

Synthesis and Aqueous Solution Properties of Hydrophobically Modified Graft Copolymer of Sodium Carboxymethylcellulose with Acrylamide and Dimethyloctyl(2-methacryloxyethyl)ammonium Bromide

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Received 14 September 1999; accepted 17 December 1999

ABSTRACT: The hydrophobically modified water-soluble graft copolymer of sodium carboxymethylcellulose with acrylamide and dimethyloctyl(2-methacryloxyethyl)ammonium bromide has been synthesized using potassium persulfate and dimethylaminoethyl methacrylate as initiators in aqueous solution. The structure and composition of the graft copolymer were characterized by infrared spectrum and elementary analysis. Molecular weight was determined by gel permeation chromatography. The solubility and viscosity of the graft copolymers in aqueous solution were investigated, as a function of copolymer concentration, added salt, temperature, shear rate, and surfactant. In addition, the intermolecular hydrophobic association in aqueous solutions in the presence of added salt and surfactant was demonstrated through the retention time from gel permeation chromatography measurement. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 78: 537–542, 2000

Key words: carboxymethylcellulose; graft copolymer; hydrophobic association; solubility; viscosity; retention time

INTRODUCTION

Water-soluble polymers modified with a small amount of hydrophobic groups (1–5 mol %) have become of great interest in recent years.¹ In particular, the hydrophobically modified polyacrylamide (HMPAM) has attained extensive research because of its important commercial applications

in enhanced oil recovery, frictional drag reduction, flocculation, superabsorbency, personal care formulation, controlled drug release, papermaking, and coatings.^{2–4} In its aqueous solution, intermolecular hydrophobic interaction occurs above a certain polymer concentration, leading to enhancing the viscosity prominently. But some disadvantages have also been found for HMPAM in practice, such as poor solubility in aqueous solution, sharp decrease of viscosity at high shear rate,⁵ and environmental damage of the effluent.

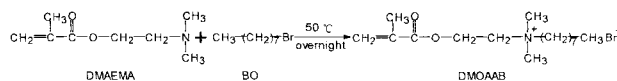
The previous studies in our laboratory show that sodium carboxymethylcellulose (NaCMC) exhibits excellent viscosification at relatively high shear rate, better solubility in water, and no environmental pollution owing to its biodegradability.⁶ What's more, the cellulose resources are very

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Contract grant sponsor: Natural Science Foundations of Guangdong Province and China.

Contract grant sponsors: State Key Laboratory of Polymer Materials Engineering, State Key Laboratory of Oil/Gas Reservoir Geology and Exploitation, Laboratory of Cellulose and Lignocellulosic Chemistry, Academia Sinica.

Journal of Applied Polymer Science, Vol. 78, 537–542 (2000)
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Scheme 1 Synthesis of DMOAAB monomer.

abundant and the production cost is low. In this report, we try to incorporate the advantages of NaCMC and HMPAM to prepare a new hydrophobically modified water-soluble graft copolymer that may effectively increase the viscosity of aqueous solution at certain range of temperature, shear rate, and surfactant concentration in the presence of added salt.

EXPERIMENTAL

Materials

NaCMC (commercial grade) was purified by washing with 80% alcohol, with a degree of substitution of 0.68 determined using conductometric titration⁷ and an average molecular weight of 1.4×10^5 measured by gel permeation chromatography (GPC). Dimethyloctyl(2-methacryloxyethyl)ammonium bromide (DMOAAB) was synthesized as described in Scheme 1 according to the literature.⁸ Acrylamide (AM) was recrystallized twice from acetone prior to use. Ammonium persulfate (APS) (analytical grade) was purified by recrystallization from water, and dimethylaminoethyl methacrylate (DMAEMA) (commercial grade) was purified by distillation under reduced pressure. 1-Bromooctylane and sodium dodecyl sulfonate (SDS), purchased from Aldrich Chemical Co., were used without further purification.

Synthesis of CAO

In a 500-mL four-necked round-bottom flask equipped with a mechanical stirrer, a thermometer, a reflux condenser, inert-gas nitrogen (N_2) inlet, and thermostated water bath, 150 mL NaCMC aqueous solution was placed, and purged with N_2 for 30 min at 40°C. Solutions of APS and DMAEMA were introduced, and the pH was adjusted to 6 or so with HCl. After 20 min, the mixed solution of AM and DMOAAB was added dropwise through a dropping funnel within 30 min. Then the solution was continuously stirred at 40°C for 4–6 h under a continuous flow of N_2 . The resulting products were washed extensively in acetone three times, and then dried under vacuum for 24 h. Further purification of the dried products was conducted by extraction with 10 mL mixed solvent (acetone/methanol/dimethylformamide/water = 60:20:10:10 by volume) per gram polymer twice to remove homopolymers and copolymers so as to obtain the pure graft copolymers CAO listed in Table I. For comparison, the graft copolymer (CA) of NaCMC and AM without DMOAAB was also prepared at the same conditions as CAO.

