New Amphoteric Graft Copolymers of Sodium Carboxymethyl Cellulose with Acrylamide And Dimethylaminoethyl Methacrylate: Aqueous Solution Properties

LI-MING ZHANG, YE-BANG TAN, ZHUO-MEI LI

Institute of Polymer Science, Zhongshan University, Guangzhou 510275, People's Republic of China

ABSTRACT: The solubility and viscosity properties of new amphoteric graft copolymers of sodium carboxymethyl cellulose with acrylamide and dimethylaminoethyl methacrylate in aqueous solutions were investigated by turbidimetry and viscometry experiments. The factors investigated include the pH of the medium, the composition of the graft copolymer, the concentration and type of added salt, temperature, aging time, and the addition of organic solvent. Unlike conventional copolymers, these graft copolymers have unique solution behavior due to the presence of both acidic and basic groups along the macromolecular backbone. In addition, their solution properties are closely related to their conformations and are partially controlled by the net electrical charge and the ionic strength. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 76: 305–310, 2000

Key words: amphoteric graft copolymers; aqueous solution properties; solubility; viscosity

INTRODUCTION

Amphoteric copolymers, which contain both acidic and basic groups along the macromolecular backbone, present great potential for many applications due to their interesting aqueous solution properties.[1–13] Unlike conventional copolymers, the solution behavior of amphoteric copolymers is usually complicated and difficult to predict as a result of the interactions between ionic groups of opposite signs. In order to choose and optimize their practical applications, it is necessary to obtain knowledge of the solution properties of amphoteric copolymers, such as solubility and hydrodynamic and conformational characteristics in solutions.

Although extensive research has been conducted on amphoteric synthetic copolymers, very few studies have been conducted on polysaccharide graft copolymers with an amphoteric character, particularly on amphoteric cellulosic graft copolymers. Recently, we synthesized and characterized a new amphoteric graft copolymer (CGAD) of sodium carboxymethyl cellulose (CMC) with acrylamide (AM) and dimethylaminoethyl methacrylate (DMAEMA).[14] We also report here on an additional investigation—of the properties of CGAD in aqueous solutions, in which special emphasis was given to its solubility and viscosity properties under different conditions.

EXPERIMENTAL

CGAD Samples and Their Characterization

The investigation used two CGAD samples with different composition and weight-average molecular weights, shown in Table I. Details of their

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Table I   Composition and Classical Light Scattering Data of Used CGAD Samples

Sample Number	Composition[a]			Light Scattering Data		
	$\%W_{AM}$	$\%W_{DM}$	$\%W_{CMC}$	dn/dc	$M_w \times 10^{-5}$ (g mol^{-1})	$A_2 \times 10^4$ (mL mol g^{-2})
CGAD-I	58.77	8.84	32.46	0.1573	4.09	4.79
CGAD-II	53.60	22.15	24.25	0.1602	5.60	9.54

[a] $\%W_{AM}$, $\%W_{DM}$, and $\%W_{CMC}$ denote the percents of AM units, DMAEMA units, and CMC units, respectively, in the graft copolymer CGAD.

synthesis, purification, structural characterization, and composition analysis were reported in the previous article.[14] Molecular weight studies were performed on a Chromatix KMX-6 low-angle laser-light scattering instrument. Refractive index increments were obtained using a Chromatix KMX-16 laser differential refractometer. The measurements were conducted at 25°C in 1.0M NaCl.

Solubility Measurements

The solubility of CGAD samples in aqueous solutions under different conditions was determined by turbidimetry. An optical transmission, T, of the order of 100%, obtained immediately after cessation of stirring, corresponds to one phase domain, while a reduced transmission indicates the beginning of phase separation.[15] The $\%T$ of the solution containing 0.1% CGAD was measured at room temperature spectrophotometrically. The variables investigated include the pH of the medium, CGAD composition, salt concentration, and type.

Viscosity Measurements

Viscometric measurements were carried out by using an Ubbelohde capillary viscometer under different conditions. Temperature were controlled with a range of ±0.02°C, and flow times were measured with an accuracy of ±0.1 s. CGAD samples were dissolving in salt solutions of varying concentration. The viscosity data were calculated according to Huggins' equation[16]

$$\eta_{sp}/C = [\eta] + k'[\eta]^2 C$$

where η_{sp} is the specific viscosity, C is the concentration of polymer, $[\eta]$ is the intrinsic viscosity, and k' is Huggins' constant. The factors investigated include the pH of the medium, CGAD composition, salt concentration and type, temperature, time, and addition of organic solvent.

