Synthesis and Solution Properties of Zwitterionic Copolymer of Acrylamide with 3-[(2-Acrylamido)dimethylammonio]propanesulfonate

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A novel zwitterionic monomer 3-[(2-acrylamido)dimethylammonio]propanesulfonate (DMADAS) was designed and synthesized in this study. Then it was polymerized with acrylamide (AM) by free radical polymerization in 0.5 mol/L NaCl solution with ammonium persulfate ($(NH_4)_2S_2O_8$) and sodium sulfate ($NaHSO_3$) as initiator. The structure and composition of DMADAS and acrylamide-3-[(2-acrylamido)-dimethylammonio]propanesulfonate copolymer (P-AM-DMADAS) were characterized by FT-IR spectroscopy, ^{1}H NMR and elemental analyses. Isoelectric point (IEP) of P-AM-DMADAS was tested by nano-particle size and potential analyzer. Solution properties of copolymer were studied by reduced viscosity. *Antipolyelectrolyte* behavior was observed and was found to be enhanced with increasing DMADAS content in copolymer. The results showed that the viscosity of P-AM-DMADAS is 5.472 dl/g in pure water. Electrolyte was added, which weakened the mutual attraction between sulfonic acid group and quaternary ammonium group. The conformation became loose, which led to the increase of reduced viscosity. The ability of monovalent and divalent cation influencing the viscosity of zwitterionic copolymer obeyed the following sequence: $Li^+ < Na^+ < K^+$, $Mg^{2+} < Ca^{2+} < Ba^{2+}$, and that of anion is in the order: $Cl^- < Br^- < I^-$, $CO_3^{2-} > SO_3^{2-} \approx SO_4^{2-}$.

Key Words : Zwitterionic copolymer, Solution property, Reduced viscosity

Introduction

Zwitterionic copolymer, a kind of charged polymer with both anionic and cationic groups on the pendant side chain of the molecular backbone, has attracted public attentions due to their unique structures and excellent properties in recent years.[1,2] There are considerable literatures on the synthesis and aqueous solution properties of random linear zwitterionic copolymer. The synthesis and characterization of diblock copolymer were not accomplished until the 1970s.[3-5] Compared with that of polyelectrolyte, electrostatic interaction of zwitterionic copolymer exhibits both electrostatic repulsion and electrostatic attraction.[6] The electrostatic interaction is influenced by internal factors (*i.e.*, nature and distribution of acid and basic substituent group, hydrophobicity) and external factors (*i.e.*, pH, temperature, ionic strength of the solution, thermodynamic quality of solvents, and so on).[7] It is known that the IEP and the antipolyelectrolyte effect are the particular properties of zwitterionic polymer. At the IEP, there are equal number of positive and negative charges along the polymer chain, giving the polymer a net charge of zero.[8] The antipolyelectrolyte effect refers to the polymer chain expansion at the IEP due to addition of small molecule electrolytes, such as NaCl, $CaCl_2$, $MgCl_2$, *etc*.[9] Their solubility is promoted by adding salts. A number of investigations have been focused on the unusual properties of zwitterionic polymer.[10-12] The preparation, characterization and application of zwitterionic polymer (or polybetaines) have been reviewed by many researchers.[13,14] Due to previously mentioned polyampho-

lytic characterization and unique salt-responsive behavior, they have been widely proposed for various industrial applications, such as water treatment,[15] multifunctional drilling-fluid additives,[16-18] salt-resistant thickeners,[19] fracturing additives,[20] cementing extra agents[21] and biomaterials to prevent postsurgical adhesions. The synthesis and aqueous solution properties of these betaine-type zwitterionic polymer were reported by several authors, including Fevola *et al.*,[22] Nelly *et al.*,[23] Ali *et al.*,[24] Lee *et al.*,[25] Zheng *et al.*,[26] Kudaibergenov *et al.*,[27] and Kudaibergenov, Jaeger *et al.*[28]

In this paper, the synthetic route of zwitterionic copolymer was initiated with synthesis of 3-[(2-acrylamido) dimethylammonio]propanesulfonate (DMADAS), followed by copolymerization with acrylamide. The study aimed at providing an interesting opportunity to examine the synthesis and aqueous solution properties of the zwitterionic copolymer. Sulfobetaine amphoteric monomer has been paid much attentions because of their chemical stability, ability of hydration, and containing a number of quaternary ammonium cations and sulfonate acid anions which are less susceptible to the influence of pH. In this paper, we study on the synthesis and characterization of copolymer of acrylamide and 3-[(2-acrylamido)dimethylammonio]propanesulfonate.

