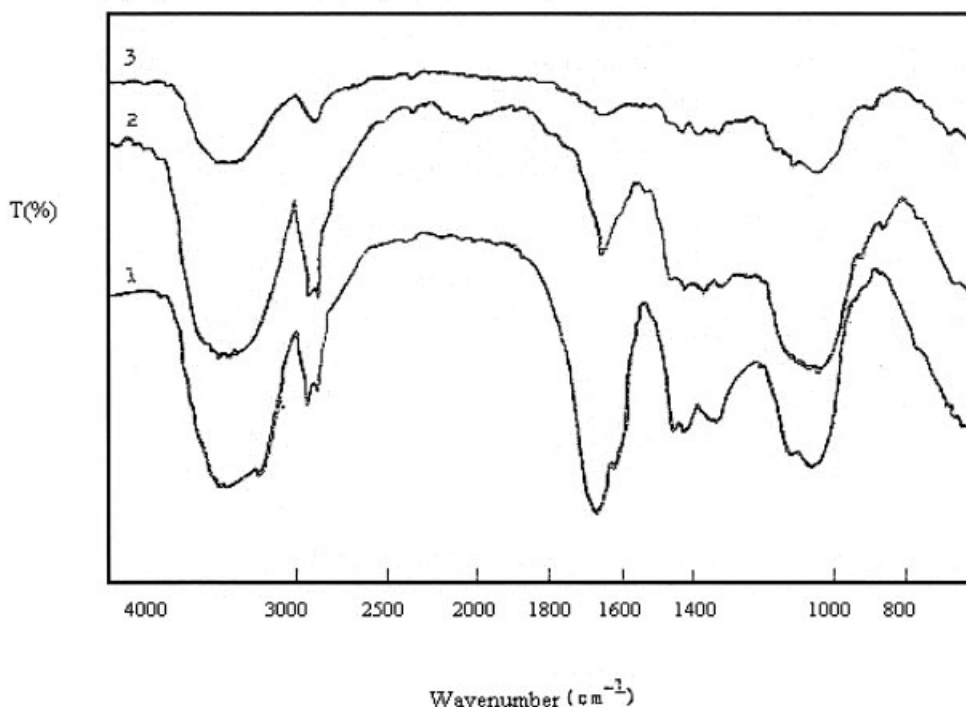| Sample	Molar ratio of CPDO to cellulose	AGU content Y (%)	DS of PDO groups (mol/AGU)[a]	Water solubility	$[\eta]$ at 25°C in cadoxen[b] and water[c] (dL/g)	Amount of solvent for the reaction (mL)	Reaction method
P1	2.56	0.83	0.45	Insoluble	0.68	100 butanol	(2)
P2	2.56	0.93	0.16	Insoluble	1.30	100 butanol	(1)
P3	8.02	0.75	0.73	Soluble	1.22 (1.01)[c]	200 acetone	(1)
P4	4.01	0.64	1.23	Soluble	0.61 (0.61)[c]	100 acetone	(1)

[a] Calculated as $162(1 - Y)/74Y$.
[b] This condition was the same as that used by Smith[12].
[c] This value was measured with an Ostwald viscometer with distilled water at 25°C.

Equation (1) shows that ceric ions reversibly form a complex with alcohols and glycols and that the disproportionation of the complex takes place. In the presence of excess substrate, the disappearance rate of the total amount of Ce^{4+} is pseudo-first-order with respect to the total Ce^{4+} concentration ($[Ce^{4+}]_T$):

$$-d[Ce^{4+}]_T/dt = k'[Ce^{4+}]_T \qquad (2)$$

where

$$k' = kK[R]/(1 + K[R]) \qquad (3)$$

Now at $t = 0$, $[Ce^{4+}]_T$ is equal to $[Ce_0^{4+}]_T$. Integrating eq. (2), we obtain

$$\ln[Ce^{4+}]_T/[Ce_0^{4+}]_T = -k't \qquad (4)$$

The Lambert–Beer law can be expressed as follows:

$$-dI/d[Ce_0^{4+}]_T = I \qquad (5)$$

where $[Ce^{4+}]_T$ and I are the concentration of the total tetravalence ceric ion and the optical density. Now at $[Ce^{4+}]_T = 0$, I is equal to I_R (where I_R is the optical density of the original polysaccharide solution). Integrating eq. (5), we obtain

$$\ln(I/I_R) = [Ce^{4+}]_T \qquad (6)$$

$$D = -\log(I/I_w) \qquad (7)$$

where D and I_w are the absorbance and the optical density of water. From eqs. (4), (6), and (7), we obtain

$$\ln(D - D_R) = -k't + C \qquad (8)$$

where C is a constant and D_R is the absorbance of the original polysaccharide solution.