RESULTS AND DISCUSSION

Solubility Properties

Figure 1 shows the effects of pH and CGAD composition on the solubility in pure water. For each sample the optical transmission, $\%T$, has a minimum. This phenomenon can be explained in terms of the interactions between acidic and basic groups along CGAD chains. At the pH corresponding to the minimum of $\%T$, the positive and negative charges, which are due to protonation of dimethylaminoethyl groups and the dissociation of carboxymethyl groups, respectively, become almost equal within a CGAD chain. This produces the strong electrostatic attractions and thus makes the CGAD chain collapse, resulting in low solubility. Except for this point, the change of $\%T$ depends on the variation of net charge along CGAD chains, attributable to the gradual conversion of dimethylaminoethyl groups from the pro-
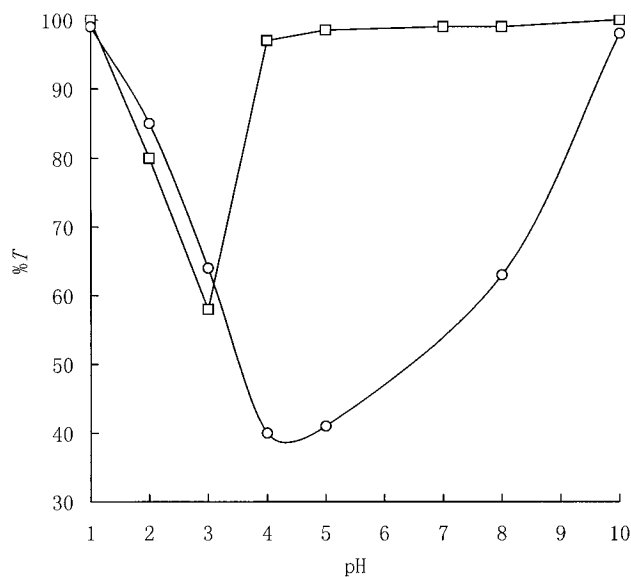

Figure 1   Effects of pH on the solubility of CGAD samples in pure water: (□) CGAD-I, (○) CGAD-II.

tonated state to the nonprotonated state and the carboxymethyl groups from the associated state to the dissociated state. The decreased net charge causes a decrease in the expansion of CGAD chain due to the weakening in intermolecular repulsion, resulting in a decrease in solubility, while the increased net charge leads to an increase in solubility. In addition, the solubility of CGAD samples is affected by their composition. For CGAD-II, with more dimethylaminoethyl groups (see Table I), for example, the %T is lower, which results from stronger electrostatic attractions from more positive and negative charges along a CGAD-II chain, and the pH corresponding to the minimum of %T is higher (see Figure 1). Different from sodium carboxymethyl cellulose (CMC), [17] CGAD-I and CGAD-II show high solubility at low pH (pH 1.0~2.0). This indicates that the grafting of the hydrophilic monomers AM and DMAEMA onto CMC improves the solubility property of CMC.

Figure 2 gives the effects of the concentration and type of added salt on the solubility of CGAD-II at a pH of 4.0, at which the minimum of %T appears. In the absence of added salt, the optical transmission of 0.1% CGAD-II is 40%. However, the %T increased when added salt is introduced and increases with enhancing salt concentration, suggesting that the addition of salt promotes solubility, a very specific property in sharp contrast with polyelectrolyte behavior.[15] In the presence of salt, there is a screening of the electrostatic inter-
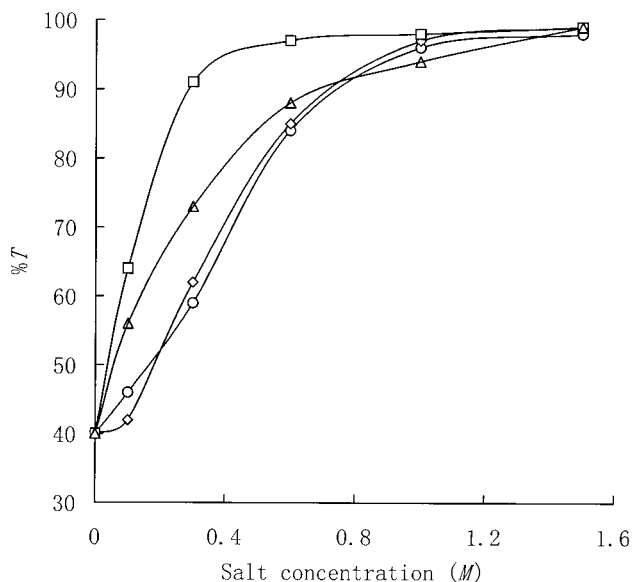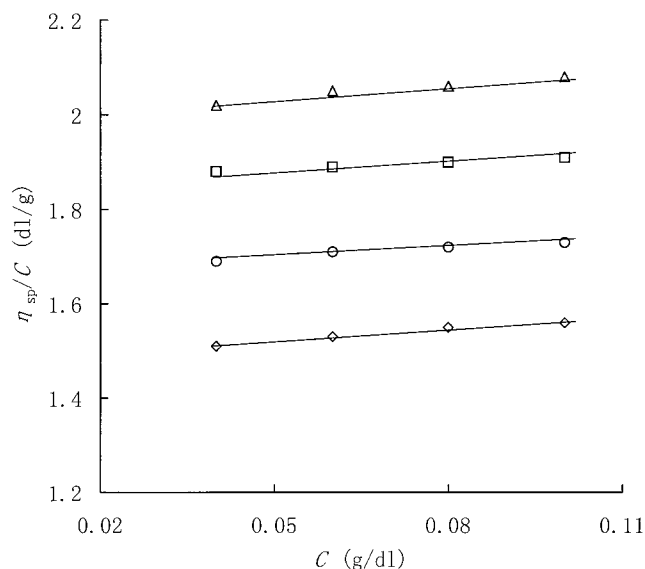

