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Low Cationic Proportion Ampholytic Polymer: Synthesis, Solution Properties and Interaction with Anionic Surfactant

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Summary

Novel ampholytic terpolymer of N-vinylformamide (NVF), vinylamine (VAm) and sodium acrylate (NA) with low cationic proportion was obtained by hydrolyzing copolymer of NVF and NA (PNVFNA). Solution properties of the polymer were investigated by methods of turbidity and viscosity experiment. The effect of sodium dodecyl sulfate (SDS) on solution viscosity was also investigated. The results showed that the turbidity curves were bimodal, and pH 3.0 was determined as the isoelectric point (IEP). At high salt concentration, polyampholyte effect was noticeable at IEP in viscosity experiment. Although the proportion of VAm in polyampholyte was lower, the solution properties were influenced markedly in the presence of SDS. At IEP, the viscosity increased more rapidly as salt concentration increased when 10^{-3} mol/L SDS contained in solution. A mechanism of SDS bound to positive sites on the collapsed globule surface was suggested.

Introduction

Polyampholytes carrying anionic and cationic charge groups on the polymer backbone [1] have attracted widespread interest because of complex solution properties and application in various fields of biotechnology [2] and medicine [3]. Ampholytic polymers in dilute solutions typically exhibit unique globule-to-coil transitions with increasing low-molecular-weight electrolyte concentration. Such transitions are accompanied by increases of the hydrodynamic volume and solution viscosity, which is called the antipolyelectrolyte effect or polyampholyte effect [1, 4]. Electrostatic interactions are primary importance for polyampholyte solubility and solution properties. Factors such as charge density, charge asymmetry, charge spacing and distribution, and solution ionic strength are all critical parameters [5].

The pH responsible systems are often called annealed polyampholyte [6], recently, such polyampholytes have caused much attention for application requiring triggerable changed in the solution viscosity [7-10]. Vinyl groups with tertiary amines are commonly used as pH-responsive cationic monomers [11, 12], whereas they can exhibit hydrophobicity at certain pH value. Polyvinylamine (PVAm) is an attractive polymer because of the very high content of primary amine groups. These both are a source of reactive centers and are readily protonated in water, giving a highly cationic polymer [13-15]. PVAm has been synthesized only via indirect routes, which hydrolysis of Poly (N-vinylformamide) (PNVF) is the most convenient method to produce PVAm [16]. However, there were little reports of polyampholytes with vinylamine as cationic units.

In the present paper, low cationic proportion polyampholytes of Poly (N-vinylamine-vinylformaminde -sodium acrylate) (PVAmNVFNA) were obtained from the hydrolization of Poly (N-vinylformamide-sodium acrylate) (PNVFNA) [17]. The structure of the copolymers was characterized by ^{13}C NMR, and the dilute solution properties of polyampholyts were investigated by methods of turbidity and viscosity experiment. Interactions between Sodium dodecyl sulfate (SDS) and PVAmNVFNA were also studied by viscosity experiment.

Experiment

Materials

Acrylic acid was purified by distillation. 2, 2'-Azobis (N, N'-dimethylene-isobutyramidine) dihydrochloride (VA-044) (Wako Chemicals Inc.) and NVF (98%)(Aldrich) were used as received. Sodium dodecyl sulfate (SDS) was recrystallized from ethanol twice. All other reagents were analytical grade, and without further purification to use.

Synthesis

The copolymers of PNVFNA were prepared in an aqueous solution at 45°C using 0.1 mol % VA-044 as the initiator. The total monomer concentration was held constant at 10 wt% in each reaction. After a designated time, the resulting polymer solution was precipitated into acetone. The polymers were further purified by reprecipitation into acetone followed by drying in the oven.

Hydrolysis

The PNVFNA precursor copolymers were subjected to alkali hydrolysis maintained solution pH > 12 at 80°C for 24h. The hydrolysate was neutralized to pH 7~8, discharged to dialysis tubing (Mn cut-off=8000~15000 g/mol) and dialyzed for 1 week, with the dialysis water being changed every 24h. The purified copolymers were isolated from water via lyophilization.

