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FORMATION OF POLYELECTROLYTE COMPLEXES BASED ON PENDANT-TYPE IMIDAZOLINIUM ORGANOSILICON POLYMER WITH POLY(SODIUM ACRYLATE)

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ABSTRACT

Three species of pendant-type imidazolinium organosilicon copolymers were synthesized by β-(*N*-ethyl-2-imidazolinium bromide)ethyl methyl diethoxy silane with dimethyl silandiol and diphenyl silandiol, respectively, and by β-(*N*-benzyl-2-imidazolinium chloride)ethyl methyl diethoxy silane with dimethyl silandiol. The polyelectrolyte complexes formed by each of them with poly(sodium acrylate) were studied. Measurements of conductometry and turbimetry showed that the formation of polyelectrolyte complexes was governed by the structure of polycations, polyions concentration, ionic strength, solvent, and pH. It was found that the formation of polyelectrolyte complexes decreased with increasing rigidity of the polymer chain, ionic strength, and the quantity of organic solvent but with decreasing dielectric constant of the solvent.

INTRODUCTION

It is well known that intermacromolecular complexes are formed by the mixing of two different macromolecular chains in solution due to secondary binding forces. Intermacromolecular complexes are divided into four classes on the basis of the main interaction forces: polyelectrolyte complexes, hydrogen-bonding complexes, stereocomplexes, and charge-transfer complexes [1]. They possess unique properties which differ from those of the initial components. Their excellent optical, dielectric, physicomechanical, and ion-exchanging properties have attracted great interest for polymer materials which have extensive application in industry, medicine, and other advanced technologies [1-7]. Therefore, intermacromolecular complexes are of considerable importance both in theory and practice.

Investigations of polyelectrolyte complexes (PECs) are more intensive in intermacromolecular complexes and are concerned with the conditions for formation of PECs, composition, stability, and so on [8-11]. However, relatively few studies on PECs of organosilicon polymers have been reported [12]. We have reported on the preparation and characterization of PECs formed by the copolymer of imidazolinium organosilicon-bisphenol A with poly(styrene sulfonate) [13]. In this paper the formation and influence of variables on PECs formed by three species of pendant-type imidazolinium organosilicon polymer (V), (VI), and (VII) with poly(sodium acrylate) are described.

EXPERIMENTAL

Materials

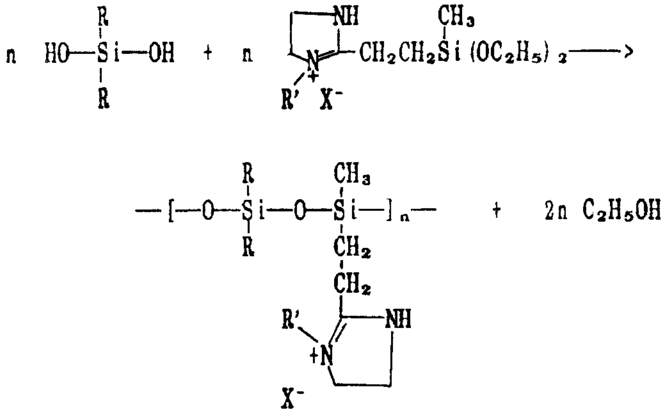
β-(*N*-Ethyl-2-imidazolinium bromide)ethyl methyl diethoxy silane (I) and β-(*N*-benzyl-2-imidazolinium chloride)ethyl methyl diethoxy silane (II) were synthesized as described previously [13]. Dimethyl silandiol (III) was prepared according to the literature and gave white needles, mp 66-67°C [14]. Diphenyl silandiol (IV), C.P. grade, was recrystallized by diethyl ether, mp 133°C.

Polymer Synthesis

Poly(sodium acrylate), a polyanion, was prepared from sodium acrylate using the $(NH_4)_2S_2O_8$-$NaHSO_3$ system as the initiator in aqueous solution. 56.4 g (0.6 mol) sodium acrylate was dissolved in 300 g distilled water, the aqueous solution was adjusted to pH 7.2 with NaOH (aqueous), and an inert gas (N_2) was bubbled through while stirring. The redox initiator, $(NH_4)_2S_2O_8$ (3.5×10^{-3} M) and $NaHSO_3$ (3.5×10^{-3} M), was introduced into the reaction solution. The polymerization was carried out at 25°C for 3 hours. The resulting poly(sodium acrylate) was precipitated by pouring the reaction solution into absolute ethanol. The precipitate was washed and purified by repeated precipitation and drying in vacuo. The degree of neutralization of NaPAA was 99.63% by the potentiometric titration method. Its intrinsic viscosity in 1 M NaCl was 7.12, corresponding to a molecular weight of 2.08×10^4 ($[\eta] = 9.25 \times 10^{-4} M^{0.9}$) [15, 16].