RESULTS AND DISCUSSION

Table I shows the experimental conditions, compositions, and characteristics of the resultant PDO–cellulose.

The anhydrous glucose unit (AGU) content in PDO–cellulose was obtained by the anthrone method[11] for the determination of the degree of substitution (DS) by PDO groups. Samples P3 and P4 were soluble in water and had high DS values by PDO groups. This showed that acetone was an excellent solvent for this Shotten–Baumann reaction between CPDO and cellulose. The by-product NaCl was insoluble in acetone, and so the reaction could proceed easily. Figure 1 shows the IR absorption spectra of PCAC, PDO–cellulose, and the starting cellulose. The spectrum of the PDO–cellulose has some characteristic absorption bands around 2960 (νC—H) and 1050 cm^{-1}(νC—O) that also appear in PDO groups and the pyranose ring of cellulose, respectively. The IR absorption and water solubility confirmed that the PDO group was introduced into the cellulose molecule. The DS of PDO groups in the obtained PDO–cellulose was less than 1.3; therefore, the reactivity of C_6 may be most preferable if we take account of its primary alcohol:

$$R \text{ is } CH_2CH(OH)CH_2(OH) \qquad (9)$$

Figure 2 shows size exclusion chromatograms of PDO–cellulose (samples P3 and P4) and CAN solutions ($4 \times 10^{-5}M$ Ce^{4+} and 0.0002N HNO$_3$). The PDO–

Figure 1 IR absorption spectra: (1) PCAC (G4), (2) PDO–cellulose (P3), and (3) cellulose.

cellulose solution without Ce^{4+} did not have an absorption of 214-nm UV under this GPC condition. From this point, it may be concluded that the PDO–cellulose–Ce^{4+} complex exited this system. Under this GPC condition, the universal calibration curve, log $[\eta]$ M_w versus the elution volume, gave a straight line for the dextran standard. Therefore, M_w of PDO–cellulose

Figure 2 Size exclusion chromatograms (by GPC) of (1) PCAC (G4), (2) PDO–cellulose (P3), and (3) CAN.

was calculated from the relationship between log $[\eta]$ M_w and the elution volume with the dextran standard (T70, T500, and T200) as the marker. The M_w values of PDO–cellulose (samples P3 and P4) were estimated to be 1,300,000 and 2,300,000, respectively. There was used cellulose (Whatman 4 filter paper) for PDO–cellulose as a starting material. The M_w value of cellulose was estimated by $[\eta]$ in cadoxene at 25°C. The following equation was used to determine the molecular weight:[12]

$$[\eta] = 0.00268M_w \tag{10}$$

The molecular weight was estimated to be 125,000.