Experimental

Materials. *N,N*-Dimethyl Acrylamide (DMAA, 99%) and 1,3-cyclopropane sulfone (99%) were purchased from Shangdong Ri Zhao Science and Technology Co. Ltd. Deionized (DI) water (electric resistance = 18 M) was used in all ex-

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periments. The dimethyl sulfoxide (DMSO) was purchased from Tianjin Damao Chemical Reagent Factory. Reagent grade salts LiCl, NaCl, KCl, KBr, KI, CaCl$_2$, MgCl$_2$, BaCl$_2$, Na$_2$CO$_3$, Na$_2$SO$_3$, Na$_2$SO$_4$, (NH$_4$)$_2$S$_2$O$_8$, NaHSO$_3$, acetone, alcohol, diethyl ether, sodium hydroxide, hydrochloric acid and acrylamide were purchased from Chengdu Kelong Chemical Regents Factory.

Characterization. Fourier transformed infrared (FT-IR) spectra was recorded with a Nicolet-560 spectrophotometer in the range 400-4000 cm^{-1}. ^{1}H NMR spectra was performed on an Avance III 400 with D$_2$O as solvent. Turbidity measurement was carried out at 490 nm, using a U-2001 Hitachi spectrophotometer at 25.0 $^{\circ}$C. Isoelectric point was tested by nano-particle size and potential analyzer (Nano-ZS) at temperature: 25.0 $^{\circ}$C. Viscosity measurement was carried out with an Ubbelohde viscometer (flow time 136.79 seconds for pure water) at 30 ± 0.1 $^{\circ}$C. The P-AM-DMADAS sample was dissolved in electrolyte solution of different cation types, anion types and pH to obtain stock solutions of approximately 0.5 g P-AM-DMADAS per 100 mL solvent. The reduced viscosity $\frac{\eta_{sp}}{C}$ was calculated by the division of η_{sp} by C (g/dL) as follows:

$$\frac{\eta_{sp}}{C} = \frac{\eta_r - 1}{C} = \frac{\frac{t}{t_0} - 1}{C}$$

Where t_0 is the flow time of solvent (1 mol/L NaCl aqueous solution), t is the flow time of the P-AM-DMADAS solution. The reduced viscosity was calculated. The determinations of t and t_0 were confined in ± 2%.

Monomer Synthesis: 3-[(2-Acrylamido)dimethylammonio]-propanesulfonate (DMADAS). The synthesis of DMADAS was carried out according to a procedure previously describ-ed in the literature.[29] DMADAS was synthesized by the ring-opening reaction of 1,3-propanesultone, then electrophilic substitution with *N,N*-dimethyl acrylamide (DMAA) in the presence of acetone at 50 $^{\circ}$C. To a 250 mL three-necked round-bottom ask equipped with a magnetic stirrer, con-denser and dropping funnel, 0.11 mol DMAA and a little polymerization inhibitor dissolved in 30 mL acetone was added, and the mixture was heated to 50 $^{\circ}$C in a thermostated water bath. 0.1 mol 1,3- SO$_3$ was dissolved in 30 mL acetone and then be added dropwise into the ask over 20 h under magnetic stirring, subsequently react at 50 $^{\circ}$C for 2 h. The DMADAS was precipitated from the reaction medium in the form of white crystal, separated by filtration, vigorously washed with acetone and diethyl ether mixture, further purified by soxhlet extractor for 48 h, and finally DMADAS was dried in vacuum oven for 2 h at 45 $^{\circ}$C to remove solvent
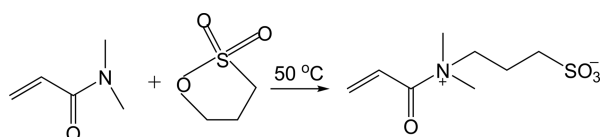
Scheme 1. Preparation of 3-[(2-Acrylamido)dimethylammonio]-propanesulfonate.
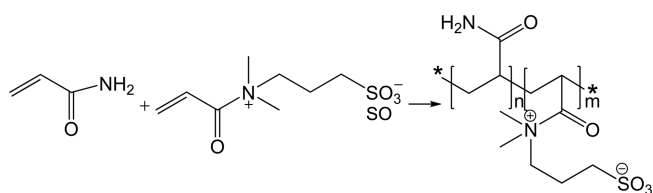
Scheme 2. Preparation of Copolymer of Acrylamide with 3-[(2-Acrylamido)dimethylammonio]propanesulfonate.

completely. The synthesis route of DMADAS is shown in Scheme 1.

Synthesis of Copolymer of Acryiamide-3-[(2-acrylamido)-dimethylammonio]propanesulfonate (P-AM-DMADAS). P-AM-DMADAS was synthesized by free radical polymeri-zation in a 0.5 M NaCl aqueous solution under nitrogen at 30 $^{\circ}$C, using 0.03% initiator (Scheme 2). In a typical synthesis, specified quantity of each monomer (AM and DMADAS) was dissolved in small volume of deionized water, which was added to a three – necked flask with a sealed mechanical stirrer, a condenser pipe, and a atmospheric dropping funnel. The pH was adjusted to 8. The necessary quantity of NaCl was added to achieve a 0.5 M NaCl solution. (NaCl was added to ensure that the polymerization medium remain homogeneous). The reaction mixture was sparged with nitro-gen after 30 minutes initiating with 0.03% sodium hydro-gensulfite and ammonium persulfate (molar ratio: 1:1.4). After a certain time, the reaction was terminated with acetone. Product under the surrounding of ethanol for 12 h is removed unreacted monomer, and P-AM-DMADAS was dried in vacuum oven for 2 h at 80 to remove solvent. The synthesis route of P-AM-DMADAS is shown in Scheme 2.