A new series of imidazolinium polysiloxane [(V), (VI), and (VII)] polycations were synthesized by the melting polycondensation of dialkyl(phenyl) silandiol with various quaternary ammonium halides of β-(2-imidazolinyl)ethyl methyl diethoxy silane. The synthetic route for condensation polymers is shown in Scheme 1.

The preparation of condensation polymers was typically carried out as follows: A 100-mL 3-necked round-bottom flask was charged with 9.3 g (0.1 mol) dimethyl silandiol and 33.9 g (0.1 mol) β-(*N*-ethyl-2-imidazolinium bromide)ethyl methyl diethoxy silane. The mixture was stirred and heated at 100°C for 16 hours



V.	$R=CH_3$	$R'=C_2H_5$	$X=Br$
VI.	$R=CH_3$	$R'=C_6H_5CH_2$	$X=Cl$
VII.	$R=C_6H_5$	$R'=C_2H_5$	$X=Br$

SCHEME 1.

under reduced pressure (0.009 kPa), and ethanol was successively distilled. The resulting polymers ranged from viscous liquid to brown gel and were dissolved in 75% ethanol and reprecipitated into absolute ethanol to give a yellowish-brown brittle solid. Elemental analyses and molecular weights of the condensation polymers are summarized in Table 1.

Preparation of Polyelectrolyte Complexes

Diluent solutions of polycation (0.1 M) and polyanion (0.1 M) were made up. A polycation solution was dropped into a polyanion solution for 2 days with stirring. The polyelectrolyte complex precipitate formed was separated by centrifuge, washed, and dried in vacuo.

TABLE 1. Condensed Polymerization of Imidazolinium Organosilicon with Silanediol

Polymer	Halogen, % Calculated	Halogen, % Found	$M_w \times 10^{-3}$ [d]
(V)[a]	23.53	23.69 (Br)	5.97
(VI)[b]	9.94	10.22 (Cl)	5.79
(VII)[c]	17.41	17.31 (Br)	5.98

[a] Copolymer of compound (I) with dimethyl silandiol.
[b] Copolymer of compound (II) with dimethyl silandiol.
[c] Copolymer of compound (I) with diphenyl silandiol.
[d] M_w was measured by GPC.

Measurement

The molecular weight of the condensation polymers was estimated by gel permeation chromatography (GPC) with Linear Ultrahydrogel Columns (Waters Associates) calibrated with PEO standards. The flow rate of the aqueous eluent was maintained at 0.7 mL/min.

The PECs were measured by means of conductometry and turbimetry. Conductivities were measured with platinum-platinum (black) electrodes (DDS-11 type) at 25°C in a high frequency. The concentration of a pair of polyion dilute solutions was 0.01 M, and the supernatant of the mixed solution was measured after 2 days. In addition, the degree of stoichiometry attained was assessed by comparison of the conductivity of the reaction mixture with that of a contrast solution made up to the composition expected for a stoichiometric reaction and complete counterion release (NaBr or NaCl solution). The turbidity of the mixed solutions at various molar ratios was measured after 2 minutes at 20°C using a 72-type photoelectric colorimeter at 590 nm.

RESULTS AND DISCUSSION

The reaction of oppositely charged polyelectrolytes NaPPA and (V) by electrostatic interaction leads to the formation of PEC. The conductivity difference used to estimate the degree of the complexation reaction is observed in Fig. 1 which presents the conductivity of the 0.01 M NaPAA-(V) reaction mixture in a salt-free solution compared with NaBr solution. The conductivity of the reaction systems decreases with an increasing mole fraction of NaPAA. There is an inflection point on the conductivity curve at 0.5 [mol NaPAA/mol NaPAA + (V)], and the con-