Therefore, the M_w value of PDO–cellulose was larger than that of the starting material cellulose. An aqueous PDO–cellulose solution may have several types of hydrogen bonds for this reason:[13] (1) intra-PDO–cellulose molecules, (2) inter-PDO–cellulose molecules, and (3) PDO–cellulose–water molecules. The hydrogen-bond formation of a water molecule can be determined by near-IR spectroscopy because water has three fundamental vibrations ($\nu1$, symmetric stretching; $\nu2$, bending; and $\nu3$, asymmetric stretching). The $2\nu1 + \nu3$ combination absorbance peak is estimated to shift to 958 nm for monomeric water and to 988 nm for entirely hydrogen-bonded water;[14] the $\nu1 + \nu2 + \nu3$ combination bond is estimated to shift to 1160 nm for monomeric water, to 1200 nm for single-hydrogen-bonded water, and to 1240 nm for double-
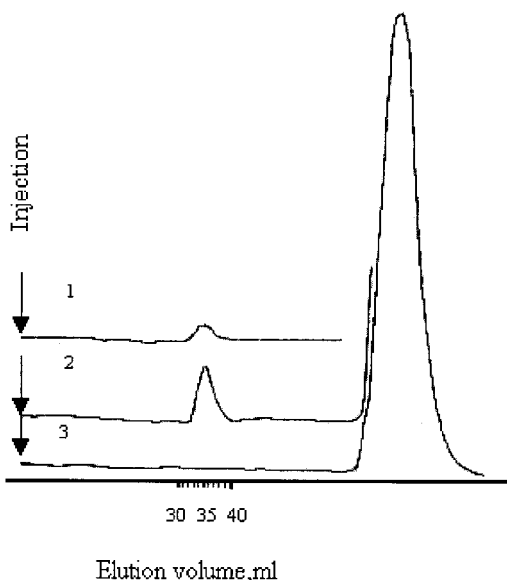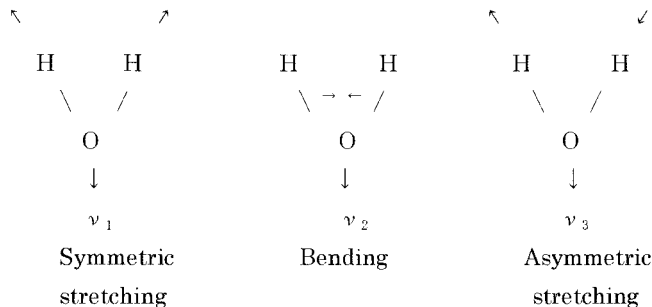
TABLE II
Near-IR Spectrum of PDO–Cellulose

Sample[a]	Absorption (nm)[b]	
	$2\nu_1 + \nu_3$	$\nu_1 + \nu_2 + \nu_3$
5.6%	971	1210
1.0%	971	1197
0.04%	969	1197
Water	967	1195

[a] P4 was used as the sample.
[b] The fundamental vibrations were as follows:

$$
\begin{array}{ccc}
\text{H}\quad\text{H} & \text{H}\quad\text{H} & \text{H}\quad\text{H} \\
\diagdown\ \diagup & \diagdown\ \rightarrow\ \leftarrow\ \diagup & \diagdown\quad\diagup \\
\text{O} & \text{O} & \text{O} \\
\downarrow & \downarrow & \downarrow \\
\nu_1 & \nu_2 & \nu_3 \\
\text{Symmetric} & \text{Bending} & \text{Asymmetric} \\
\text{stretching} & & \text{stretching}
\end{array}
$$

hydrogen-bonded water.[15] Table II shows that the $2\nu1 + \nu3$ peak and $\nu1 + \nu2 + \nu3$ peak shift to a larger wavelength with an increase in the PDO–cellulose concentration. These mechanisms can be proposed for the gelation and micelle formation due to the comparable accessibility of PDO–cellulose to both PDO–cellulose and water. Figure 3 shows the D variation of a polymer solution (1.1% PDO–cellulose, 2.1% water-soluble starch, and 3.1% dextran) oxidized by Ce^{4+} with time.

Figure 4 shows the relationship between $\ln(D - D_R)$ and time. The overall kinetic constant (k') of Ce^{4+} consumption was calculated from the slopes of $\ln(D - D_R)$ versus time. k' included $k_1' = 1.3 \times 10^{-4}\ s^{-1}$ and $k_2' = 6.0 \times 10^{-5}\ s^{-1}$ for water-soluble starch (Pfaltz and Baur Co.), $k_1' = 6.4 \times 10^{-4}\ s^{-1}$ for dextran (T-70), and $k_1' = 1.4 \times 10^{-3}\ s^{-1}$ and $k_2' = 5.7 \times 10^{-4}\ s^{-1}$ for PDO–cellulose (sample P4). The results show also that there were two mechanisms of oxidation by Ce^{4+} with PDO–cellulose. The first step of the oxidation mechanism by Ce^{4+} depended on the PDO group, and the second step was caused by the reducing end and the amorphous properties of the PDO–cellulose molecule.[16] Table III shows the polymerization conditions, compositions, and characteristics of PCACs. Sample G8 had maximum values for the grafting percentage [(weight of graft-polymerized AM/weight of PDO–cellulose in the copolymer) ×100], the conversion [(weight of the polymerized monomer/weight of the total monomer) × 100], and [η] in 0.1M Na_2SO_4 at 25°C. These polymerization conditions may be the best of all the conditions. When the initiator Ce^{4+} concentration is higher, the conversion become lower. This is why the initiator Ce^{4+} acted as a terminator for the active sites of the PDO–cellulose molecules under

these conditions.[17] When the weight ratio of AM to PDO–cellulose increased, the conversion perhaps also increased. The IR absorption spectra of PCACs showed some characteristic absorption bands around 3200 (νN—H), 1670 (νC=O), and 1050 cm^{-1} (νC—O), which were attributed to AM, the carbonyl group of AM, and the pyranose ring of PDO–cellulose, respectively.