Figure 3 Dependence of η_{sp}/C on C for CGAD-II at 30°C and pH 6.0 (○) in 0.6M NaCl, (◇) in 0.8M NaCl, (□) in 1.5M NaCl, (△) in 1.0M NaCl.

actions, and the attractive forces are smaller than in pure water. The addition of a sufficient amount of salt tends to reswell the collapsed polymeric chain, which becomes soluble. For salt solutions containing a common anion (Cl⁻) but different cations (Na⁺, K⁺, Mg²⁺, Ca²⁺), the data from Figure 2 show that Mg²⁺ is more efficient at promoting solubility. It seems that the divalent cation Mg²⁺, with a smaller ionic radius, has a greater binding affinity for the carboxymethyl group (—CH₂COO⁻) of CGAD-II than do Na⁺, K⁺, and Ca²⁺ and which is more favorable to collapsing the ionically crosslinked network and expanding the CGAD chain.

Viscosity Properties

The intrinsic viscosity [η] is a good measure of the hydrodynamic volume of polymers containing the same molecular weight and can provide a reasonable assessment of macroscopic solution behavior.[13,18−21] Determining the [η] of CGAD samples under different conditions reflects the influence of these conditions on the hydrodynamic volume of the polymer chains. For aqueous CGAD salt solution, the reduced viscosity (η_{sp}/C) generally increases in a linear manner with increasing polymer concentration (C) (see Figure 3). Thus, the [η] can be obtained from the plot of η_{sp}/C versus C by extrapolating the curves-to-zero concentration according to Huggins' equation.[16]

The [η] versus pH curves of CGAD-I and CGAD-II dissolved in 0.6M NaCl at 30°C are

Figure 2 Effects of added salts on the solubility of CGAD-II at pH 4.0: (□) MgCl₂, (△) CaCl₂, (◇) KCl, (○) NaCl.

shown in Figure 4. The $[\eta]$ of CMC increases with pH, indicating that the charge density is one of the important factors dominating the viscosity of CMC solution. In contrast with CMC,[17] CGAD-I and CGAD-II have their minimum $[\eta]$ near the isoelectric points of pH 3.0 and pH 4.0, respectively, due to the intramolecular ionic attraction and the lack of ionic repulsion. On the higher or lower pH side of isoelectric point, the $[\eta]$ of CGAD-I and CGAD-II increases gradually when the positive or negative net-charge density becomes higher with the change of pH, suggesting that the intramolecular ionic repulsion between charges of the same sign makes the polymer chains adopt an extended conformation. These effects are similar to the effects of pH on solubility (see Figure 1).

