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ORIGINAL PAPER

Synthesis, characterization, and aqueous solution behavior of copolymers of acrylamide and sodium 10-acryloyloxydecanoate

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Abstract A new water-soluble monomer of sodium 10-Acryloyloxydecanoate (NaAD), which possesses a hydrophobic group and an ionizable group, was synthesized from acryloyl chloride and 10-hydroxydecanoic acid, and the series of copolymers of NaAD with acrylamide (AM) were prepared by the free radical polymerization in aqueous solution using ammonium persulfate as the initiator. The feed ratio of NaAD:AM was varied from 5:95 to 70:30 mol%, with the total monomer concentration held constant at 0.5 M. The copolymer compositions were determined from elemental analysis. The molecular weights of the copolymers were determined by gel permeation chromatography ranged from 0.76×10^6 to 1.37×10^6 g/mol. All copolymers were soluble in deionized water and salt solutions at pH > 5. The dilute and semidilute solution behavior of the copolymers was studied as a function of composition, pH, and added electrolytes, and the results indicated that NaAD30 exhibited much higher viscosity values. At moderate pH values, the copolymers coils become slightly more expanded and intermolecular association interactions occur, which was indicated by fluorescence and apparent viscosity measurements. Upon the addition of NaCl and in low pH, viscosities tended to decrease because of the disruption of the intermolecular associations.

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Introduction

Water-soluble polymers with hydrophobic substituents have been extensively studied from the theoretical and experimental points of view due to their important role as thickeners and viscosity modifiers in a variety of water-borne technologies including enhanced oil recovery, drag reduction, flocculation, superabsorbency, and personal care and coatings compositions [1–3]. These hydrophobically modified water-soluble polymers (HMWSP) consist primarily of a hydrophilic macromolecular backbone with a few percent of hydrophobic groups incorporated within the structure [4–7]. The incorporation hydrophobic groups in the hydrophilic network cause the hydrophobes to cluster together into aggregates acting as transitory physical cross links. The interesting feature of HMWSP is their ability to produce highly viscous aqueous solutions above a threshold polymer concentration. This viscosity enhancement, much higher than the viscosity of the unmodified precursor under the same conditions, is due to the strong tendency of their hydrophobic parts to form intermolecular aggregates in aqueous solutions [8–10].

Hydrophobically modified polyacrylamides are an important type of associating polymers. One method to copolymerize acrylamide (AM) with a hydrophobic comonomer is a micellar polymerization technique in which the hydrophobe is solubilized into micelles dispersed in a water continuous medium. As polymerization proceeds, hydrophobic monomers are incorporated in the copolymer structure as a series of blocks along the AM backbone because of the high concentration of hydrophobic units in the micelles. This structure was first proposed by Peer [11] and subsequently demonstrated by the use of fluorescent probes such as pyrene. The micellar copolymer was purified by successive precipitation into acetone, redissolution into water, dialysis to remove the surfactant, and freeze drying to gain pure production.

However, the hydrophobe content in hydrophobically associating polyacrylamides is very limited to maintain the solubility in water [12–17]. An additional problem arises from the difficulty to prepare copolymers with both high associativity and good water solubility. McCormick et al. [5] found that dodecylacrylamide cannot be incorporated at a content higher than 0.5 mol%. Comonomers with shorter alkyl chains, such as octylacrylamide, can be used at higher contents, but this results in copolymers with only weak associative properties. As a consequence, the range of hydrophobic modification is rather limited, and therefore the rheological properties cannot be controlled over a large variety.

The copolymerization of AM with short alkyl chain length anionic comonomers has been investigated. These ionic comonomers are potassium or sodium styrenesulfonate, sodium 2-sulfoethyl methacrylate, sodium 3-acrylamido-3-methlbutanoate, and sodium acrylate [6]. It was observed that the synthesis and the solution properties of the resulting copolymers depend on the ionic strength and polarity of the solvent. The solution properties of these copolymers have been studied with respect to the composition, the effect of temperature and electrolyte, as well as aging.

In this article, we aim to synthesize water-soluble copolymer from AM, incorporating a high molar proportion of long alkyl chain length anionic NaAD to an extent of about 5–70 mol%. In addition, we report solution structures of the copolymers at different pH and in the presence of electrolyte, employing well established fluorescence and viscosity studies.

Experimental

Materials

AM from recrystallized twice from acetone and vacuum dried at room temperature was used in the polymerization experiments. 10-hydroxydecanoic acid (HDA, Tianyuan Fine Chemicals Co, Ltd.) was recrystallized twice from the mixture of acetone–petroleum ether and vacuum dried at room temperature. Ammonium persulphate, acetone, and dichloromethane were purchased from Beijing Yili Fine Chemicals Inc. and used as received. Deionized water was used in all the experiments. All other reagents were purified by common purification procedures.