NMR Experiment

The sample for NMR spectroscopy analysis was dissolved in D_2O. ^{13}C NMR spectra were obtained at Bruke AV 600MHz NMR spectroscopy. For the quantitative determination of the polymer composition, a gated decoupled pulse sequence with a 6.70 s relaxation delay was used to suppress nuclear Overhauser effect.

Size Exclusion Chromatography Experiment

Aqueous size exclusion chromatography (SEC) 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 analysis was conducted at 30°C. Poly (sodium acrylate) standards (Mp 900~1100000 g/mol) were used with a mobile phase of 0.1M $NaNO_3$ aqueous solution for PNVFNA and 0.2M Na_2SO_4 (5mM sodium phosphate buffer, pH 7.5) aqueous solution for PVAmNVFNA at a flow rate of 0.5 mL/min.

Turbidity

The pH value of polymer solution was adjusted by 0.1 mol/L NaOH aqueous solution and hydrochloric acid. Turbidity measurements were carried out at 280nm, using Lambda 900 UV/VIS/NIR Spectrometer (PerkinElmer Instruments), at ambient temperature.

Viscometry

Reduced viscosity was made at 25 ± 0.1°C with an Ubbelohde dilution-type viscometer, and all the flow time was above 100s.

Results and Discussion

Synthesis and Characterization

The copolymer of NVF and NA was synthesized firstly using water-soluble VA-044 as initiator, and then hydrolyzed to form low cationic proportion polyampholyte. The structure of PNVFNA was characterized by ^{13}C NMR (shown in Figure 1), and the composition of copolymers was calculated from the integral area of the chemical shift at 183.61 ppm (**C**OO$^-$), 166.37 ppm and 163.15 ppm (**C**HO). The molecular weight and polydispersity (PDI) of copolymers were determined by aqueous SEC, and the results were listed in Table 1. As shown in Table 1, the composition in copolymers is similar to that of in feed and low cationic proportion polyampholyte ($PVAm_9NVF_{25}NA_{66}$) is successfully synthesized.

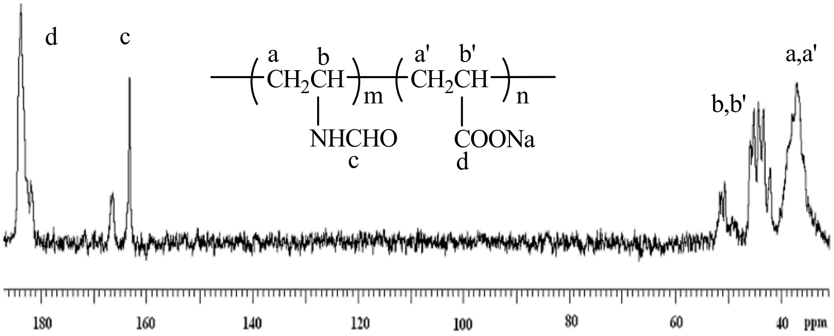


Fig.1. Representative inverse gated decouple ^{13}C NMR spectrum of $PNVF_{34}NA_{66}$ in D_2O.

Table 1. Monomer feed ratios and copolymer compositions for PNVFNA and PVAmNVFNA.