Analysis and Measurements

1. The infrared (IR) spectra of graft copolymers were recorded with a NICOLET FT-IR 20SX spectrophotometer, KBr pellet.
2. The analysis of the composition for graft copolymers was determined by HERAEUS CHN-O-Rapid element meter.
3. The molecular weight (MW) of graft copolymers was obtained using Waters-244GPC:

Table I Parameters of Graft Copolymers Obtained by EA and GPC

Sample	Feed Ratio			N (%)	Br (%)	Compositions of Copolymers			Yield (%)	M_w ($\times 10^6$)
	E/g	F/g	G/g			E/%	F/%	G/%		
CA	3	10	0	14.517	0	26.38	73.62	0	76.92	1.31
CAO-1	3	10	1.00	14.697	1.119	21.56	73.54	4.90	71.43	0.63
CAO-2	3	10	0.51	15.060	0.349	22.40	76.06	1.54	74.02	0.87
CAO-3	4	10	0.78	13.063	0.744	31.16	65.59	3.25	67.66	0.71

E, F, and G denote NaCMC, AM, and DMOAAB, respectively.

Reaction conditions: [APS] = $3 \times 10^{-3}M$; [DMAEMA] = $3.5 \times 10^{-3}M$; pH = 6; 4 ~ 6 h; 40°C.

$$\text{Yield (\%)} = \frac{\text{Mass of the graft copolymers}}{\text{Mass of the raw materials}} \times 100.$$

Table II Dependence of Solubility on the Content of Hydrophobe in Graft Copolymers

Sample	CA	CAO-1	CAO-2	CAO-3
Transmittance (%)	98	83	94	87

Determined conditions: polymer concentration, 0.4%; solvent, deionized water; 30°C.

Ultrahydrogel 1000 column; standard specimen, pullulan; eluant, mixture of water and methanol containing 0.1M NaNO₃; temperature, 30°C. The polymer concentrations were obtained using Chromatix KMX-16 differential refractometer.

- The viscosity measurements of aqueous solution for graft copolymers were performed on a Contraves LS 30 low-shear rheometer at low shear rate, on a Haake Rheocontroller equipped with CV20C RV20 PK45-4.0 rotasystem at high shear rate.
- Hydrophobic associations were identified in the light of retention time gained by GPC.

RESULTS AND DISCUSSION

Structure Characteristics of Graft Copolymer

IR Analysis

The FTIR spectra of graft copolymers CAO manifest the peaks of NaCMC (cycloether, 1068 cm⁻¹; —COO⁻, 1592 cm⁻¹, and 1412 cm⁻¹), AM (3200 cm⁻¹, 1650 cm⁻¹, 1330cm⁻¹), and DMAOAB [—(CH₂)_nCH₃ n > 4, 723 cm⁻¹; —COO—, 1180 cm⁻¹, weak peaks], confirming that CAO consists of the components of NaCMC, AM, and DMOAAB.

Composition Analysis

According to the data of elemental analysis (EA) for nitrogen (N%) and bromide (Br%), the contents of NaCMC (A%), AM (B%), and DMOAAB (C%) in 100 g CAO can be calculated as follows:

$$A = 100 - B - C$$

$$B = \left(\frac{N}{14} - \frac{C}{349.9} \right) \times 71$$

$$C = \frac{\text{Br}}{79.9} \times 349.9$$

where 14, 79.9, and 71, 349.9 represent the atomic mass of nitrogen and bromide, the molecular weight of AM and DMOAAB, respectively. The results are listed in Table I.

Aqueous Solution Properties

Solubility

The graft copolymers with various contents of DMOAAB exhibit the difference of solubility in deionized water according to the transmittance of the solution determined by a spectrophotometer (Table II). As usual, the larger transmittance indicates the better homophase formed between polymer and water, i.e., good solubility.⁹ It has been found that the solubility of CAO with hydrophobe is less than that of CA without hydrophobe, and the solubility of CAO reduces with the increase of hydrophobe. But because of CAO containing hydrophilic groups of quaternary ammonium cation, —CONH₂ and —COO⁻, CAO is still water soluble under certain condition. For instance, CAO-1 with high content of hydrophobe can dissolve completely in water within a day on agitating at 30°C.