Results and Discussion

DMADAS Synthesis. DMADAS was synthesized by DMAA with the ring-opening reaction of 1,3-propanesul-tone as shown in Scheme 1. The absorption bands at 1197.1 and 1043.6 cm^{-1} can be ascribed to be asymmetric and symmetric stretching vibrations of sulfonic acid groups.[30] 3090 cm^{-1}, 1415.2 cm^{-1}, 922.1 cm^{-1} show the peak of double bond. The peak at 1635.0 cm^{-1} reveals the existence of the stretching vibration of canbonyl group. 1487.0 cm^{-1} can be flexural vibration of methylene. 3447.5 cm^{-1} is the absorbed water of sulfonic acid group. The peaks at 2960 cm^{-1} and 1487.0 cm^{-1} in Figure 1(a) represent the asymmetrical stretch vibration and asymmetrical variant vibration of methyl, respectively.[31] Monomer structure was confirmed by FT-IR and ^{1}H NMR as shown in Figures 1 and 2.

P-AM-DMADAS Synthesis. The synthesis of P-AM-DMADAS was carried out by copolymerization AM and DMADAS, in different ratios of initiator concentration, solution pH, NaCl aqueous solution concentration, temper-ature and time. The corresponding reduced viscosity is shown in Table 1. The P-AM-DMADAS structure was con-firmed by FT-IR and ^{1}H NMR as shown in Figure 1 and 3.

The results in Table 1 indicate that the reduced viscosity

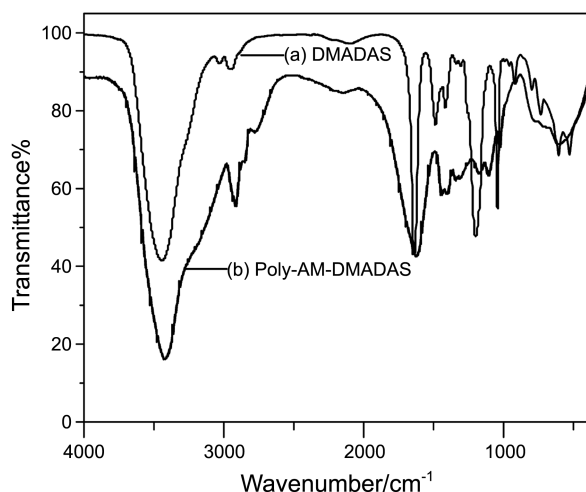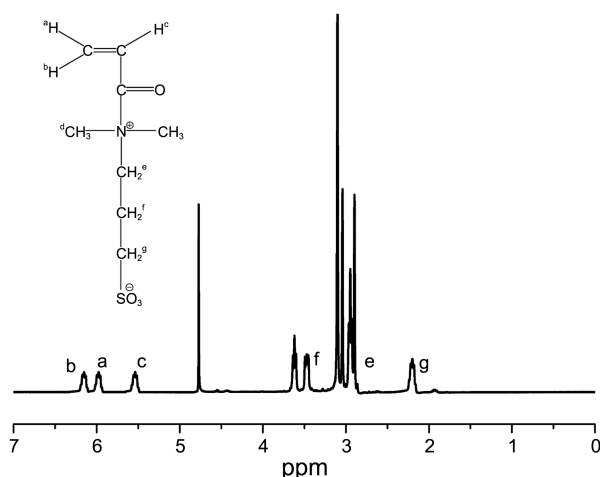**Table 1.** Synthesis of the P-AM-DMADAS

Monomer[a]	t/h	T/°C	Initiator (w%)[b]	Solid[c] (w%)	NaCl (mol/L)	Reduced viscosity (dl/L)
5:95	6	25	0.03	15	0.5	5.243
5:95	8	25	0.03	15	0.5	5.472
10:90	8	35	0.03	15	0.5	5.035
5:95	8	25	0.05	15	0.5	5.243
5:95	8	25	0.03	25	0.5	5.073
15:85	6	35	0.03	15	0.5	4.958

[a]The monomer ratio of DMADAS and AM. [b]The molar ratio of n((NH$_4$)$_2$S$_2$O$_8$):n(NaHSO$_3$) = 1.4:1. [c]The solid content

depends on initiator concentration, NaCl aqueous solution concentration, temperature and time. For a 5% content of DMADAS and acrylamide reacting for 8 h, the reduced viscosity of the polymer achieved 5.472 dl/g at 25 °C, initiator content 0.03%, solid concentration 15% and NaCl aqueous solution concentration 0.5 mol/L.

