

Polyelectrolyte Complexes Formed by Hyperbranched Poly(sulfone-amine) Hydrochlorate and Poly(sodium acrylate)

Li Zhou,¹ Liangyu Yan,¹ Jie Xue,¹ Liang Chen,¹ Yanping Wang,¹ Zhifeng Jia,² Xinyuan Zhu,^{1,2} Deyue Yan¹

¹School of Chemistry and Chemical Technology, State Key Laboratory of Metal Matrix Composites, Shanghai Jiao Tong University, 800 Dongchuan Road, Shanghai 200240, People's Republic of China

²Instrumental Analysis Center, Shanghai Jiao Tong University, 1954 Huashan Road, Shanghai 200030, People's Republic of China

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ABSTRACT: A new type of polyelectrolyte complexes formed by hyperbranched poly(sulfone-amine) hydrochlorate and poly(sodium acrylate) has been reported. It has been found that the stoichiometry between polycation and polyanion is 1.16, which means that hyperbranched polyelectrolyte can also form the compact complexes in spite of the ill-defined structure. Moreover, the effect of various pa-

rameters, such as the architecture of poly(sulfone-amine), molecular weight of polymer, concentration and low molecular salt, on the complexation is also discussed. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 2323–2329, 2007

Key words: hyperbranched polymer; polyelectrolytes; water-soluble polymers; complexes; stoichiometry

INTRODUCTION

It is well known that the interaction between two oppositely charged polyelectrolytes in aqueous solution results in the formation of a polyelectrolyte complex (PEC).^{1–4} Such polyelectrolyte complexes formed by polyelectrolyte pairs have been extensively studied for many years because of the potentially attractive applications in industry, such as flocculants, binders, drug delivery, etc.⁵

Starting with the systematic research promoted by Michaels,^{6,7} most investigations on polyelectrolyte complexes were focused on the linear polyelectrolytes.^{8,9} Recently, the complexation behavior of dendrimer with linear counterpart has attracted much attention.^{10–16} It has been found that the dendritic polyelectrolyte with perfectly topological structure can be fully penetrable for rather flexible oppositely charged linear polymer to form the stoichiometric complex, but this is not the case for rigid oppositely charged polyelectrolyte, which binds only to the dendrimer shell.^{10–11} Different from the dendrimer,

the hyperbranched polymer has an ill-defined structure. It can be synthesized by one-pot strategy, thus it is more competitive in practical applications than the dendrimer. However, up to date, only a few reports concern the complexation of hyperbranched polyelectrolyte.^{17–19} It is thought that due to the irregularly highly branched structure, the hyperbranched polyelectrolyte can only form the nonstoichiometric complexes.^{17–19}

In the present work, we studied the complexation behavior of hyperbranched poly(sulfone-amine) hydrochlorate with a flexible linear poly(sodium acrylate) in aqueous solution. To our surprise, the experimental results indicate that the hyperbranched polyelectrolyte can form the stoichiometric complexes in spite of the ill-defined structure. Moreover, the effect of various parameters, such as the architecture of poly(sulfone-amine), molecular weight of polymer, concentration and low molecular salt, on the complexation is also discussed.