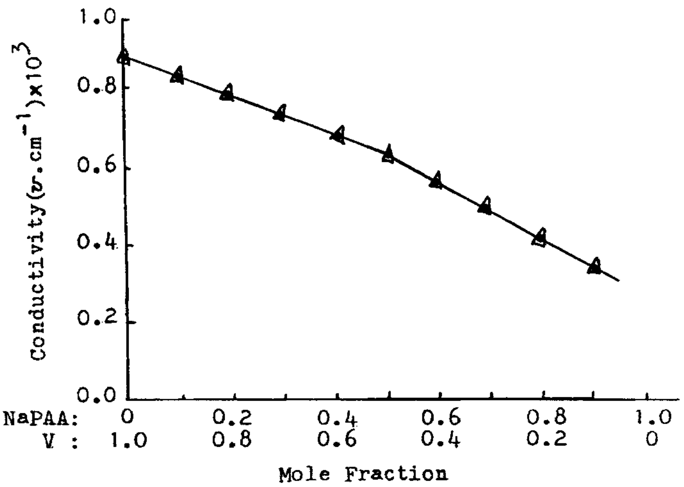


FIG. 1. Conductances of NaPAA-(V) system and contrast solution. 10^{-2} mol/L NaPAA, 10^{-2} mol/L (V); 25°C; pH 7.0. (●) NaPAA-(V) system; (△) contrast solution (NaBr solution).

ductivity curve of formation of PEC completely coincides with that of the NaBr solution. These results indicate that the conductivity of the reaction mixture is proportionally equal to that expected for a stoichiometric reaction (1:1 composition) involving the complete release of the counterions, and that two components were incorporated in a one-to-one equivalence ratio and the ionic function were completely reacted.

Figures 2 and 3 show the conductivity of the NaPAA-(VI) and NaPAA-(VII) reaction systems compared with their contrast solutions (the former was NaCl solution and the latter was NaBr solution). The equivalent conductance of the reaction mixture was less than that of the contrast solution on the side of the equivalence point where NaPAA is present in the smaller amount. It was found that the deviation for the conductivity of the NaPAA-(VII) reaction mixture was more than that for NaPAA-(VI). The results indicate that a certain fraction of ionic groups have not reacted in forming the PEC. These are explained in terms of steric restrictions arising from the more tightly coiled conformation of the polycation. Thus, by comparing three series structures of polycation electrolytes (V), (VI), and (VII), where $R = CH_3$, $R' = C_2H_5$, and $X = Br$ (V), the stoichiometry of the polyanion-polycation complex can be easily obtained due to the more flexible coiled conformation of polysiloxane, whereas replacement of the R' group bound on the N atom of quaternary ammonium halide in the polycation electrolyte by phenyl (VI) and that of the R group on the main chain by phenyl (VII) have more stiffly coiled conformations due to steric hindrance of the giant phenyl group. Because the open, extended conformation of the polycation chain decreases, the electrolytic interaction of approaching ionic groups of the polyions and a fraction of ionic groups inaccessible for reaction will be moderated. On the other side of the equivalence point, complete reaction of all the ionic groups of (VI) or (VII) can be satisfied by

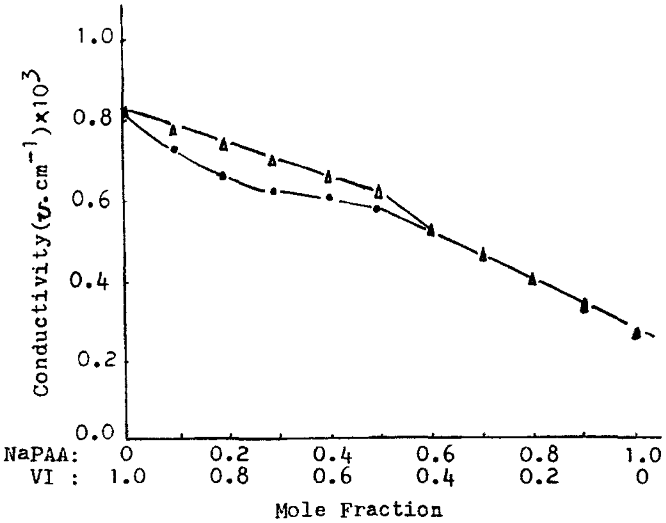


FIG. 2. Conductances of NaPAA-(VI) system and contrast solution. 10^{-2} mol/L NaPAA, 10^{-2} mol/L (VI); 25°C; pH 7.0. (●) NaPAA-(VI) system; (△) contrast solution (NaCl solution).