	NVF (in feed, mol %)	*NVF (in polymer, mol %)*	*VAm (in polymer, mol %)*	*Mw (10^{-5})*	*PDI*
$PNVF_{34}NA_{66}$	40	34.4	0	5.4	4.87
$PVAm_{9}NVF_{25}NA_{66}$	-	25.0	9.4	4.9	3.03
$PNVF_{72}NA_{28}$	80	71.8	0	5.3	4.07
$PVAm_{41}NVF_{31}NA_{28}$	-	30.6	41.2	4.4	-

Turbidity titration

Figure 2 shows the relationship between the polymer concentration and the amount of salt with polymer solution and turbidity. At the isoelectric point (IEP), the polyampholyte solution is expected to show maximal turbidity. However, the shape of each curve exhibits two maxima and one minimum, and pH 3.0 is considered as IEP of $PVAm_{9}NVF_{25}NA_{66}$. The similar phenomenon was also observed by C. S. Patrickios [18]. A possible explanation provided by them: as the excess charge is very small, the electrostatic repulsion is too weak to inhibit aggregation but sufficient to increase the spacing of the components of an aggregate compared with the isoelectric point. As seen in Figure 2, turbidity is increased with increase of salt and polymer concentration, but the IEP is not shifted. The turbidity experiment couldn't carry out at higher polymer concentration (> 0.05 g/L) because the precipitation took place immediately around the IEP. The 0.02 g/L polymer solution could stabilize several hours at IEP, thus the concentration was selected to investigate the effect of salt concentration on the turbidity as well as viscosity experiments except specially mentioned.

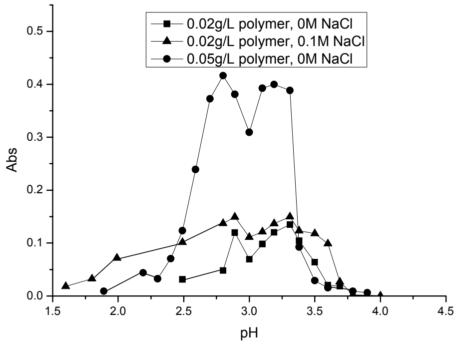


Fig.2. Effect of salt and polymer concentration on turbidity curves of $PVAm_{9}NVF_{25}NA_{66}$.

Viscosity analysis of polyampholyte solution

Figure 3 shows the effect of salt concentration on reduced viscosity as a function of solution pH of $PVAm_{9}NVF_{25}NA_{66}$. The reduced viscosity shows an unconspicuous lowest point around pH 3.0, and increases rapidly as pH > 3.0 in the absence of salt. When pH is lower than 3.0, the polymer carries positive charge, and the reduced viscosity is little changed because of VAm fully protonized under pH 3.0. In contrast, the polymers take negative charge above IEP; the polymer chain expansion due to electrostatic repulsion and cause the reduced viscosity to increase.

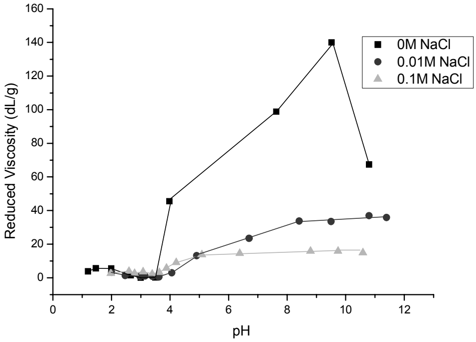


Fig.3. Effect of salt concentration on reduced viscosity as a function of solution pH of PVAm$_9$NVF$_{25}$NA$_{66}$, C$_{polymer}$= 0.02 g/L.

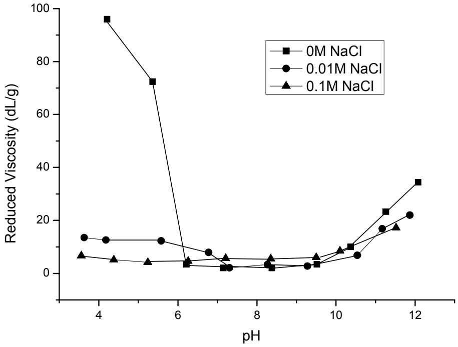


Fig.4. Effect of salt concentration on reduced viscosity as a function of solution pH of PVAm$_{41}$NVF$_{31}$NA$_{28}$, C$_{polymer}$= 0.02 g/L.