Viscosity Behaviors

Effect of polymer concentration. The viscosity of aqueous solutions for graft copolymers increases with increasing polymer concentration (Cp) (Fig. 1), which is in agreement with the general regu-

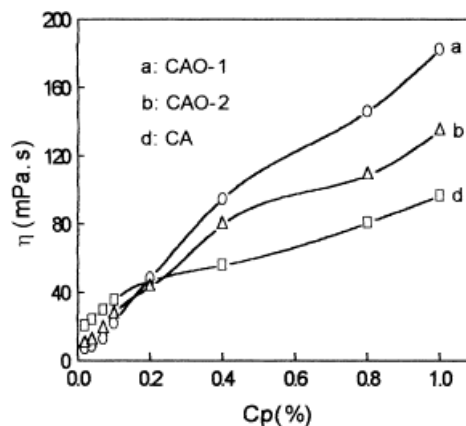


Figure 1 Plot of the viscosity of aqueous solution for graft copolymers as a function of polymer concentration: 30°C; 10 s⁻¹.

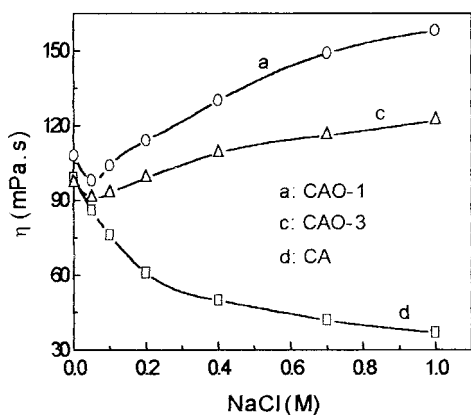


Figure 2 Plot of the viscosity of aqueous solution for graft copolymers as a function of salt concentration: Cp, 0.5%; 25°C; 10 s⁻¹.

larity. But it is interesting to find that for CAO-1 with lowest molecular weight (see Table I), the increment of η is the largest and its viscosity is much larger than CAO-2 and CA. This is attributed to the least ratio of NaCMC and the highest content of hydrophobe in CAO-1. The lowest proportion of NaCMC bearing semi-rigid backbone is favorable to hydrophobic association and less polyelectrolyte effect. The highest content of hydrophobe (DMOAAB) causes the nearest space for hydrophobic pendant groups of adjacent chains, therefore interactions between hydrophobic groups are strengthened, forming plenty of bridged crosslinking complexes containing hydrophobe, hydrophile, and solvent.¹⁰ It is noteworthy that the graft copolymer with very low level of DMOAAB displays interesting solution properties. For example, the solution viscosity of CAO-2 with 1.54% DMOAAB is much larger than that of CA with the highest molecular weight of 1.31×10^6 at the Cp more than 0.2%, but it is lower than the viscosity of CA solution at the Cp less than 0.2%. This is because the intermolecular hydrophobic associations exceed greatly intramolecular associations at high Cp over 0.2% and the intramolecular associations become the major ones at Cp below 0.2%.

Effect of added salt. It can be seen from Figure 2 at NaCl concentration from 0 to 0.05M, the solution viscosity of graft copolymers decreases with the increase of NaCl content, as is analogous with literature.² However, at NaCl concentration over 0.05M, the viscosity of CAO and CA solution exhibits two opposite tendencies with increasing NaCl content: viscosity of CAO is enhanced

nearly linearly, but that of CA drastically falls down. It is well known that the addition of NaCl to the polyelectrolyte solution causes electrostatic screening of the charged groups and a striking reduction in hydrodynamic volume leading to the decrease of viscosity; CA is consistent with this rule. As for CAO, it is necessary to take the specialty of hydrophobe into account. The polarity of solvent promoted by NaCl motivates intermolecular hydrophobic association, which results in increase of viscosity.¹¹ The electrostatic shield of Cl⁻ to cation of quaternary ammonium of DMOAAB will weaken the repulsion between positive charges of DMOAAB, leading to easier hydrophobic association. In addition, the ionic species may enhance ordering of the hydrophobic microdomains in favor of viscosity enhancement.² It can be inferred that for CAO solution in the presence of added salt, the more the hydrophobe content, the higher the viscosity. As shown in Figure 2, in 1M NaCl solution, the viscosity of 0.5% CAO-1 solution is high up to 158 mPa.s, that of CAO-3 solution is only 120 mPa.s.