Figure 5 shows the GPC chromatogram of PCAC (G9). Two peaks can be observed. One is a single pattern of the chromatogram for the graft copolymer, and the other is a pattern of cerium salt. These were detected by 214-nm UV, and only a water solvent could be detected by the refractive index (RI). After purification by the sedimentation method of acetone, the peak of the cerium salt vanished.

Therefore, there should be no PAM homopolymer or unreacted PDO–cellulose. GPC also indicated that the hydrodynamic volumes of the graft copolymers decreased in the following order, in agreement with M_w of the grafted AM chain: G8 > G9 > G7 > G6 > G4. The number of the branch PAM chains per molecule [number of graft sites = grafting (%) × M_w of the backbone polymer/100 × M_w of the branch polymer) of PDO–cellulose was 0.7–1.58 for P4 and 0.63–0.87 for P3. The elementary reactions thus considered are as follows (in the PDO–cellulose molecule). For initiation,
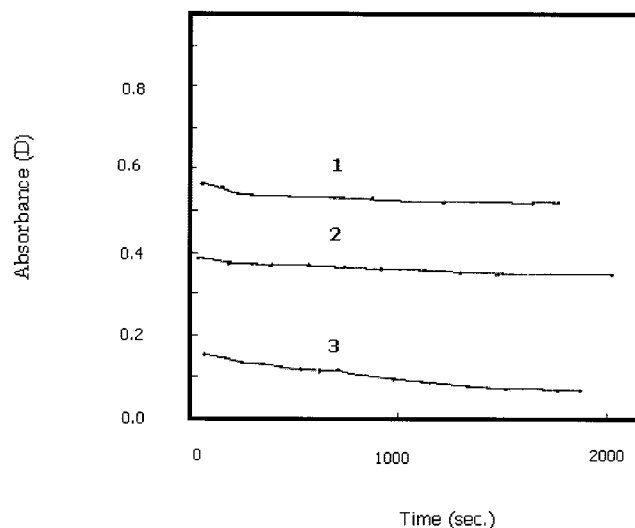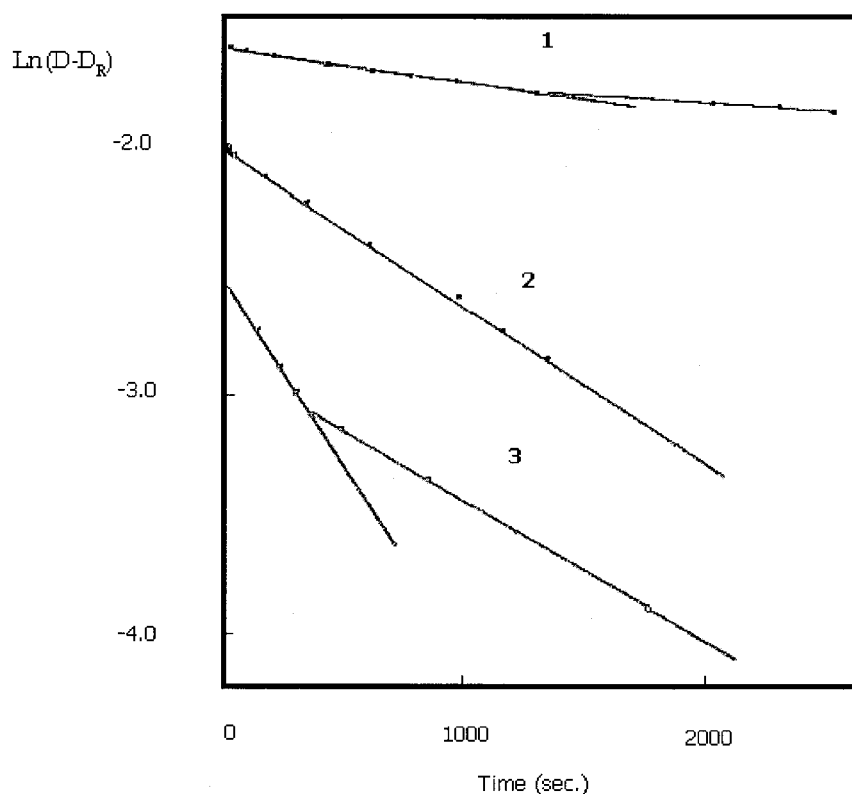
$$R\text{cell—OH} + Ce^{4+} \rightarrow \text{Complex} \rightarrow Ce^{3+} + H^+$$
$$+ [R\text{cell} = 0]^{\bullet} \quad (11)$$