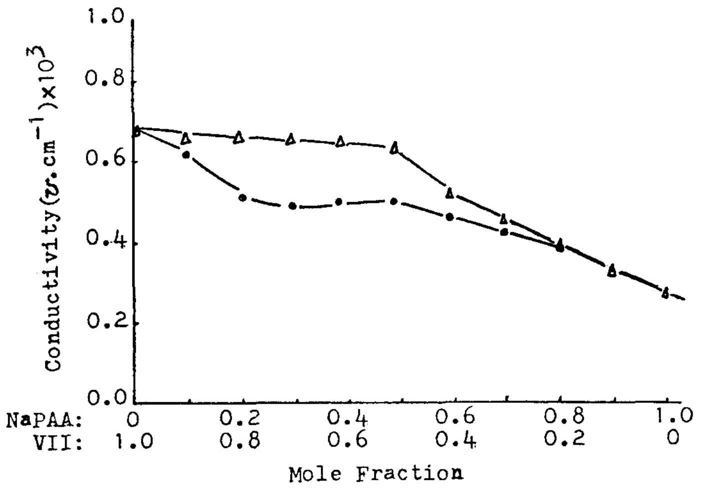


FIG. 3. Conductances of NaPAA-(VII) system and contrast solution. 10^{-2} mol/L NaPAA, 10^{-2} mol/L (VII); 25°C; pH 7.0. (●) NaPAA-(VII) system; (△) contrast solution (NaBr solution).

excess NaPAA when the mole fraction of NaPAA is 0.6 (composition 1.5:1) and 0.8 (composition 4:1) for NaPAA-(VI) and NaPAA-(VII) reaction mixtures, respectively. This suggests that the steric influence of the giant phenyl substituent on the main chain is more effective than that on the pendant group.

The formation of PEC can be also studied by a turbidimetric method. Figure 4 shows the dependence of the turbidity of the NaPAA-(V) reaction mixture on the

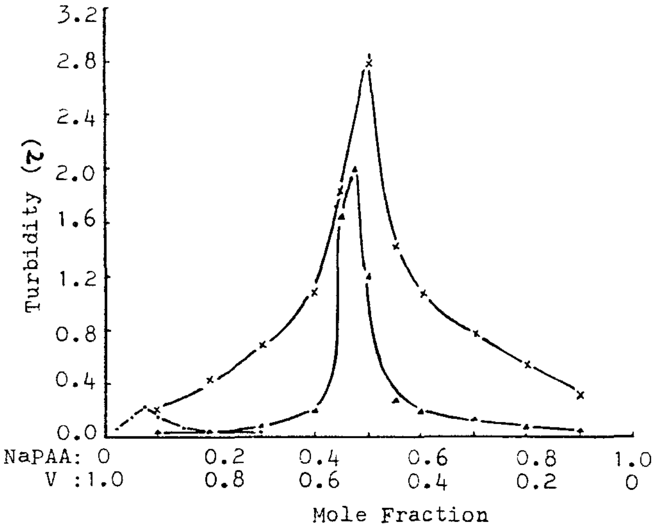


FIG. 4. Effect of NaPAA-(V) system concentration on turbidity. (×) 1 × 10^{-2} mol/L NaPAA, 1 × 10^{-2} mol/L (V); (▲) 0.5 × 10^{-2} mol/L NaPAA, 0.5 × 10^{-2} mol/L (V); (●) 0.3 × 10^{-2} mol/L NaPAA, 0.3 × 10^{-2} mol/L (V); 20°C; pH 7.0.

mole fraction at various concentrations of a pair of polyion solutions. It was found that the turbidity of the NaPAA-(V) reaction mixture increases rapidly with an increasing mole fraction of NaPAA. At a 0.01 M concentration, the maximum turbidity attained was 2.8 at 0.5 mole fraction of NaPAA, which was described as a stoichiometric reaction (composition 1:1). The turbidity decreased with a decreasing concentration of polyion solution because the total yield of PEC was reduced. In addition, the turbidity peaks deviated on the side of the equivalence point where NaPAA was present in a smaller amount, which may be interpreted as due to the dissociation of PEC at high dilution. This remains to be further verified.