EXPERIMENTAL

Materials

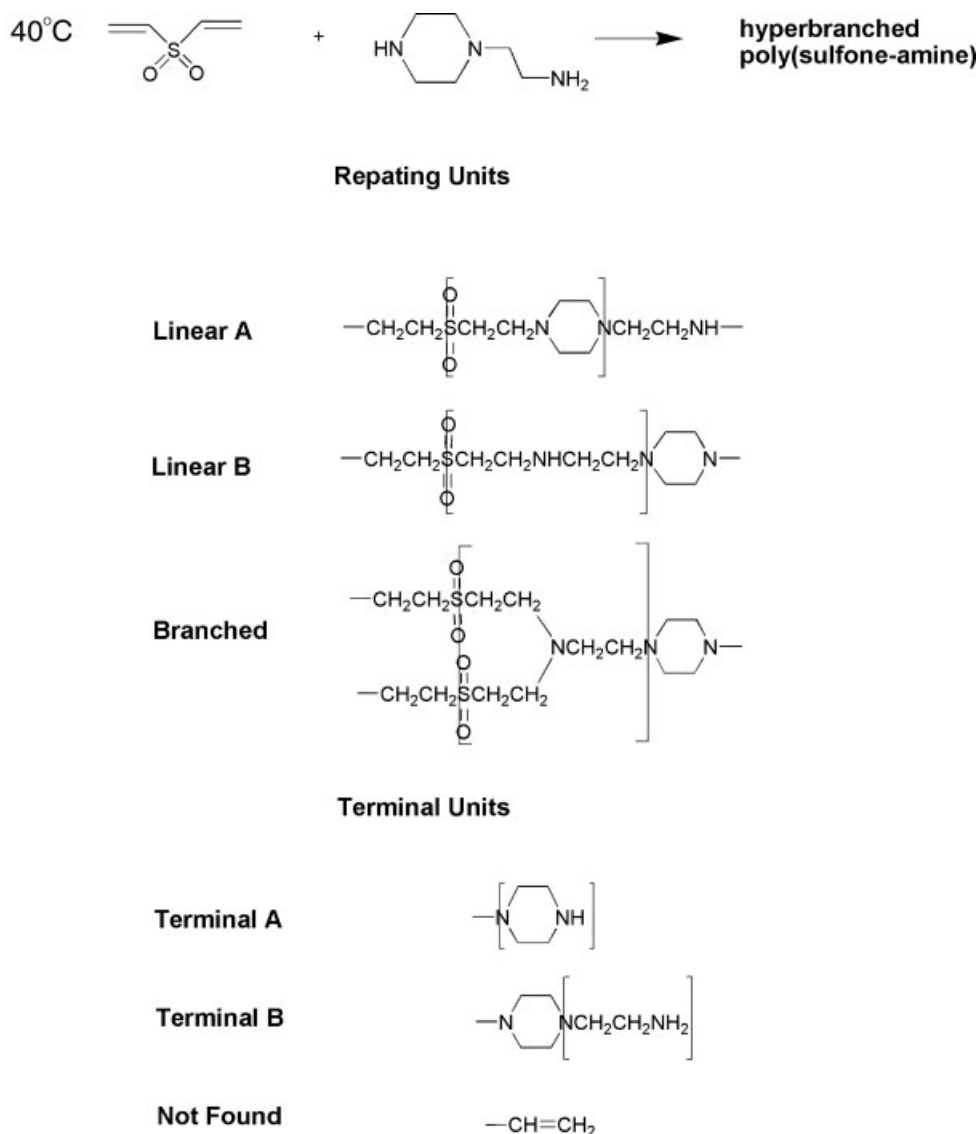
Poly(acrylic acid) I (PAA-I, $M_w = 1000$) was purchased from Tianjin Kernel Chemical Reagent Development Center, China. Poly(acrylic acid) II (PAA-II, $M_w = 100,000$), 1-(2-aminoethyl)piperazine (AP), divinyl sulfone (DV) were purchased from Aldrich Chem. Corp. Inc., and used without further purifica-

Correspondence to: X. Zhu (xyzhu@sjtu.edu.cn).

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Scheme 1 The molecular structure of hyperbranched poly(sulfone-amine).^{21,22}

tion. Poly(sodium acrylate) (NaPA-I or NaPA-II) aqueous solution was prepared by neutralization of PAA-I or PAA-II solution in distilled water with the equivalent amount of NaOH. NaCl, KCl, NH_4Cl , NaNO_3 , Na_2SO_4 , and NaOH are A. P. grade and used as received.