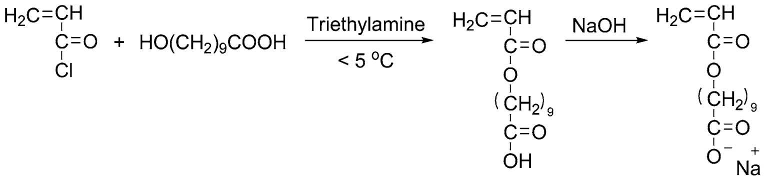
Synthesis

Synthesis of monomer 10-acryloyloxydecanoic acid (ADA)

ADA monomer was synthesized by referring to the method reported by Finkelman et al. [18]. A mixture of 10-hydroxydecanoic acid (18.8 g, 0.1 mol) and triethylamine (20.2 g, 0.2 mol) in dichloromethane (80 mL) was added by drop to a solution of acryloyl chloride (18 g, 0.2 mol) in dichloromethane (40 mL) at 0 °C. To avoid a temperature increase by mixing, this process was conducted carefully by spending over 5 h at 0 °C, then left overnight at room temperature. After removing triethylamine HCl salt by filtration, the solvent was evaporated. The ADA, obtained as a yellowish liquid in a yield of 80% (19.5 g), was characterized by ^{1}H NMR to be ca. 98% pure with ca. 2% unreacted 10-hydroxydecanoic acid remaining. IR (liquid petrolatum, cm^{-1}): 1710 (C=O of ester), 1637 (C=C), 2500–3700 (–OH of carboxylic acid); ^{1}H NMR (600 MHz, $CDCl_3$, δ, ppm): 6.4 and 5.8 ($\sim$2H, m, CH_2=C–); 6.1(1H, br, C=CH–); 4.2($\sim$2H, t, –CH_2OCO–); 2.3($\sim$2H, t, –CH_2COOH); 1.6($\sim$4H, br s, –CH_2–); 1.3($\sim$10H, br s, –CH_2–).

Synthesis of copolymers of NaAD with AM

The homopolymer of AM and the copolymers of AM with sodium 10-Acryloyloxydecanoate (NaAD) (Scheme 1) were prepared in aqueous solution at 50 °C using 0.1 mol% ammonium persulphate as the initiator. Each reaction was conducted in a 250 mL, three-necked flask equipped with a mechanical stirrer and nitrogen inlet tube. A designated amount of ADA was partially dissolved in



Scheme 1 Synthetic pathway for preparation of sodium 10-Acryloyloxydecanoate (NaAD)

Table 1 Reaction parameters for the copolymerization of acrylamide (M_1) with sodium 10-Acryloyloxydecanoate (M_2) and homopolymerization of PAM

Sample	M_1:M_2	Conv. (%)	wt[a]		M_2 in copolymer (mol%)	$M_n \times 10^{-6}$ [c]	M_w/M_n[c]
			%C	%N			
PAM	100:0	95	50.70[b]	19.72[b]	0[b]	1.25	3.5
NaAD5	95:5	70	47.26	15.20	4.6 ± 0.2	0.58	3.8
NaAD10	90:10	76	47.45	12.36	10.2 ± 0.4	0.42	3.4
NaAD20	80:20	63	48.49	10.15	16.5 ± 0.4	0.31	2.7
NaAD30	70:30	67	49.67	8.03	24.5 ± 0.6	0.37	3.6
NaAD50	50:50	65	50.22	4.40	44.21 ± 1.1	0.23	4.1
NaAD70	30:70	56	55.19	1.48	75.7 ± 2.3	0.26	3.6

[a] Calculating from the data of elemental analysis, [b] theoretical value, [c] obtained from GPC

deionized water followed by the addition of an equimolar amount of NaOH. A designated amount of AM dissolved in deionized water was then added to the neutralized ADA solution, and the pH of the entire mixture was adjusted to 9.0 ± 0.1 by dropwise addition of 0.5 M NaOH. The pH adjustment was performed to ensure that all of the carboxylate monomer was in the sodium salt form. Each reaction mixture was then deaerated with oxygen-free nitrogen for 20 min. The designated quantity of ammonium persulphate initiator, dissolved in deionized water, was injected into the reaction vessel. The total monomer concentration in each reaction was held constant at 0.5 M. After designated reaction intervals, the resulting polymer was diluted with deionized water and isolated from the reaction medium using ethanol as precipitating solvent. The polymer was finally dried under vacuum at room temperature. Structural characterization was used by nuclear magnetic resonance (NMR) and infrared spectra (IR). ^{1}H NMR (600 MHz, D_2O, δ, ppm): 4.0 (–O–CH_2–, in side chains); from 2.4 to 2.1 (–CH–, in main chains); from 1.6 to 1.4 (–CH_2–, in main chains); from 1.2 to 1.1 (–CH_2–, in side chains). IR (KBr, thin film, cm^{-1}): 1710 (C=O of ester), 1650 (C=O of carboxylate). Polymer composition was determined by the elemental analysis and the ^{1}H NMR. These data from two methods are similar. Weight-average molecular weights were determined by gel permeation chromatography (GPC). Conversions were determined gravimetrically and were controlled at low level (below 40%). Reaction parameters for the copolymerization of AM with NaAD and the homopolymerization of AM are listed in Table 1.

Characterization

Elemental analysis

Elemental analyses for carbon, hydrogen, and nitrogen of the copolymers were obtained by an Elemental Analyser Vario EL (Elementar). The copolymer compositions were calculated using C/N ratios.

Spectroscopic measurement

IR were recorded by a Bruker VERTEX 70 spectrophotometer using KBr pellets. The proton NMR spectra were obtained in $CDCl_3$ or D_2O by a Bruker AV 600 spectrometer.