Effect of temperature. Figure 3 shows the dependence of solution viscosity on temperature. The viscosity of CA solution reduces gradually with increasing temperature due to weakening solvation and disruption of intermolecular hydrogen bond of CA. But for CAO solution, the behavior is quite different: the viscosity increases with increasing temperature within certain range to maximum and then drops down remarkably. Obviously there exist two opposite effects of temperature on viscosity of CAO solution. Because the hydrophobic interaction is an endothermic pro-

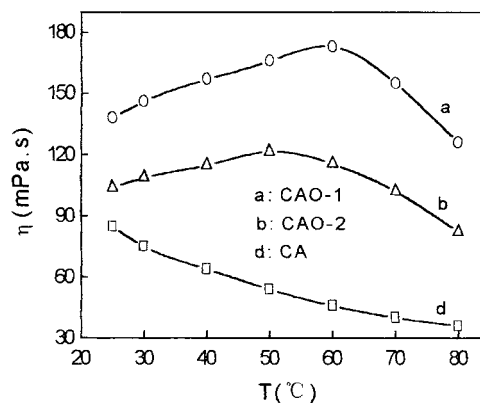


Figure 3 Plot of the viscosity of aqueous solution for graft copolymers as a function of temperature. Cp, 0.8%; 10 s⁻¹.

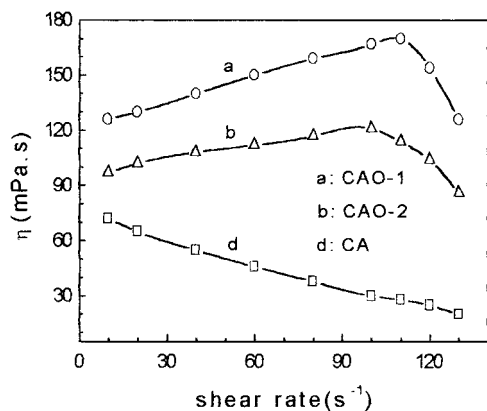


Figure 4 Plot of the viscosity of aqueous solution for graft copolymers as a function of shear rate. Cp, 0.6%; 25°C (from Haake rheometer).

cess driven by entropy,² rising temperature is favorable for intermolecular hydrophobic association resulting in enhancement of the solution viscosity. But at higher temperature, the active movement of molecules would destroy the hydrophobic association and the dehydration of the hydrophilic groups would give birth to the coiling loose structure of molecular chains. These latter two effects would result in decreasing viscosity of CAO solution. As shown in Figure 3, the solution viscosity of CAO-1 with more hydrophobe is higher than CAO-2 and η_{\max} of CAO-1 solution appears at higher temperature than CAO-2 solution. This infers that CAO with higher content of hydrophobe can keep its higher solution viscosity up to higher temperature. It is possible to vary the content of the hydrophobe in CAO to meet different requirements for viscosity of aqueous solution in practice.

Effect of shear rate. Figure 4 shows the viscosity-shear relationships of graft copolymers. The viscosity of CA falls down with increasing shear rate. But increasing the shear rate from 10 to 110 s^{-1} results in a large increase in viscosity of CAO-1 followed by a decrease at higher shear rate. Sample CAO-2 shows moderate viscosity increment. It is reported² that this peculiar viscosity behavior of CAO solution may be a result of an increase in the order of the hydrophobic domains induced by the application of shear, thus the hydrophobic domains are enhanced by groups that had not participated in the intermolecular association before the utilization of shear. Further increment in shear rate (110 s^{-1}) leads to the breakage of intermolecular associations and the copolymers ex-

hibit shear-thinning behavior on account of the physical reversibility of the association frame.¹²

Effect of SDS. Figure 5 illustrates the viscosity feature of graft copolymers in the presence of surfactant SDS. When SDS is added to the aqueous solution of CA, a continuous and steady decrease of the viscosity is observed. This is equivalent to the augment of the ionic strength of the solution. However, the solutions of CAO-1 and CAO-2 display completely different viscosity behaviors on addition of SDS. The viscosity rises noticeably at SDS concentration less than its critical micelle concentration (cmc, $\approx 8 \times 10^{-3} \text{ mol/L}$),¹³ up to a maximum and then down rapidly above cmc. Despite the unfavorable electrostatic repulsion between CAO and SDS, hydrophobic interaction becomes the driving force of association. The hydrophobic alkyl groups of CAO and SDS form mixed hydrophobic clusters containing two or more distinct polymer chains¹³ resulting in the increase of hydrodynamic volume of CAO and the increase of viscosity of CAO solution. At approximate cmc of SDS, maximum of crosslinking of the polymer chains is realized through mixed hydrophobic clusters. Accordingly, the viscosity of CAO reaches maximum. Well above cmc, SDS micelles are in large excess, the polymer-alkyl groups are distributed in a maximum number of SDS micelles rather than involved in a small amount of clusters for mixed micelles containing two or more chains. Thus, effective crosslinking is prevented and the network structure is broken down, and eventually results in the descent of viscosity.