The turbidity of the mixture in the presence of 1 × 10^{-2} M to 2 × 10^{-2} M NaBr was evidently smaller than that in salt-free solution (Fig. 5). It seems reasonable to consider that the polyion chain was in an open, extended conformation in salt-free solution or in the presence of a low concentration of salt. The ionic groups approached each other enough to complete the electrostatic interaction. Because NaBr is dissociated into Na^+ and Br^- ions in the presence of added NaBr, it will accelerate the accumulation of released counterions in the neighborhood of reacting groups and moderate the electrostatic interaction of two oppositely charged polyelectrolytes.

Figure 6 shows that the turbidity curve of the NaPAA-(V) system in C_2H_5OH–H_2O is the same as in aqueous solution, but the peak decreases with increasing C_2H_5OH concentration in the C_2H_5OH/H_2O ratio. It is suggested that PEC is formed by the interaction between the oppositely charged polyelectrolytes in aqueous solution with stoichiometry (composition 1:1), while the hydrophobic interaction for NaPAA and (V) was considerably weakened. When Me_2CO-H_2O or DMF–

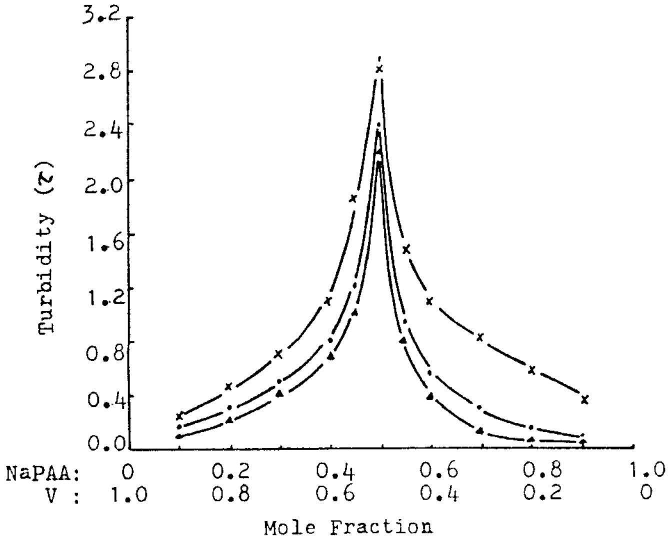


FIG. 5. Effect of micro salts (NaBr) concentration on turbidity. (×) 1 × 10^{-2} mol/L NaPAA and 1 × 10^{-2} mol/L (V) in salt-free solution; (●) 1 × 10^{-2} mol/L NaPAA and 1 × 10^{-2} mol/L (V) in 1 × 10^{-2} mol/L NaBr; (▲) 1 × 10^{-2} mol/L NaPAA and 1 × 10^{-2} mol/L (V) in 2 × 10^{-2} mol/L NaBr; 20°C; pH 7.0.

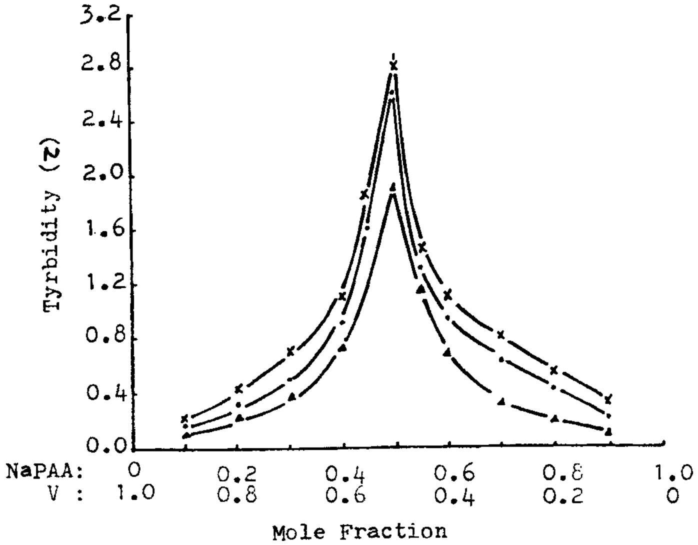


FIG. 6. Effect of C_2H_5OH concentration on turbidity. (×) 1 × 10^{-2} mol/L NaPAA and 1 × 10^{-2} mol/L (V) in aqueous solution; (●) 1 × 10^{-2} mol/L NaPAA and 1 × 10^{-2} mol/L (V) in C_2H_5OH-H_2O (20:80); (▲) 1 × 10^{-2} mol/L NaPAA and 1 × 10^{-2} mol/L (V) in C_2H_5OH-H_2O (40:60); 20°C; pH 7.0.