Synthesis and characterization of hyperbranched poly(sulfone-amine) hydrochlorate²⁰⁻²²

Mixtures of 2.433 g (20 mmol) of DV, 2.606 g (20 mmol) of AP, and 15 mL of water were reacted at 40°C with stirring for 120 h under nitrogen, and then the reaction product was poured into the mixture solution containing 500 mL of methanol and 10 mL of HCl (8M). The precipitate was collected by filtration and dried under vacuum at 80°C , and the hyperbranched

poly(sulfone-amine) hydrochlorate (HPSA-HCl) was obtained. $M_n = 33,850$, $M_w/M_n = 1.32$. The molecular structure of hyperbranched poly(sulfone-amine) is represented in Scheme 1. Ratio and molar mass for various structure units of poly(sulfone-amine) are shown in Table I.

Synthesis and characterization of linear poly(sulfone-amine) hydrochlorate²³

Linear poly(sulfone-amine) hydrochlorate (LPSA-HCl) was prepared as follows, using the report by Pan et al.²³: 0.243 g (2 mmol) of DV was added into a solution of 0.261 g (2 mmol) of AP in 9 mL of chloroform. The reaction was carried out at -15°C for 7 days under stirring, and then the reaction mixture was concentrated under a reduced pressure, fol-

TABLE I
Ratio and Molar Mass for Various Structure Units of Poly(sulfone-amine)^{21,22}

	Ratio	M
Linear A	0.47	137
Linear B	0.12	110
Branched	0.23	169
Terminal A	0.06	78
Terminal B	0.12	51
Degree of Branching	0.41	

lowed by precipitation into the mixture solution containing 300 mL cold petroleum ether and 1 mL of HCl (8M). The polymer was obtained by filtration and dried under vacuum at 40 °C. $M_n = 37,698$, $M_w/M_n = 1.24$. The absence of ¹³C-NMR signals corresponding to branched units confirms Pan's observation²³ that only the linear poly(sulfone-amine) forms at low reaction temperature.^{21,22} The molecular structure of linear poly(sulfone-amine) is represented in Scheme 2.

Measurements

Turbidimetric measurements were carried out with the help of the spectrophotometer "722" (China) at wavelength $\lambda = 500$ nm at room temperature. The pH of the solutions was adjusted with 0.1M NaOH, and the pH value was determined using a PHS-2C pH-meter. Dynamic light scattering (DLS) measurements were performed in aqueous solution using a Malvern Zetasizer 3000HS apparatus (Malvern Instruments, UK) equipped with a 125 mW laser operating at $\lambda = 633$ nm. All the DLS were measured at room temperature and at a scattering angle of 90°.

RESULTS AND DISCUSSION

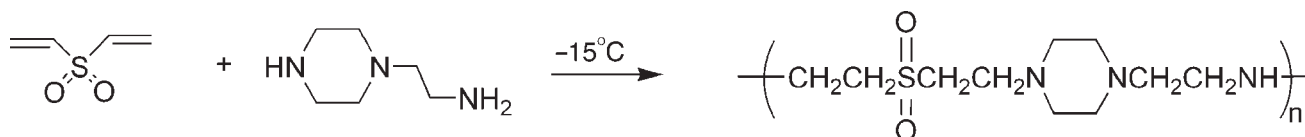
It has been well realized that if no specific interactions exist between two kinds of different polymers, the random coils of component polymers isolate from each other in dilute solution.²⁴ On the other hand, when polymer-polymer interacts with each other in solution, the hydrodynamic volume of polymer chains can be changed. Especially, in the pres-

ence of strong attractive interaction between polymer pair, such as the electrostatic interaction or hydrogen bonding, the contraction or collapse of the component polymer coils results in the phase separation. In the meantime, the solution becomes turbid. Therefore, turbidimetric measurement has become a simple and effective technique for monitoring the complexation of polymer blend solutions.