The effects of added salt on the $[\eta]$ of CGAD-II are shown in Table II for NaCl and MgCl$_2$ as representative mono- and divalent species. It is seen that increasing the salt concentration up to 1.0M is accompanied by an obvious increase in the $[\eta]$, but beyond that point the $[\eta]$ decreases. Within the salt concentration range of 0.3M to 0.8M, MgCl$_2$ leads to significantly higher chain expansion than NaCl. In pure water and for NaCl concentrations up to 0.3M, the CGAD-II sample is insoluble. These effects are also in good agreement with the effects of added salt on the %T (see Figure 2), indicating the fundamental difference between polyampholytes and polyelectrolytes. On the other hand, for a higher salt concentration, of
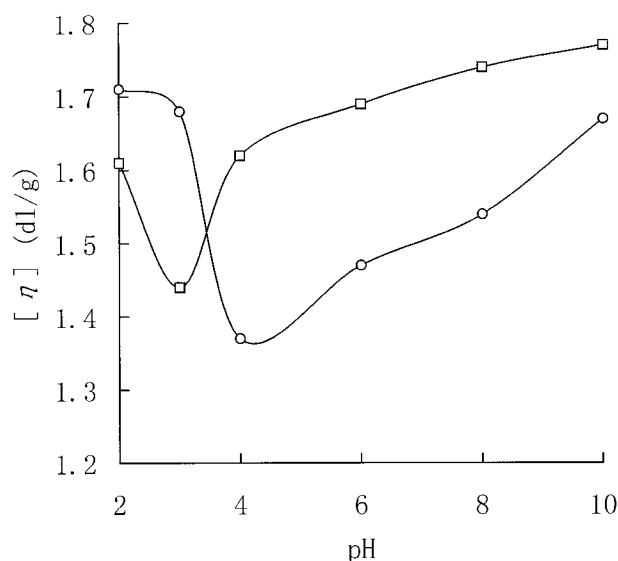
Table II Effect of Added Salt on the $[\eta]$ of CGAD-II in Aqueous Solutions at 30°C and pH 6.0

Salt Concentration (M)	$[\eta]$ (dl g^{-1})	
	NaCl	MgCl$_2$
0.3	$\times$	0.89
0.6	1.52	1.83
0.8	1.68	
1.0	1.96	1.92
1.5	1.87	1.79

$\times$, insoluble

1.5M, the decrease in the $[\eta]$ of CGAD-II with an excess of charge at pH 6.0 may be interpreted as the competitive result of the polyelectrolyte effect, which tends to collapse the coil in salt solution, and the polyampholyte effect, which tends to expand the coil in salt solution.

Table III illustrates the effect of temperature (T) on the $[\eta]$ of CGAD-I and CGAD-II in aqueous NaCl solutions. The decrease in the $[\eta]$ with increasing T indicates a decrease in the hydrodynamic volume of CGAD macromolecule. This is due to the conformational and solvent changes associated with increasing T. According to Rangarai et al.,[22,23] the increase in the temperature of a polymer solution produces two antagonistic effects. First, an increase in temperature generally leads to an increase in solvent power, that is, the solubility of the polymer in a solvent increases. This results in the uncoiling of the polymer chains, leading to increase in $[\eta]$ with temperature. Second, increase in temperature may lower the rotational barrier, thereby enhancing the degree of rotation about a skeletal bond and forcing the molecular chains to adopt a more compact coiled configuration. This leads to a decrease in $[\eta]$ with an increase in temperature. In addition, the variation of $[\eta]$ with temperature depended on the salt concentration and CGAD composition (see Table III). The plots of ln $[\eta]$ versus T^{-1} are linear in all the cases, and therefore the temperature effect can be explained better by the Arrhenius-type equation[24]

$$[\eta] = Ae^{E_a/RT}$$

where R is the gas constant, E_a is the activation energy, and A is a preexponential parameter. Thus, E_a, reflecting the sensitivity of the solutions toward temperature, can be determined, as

Figure 4 Effects of pH on the $[\eta]$ of CGAD-I and CGAD-II in 0.6M NaCl solutions ($\square$) CGAD-1, ($\bigcirc$) CGAD-3.

Table III   Effect of Temperature on the [η] of CGAD Samples in Aqueous Salt Solutions at pH 6.0

Systems	T (K)	$[\eta]$ (dL g^{-1})	E_a (kJ mol^{-1})	R
CGAD-I/0.6M NaCl	303	1.58	3.96	0.937
	313	1.54		
	323	1.50		
	333	1.36		
CGAD-II/0.6M NaCl	303	1.52	12.78	0.983
	313	1.31		
	323	1.05		
	333	0.98		
CGAD-II/1.0M NaCl	303	1.96	9.28	0.984
	313	1.78		
	323	1.50		
	333	1.43		

R is the corresponding determination coefficient.

shown in Table III. Comparing the magnitudes of E_a shows that the temperature affects the [η] by increasing with increasing $W_{DM}\%$ in the graft copolymer (see Tables I and III) and that an increase in the salt concentration weakens the sensitivity to temperature (see Table III).