IR. With respect to P-AM-DMADAS, in Figure 1(b) the peak at 3431.2 cm^{-1} is the asymmetric stretching vibration of N-H bond,[32] and 1633.6 cm^{-1} is the stretching vibration of carbonyl group. The absorption bands at 1179.5 cm^{-1} and 1038.5 cm^{-1} can be ascribed to be asymmetric and symmetric stretching vibrations of sulfonic acid groups.[30] The peaks at 2925.2 cm^{-1} and 1452.9 cm^{-1} represent the asymmetrical stretch vibration and curve vibration of methyl, and 1318.1 cm^{-1} is stretching vibration of C–N in –N–(CH$_3$)$_3$, respectively.[31] The peak at 1452.9 cm^{-1} is mixed in-plane bending vibration of C–N and N–H and 2787.9 cm^{-1} is the stretching vibration of methylene. From Figure 1(b), we can see characteristic absorption peak of acrylamide, and the peak 2943.3 cm^{-1} disappeared. These observations can confirm the successful chemical copolymerization of DMADAS and AM.

^{1}H NMR. Figure 2 shows the ^{1}H NMR spectrum of DMADAS. The chemical shifts at δ 3.5 ppm, 2.2 ppm, and 2.9 ppm can be attributed to the protons of being connected

Figure 2. ^{1}H NMR spectrum of DMADAS.

methylene group, and the peak at δ 3.14 ppm can be ascribed to the methyl proton adjacented to the nitrogen atom of dimethylamino group –N(CH$_3$)$_2$, respectively. The chemical shifts at δ 5.68 ppm, 6.08 ppm, and 6.19 ppm also can be attributed to the multiple absorption of CH$_2$=CH–. These results indicate that zwitterionic monomer DM is obtained.

In the ^{1}H NMR spectrum of P-AM-DMADAS, the peak at δ 3.14 ppm is the absorption of −CH$_3$ linking with N. The peaks at δ 3.5 ppm, 2.2 ppm, and 2.9 ppm are attributed to the protons of being connected methylene group, the peaks at δ 1.68 ppm and δ 2.29 ppm are the absorption of −CH$_2$− and CH in the main chain, respectively. The peaks at δ 2.25 ppm and δ 2.142 ppm are the absorption of CH and −CH$_2$− in the acrylamide, respectively. The spectrum indicates the disappearing of chemical shift of CH$_2$=CH– and presence of the absorption of acrylamide. So there is the occurrence of the binary copolymerization.

Properties of P-AM-DMADAS Solubility Measurement. The solubility behavior of P-AM-DMADAS is shown in Table 2. The solubility of polyelectrolyte is found to be soluble in most polar solvents, such as water, methanol, ethanol, and so on. However slightly soluble in THF,
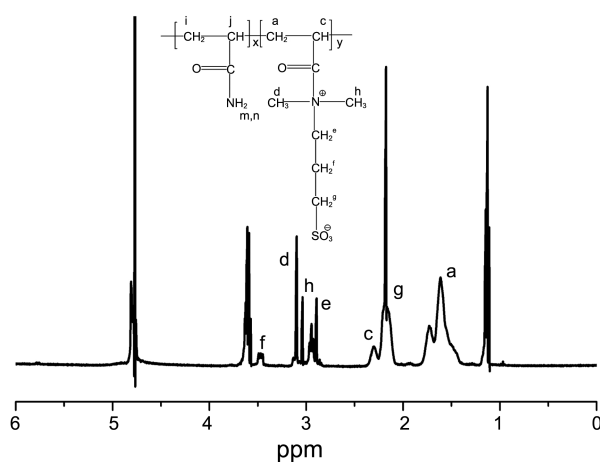

Figure 1. The FT-IR spectra of DMADAS and P-AM-DMADAS.

Figure 3. ^{1}H NMR spectrum of zwitterionic copolymer (P-AM-DMADAS).

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Table 2. The solubility behavior of P-AM-DMADAS

Solvent	Polarity Index	Solubility
Water	10.2	+
Dimethylsulfoxide	7.20	±
Tetrahydrofuran	4.20	±
Dimethylacetamide	6.40	±
Methanol	6.60	−
Ethanol	4.30	−

(+) indicates soluble; (−) indicates insoluble; (±) indicates partially soluble.

especially soluble in deionized water at pH value from 3 to 13, which is similar to previous study.[33] Unlike the most reports,[34,35] the zwitterionic copolymer is found to be soluble in water. The hydrophobic groups of these polymers interrupt the intra- and inter-ionic associations and cause the solution of the polymer in deionized water.[36] The solubility behavior of zwitterionic copolymer (at IEP) in the present study can be interpreted by the big steric hindrance between positive and negative charges along the main chain. Because anionic and cationic groups increase the polarity of polymer chain, it is also found that the zwitterionic copolymer can be soluble in most polar solvents.