Figure 1 gives the variation of the transmittance of HPSA-HCl/NaPA-I aqueous solution versus the content of NaPA-I. It can be found that the transmittance decreases greatly with the addition of NaPA-I into HPSA-HCl aqueous solution. Apparently, the electrostatic attraction results in the formation of water-insoluble polyelectrolyte complexes. After NaPA-I reaches 40 wt %, the transmittance of the blend solution begins to increase with NaPA-I content. It can be inferred that the excess of NaPA-I makes the complexes more and more hydrophilic. Finally, when the content of NaPA-I exceeds 50 wt %, the polyelectrolyte complexes become soluble so that the transmittance keeps unchanged.

The formation of HPSA-HCl/NaPA-I complexes can be further confirmed by DLS experiments. Because of the cooperatively electrostatic attraction, the mutual screening of hydrophilic parts of the interacting macromolecules leads to strong hydrophobization of the resultant complexes in aqueous solution. The polymer complexes coil up into a compact structure, and then the water-insoluble particles are formed. The variation of particle size with NaPA-I content is shown in Figure 2. Without NaPA-I component, the HPSA-HCl aqueous solution is homogeneous, so no particle exists in the system. When NaPA-I content arrives at 10 wt %, the water-insoluble particles appear because of the strong electrostatic complexation. With increasing NaPA-I content from 10 to 40 wt %, the particle size of electrostatic complexes changes from 110 to 580 nm. However, further increasing NaPA-I content decreases the particle size. As soon as NaPA-I content is higher than 50 wt %, a transparent and homogeneous solution is obtained, and DLS experiments show the compact particles no longer exist in the system.

Both turbidimetric measurements and DLS experiments show that the most compact structure is formed at the 3 : 2 mass ratio of HPSA-HCl to NaPA-I. Therefore, the stoichiometry of HPSA-HCl/NaPA-I



Scheme 2 The molecular structure of linear poly(sulfone-amine).²³

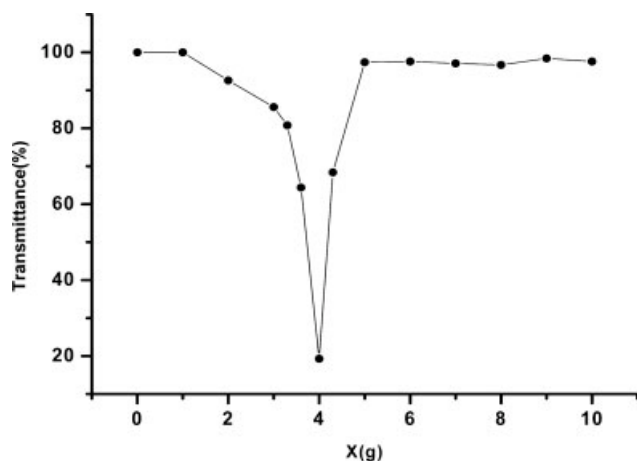


Figure 1 Transmittance of the blend solution versus mixing composition during the formation of polyelectrolyte complexes (X g 0.3 g/L NaPA-I + $(10 - X)$ g 0.3 g/L HPSA-HCl = 10 g).

complexes can be calculated. According to Scheme 1 and Table I, the average molecular weight of repeat unit of the hyperbranched poly(sulfone-amine) is

$$0.47 \times 137 + 0.12 \times 110 + 0.23 \times 169 + 0.06 \times 78 + 0.12 \times 51 = 127.26 \quad (1)$$

Because there are one and a half of nitrogen atoms in each repeat unit of HPSA, the correspondent molecular weight of repeat unit of the hyperbranched poly(sulfone-amine) hydrochlorate is

$$127.26 + 1.5 \times 36.5(\text{HCl}) = 182 \quad (2)$$

Considering the molecular weight of repeat unit of NaPA-I is 94, the stoichiometry of the polycation to polyanion for HPSA-HCl/NaPA-I complexes is

$[\text{NH}_4^+]/[\text{COO}^-] = [1.5 \times (3/182)]/(2/94) = 1.16$

Generally speaking, it has been observed that hyperbranched polymers readily form the loose complexes due to the irregularly hyperbranched structure. Different from the previous observations, our experimental results show that the irregularly hyperbranched HPSA-HCl can also form compact polyelectrolyte complexes with the linear NaPA-I.