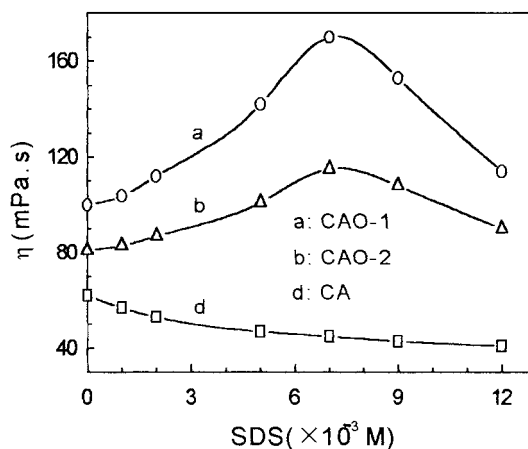


Figure 5 Plot of the viscosity of aqueous solution for graft copolymers as a function of SDS concentration. Cp, 0.4%; 25 °C; 10 s^{-1} .

Table III Retention Time of CAO-1 as a Function of Concentrations of NaCl and SDS by GPC

Polymeric Water Solution	Eluant	Rt (min)
0.5% CAO-1 + 0.1M NaCl	0.1M NaCl	12.8
0.5% CAO-1 + 0.5M NaCl	0.5M NaCl	12.4
0.5% CAO-1 + 0.1M NaCl + 0.002M SDS	0.1M NaCl + 0.002M SDS	12.6
0.5% CAO-1 + 0.1M NaCl + 0.006M SDS	0.1M NaCl + 0.006M SDS	11.7
0.5% CAO-1 + 0.1M NaCl + 0.01M SDS	0.1M NaCl + 0.01M SDS	12.0

Determined conditions: driving speed, 0.6 mL/min; temperature, 30°C; polymer concentrations are inspected by Chromatix KMX-16 differential refractometer.

Evidence of Hydrophobic Associations

GPC was used to study the intermolecular hydrophobic association in CAO solution. In general, the shorter the retention time (Rt), the larger hydrodynamic volume of the polymer due to the intermolecular aggregation. Table III describes Rt of CAO-1 solution containing various contents of NaCl and SDS. When the concentration of NaCl is raised from 0.1M to 0.5M, Rt decreases from 12.8 to 12.4 min. But there is the quite pronounced difference of the influence of SDS on Rt. For example, at 0.1M NaCl, Rt varies from 12.6 to 11.7 min as SDS concentration increases from 0.002 to 0.006M. However, Rt rises from 11.7 to 12.0 min with increasing SDS from 0.006 to 0.01M. The above results are consistent with the η -NaCl plot in Figure 2 and η -SDS plot in Figure 5. It has been demonstrated, once more, that the intermolecular hydrophobic association is the main effect on the peculiar viscosity behavior of CAO aqueous solution.

CONCLUSIONS

The graft copolymers are of good solubility in water, even if the content of hydrophobe (DMOAAB) in CAO-1 is up to 4.9%. The dependence of solution viscosity (η) for CAO on Cp increases greatly with the increment of hydrophobe. The upward slope of the plots of η versus Cp above 0.2% is much larger than that below 0.2%. Solution viscosity increases drastically with the addition of NaCl, but nonmodified CA without DMOAAB exhibits opposite tendency. Temperature in the range of 20 to 60°C is favorable to intermolecular hydrophobic association. Solution viscosity rises with the increment of shear rate less than 110 s⁻¹. An increase in the solution viscosity of CAO is observed on the addition of

SDS below cmc and the continuous addition of SDS above cmc leads to dropping viscosity. But the solution viscosity of CA without DMOAAB is diminished with increasing SDS. Retention time attained by GPC is capable of demonstrating the interchain associations of hydrophobic groups of CAO.

The authors appreciate support from the State Key Laboratory of Polymer Materials Engineering, the State Key Laboratory of Oil/Gas Reservoir Geology and Exploitation and the Laboratory of Cellulose and Lignocellulosic Chemistry, Academia Sinica.

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