A plot of [η] versus time for CGAD-I in 0.6M NaCl solutions is shown in Figure 5. It is seen that the [η] decreased from 1.82 dl/g to 1.60 dl/g within 30 days. Apparently, there is a collapse of the polymer coil with time. It's interesting that the coil does not collapse enough for the polymer to precipitate from the solution. This aging char-

acteristic contrasts with the behavior reported for other polyampholytes.[10,25]

Measurements of the [η] have also been carried out in 1.0M NaCl–methanol mixtures at 30°C and pH 6.0 (see Figure 6). The addition of methanol to the aqueous NaCl solution of CGAD-II changes the hydrodynamic characteristic of the latter. An analogous phenomenon was observed by Bekturov et al.[3,26] The addition of methanol may result in the following effects:

- causing the association of amphoteric polyion with counterions due to a decrease of the
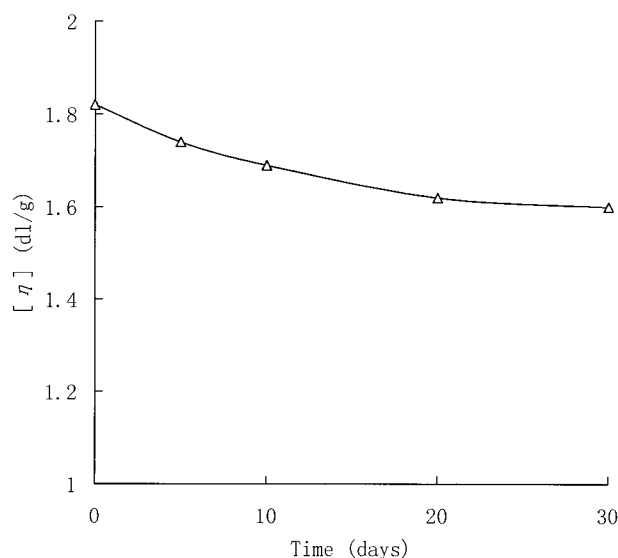

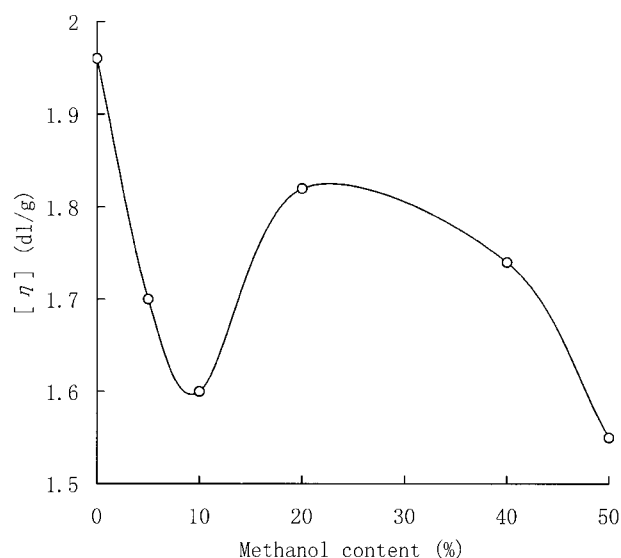**Figure 5**   Effect of aging time on the [η] of CGAD-I in 0.6M NaCl solution at 30°C and pH 6.0.

Figure 6   Effect of addition of methanol on the [η] of CGAD-II in 1.0M NaCl solution.

solvent dielectric permeability, which results in a decrease of [η].

- increasing the repulsion of fixed charges due to a decrease of the solvent dielectric permeability, which results in an increase of [η].
- weakening the screening of NaCl to the electrostatic attractions in the CGAD chains due to the decrease of NaCl dissociation, which results in a decrease of [η].

Thus, the change of the [η] with methanol content may be interpreted as the comprehensive result of these effects.

CONCLUSIONS

New amphoteric graft copolymers of CMC with AM and DMAEMA display interesting solution behavior. Turbidimetry experiments demonstrate that the solubility of CGAD macromolecules is related to the pH of the medium, the composition of the graft copolymer, and the concentration and type of added salt. Viscometry experiments indicate that the hydrodynamic and conformational characteristics for CGAD macromolecules in aqueous solutions are affected by the pH of the medium, the composition of the graft copolymer, and the concentration and type of added salt, as well as temperature, aging time, and the addition of methanol. At the isoelectric point, the %T and the [η] of CGAD have a minimum. On the higher or lower pH side of the isoelectric point, the %T and the [η] of CGAD increase gradually when positive or negative net-charge density becomes higher with the change of pH. In contrast with common cationic and anionic polyelectrolytes, the solubility and the [η] of CGAD may be promoted by the addition of salt. With the increase of temperature and aging time, the [η] of CGAD decreases. The temperature effect on the [η] increases with increasing W_{DM}% in CGAD, and an increase in salt concentration weakens the sensitivity of the CGAD solution to temperature. The solution properties of CGAD are partially controlled by the net electrical charge and are fixed by its composition and the ionic strength.

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