GPC

The molecular weights and molecular weight distributions of the polymers were determined with a GPC instrument. The GPC system was comprised of a Waters 515 HPLC pump, two columns (a guard column and Ultrahydrogel-2000 and Ultrahydrogel-1000 column from Waters) connected in series, and Waters 2414 refractive index detector. All the analyses were conducted at 30 °C. Poly(sodium acrylate) standards were used with a mobile phase of 0.1 M $NaNO_3$ aqueous solutions.

Solution properties measurements

Fluorescence spectra

Steady-state fluorescence spectra were recorded on a Hitachi F-4500 fluorescence spectrometer using a 1 cm path length quartz cuvette. All measurements were performed at ambient temperature. The slit width of excitation and emission was kept at 3 nm during measurements. The excitation wavelength (λ) was set at 337 nm. The ratio of the intensities of the third I_3 (384 nm) to first I_1 (373 nm) vibronic peak of fluorescence spectrum of pyrene probe was used as an estimate of micro polarity of pyrene microenvironment [19, 20]. As pyrene exhibits least solubility in water (1×10^{-7} M), a required volume of stock solution of pyrene in ether (1×10^{-5} M) was pipetted out into a standard flask and a thin film of pyrene was deposited on the sides of the flask, through evaporation of solvent by bubbling N_2 gas. The effective concentration of pyrene was maintained at 1×10^{-6} M in all the solutions.

Potentiometric titration

The pH measurements for potentiometric titrations were conducted at 25.0 ± 0.5 °C with DelTA 320 digital pH meter fitted with a Ross Sure-Flow

8175 pH electrode. The meter was calibrated via a three-point calibration method. The polymer concentrations for titration were 0.10 g/dL; minimal volume variation during titration was achieved by the addition of microliter aliquots of the titrant. Polymer solutions were adjusted to pH 10 with concentrated NaOH to ensure the complete neutralization of all carboxylic acid groups and then were back-titrated with a 0.0469 M HCl standard solution. The degree of ionization (α), defined as the fraction of acid groups dissociated, was determined for each addition of titrant, using the relationship, $\alpha = C_A/C_{HA}$, where C_A is the concentration of the dissociated acid group and C_{HA} is the total concentration of acid group in the sample [21].

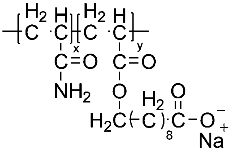
Rheological study

Viscosity measurements were performed with a Brookfield DV-III Ultra rheometer. The prepared copolymers were dissolved in water to achieve the desired concentration. Adjustments to pH were accomplished by adding small aliquots of a concentrated HCl or NaOH solution via a microsyringe. All measurements were conducted at 30 °C, and samples were covered to prevent evaporation during the tests. All solution viscosities were determined at 30 °C at appropriate shear rate.

Results and discussions

Polymer syntheses and compositional analysis

NaAD and AM monomers were copolymerized successfully in water (Scheme 2). The copolymers of NaAD with AM were synthesized by varying the feed molar ratio of AM:NaAD from 100:0 to 70:30. The reaction parameters and resulting copolymer compositions are presented in Table 1. The copolymers are named according to the feed composition of comonomer NaAD. The numbers appended to the acronym NaAD represent both the mol% of NaAD present in the feed into the copolymers. The degree of NaAD incorporation in each of the copolymers was determined by elemental analysis for carbon and nitrogen contents. Elemental analyses were conducted at low polymer conversion to assess the effects of compositional drift. The copolymer compositions as a function of feed composition for the NaAD series are shown in Fig. 1. It is found that the copolymer compositions are in good agreement with the feed composition. Thus, it can be concluded that the effects of compositional drift are minimal. These experimental values follow closely the dashed line representative of an ideal random



Scheme 2 Structural composition of copolymers of acrylamide with sodium 10-Acryloyloxydecanoate (the NaAD series)

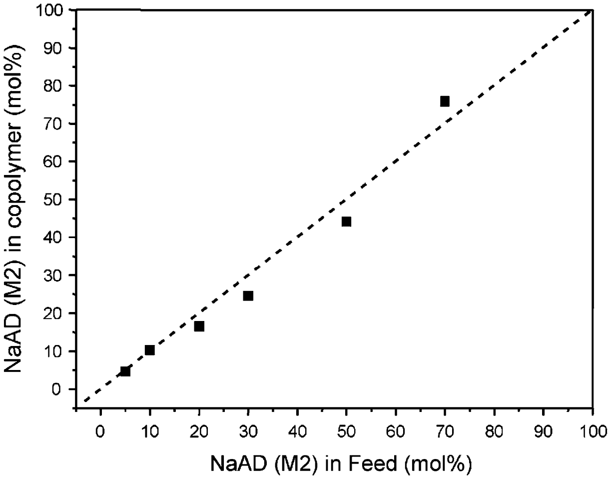


Fig. 1 Mole percent NaAD incorporated into the copolymers as a function of comonomer composition in the feed. The *dashed line* represents an ideal random incorporation

polymerization. NaAD and AM incorporation in both the NaAD and NaAD series approximates the feed compositions indicating similar reactivities of the respective monomers.

