Ordering in Poly(allylamine hydrochloride) Gels

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ABSTRACT: Poly(allylamine hydrochloride) gels were prepared using *N*,*N*′-methylenebis(acrylamide) or glutaraldehyde as cross-linking agents. The gels were found to collapse when equilibrated with sodium salts of various organic acids. A less precipitous volume change was observed when equilibrated with NaCl and NaI. A small-angle X-ray scattering (SAXS) study was performed on the gels. A single broad peak was observed for the collapsed gels with the sodium salts of organic acids such as *p*-styrenesulfonate whereas no peak was found for the inorganic salts. The strong maximum in the SAXS patterns was attributed to the presence of ordered structures in the collapsed gels. The peak position shifted toward lower angles as the size of counterion was increased. A change in the peak position, though small, was noticed with variation in the charge density of the polymer, except for the less charged gel prepared at pH 10.5 which did not even collapse.

Introduction

Polyelectrolyte gels are used in many applications such as superabsorbent materials, separation process, and controlled drug delivery.[1−4] These gels exhibit discrete volume transitions with small variations in the temperature, pH, and solvent compositions.[5−8] Scattering techniques have been widely used to understand the structure of the gels at the point of volume transition.

Shibayama et al. studied the behavior of copolymer gels of *N*-isopropylacrylamide (NIPAM) and ionized acrylic acid as functions of temperature, concentration, and charge density.[9,10] They observed a scattering maximum at elevated temperatures. The maximum was attributed to a microphase separation, which occurred even before the onset of the volume phase transition of the gel due to a balance between opposing hydrophobic and electrostatic forces. Schosseler et al. carried out scattering studies on weakly charged acrylic acid gels.[11,12] They also observed the scattering maximum and attributed it to the frozen-in heterogeneities existing in the weakly charged gels due to the inhomogeneous distribution of cross-links. All these studies were on partially charged gels.

Fully ionized gels also show distinct volume transitions with change in the salt concentration. When a polyelectrolyte gel is placed in salt solution, the effect of binding of counterions with polymer ions plays an important role. Starodoubtsev et al. studied the deswelling behavior of fully ionized poly(diallyldimethylammonium chloride) (PDADMACl) with sodium salts of chloride, bromide, iodide, and acetate in aqueous media.[13] They observed that at a critical concentration of sodium iodide the phase transition of the network to the collapsed state took place whereas other salts did not initiate the collapse of the gel network. The observed behavior was explained in terms of the formation of ion pairs and multiplets. No scattering data were reported on these gels. Recently, Budtova and Navard reported that when dried polyacrylate−acrylic acid gel was treated with $CuSO_4$ or $AgNO_3$ solutions, gels were swollen initially and contracted due to the penetration of metal ions into the gel network.[14,15] They observed that an insoluble layer was formed on the surface of the gel and accompanied by the formation of a birefringent core, and they demonstrated the existence of various swelling paths depending on the gel interaction with metal ions and their concentration.

To understand the influence of ionic strength on the structure of the fully ionized gels, poly(allylamine hydrochloride) (PAAMHCl) gels were chosen in the present study. Until now there are no reports on this gel system. The swelling behavior of PAAMHCl gels in various salt solutions, the structure of the collapsed gels, and the effect of the charge density are presented in this paper.

Experimental Section

Poly(allylamine hydrochloride) (PAAMHCl) powders (PAA HCl−H, the weight-average molecular weight, $M_w = 10^5$, with $M_w/M_n \sim 3$, where M_n is the number-average molecular weight) supplied by Nitto Boseki Co., Ltd., Japan, were purified by ultrafiltration using Amicon membranes of PM10. The solutions thus obtained were freeze-dried, and the resultant powders were used for the preparation of the gels. Cross-linking agents *N*,*N*′-methylenebis(acrylamide) (MBA) and 25% solution of glutaraldehyde (GA) and sodium chloride, citrate, benzoate, benzenesulfonate, and 2-naphthalenesulfonate from Wako Chemicals, Japan, *p*-ethylbenzenesulfonate and *p*-styrenesulfonate from Tokyo Kasei, Japan, and sodium iodide from Yoneyama Chemical Industries, Japan, were used without further purification. Milli-Q reagent grade water was used for all the experiments.