Light Transmittance of P-AM-DMADAS with the Different DM Content. The solution behaviour of zwitterionic copolymer was mostly dependent on the amount of DMADAS incorporated into the copolymer. When the content of DMADAS is 15 mol % or less, the copolymer is soluble in deionized water and displayed a tendency of intermolecular association. With the content of DMADAS lowering, the solubility was improved. However, with the content of DMADAS increasing, the solubility reduced gradually. When the content of DMADAS is more than 15%, the aqueous solution became turbid. Adding electrolyte, such as NaCl, can improve the solubility. When the content of DMADAS is high, the role of intra- and inter-chain association was outlined resulting in insolubility in pure water due to the formation of ionically cross-linked network structures. However, it can be soluble in saline water because of the disruption of the ionic networks. Moreover, since this behavior is typical of most zwitterionic copolymer composed of sulfobetaine with three methylene units between the cationic and anionic groups, the lack of solubility is attributed to the attractive dipole coulombic interactions. These interactions,

Table 3. Dissoluvabilities of P-AM-DMADAS with different DMADAS content in water and in NaCl solution

Sample	Light transmittance, %				
	H₂O	c(NaCl)/(mol/L)			
		0.03	0.06	0.12	0.15
DMADAS -5%	98.6	98.7	98.7	98.7	98.8
DMADAS -10%	83.2	91.9	92.7	95.5	96.4
DMADAS -15%	68.9	87.6	91.9	92.4	93.4

c(P-AM-DMADAS) = 0.2 g/dl.

Table 4. Comparison of measured and calculated values with different DMADAS content

n(DMADAS): n(AM)	Calculated value / Measured value	C(%)	N(%)	0(%)	S(%)
5/95	Calculated	27.63	3.57	13.73	3.39
	Measured	27.63	3.56	13.73	3.40
10/90	Calculated	27.68	3.69	13.65	3.32
	Measured	27.67	3.68	13.66	3.33
15/85	Calculated	27.72	3.82	13.58	3.25
	Measured	27.70	3.85	13.56	3.24

however, can be shielded by the addition of electrolyte, resulting in solubilization of the polymer. This is a typical behaviour of poly(vinylsulfobetaines) and has been observed in numerous studies.[37,38] The result was shown in Table 3. In the course of experiment, I carried out dissoluvability measure from 0.03 mol/L to 0.3 mol/L. From 0.15 mol/L to 0.3 mol/L, the light transmittance is no change. So this concentration (from 0.03 mol/L to 0.15 mol/L) was chosen.

Elemental Analysis of Zwitterionic Copolymer with Different DMADAS Content. From Table 4, it can be seen there are many differences between measured and calculated value of zwitterionic copolymer with different DMADAS content. When n(DMADAS): n(AM) is 5:95, the difference is the smallest. With the DMADAS content increasing, the difference become obvious. Because the zwitterionic monomer has a low activity, the higher the concentration of DMADASis, the more DMADAS is not connected-up. However, from the whole table, monomers can be reacted accordingto thedosing ratio.

Influence of pH on the Reduced Viscosity of Zwitterionic Copolymer in Pure Water. A characteristic feature of zwitterionic copolymer (in particular it is composed of weak acid and base species) is that it possess an isoelectric point (IEP). The IEP is defined as pH at which the zwitterionic copolymer is electrical neutral.[39] The solubility of zwitterionic copolymer at the IEP is very much dependent upon the copolymer structure and composition. For example, zwitterionic copolymer tend to be soluble above and below the IEP and precipitated at/around this critical pH. This is because at IEP, the interaction force is the largest, molecular chain crimp degree is the largest, hydrodynamic volume is the smallest. IEP may be determined experimentally by electric potential, or by measuring the reduced viscosity. Ascoli and BotreÂ[40] confirmed the IEP by measuringthe reduced viscosity.

Figure 4 represents the effect of pH on the reduced viscosity of P-AM-DMADAS in pure water. The adjustment of pH was achieved *via* the addition microliter aliquots of NaOH or HCl. The pH of solution was measured by the PB-10 pH meter. In the absence of electrolyte, the reduced viscosity change of P-AM-DMADAS is not obvious from pH 3 to 12. Because the sulfonate moiety is a kind of weak conjugate base, it will remains the anionic form at all attainable pH value,[33] so it is relatively insensitive to pH of the aqueous solution. Meanwhile, for P-AM-DMADAS, at
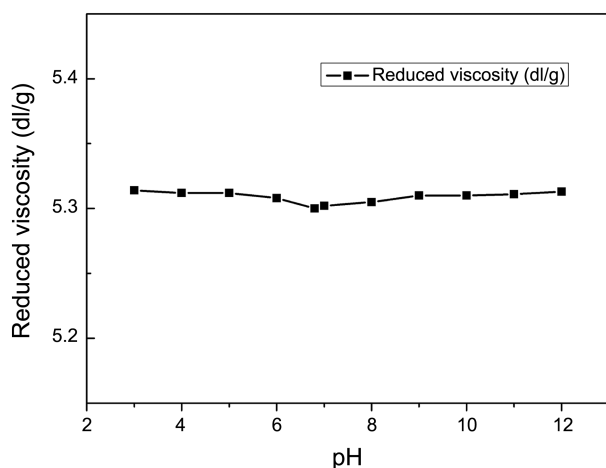
Figure 4. Influence of pH on the reduced viscosity in a dilute (0.01 g/mL) solution of zwitterionic copolymer (P-AM-DMADAS, PH_{IEP} = 6.8).