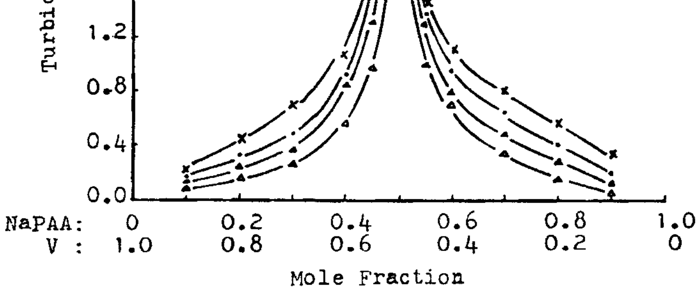


FIG. 7. Effect of various organo solvents on turbidity. (×) 1 × 10^{-2} mol/L NaPAA and 1 × 10^{-2} mol/L (V) in aqueous solution; (●) 1 × 10^{-2} mol/L NaPAA and 1 × 10^{-2} mol/L (V) in C_2H_5OH-H_2O (20:80); (▲) 1 × 10^{-2} mol/L NaPAA and 1 × 10^{-2} mol/L (V) in Me_2CO-H_2O (20:80); (△) 1 × 10^{-2} mol/L NaPAA and 1 × 10^{-2} mol/L (V) in DMF-H_2O (20:80); 20°C; pH 7.0.

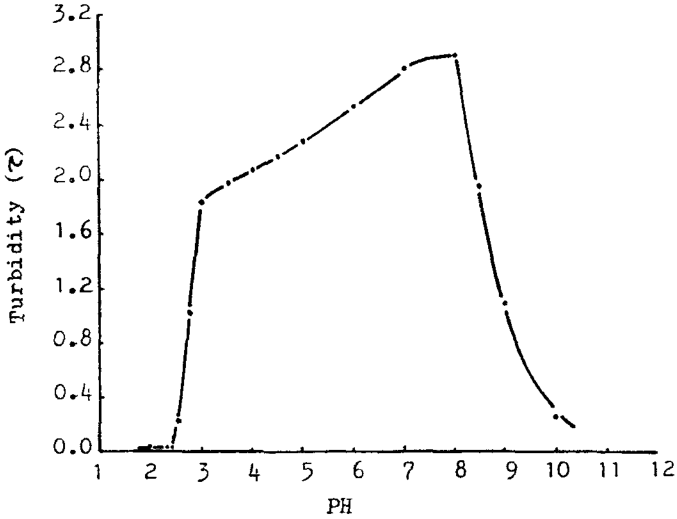


FIG. 8. Effect of pH value on turbidity. 1 × 10^{-2} mol/L NaPAA and 1 × 10^{-2} mol/L (V) in aqueous solution; 20°C.

H_2O is used as solvent, the turbidities are lower than when C_2H_5OH-H_2O is used (Fig. 7). It is possible to state that the dissociation of polyelectrolyte components is lowered with a decreasing dielectric constant (ϵ) of the solvent (ϵ: $H_2O > C_2H_5OH > Me_2CO >$ DMF).

Obviously, the effect of the pH value of the NaPAA-(V) system on the formation of PEC is also potent (Fig. 8). When the pH value is higher than 8.5 or less than 3.0, the turbidities decrease drastically because the dissociation of NaPAA is restrained at pH > 8.5, and NaPAA is transformed into PAA (acidic form at pH < 3). Thus while the turbidities increase with increasing pH value in the 3.0–8.5 range, this range is more favorable for the formation of PEC.

CONCLUSION

1. Three species of novel pendant-type imidazolinium organosilicon polymers, (V), (VI), and (VII), have been synthesized.
2. The PECs based on three imidazolinium organosilicon polymers with poly(sodium acrylate) were synthesized.
3. Measurement of conductimetric titration indicates that the composition of NaPAA-(V) is 1:1, that of NaPAA-(VI) is 1.5:1, and that of NaPAA-(VII) is 4:1 (mole ratio).
4. Measurement of turbimetry shows that the formation of a PEC is affected by the polycation's structure and such environmental factors as polyion's concentration, ionic strength, organic solvent, and pH value.

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