Effect of copolymer composition on the dissociation behavior in the absence of electrolytes

The dissociation behavior of the copolymers has been compared. Figure 2 shows the dissociation isotherms for copolymers with various ADA compositions. At the same pH, it is observed that within the series the degree of ionization (α) changes depending on the number of carboxylate groups in the copolymer, which show trends of decreasing α for carboxylate groups with increasing the mole percent of NaAD in the copolymer. The dissociation of NaAD20 begins at pH = 3.5 and NaAD70 begins at pH = 5.5. At pH = 7, the copolymer NaAD20, 80% of the carboxylic groups can dissociate, but only about 40% of the carboxylic groups of NaAD70 can dissociate. This result shows that the carboxyl groups exhibit different ionization capacities in series copolymer. The possible reasons are as follows; the higher the NaAD content in the copolymer the lower the distance between –COOH groups. Consequently, the carboxylic groups are closer at higher NaAD ratios, and they can interact via hydrogen bonding making ionization more difficult at pH lower than p*K*a.

Effect of ionic strength on the dissociation behavior

Figure 3 depicts the potentiometric titration curves of the NaAD copolymers in pure water and 0.5 M NaCl. Titration behavior conducted in pure water is analogous to that in salt solution and the minor difference from the respective potentiometry

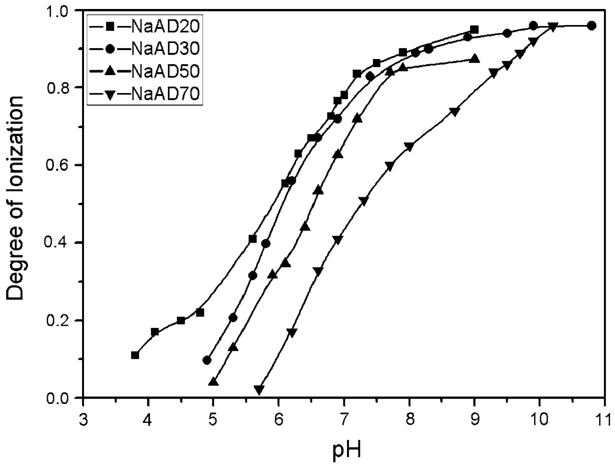


Fig. 2 The degree of ionization (α) as a function of pH for the 0.1 g/dL aqueous solutions of copolymer

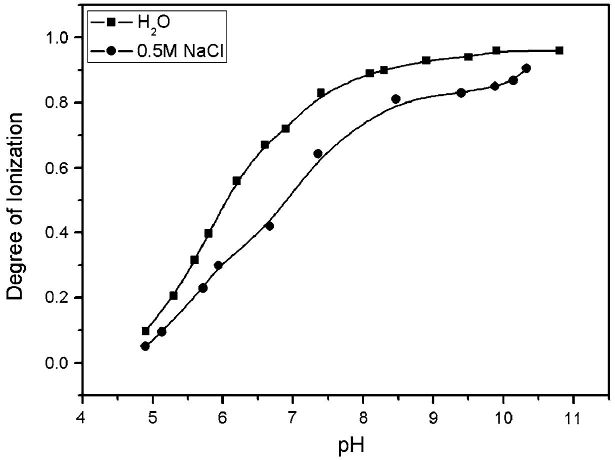


Fig. 3 The degree of ionization (α) as a function of pH for the 0.1 g/dL solutions of copolymer NaAD30

curves is that the degree of ionization is slightly lower in 0.5 M NaCl than that in pure water. The increasing hydration of the charged groups in the presence of the added electrolytes can be explained that the increasing local interaction due to the random coil conformation of the chains caused by charge shielding. And the greater conformational changes are observed in pure water due to the absence of charge shielding. This is likely due to the lack of conformational change occurring as a function of the degree of ionization (α). In other words, the charge–charge interactions greatly diminish in salt solutions as compared with in pure water. The polymers in pure water are much more extended due to electrostatic repulsion and are much more sensitive to pH changes.

Effect of copolymer composition on the solution viscosities

The effects of increasing polymer concentration on the apparent viscosities of the NaAD copolymers with various hydrophobic group contents are shown in Figs. 4 and 5. The measurements were conducted at pH = 8.5 and hence almost all of the anionic comonomers should be neutralized. Because of the polyelectrolytic nature of the copolymers, relatively high apparent viscosities are observed at low polymer concentration due to coulombic repulsions between the anionically charged comonomers.

The magnitude of the apparent viscosity is affected not only by molecular weight but also by charge density effects. For instance, NaAD30, which has lower molecular weight than NaAD20, exhibits much higher viscosity values due to the higher content (mol%) of NaAD incorporated into the copolymer. The anionic groups of NaAD30 are inherently closer to neighboring anionic sites resulting in a greater degree of chain extension. However, an interesting trend is also noted for the series. The copolymer containing the highest incorporation of charged comonomers (NaAD70) exhibits the lowest apparent viscosities, but the copolymers containing 20–50 mol% NaAD exhibit the highest apparent viscosities. The electrostatic repulsions of the NaAD70 containing the highest carboxylate groups are sufficient to prevent interpolymer aggregation through hydrophobic associations. Similar observations have been reported for other intramolecular associative copolymers [22, 23] and have been attributed to a transition from random coil to tighter hypercoil. McCormick et al. found that for the AM copolymers, the highest viscosity values were obtained when there was ~10–35 mol% incorporation of either NaAMBA [24, 25] or NaAMPS [26], while for AM-NaA copolymers [23], 50 mol% NaA incorporation yielded the highest viscosity. This behavior results from numerous factors which affect the hydrodynamic volume, including molecular weight, mol% of anionic comonomer, and the extent of hydration of the polymer coil.