In Figure 3, the viscosity decreases as salt concentration increases when pH >3.0, which is attributed to polyelectrolyte effect. As mentioned by C.L. McCormick [1], the IEP represents the pH at which the polyampholyte is electrically neutral and also at this point the copolymer is in its most compact conformation as reflected by the minimum in reduced viscosity. Figure 4 shows effect of salt concentration on reduced viscosity verse solution pH of PVAm$_{41}$NVF$_{31}$NA$_{28}$. The minimum viscosity exhibits about at pH 8.5, and so the IEP of PVAm$_{41}$NVF$_{31}$NA$_{28}$ is considered as pH 8.5. Compared PVAm$_{41}$NVF$_{31}$NA$_{28}$ (shown in Figure 4) with PVAm$_9$NVF$_{25}$NA$_{66}$, polyelectrolyte effect is also evident above or below IEP, and at IEP the reduced viscosity increases along with salt concentration increase, meaning that polyampholyte effect is also visible. Michael J. Fevola et al. [12] had stated that the magnitude of coil expansion (as implied from the viscosity increase) became greater with increasing ionic comonomer content because of greater electrostatic interactions at higher charge densities. At pH 3.0, 9.4mol % VAm units (pKa 8.4) [20, 21] are protonized, and 9.2mol % NA (pKa 4.75) units exists [22]. Therefore, for PVAm$_9$NVF$_{25}$NA$_{66}$, one of reason for unnoticeable viscosity increase is low ionic proportion at IEP. As shown in Figure 5, viscosity increase is small when salt concentration is below 0.1 mol/L, while viscosity increase is obvious at higher salt concentration. Considered this fact, another reason for unconspicuous viscosity increase in Figure 3 is low salt concentration used.

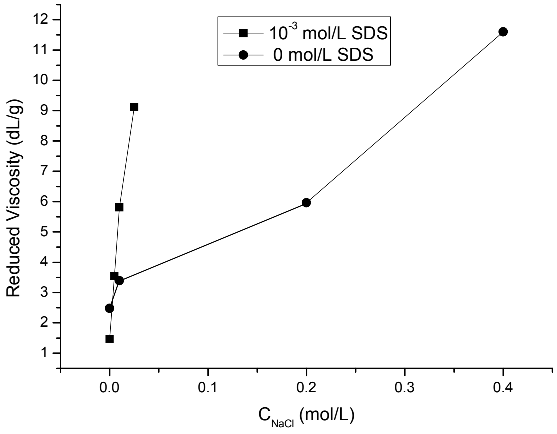


Fig.5. Reduced viscosity as a function of salt concentration at the IEP of $PVAm_9NVF_{25}NA_{66}$ compared without SDS with 10^{-3} mol/L SDS, $C_{polymer}$= 0.02 g/L.

Viscosity analysis of polyampholyte interaction with anionic surfactant (SDS)

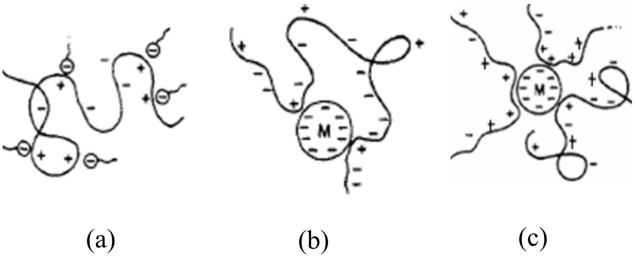
Interactions between polyampholyte and surfactants are also extensively studied due to their applications in industrial and biological processes [23]. The interaction between PVAm and SDS had been studied by S. M. Bystryak [24] and S. Q. Zhou [25], and the results showed that SDS strongly influenced the properties of PVAm. The effect of SDS on low cationic polyampholyte solution viscosity was detected in this section.