The relationship between structure and properties of polyelectrolyte complexes can be adjusted in a large range by varying composition, temperature, concentration, molecular weight of polymer, low molecular salt, the nature of solvent, and so on.¹⁻⁴ In the present work, we reported the influence of the architecture of poly(sulfone-amine), molecular weight of PAA, polymer concentration, and low molecular salt on the complexation behaviors.

Firstly, the influence of branched structure of poly(sulfone-amine) on the complexation is discussed. Both hyperbranched and linear PSA-HCl were synthesized, and then complexed with linear NaPA-I respectively. 50 mL solutions containing the mixture of 30 mL 0.3 g/L HPSA-HCl or LPSA-HCl with 20 mL 0.3 g/L PAA-I were titrated with 0.1M NaOH solution. The turbid titration curves of PAA-I with HPSA-HCl and LPSA-HCl are plotted in Figure 3. It can be seen that for both HPSA-HCl and LPSA-HCl, the shape of titration curves are quite similar to each other and the minimum transmittance occurs at about pH = 5. This experimental result indicates that the branched structure of poly(sulfone-amine) has only a little influence on the complexation behavior because linear polyamine can form the com-

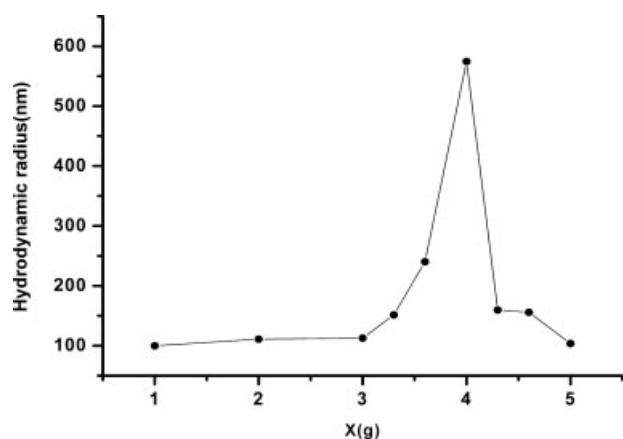


Figure 2 Hydrodynamic radius of the blend solution versus mixing composition during the formation of polyelectrolyte complexes (X g 0.3 g/L NaPA-I + $(10 - X)$ g 0.3 g/L HPSA-HCl = 10 g).

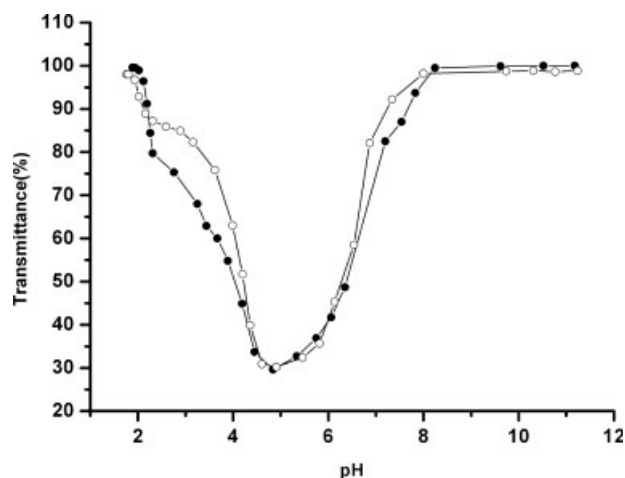


Figure 3 Effect of the branched structure of poly(sulfone-amine) on the formation of polyelectrolyte complexes: (O) HPSA-HCl/NaPA-I, (●) LPSA-HCl/NaPA-I.

compact complex with poly(acrylic acid) very easily.^{1,2,4,8,9} Figure 3 supports the earlier-mentioned conclusion that HPSA-HCl can form the stoichiometric complex with NaPA regardless of the irregularly hyperbranched structure.