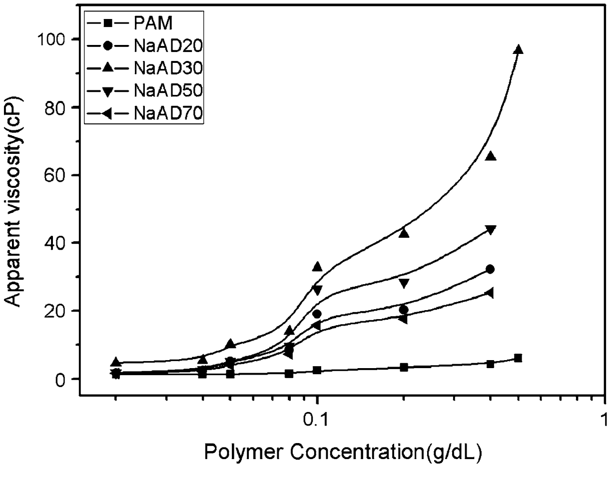


Fig. 4 Apparent viscosity as a function of polymer concentration for NaAD copolymers with various hydrophobic group contents in deionized water determined with a shear rate of 6.12 s^{-1} at 30 °C

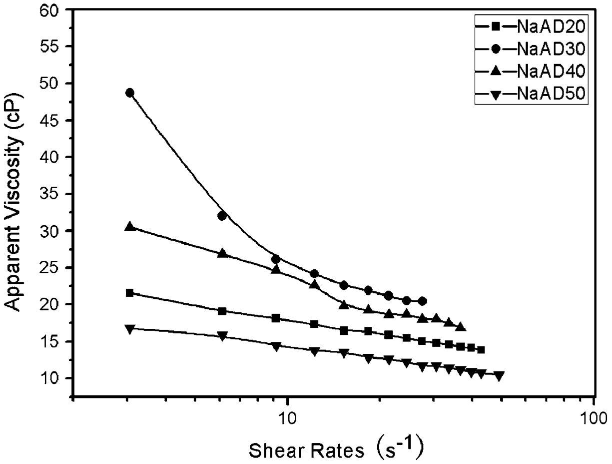


Fig. 5 Comparison of apparent viscosities and their dependence on shear rate for copolymer of varying contents of the NaAD unit ($C_p = 0.1$ g/dL, pH = 8.5)

It is worth to note that there are two break points in the curves of Fig. 4. The common viscosity–concentration curve of HAWSPs (hydrophobically associative water-soluble polymers) has only one break point (cac, critical association concentration) which indicates the transition from intramolecular association to intermolecular association. The cacs of these copolymers were presented in the first break points which were below 0.1 g/dL except for PAM. While polymer concentration is above cac, the viscosities of NaAD series are not as high as had been predicted and thus provide the second break point. The possible reason of this exceptional curve is that coulombic repulsions among anionic charges prevent the intermolecular association and make the viscosity decrease.

Figure 5 depicts the shear-thinning behavior of copolymers with NaAD units (0.1 g/dL aqueous solutions). The viscosities of all the samples decrease with the increment of shear rate because the shear force destroys the intermolecular association which forms the hydrophobic domains and physical networks.

Effects of polymer concentration on the solution viscosities

Apparent viscosity as a function of shear rate was measured for NaAD30 sample at different concentrations as shown in Fig. 6. It can be seen that the copolymer gives rise to weakened viscosity diminishes in the low-shear region, the higher the concentration, the larger is the effect. When the time scale of the imposed deformation is larger than the relaxation time of the polymeric chains, the deformed chains can fully relax to its unperturbed state. This allows the dissociated hydrophobes to reassociate to form hydrophobic junctions, where the balance of inter- and intra-molecular junctions is restored. Thus, Newtonian behavior can be achieved in low concentration region as shown in Fig. 5. This is a clear indication that hydrophobic interactions occur between chains, which leads to polymolecular

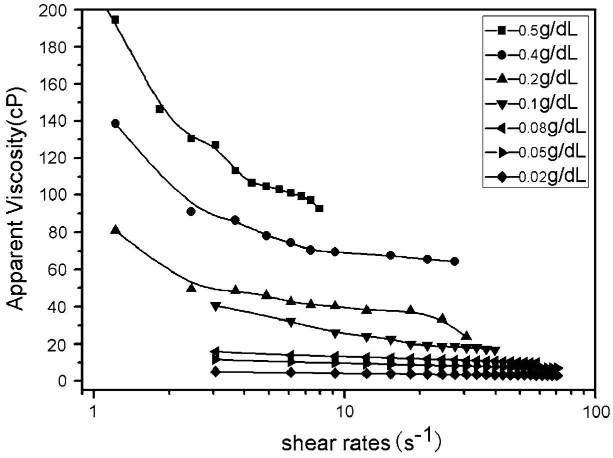


Fig. 6 Apparent viscosity of NaAD30 sample at various concentrations and shear rates

structures with a high hydrodynamic volume. As the polymer concentration increases beyond a critical value, a shear rate region in which viscosity decreases with shear is observed. This considerable loss in viscosity for the copolymer corresponds to the progressive rupture of the intermolecular associations upon increasing the shear rate, and these are no longer effective at the highest shear values.