Table 2 shows copolymer solution viscosity as a function of SDS concentration at pH 2.5, 3.0 and 5.0. At pH 5.0, the reduced viscosity decreases obviously after adding SDS, from 61.9 to 13.52. The reason is that Na^+ releases from surfactant after SDS binding to positive units, and hence electrostatic repulsion is screened to some extent. In the case of below the critical micelle concentration (CMC) of SDS (8.5 mM), viscosity increases as SDS increases. The charged surfactant binds to polyampholyte chain as shown in Scheme 1 (a), and causes coil expansion because of residual negative charge. However, micelles are formed above the CMC of SDS, and binding intramolecluar micellar as shown in Scheme 1(b) makes polyampholyte coil collapse and the viscosity decrease. J. Greener et al. [26] stated that the “cross-linking” association as shown in Scheme 1(c) contributed port of viscosity increase, whereas it couldn’t explain viscosity increase at pH 2.5 for no micelle formed under low SDS concentration used.

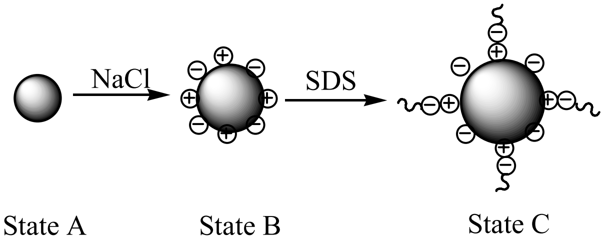
Table 2. Effect of SDS concentration on reduced viscosity at pH 2.5, 3.0 and 5.0 of $PVAm_9NVF_{25}NA_{66}$ in the absence of salt, $C_{polymer}$= 0.02 g/L.

SDS (mol/L)	η_{sp} (dL/g)		
	pH 2.5	pH 3.0	pH 5.0
0	2.51	0.09	61.90
10^{-3}	2.45	1.47	13.52
5×10^{-3}	14.92	14.18	18.99
10^{-2}	17.31	17.04	16.51

Figure 5 also shows viscosity versus NaCl concentration compared without SDS with 10^{-3}mol/L SDS at the IEP of $PVAm_9NVF_{25}NA_{66}$. The reduced viscosity increases with increasing salt concentration in spite of adding SDS, however, the magnitude of the slopes which indicates the extent of conformational change induced by the addition of electrolytes [27] is great difference. At higher salt concentration without SDS, reduced viscosity increases distinctly, indicating classic polyampholyte behaviour. Reduced viscosity increases more rapidly when SDS is added, and that can be explain as shown in Scheme 2. At IEP, ampholytic polymers in dilution solution typically exhibit coil-to-globule transition (State A) because of electrostatic attraction. Added electrolytes, charge attractions between the ionic sites are shielded, leading to the increase of hydrodynamic volume because the polymer coil assumes a more extended conformation (State B). With the addition of SDS, SDS binds to the positive sites of the globule surface, and causes more extended chain conformation for electrostatic repulsion (State C), and hence solution viscosity is increased rapidly. The viscosity increase in Table 2 and Figure 7 at pH 3.0 can be explained by the same way.



Scheme 1. Possible association modes of polyampholyte molecules with negative charged surfactants that cited from ref 24: (a) simple attachment of free surfactant; (b) intramolecular micellar binding; (c) cooperative micellar binding (“cross-linking”).



Scheme 2. Mechanism of coil expansion in the presence of salt and SDS at IEP of polyampholyte. State A represented globule conformation of polyampholyte at IEP. State B illustrated coil expansion caused by polyampholyte effect. State C displayed that added SDS also led to coil expansion.