Figure 3 Absorbance variation of aqueous polymer solutions oxidized by Ce^{4+} with the time (s): (1) 1% PDO–cellulose (P4), (2) 1% water-soluble starch ($M_w = 11.9 \times 10^4$), and (3) 1% dextran ($M_w = 7 \times 10^4$).
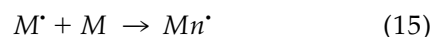
Figure 4 Relationship between $\ln(D - D_R)$ and the time (s) for aqueous polymer solutions oxidized by Ce^{4+}: (1) water-soluble starch ($M_w = 11.9 \times 10^4$), (2) 1% dextran ($M_w = 7 \times 10^4$), and (3) 1% PDO–cellulose (P4).

Rcell—OCH$_2$CH(OH)CH$_2$(OH)

$\quad$ + Ce^{4+} → Complex → Rcell—OCH$_2$ĊH(OH)

$\qquad\qquad\qquad$ + HCHO + Ce^{3+} + H$^+$ $\quad$ (12)

or

$\quad$ Rcell—OCH$_2$CHO + ĊH$_2$(OH) + Ce^{3+} + H$^+$ $\quad$ (13)

For propagation,

$$RM^{\bullet} + M \ \rightarrow \ RMn^{\bullet} \qquad (14)$$

$$M^{\bullet} + M \ \rightarrow \ Mn^{\bullet} \qquad (15)$$

For termination,

$$RMn^{\bullet} + RMn^{\bullet} \ \rightarrow \ \text{Copolymer} \qquad (16)$$

$$RMn^{\bullet} + Mn^{\bullet} \ \rightarrow \ \text{Copolymer} \qquad (17)$$

where RM · and M are the copolymer radical and AM monomer, respectively. The termination reaction should be a diffusion-controlling reaction. The in-

TABLE III
Experimental Conditions, Compositions, and Characteristics of PCACs

Sample	G4	G6	G7	G8	G9
CAN/PDO–cellulose (mmol/g)[a,b]	0.550	0.492	0.077	0.077	0.077
AM/PDO–cellulose (w/w)	4.3	4.3	4.3	8.8	4.3
Starting PDO–cellulose	P3	P3	P3	P4	P4
Grafting (%)	80	130	138	550	170
Conversion (%)	19	30	32	62	38
$[\eta]$ in 0.1M Na$_2$SO$_4$ at 25°C (dL/g)	1.8	2.1	2.0	5.8	4.7
M_w of the grafted AM chain ($\times 10^{-6}$)	1.62	1.95	2.05	7.95	5.63
Number of graft sites	0.63	0.87	0.87	1.58	0.70

[a] Moles of CAN/amount of PDO–cellulose.

[b] 0.1N HNO$_3$ was used at the rate of 10 mL/g of PDO–cellulose with G4 and G6 and at the rate of 11 mL/g of PDO–cellulose with the others.
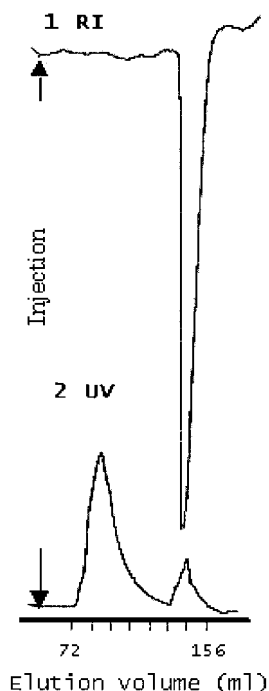
Figure 5 Size exclusion chromatogram (by GPC) of PCAC (G9): (1) RI and (2) 214-nm UV.

crease in the molecular weight by the propagation step negatively affects the termination step by an increase in the viscosity. The termination equation, eq.