It is evident from Fig. 6 that at higher polymer concentration, the onset of shear-thinning behavior occurs at lower shear rates. An explanation of the molecular behavior of the system for shear thinning involves a change in the relative amount of intra- and inter-molecular associations with shear. In the case where intra- and inter-polymer associations are competing depending on the polymer conformation, shear thinning is often observed arising from a transition from inter- to intra-polymer associations induced under shear conditions. A strong shear-thinning effect indicates that a large fraction of the elastically active inter-polymer junctions have been severed. With increasing polymer concentration, the formations of higher number of mechanically active hydrophobic junctions and aggregation number in the network are expected to retard the relaxation behavior of the polymeric chains. When the relaxation time of the polymer chains is slower than the time scale of imposed deformation, the dissociated hydrophobes are not able to reassociate to restore the network junctions. Instead, they reorganize to form a network structure containing junctions with lower aggregation number, which contributes to a reduction in the strength of the network and overall resistance to shear deformation. A consequence of this is the shifting of shear-thinning behavior to lower shear rates with increasing polymer concentration.

Effects of added electrolytes on the solution viscosities

To further investigate the associative behavior, the apparent viscosity of the NaAD30 copolymers was determined at a shear rate of 6.12 s^{-1} at 30 °C as a

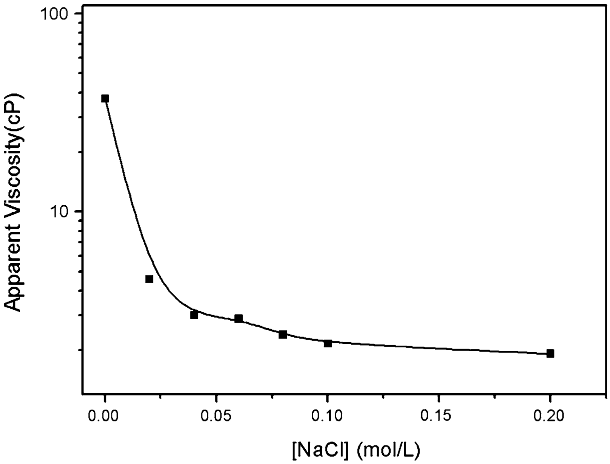


Fig. 7 Apparent viscosity of NaAD30 as a function of [NaC1] at pH 8.5 (Polymer concentration: 0.1 g/dL)

function of increasing sodium chloride concentration was examined and the results presented in Fig. 7. It is apparent that the addition of a small amount of NaCl causes a substantial decrease in the apparent viscosity, and then the viscosity decreases only slightly as the salt concentration is further increased. The polyelectrolyte effect vanished when the sodium chloride concentration exceeds 0.1 mol/L. Viscosity studies indicate that the anionic repulsions are shielded and the hydrodynamic volume decreases as the polymer chain relaxes into the a more compact configuration as salt is added. Furthermore, these interactions are strongly influenced by coulombic repulsions between the carboxylate groups with long alkyl chains as evidenced by the disruption (shielding) of these interactions with the addition of electrolytes. The disruption of intermolecular associations of charge groups by the addition of electrolytes has been observed previously by McCormick's group and others [27–31]. As the concentration of sodium chloride is increased, the apparent viscosity of the copolymers decreases as polymer coil shrinks, indicating that polymer chains collapse as a result of an electrostatic shielding of charges.

Effects of pH on the solution viscosities

The anionic moiety of the NaAD30 mer unit is based on a carboxylate group and, therefore, should be responsive to changes in the pH of the aqueous media. Variation in pH can impart significant change in solution properties. Figure 8 shows the apparent viscosity of NaAD30 at a concentration of 0.1 g/dL as a function of selected pH in deionized water. The apparent viscosities of the polymer solutions initially increase with increasing pH and then decrease.

At the lowest pH value, the carboxylic groups of the NaAD30 mer units become protonated; therefore, the polymer is only marginally soluble in aqueous solution and likely exists in a collapsed state with most hydrophobes participating in

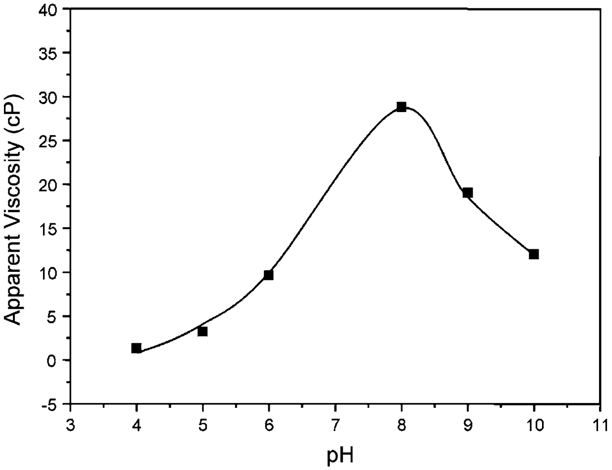


Fig. 8 Apparent viscosities of NaAD30 in deionized water as a function of pH (Polymer concentration: 0.1 g/dL)

intra-polymer versus interpolymer associates. As the pH is increased over this range (5–7), the polymer becomes partially ionized, and limited chain (backbone) extension occurs. At pH values between 7 and 8.5, a larger change in viscosity for the NaAD30 copolymer is observed. Ionization of the carboxyl functional groups into a conformationally extended, energetically favorable state occurs. At these pH values, the degrees of ionization are sufficient to overcome hydrophobic forces and disrupt intra-polymer aggregates, resulting in reordered, extended structures with more efficient network formation. Charge–charge repulsions of the carboxylate groups force an uncoiling of the polymer resulting in larger hydrodynamic volumes and, thus, enhanced viscosity values. The degree of ionization of the copolymer increases with increasing pH, disrupting intramolecular associations. The copolymer reaches maximum charge density at the pH at which the highest apparent viscosity is achieved. Further increase in pH increases the concentration of sodium ions in the solution; therefore, the interaction between the charged groups along the polymer backbone is shielded, causing polymer coil collapse.