Distinct from the small molecular complexes, the strong cooperative interactions exist in the polymer complexes. Therefore, the polyelectrolyte complexes can be formed only above a critical molecular weight, and the cooperative interactions are strengthened by increasing the molecular weight of polymers.^{2,4} Here, two kinds of NaPA with different molecular weights have been used to complex with HPSA-HCl, and 50 mL solutions containing the mixture of 30 mL 0.3 g/L HPSA-HCl with 20 mL 0.3 g/L PAA-I or PAA-II were titrated with 0.1M NaOH solution. During the titration, the obvious phase separation happens and the white polyelectrolyte complexes precipitate from the solution for PAA-II system. However, for PAA-I, there is no any precipitate although the solution also becomes turbid. So, it can be concluded that the higher molecular weight of NaPA strengthens the cooperative interactions between polycation and polyanion, which favors the formation of polyelectrolyte complexes.

In the aqueous solution, the complexation between HPSA-HCl and NaPA-I occurs only in a certain range of pH value. It has been pointed out that the pH range for water-insoluble complexes can be considered as criteria for the ability to form polyelectrolyte complexes.^{25,26} The wider the pH range is, the higher the ability to form complexes is. Figure 4 shows the dependence of solution turbidity of the HPSA-HCl/PAA-I mixtures on pH at different polymer concentrations, and the corresponding critical pH values and the pH ranges for the formation of water-insoluble polyelectrolyte complexes are shown

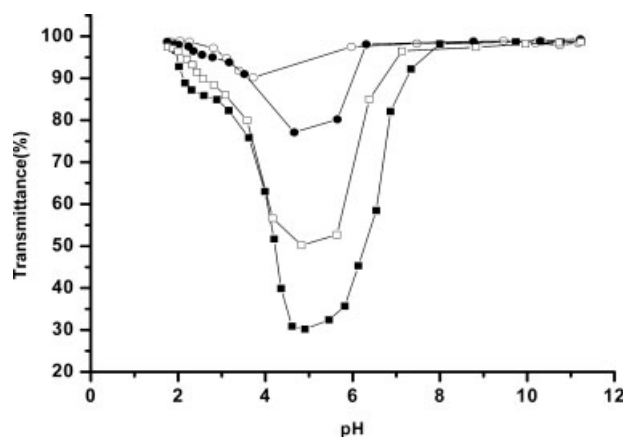


Figure 4 Effect of the concentration on the formation of HPSA-HCl/NaPA-I polyelectrolyte complexes: [HPSA-HCl] = [PAA-I] = 0.3 g/L (■), 0.15 g/L (□), 0.075 g/L (●), 0.03 g/L (○).

TABLE II
Critical pH Values and pH Ranges for the Formation of Insoluble Polyelectrolyte Complexes between HPSA-HCl and NaPA-I

Concentration (g/L)	pH (High critical)	pH (Low critical)	pH range (For insoluble PEC)
0.3	8.04	1.75	6.29
0.15	7.18	1.87	5.31
0.075	6.27	2.04	4.23
0.03	5.98	2.25	3.73

in Table II. It can be seen that the pH range for water-insoluble complexes becomes wider and wider with the increase of polymer concentrations. It indicates that the interpolyelectrolyte complexes are easily formed at a higher polymer concentration.

The influence of low molecular salt additives on the complexation behaviors has also been studied. Figure 5 gives the relationship of solution turbidity with NaCl content. Adding NaCl into 50 mL solutions containing the mixture of 30 mL 0.3 g/L HPSA-HCl with 20 mL 0.3 g/L PAA-I, the transmittance decreases because of the deterioration of solvent quality. However, as soon as the concentration of NaCl is higher than 0.2 mol/L, the transmittance starts increasing. Apparently, owing to the electrostatic attraction, the counterions are concentrated around the polycation or polyanion, which leads to the destruction of polyelectrolyte complexes. Consequently, the addition of salt into polyelectrolyte complex solution induces the competition between the salting-out effect and the screening effect: When the amount of salt is low, the salting-out effect is much stronger than the screening effect. On the contrary, provided that a lot of salt is added, the latter effect dominates the former.