Figure 6 shows the effect of polymer concentration on viscosity as 10^{-3} mol/L SDS contained in polymer solution. It could find that there is little difference in reduced viscosity in the range of 0.02~0.2 g/L at pH 2.5 and 3.0, indicating no concentration dependence on solution behaviour after adding SDS. At pH 5.0, solution behaviour is more complex. 0.05 g/L polymer concentration gives rise to the maximum viscosity

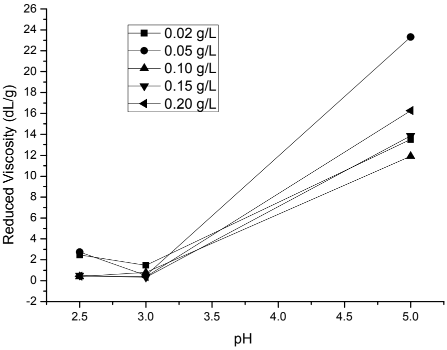


Fig.6. Effect of polymer concentration on reduced viscosity at pH 2.5, 3.0 and 5.0 of $PVAm_9NVF_{25}NA_{66}$ in the absence of salt, $C_{SDS}=10^{-3}$ mol/L.

and 0.10 g/L polymer concentration gives rise to the minimum viscosity. The causation is still not clear.

Figure 7 represents three dimensional (3D) plots of the combined pH- responsive and salt-responsive characteristics of $PVAm_9NVF_{25}NA_{66}$ in the present of 10^{-3} mol/L SDS. With the same amount of salt concentration, viscosity is lowest at pH 3.0. The reduced viscosity decreases when salt concentration increases at pH 5.0, while increases at pH 2.5 and 3.0. At pH 5.0, viscosity decreases because of polyelectrolyte effect. It was surprising that viscosity increased at pH 2.5 where the polymer chain carried positive charge. The possible reason was that the salt shielded part of electrostatic attraction between SDS and positive charged polyampholyte chain, making coil expansion.

It must specially mention that all the solution used was transparent after adding SDS except for a little blue for 0.2 g/L polymer solution with 10^{-3} mol/L SDS at pH 5.0. It also found that there must be a threshold SDS concentration for effective

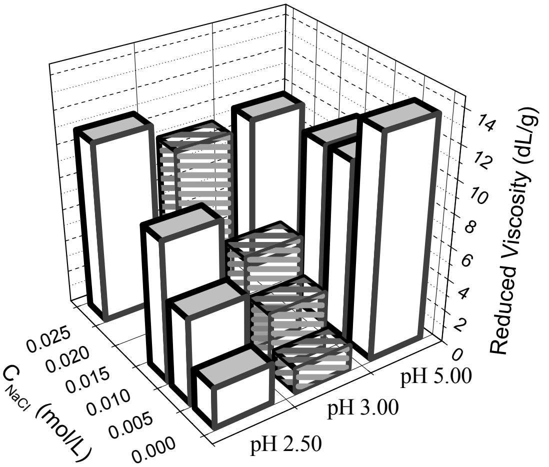


Fig.7. 3D plots of reduced viscosity as functions of salt concentration and solution pH of $PVAm_9NVF_{25}NA_{66}$, $C_{polymer}=0.02$g/L, $C_{SDS}=10^{-3}$ mol/L.

interaction with polymer because 10^{-4} mol/L SDS contained $PVAm_9NVF_{25}NA_{66}$ solution still showed obviously turbidity around IEP. The fact illustrated the interaction between $PVAm_9NVF_{25}NA_{66}$ and SDS.

Conclusions

Low cationic proportion polyampholyte of $PVAm_9NVF_{25}NA_{66}$ was successfully synthesized, and the solution properties were investigated by methods of turbidity and viscosity. The IEP (pH 3.0) of $PVAm_9NVF_{25}NA_{66}$ was determined by turbidity experiment. Because of low ionic proportion of polyampholyte at pH 3.0, polyampholyte effect was indistinct. At high salt concentration, reduced viscosity increased in evidence as salt concentration increased, indicating classic polyampholyte behaviour. The interactions between $PVAm_9NVF_{25}NA_{66}$ and SDS were complex. It found viscosity increased more rapidly as salt concentration increased at IEP even though low SDS concentration used. That was owed to the electrostatic attraction between negative charged SDS and positive sites on the polyampholyte globule surface.

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