Fluorescence studies

The fluorescence behavior of pyrene in presence of aqueous polymeric solutions has been employed to investigate micro polarity of polymeric structures. Pyrene, employed as an external fluorescence, is predominantly solubilized inside non-polar microdomain, and the ratio I_3/I_1 of the third (385 nm) to first (374 nm) peak intensities of pyrene is highly sensitive to micro polarity of the environment and increases with an increase in non-polarity of microenvironment [20]. It could be seen in Fig. 9 that I_3/I_1 of copolymer NaAD30 increases progressively from about 0.65–0.82 with an increase in concentration of polymer solution from 0 to 0.02 g/dL. A further increase in concentration of polymer solutions results in a

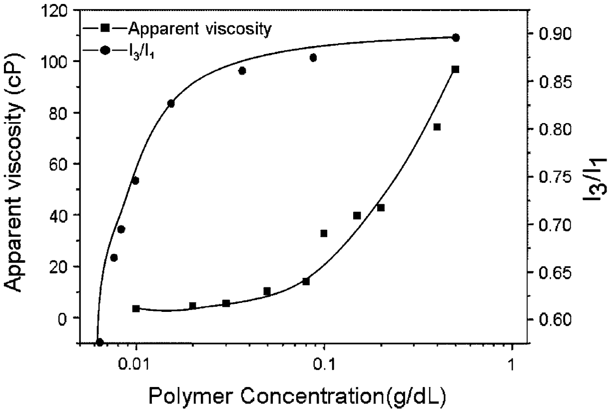


Fig. 9 Apparent viscosity and I_3/I_1 as a function of polymer NaAD30 concentration (in H_2O, pH: 7.5)

small increase in I_3/I_1 ratio, which reaches a maximum of about 0.90. It has been well demonstrated that the polar microenvironment of pyrene, as in water contributes to I_3/I_1 of about 0.62. Also, aqueous solution of polymeric hydrophiles, almost devoid of non-polar microdomains and exhibiting open chain conformation result in low I_3/I_1 ratio of about 0.63 [32]. Furthermore, the concentration of pyrene solubilized in polymer NaAD30 solution highly exceeds the limiting solubility of pyrene in water (<1 μM). These results indicate that most of pyrene molecules in the copolymer solution are incorporated into hydrophobic microdomains formed by the copolymer. This information agrees favorably with that obtained from viscosity studies.

To investigate the effect of pH and NaCl concentration on association for NaAD30, the I_3/I_1 ratio at $C_p = 1.0$ g/L was measured as a function of pH and NaCl concentration at 30 °C (Fig. 10). At acidic pHs, the apparent viscosities (Fig. 8) are small, which indicates that the copolymer chain adopts a collapsed conformation in a low-pH region. On the other hand, the I_3/I_1 ratios at various values of acidic pH are larger (Fig. 10a). This observation implies that NaAD30 is able to incorporate pyrene molecules into hydrophobic microdomains formed from the self association of the pendent alkyl carboxylic groups under acidic conditions and that the number of the hydrophobic microdomains is large enough to incorporate all pyrene molecules present in the solution when C_p is 0.1 g/dL at acidic pHs. At basic pHs, the pendent carboxylic groups in the copolymer are deprotonated. Since the content of the ADA unit in the copolymer is as high as 30 mol%, the polymer chain is crowded with decanoate chains. In such a situation, all alkyl chains in the ADA unit may not be completely kept from associating together, but some alkyl chains may interact to form hydrophobic microenvironments along the polymer chains. Some pyrene molecules may be trapped in the hydrophobic microenvironment, thus showing a decrease in I_3/I_1 at basic pHs. Addition of salt to a solution of pyrene labeled polyelectrolyte screens the charges, which favors greater association (Fig. 10b).