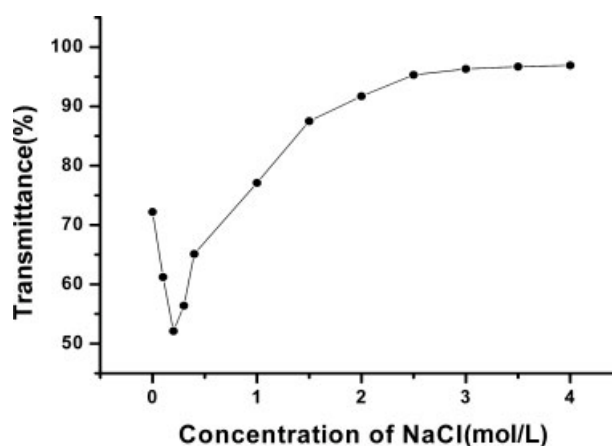


Figure 5 Effect of NaCl on the formation of HPSA-HCl/NaPA-I polyelectrolyte complexes.

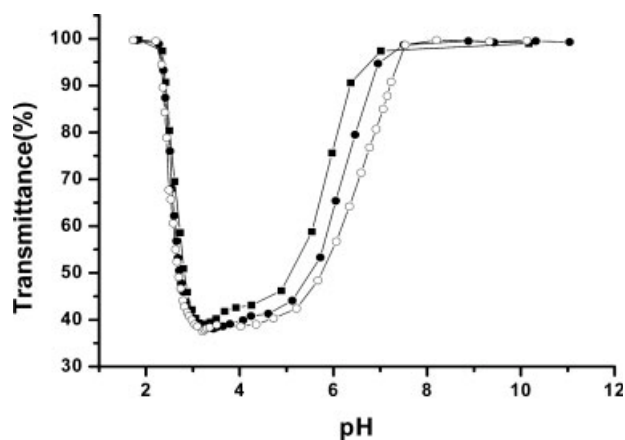


Figure 6 Effect of the radius of cations of low molecular salts on the formation of HPSA-HCl/NaPA-I polyelectrolyte complexes: (■) 0.1 mol/L NaCl, (●) 0.1 mol/L KCl, (○) 0.1 mol/L NH_4Cl .

Adding NaCl, KCl, and NH_4Cl into 50 mL aqueous solutions containing the mixture of 30 mL 0.3 g/L HPSA-HCl with 20 mL 0.3 g/L PAA-I, the titration curves will be changed. Figure 6 gives the influence of the radius of cations on complexation. When pH is <3 , all titration curves overlap together, indicating no effect of cations on the complexation. As at pH >3 , the salting-out effect is strengthened by increasing the radius of cations, which facilitates the complex formation.

On the other hand, the influence of the anion radius on the complexation has also been investigated. The transmittance curves of HPSA-HCl/NaPA-I solution in the presence of NaCl or NaNO_3 are presented in Figure 7 by adding NaCl or NaNO_3 into 50 mL solutions containing the mixture of 30 mL 0.3

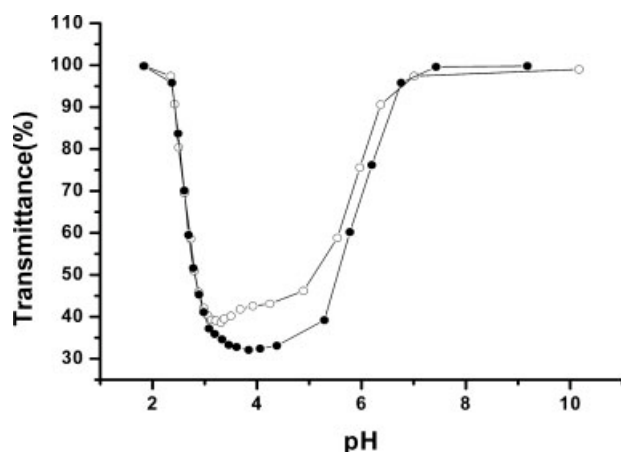


Figure 7 Effect of the radius of anions of low molecular salts on the formation of HPSA-HCl/NaPA-I polyelectrolyte complexes: (○) 0.1 mol/L NaCl, (●) 0.1 mol/L NaNO_3 .