Figure 5. Influence of NaCl solution concentration on the reduced viscosity of zwitterionic copolymer with different DMADAS content.

low pH, the sulfonic acid groups are shielded by exceed H^+, leading to weak repulsive forces slightly. The enhanced ionization of quaternary amine groupscan compensate for sulfonic acid groups and relieve the repulsive force among sulfonic acid groups, so the polymer coiled. With increasing pH, the electrostatic repulsion of negative charge increases, leading to extended conformation and large hydrodynamic volume. At about 7, sulfonic acid groups and quaternary amine groups interattract, the reduced viscosity is the lowest,which is consistent with IEP (pH_{IEP} = 6.8).

Viscosity Behavior of Zwitterionic Copolymer in Aqueous Salt Solutions. Influence of NaCl solution concentration on the reduced viscosity of zwitterionic copolymer with different DMADAScontent is shown in Figure 5. It can be seen thatthe reduced viscosity increases with the increase of NaCl solution concentration. Further, the higher DMADAS content of the copolymer is, the bigger increase range of reduced viscosity is with increasing NaCl solution concentration. Classical antipolyelectrolyte behavior is exhibited by P-AM-DMADAS. Because the number of cations and anions is equal, the electrostactic attraction existing between internal and external molecules constrain the chain extension. In aqueous solution, the electrostatic attraction can cause intramolecular aggregate among intragroups and intrachains, leading to decrease of hydrodynamic volume and closeness of conformation (indicated by relatively lower reduced viscosity). But in aqueous salt solution, the electrostatic attraction can be effectively screened by ions of electrolyte, leading to increase of hydrodynamic volume and expansion of the coil (indicated by the increase of reduced viscosity). When the higher the content of DMA-DAS is, the more obvious the shielding effect is, the larger the reduced viscosity is. However, the typical polyelectrolyte effect can be shown in the curve with concavity of polyacrylamide (PAM, the degree of hydrolysis 10%). The reduced viscosity of PAM is decreased significantly with the increase of NaCl concentration. The decreases in the hydrodynamic volume and coil twist (indicated by the decrease of reduced viscosity
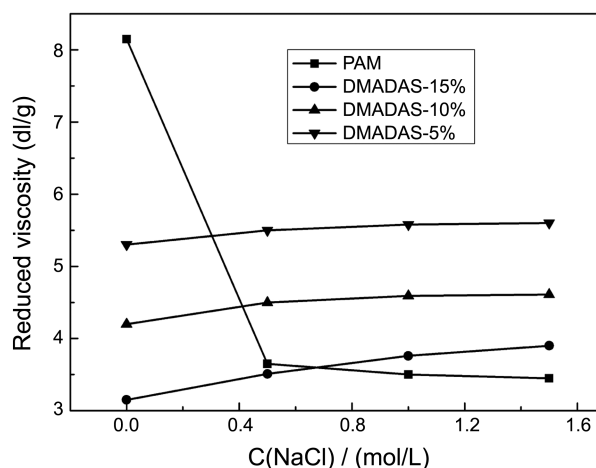
and deposition) are contributed to the shielding of electrostatic repulsion among the negative charges by the small-molecule electrolyte. Because the interaction force of PAM is only electrostatic repulsion in aqueous solution, the polymer chain is expanded. In salt solution, the small-molecule electrolytes shield the repulsion and the reduced viscosity decrease.

Influence of Electrolyte on the Reduced Viscosity of Zwitterionic Copolymer. The influence of various electrolytes with a common anion (Cl^-) on the reduced viscosity of zwitterionic copolymer (DMADAS content is 5%) is shown in Figure 6. The influencing ability of monovalent and divalent cations on the reduced viscosity of zwitterionic copolymer obeys the following sequence: $Li^+ < Na^+ < K^+$ for LiCl, NaCl and KCl, and $Mg^{2+} < Ca^{2+} < Ba^{2+}$ for $MgCl_2$, $CaCl_2$ and $BaCl_2$, respectively, which were proved by the change range of reduced viscosity. It is indicated that the divalent cation with a small charge density is easily attracted to the sulfonate group, leading to the reduce of the electrostatic interactions between cations and anions. So the residual cationic groups along the polymer chain exhibit
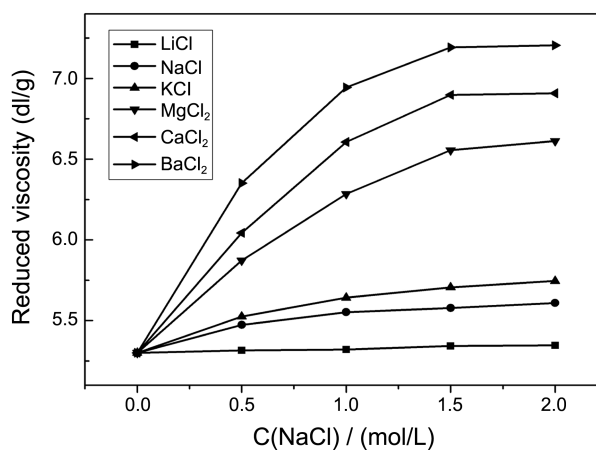