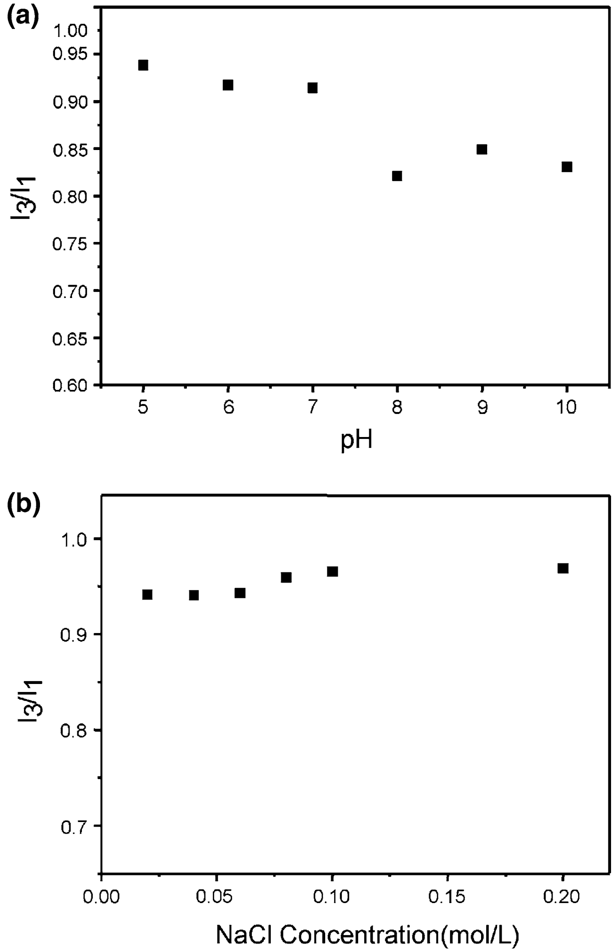


Fig. 10 I_3/I_1 as a function of solution pH (**a**) and NaCl concentration (**b**) for a 0.1 g/dL solution of NaAD30

Conceptualized model

A hypothetical model for the effects of concentration, acidic, and saline media is conceptually illustrated in Fig. 11. The hydrophobic groups on the copolymers exhibit concentration-dependent association. In region (I), low hydrophobic concentration, low copolymer concentration, or both conditions are insufficient to bring about significant associations which are not sufficient to cause appreciable viscosity enhancement. In region (IV), ordered associations or domains result in microphase networking and large increases in apparent viscosity. Viscosity and I_3/I_1 studies indicate that intramolecular associations may result at low pH or in the presence of electrolyte (Figs. 7, 9, and 10). As the pH decreases, the I_3/I_1 ratios show apparent increases (Fig. 10a), indicating in region (III). The intra-chain

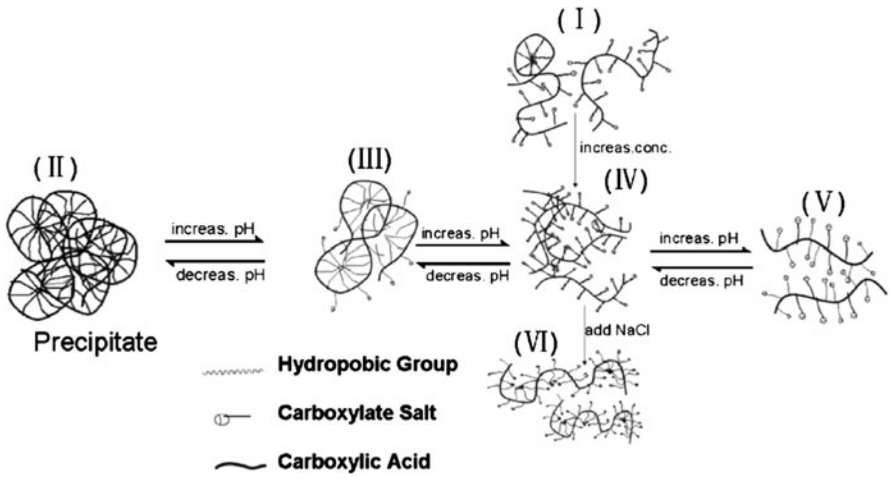


Fig. 11 Schematic of aggregated structures illustrating the effects of polymer concentration, pH, and added electrolytes

association of the protonated pendent alkyl carboxyl groups causes the polymer chain to collapse which is consistent with decreased apparent viscosities (Fig. 7). At extremely low pH, the copolymer is obtained as a curdy precipitate in aqueous solution (II). At this stage, for NaAD30, the degree of ionization <0.2 results in insolubility, possibly because of too many intra-molecule associations for hydration. At basic pHs, on the other hand, the electrostatic repulsion between the pendent alkyl carboxylate anions causes the polymer chain to adopt an open chain conformation. The slight decrease in apparent viscosity as observed (Fig. 8) by viscometry with added NaOH at high pH is due to increased ionic strength (V). Viscosity is at a minimum for NaAD30 at pH 8 in 0.2 M NaCl but at a maximum in deionized water (Figs. 7 and 8). Values of I_3/I_1 at low pH in deionized water and in 0.2 M NaCl are measured. This value equals or exceeds the highest value of I_3/I_1 for pyrene in the hydrophobic interior of surfactant micelles [33], suggesting a high degree of microdomain organization.

Conclusions

Copolymers of AM with NaAD were prepared in aqueous solution. Elemental analysis and ^{1}H NMR were used to determine the copolymer compositions. Molecular weights range from 0.5 to 1.5 × 10^6 g/mol was obtained by GPC. The aqueous solution behavior of copolymers has been investigated as a function of copolymer concentration, pH, and added electrolytes on the viscosity profiles. Hydrophobic association behavior of copolymer series is observed by pyrene fluorescence probe method. In the absence of added electrolytes, copolymers containing approximately 30 mol% of the anionic comonomer exhibit the highest viscosities near pH 8. Furthermore, solution behavior studies were conducted on copolymers incorporating 30 mol% to assess the effects of polymer concentration, pH, and added electrolytes on the rheological and fluorescence profiles. The decanoate group imparts considerable salt- and pH-responsiveness. As the electrolyte concentration increases, the shielding or elimination of electrostatic repulsions between carboxylate groups shrinks the polymer chain. At low pHs, the copolymer chain adopts a collapsed conformation as a result of the self association of the pendent alkyl carboxylic groups under acidic conditions.

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