g/L HPSA-HCl with 20 mL 0.3 g/L PAA-I. Similar to Figure 6, different kinds of anions have almost no effect on the complexation behavior as pH <3 , while increasing the radius of anions strengthens the complexation ability as pH >3 because of the strong salting-out effect.

Finally, the effect of valence of anions of low molecular salts on the formation of polyelectrolyte complexes is discussed. The titration curves are recorded by adding NaCl or Na_2SO_4 into 50 mL solutions containing the mixture of 30 mL 0.3 g/L HPSA-HCl with 20 mL 0.3 g/L PAA-I. Figure 8 gives the variation of transmittance versus pH values in NaCl or Na_2SO_4 solutions. It can be found that although the amount of sulfate anion is only half of chloride anions, the complexation ability in Na_2SO_4 aqueous solution is much stronger than that in NaCl solution. It means that the enhancement of anion valence facilitates the formation of polyelectrolyte complexes because the solvent quality deteriorates by increasing the ion valence of salt.

CONCLUSIONS

The complexation behavior between hyperbranched poly(sulfone-amine) hydrochlorate (HPSA-HCl) and poly(sodium acrylate) (NaPA) in aqueous solution has been studied. Different from the previous observations, our experimental results show that the ill-defined HPSA-HCl can form stoichiometric polyelectrolyte complexes with the linear NaPA. Interestingly, it is found that the branched structure of poly(sulfone-amine) has only a little influence on the complexation behavior. With the increase of the molecular weight of NaPA, the cooperative interactions between polycation and polyanion are strengthened,

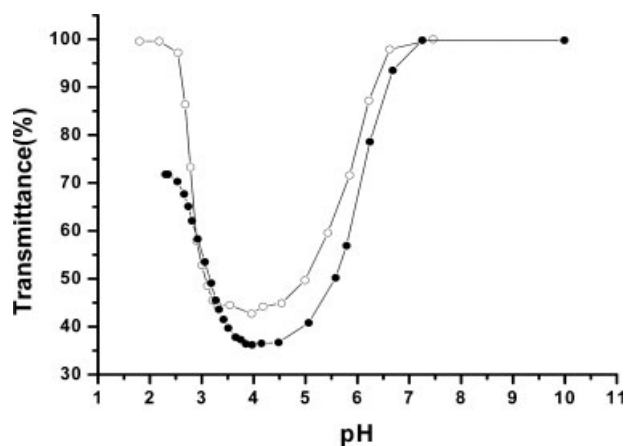


Figure 8 Effect of the valence of anions of low molecular salts on the formation of HPSA-HCl/NaPA-I polyelectrolyte complexes: (○) 0.2 mol/L NaCl, (●) 0.1 mol/L Na_2SO_4 .

which favors the formation of polyelectrolyte complexes. At high polymer concentration, the polyelectrolyte complexes can be easily obtained. Adding salts into polyelectrolyte complex solution, a competition exists between the salting-out effect and the screening effect. When the amount of salts is low, the salting-out effect is dominant. On the contrary, the screening effect is much strong at high salt concentration. Moreover, all kinds of salts have the same influence on the complexation behavior when pH is below 3. However, increasing the radius of both cations and anions facilitates the complex formation as $\text{pH} > 3$. Addition of high valence of anions in aqueous solution is favorable for the electrostatic attraction between oppositely charged polyelectrolytes.

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