Figure 6. Effect of cation on the reduced viscosity of P-AM-DMADAS (Polymer concentration = 0.5 g/dL).
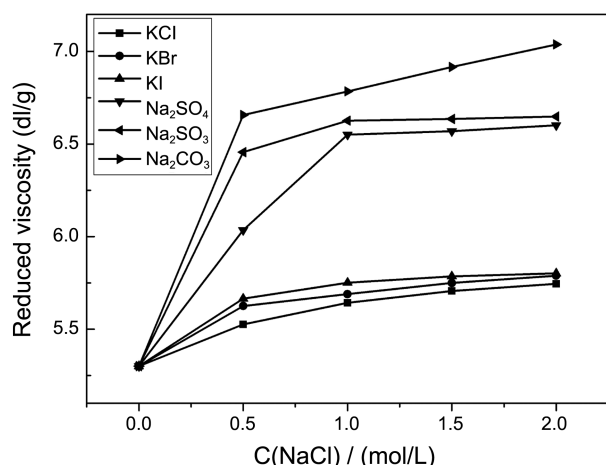
Figure 7. Effect of anion on the reduced viscosity of P-AM-DMADAS (Polymer concentration = 0.5 g/dL).

electrostatic repulsion to extend the polymer chain. These tendencies conform to the previous work.[24,25]

The data of reduced viscosity under the effect of various anions with a common cation (K^+) or (Na^+) is shown in Figure 7, of which the increase is the following order: $Cl^- < Br^- < I^-$ for KCl, KBr and KI, $CO_3^{2-} > SO_3^{2-} \approx SO_4^{2-}$ for Na_2CO_3, Na_2SO_3 and Na_2SO_4. The result confirm the order of interaction of the anion with quaternary ammonium group. This can be correlated to the polarizability increase of the anions from Cl^- to I^-. The anion with a small charge density was easily polarized as it approaches and becomes bound to the quaternary ammonium groups on the polymer unit. The reduced viscosity increases with the increasing polarizability of the ion. A similar tendency was also observed in the previous work.[24,25] Meanwhile, according to the Pearson theory,[41] the quaternary ammonium group and sulfonate group on the polymer unit can be considered as a soft acid and a soft base, respectively. The soft quaternary ammonium and sulfonate ion bind more effectively to large and highly polarizable counterions. Thus soft base (anion) from a salt (larger anionic radius) bind more easily to site on the quaternary ammonium group than hard base, and soft acid (cation) from a salt (larger cationic radius) bind more easily on the sulfonate group than hard acid.

Conclusion

A sulfobetaine monomer, 3-[(2-acrylamido)dimethylammonio]propanesulfonate, was synthesized and copolymerized with acrylamide in this paper. The success in polymer synthesis was confirmed by FT-IF and ^{1}H NMR analyses. The antipolyelectrolyte behavior and the remarkable increase of reduced viscosity with the addition of salt were observed. The reduced viscosity was enhanced with increasing DMADAS content in copolymer due to the screening of the electrostatic attractive interaction between the cationic and anionic groups in the zwitterionic copolymer. It was suggested that the coulombic interactions and hydration effects are the main factors affecting the solubility behavior of zwitterionic

copolymer. The solution properties of zwitterionic copolymer were controlled by electrostatic interactions of different group types, such as sulfonic group and quaternary ammonium group, and by extra factors, such as pH, small electrolyte, concentration, and so on. Copolymer exhibited the greatest increase in viscosity as the concentration of electrolyte increased. The influent ability of charge on the reduced viscosity of zwitterionic copolymer obeys: $Li^+ < Na^+ < K^+$, $Mg^{2+} < Ca^{2+} < Ba^{2+}$, $Cl^- < Br^- < I^-$ and $CO_3^{2-} > SO_3^{2-} \approx SO_4^{2-}$.