(17), must take place before eq. (16) when the viscosity is high.[18]

Figure 6 shows the relationship between the grafted PAM M_w and the grafting percentage. There was also a correlation between the M_w values of the reactant PDO–cellulose and the branch PAM in the product. Thus, the M_w value of the branch PAM must be determined when higher PDO–cellulose is used as the starting material. It may be concluded from the results that PDO–cellulose is suitable as a starting material for the AM copolymer for EOR and that the copolymer is produced by a mechanism similar to that determined for matrix polymerization by Kargina et al.[19]

CONCLUSIONS

A water-soluble PCAC has been developed for EOR with AM and PDO–cellulose, which is formed through the addition of glycols to cellulose by a Shotten–Baumann reaction between CPDO and cellulose.

PDO–cellulose has a high reactivity for graft polymerization because there are two mechanisms of oxidation by Ce^{4+} with PDO–cellulose. The first step of the oxidation mechanisms by Ce^{4+} must depend on the PDO groups, and second step must be caused by the reducing end groups of PDO–cellulose.

The molecular weight of PDO–cellulose has been evaluated by a GPC method and estimated to be
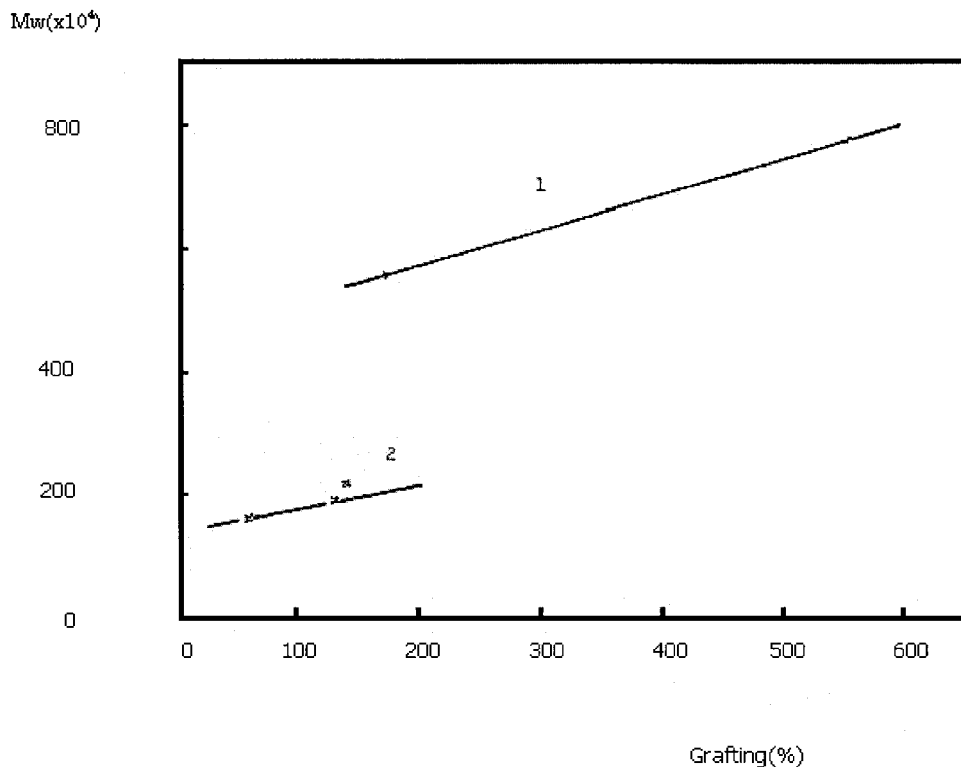
Figure 6 Relationship between the grafting percentage and the molecular weight of the branch PAM: (1) backbone polymer P4 ($M_w = 2.3 \times 10^6$) and (2) backbone polymer P3 ($M_w = 1.3 \times 10^6$).

1,000,000–3,000,000. The hydrogen-bonding formation of water molecules in PDO–cellulose solutions has been confirmed by near-IR spectra. This is why the huge PDO–cellulose molecule should be formed by hydrogen bonding.

As we expected, a PCAC solution has high viscosity and viscoelasticity. There is also some correlation, like that of matrix polymerization, between the molecular weights of the reactant PDO–cellulose and the branch PAM.[19]

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