References

1. Andrew, B. L.; Charles, L. M. *Chem. Rev.* **2002**, *102*, 4177-4189.
2. Xuan, F. Q.; Liu, J. S. *Polym. Int.* **2009**, *58*, 1350-1361.
3. Kamachi, M.; Kurihara, M.; Stille, J. K. *Macromolecules* **1972**, *5*, 161-167.
4. Kurihara, M.; Kamachi, M.; Stille, J. K. *J. Polym. Sci., Polym. Chem. Ed.* **1973**, *11*, 587-610.
5. Varoqui, R.; Tran, Q.; Pefferkorn, E. *Macromolecules* **1979**, *12*, 831-835.
6. Andrey, V. D.; Micheal, R. *J. Phys. II France* **1995**, *5*, 677-697.
7. Xiao, H.; Tao, R.; Cui, W. *J. Appl. Polym. Sci.* Published online.
8. Dobrynin, A. V.; Colby, R. H.; Rubinstein, M. *J. Polym. Sci. Part B: Polym. Phys.* **2004**, *42*, 3513.
9. Ibraeva, Z. E.; Hahn, M.; Jaeger, W.; Bimendina, L. A.; Kudaibergenov, S. E. *Macromol. Chem. Phys.* **2004**, *205*, 2464-2472.
10. Xu, S.; Cao, L.; Wu, R.; Wang, J. *J. Appl. Polym. Sci.* **2006**, *101*, 1995.
11. Das, M.; Kumacheva, E. *Colloid Polym. Sci.* **2006**, *284*, 1073.
12. Baker, J. P.; Blanch, H. W.; Prausnitz, J. M. *Polymer* **1995**, *36*, 1061.
13. Gui, Z.; Qian, J.; An, Q.; Xu, H.; Zhao, Q. *European Polymer Journal* **2009**, *45*, 1403-1411.
14. Berlinova, I. V.; Dimitrov, I. V.; Kalinova, R. G.; Vladimirov, N. G. *Polymer* **2000**, *41*, 831-837.
15. Armentrout, R. S.; McCormick, C. L. *Macromolecules* **2000**, *33*, 419-424.
16. Zhang, L. M.; Tan, Y. B.; Li, Z. M. *Carbohydr. Polym.* **2001**, *44*, 255-260.
17. Zhang, L. M.; Chen, D. Q. *Macromol. Mater Eng.* **2003**, *288*, 252.
18. Zhang, L. M.; Tan, Y. B.; Li, Z. M. *Colloid Polym. Sci.* **1999**, *277*, 1001-1004.
19. Zhang, J.; Zhang, L. M.; Li, Z. M. *Appl. Polym. Sci.* **2000**, *78*, 537.
20. Bruton, J. R.; McLaurine, H. C. SPE26327, 1993.
21. Peiffer, D. G.; Btunswick, E. *et al.* US 4626285, 1986.
22. Fevola, M. J.; Bridges, J. K.; Kellum, M. G.; Hester, R. D.; McCormick, C. L. *J. Appl. Polym. Sci.* **2004**, *94*, 24-39.
23. Nelly, B.; Andren, L. *Polymer* **1996**, *10*, 2011-2019.
24. Ali, S. A.; Rasheed, A. *Polymer* **1999**, *40*, 6849-6857.
25. Lee, W.-F.; Huang, G.-Y. *Polymer* **1996**, *37*, 4389-4395.
26. Zheng, Z.; Timothy, C.; Sheng, F. C.; Shao, Y. J. *Langmuir* **2006**, *22*, 10072-10077.
27. Kudaibergenov, S. F.; Ciferri, A. *Macromol. Rapid Commun.* **2007**, *28*, 1969-1986.
28. Kudaibergenov, S.; Jaeger, W.; Laschewsky, A. *Advances in Polymer Science* 2006; pp 157-224.
29. Liaw, D.-J.; Huang, C.-C. *Macromol. Chem. Phys.* **2000**, *201*, 1101-1107.
30. Cheng, X. X.; Zhang, X. F.; Liu, J. S.; Xu, T. W. *European Polymer Journal* **2008**, *44*, 918-931.
31. Jia, X.; Zhang, Y. J. *J. Appl. Polym. Sci.* **2010**, *118*, 1152-1159.

32. Ye, L.; Huang, R.; Wu, J.; Hoffmann, H. *Colloid Polym. Sci.* **2004**, *282*, 305-313.
33. Kathmann, E.; White, L.; McCormick, C. *Macromolecules* **1997**, *30*, 5297-5304.
34. Lufrano, F.; Squadrito, G.; Patti, Q.; Passalacqua, E. *J. Appl. Polym. Sci.* **2000**, *77*, 1250.
35. Andrew, B.; Lowe; Charles, L. *Chem. Rev.* **2002**, *102*, 4177-4189.
36. Liaw, D. J.; Huang, C. C. *Macro Chem. Phys.* 2000; in press.
37. Liaw, D. J.; Lee, W. F.; Whung, Y. C.; Lin, M. C. *J. Appl. Polym.*

Sci. **1987**, *37*, 999.
38. Salamone, J. C.; Volksen, W.; Olson, A. P.; Israel, S. C. *Polymer* **1978**, *19*, 1157.
39. Alfrey, T.; Morawetz, H.; Fitzgerald, E. B.; Fuoss, R. M. *J. Am. Chem. Soc.* **1950**, *72*, 1864.
40. Ascoli, F.; BotreÂ, C. *J. Polym. Sci.* **1962**, *62*, S56-S59.
41. Pearson, R. G. *Journal of the American Chemical Society* **1963**, *85*, 3533-3539.