The degree of neutralization of the polymer was determined by Mohr titration using standard 0.1 N $AgNO_3$ solution. Potassium chromate was used as an indicator. The degree of neutralization was found to be 0.96; in other words, polymer was ionized and was in the form of $-NH_3^+$ and Cl^-. Gels were prepared using GA as a cross-linking agent. The ratio of GA moles to the monomer units present in the polymer was maintained at 0.03, and the concentration of the monomer employed was 1.75 M. Transparent gels were obtained at room temperature when an appropriate amount of GA was added to the polymer solution under stirring. To prepare the PAAM solutions at various pH values, the polymer solution was treated with strong anion-exchange resin (Bio Rad AG-1X8), and the resultant solutions were tested for the absence of chloride by treating with $AgNO_3$ solution. The pH of the resultant solution was found to be 11.5, and the pH of the solution was adjusted to 7.2, 8.9, and 10.5 by adding HCl to

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the polymer solution. Since GA cannot be used as a cross-linking agent at higher pH values, MBA was instead used. A suitable amount of polymer (monomer concentration 1.75 M) was dissolved in water, MBA (ratio of MBA moles to monomer units = 0.03) was added under stirring, and the reaction mixture was further stirred at 80 °C. A transparent gel was obtained within a few minutes. All the gels were washed with a large amount of water for 2−3 weeks by intermittently changing the water. The resultant highly swollen gels were used for further studies.

Gels were equilibrated with sodium chloride, iodide, citrate, benzoate, benzenesulfonate, *p*-styrenesulfonate, *p*-ethylbenzenesulfonate, and 2-naphthalenesulfonate of 0.07 M concentration. The ratio of the number of moles of sodium salts to the number of moles of monomers of the polymer was maintained at 6. The concentration of the polymer in the swollen gel was 0.008 g/g. Swelling ratios were evaluated from the ratios of the weight of the gels under the experimental conditions to the weight of the fully swollen gel when equilibrated with water. A laser scanning microscope (LSM), model No. 410, Carl Zeiss, Germany, was also employed to determine the swelling ratios of the gels. The area of the gel when equilibrated with water was measured, water was removed from the sample holder, salt solution was introduced, and the area of the gel piece was measured at regular intervals of time.

Small-angle X-ray scattering measurements were carried out with a Rigaku SAXS apparatus. A 14 kW rotating-anode generator (Rotaflex RU-300, target: Cu, wavelength of X-ray = 154 Å) was used. The X-ray beam was collimated by a Kratky U-slit camera and directed at the gel (contained in a quartz capillary). The scattered X-rays were detected by a position-sensitive-proportional counter (PSPC). The entrance slit width of 70 μm was used. The temperature of the measurement was maintained at 25 °C. Blank runs were obtained without gels for salt solutions, which were previously in equilibrium with the gels. Gel pieces were inserted into quartz capillaries (2 mm diameter from Glas, Germany) containing the blank solution. The transmittances of the blank solution and samples were taken into account in correction, and the scattering intensity of the blank was subtracted from that of the sample. The initial concentration of the raw gel employed for the SAXS was 14 wt % unless otherwise specified. Gel pieces were not uniformly packed in the capillary, and hence desmearing was not carried out for the scattering data.

Results and Discussion

Figure 1a shows the swelling curves (by weight) of the PAAMHCl gels when equilibrated for 1 week in sodium chloride, iodide, and *p*-styrenesulfonate solutions. With increase in the salt concentration, the gels contracted, and precipitous transitions were observed in sodium *p*-styrenesulfonate and sodium iodide solutions whereas a less sharp transition was observed in sodium chloride solutions. An increase in the salt concentration resulted in an increase in the osmotic pressure in the outside solution, thus causing contraction. The collapse of the gel in sodium *p*-styrenesulfonate was rather drastic, showing an important influence of the counterions on the swelling/deswelling of the gels. Starodoubtsev et al. also observed such sharp transitions when they treated poly(diallyldimethylammounium chloride) (PDADMACl) with sodium iodide.[13] They attributed this behavior to the higher polarizability of the iodide ions, resulting in enhanced ion-pair formation, thereby decreasing the osmotic pressure and hence collapse of the gel. In addition to osmotic pressure, the electrostatic interactions between the cationic polymer and the aromatic sulfonate ion might have also played a role in collapse of the gel.

The swelling ratio was also obtained as a function of time by optically measuring the area of the PAAMHCl gel samples and are presented in Figure 1b. Even though a salt concentration of 0.07 M was used for the preparation of complexes, a salt concentration of 0.01 M was used for the swelling experiments. Within a few minutes of contact between gel and sodium *p*-styrenesulfonate (0.01 M), a sharp decrease in the area of the gels was observed, whereas such sharp collapse of the gel was not observed in NaI solution in contrast with Starodoubtsev et al.'s observation.[13] In other words, a jump-wise transition to the collapsed state was not observed in NaI solution. The aromatic sulfonate ions replaced the chloride counterions, as was confirmed by the absence of precipitate when the collapsed gel was treated with $AgNO_3$ solution. Because of deswelling of the gel, the dielectric constant of the gel decreases, causing the formation of ion pairs.[16] The formation of ion pairs further lowers the osmotic pressure in the gel network, and this process continued until

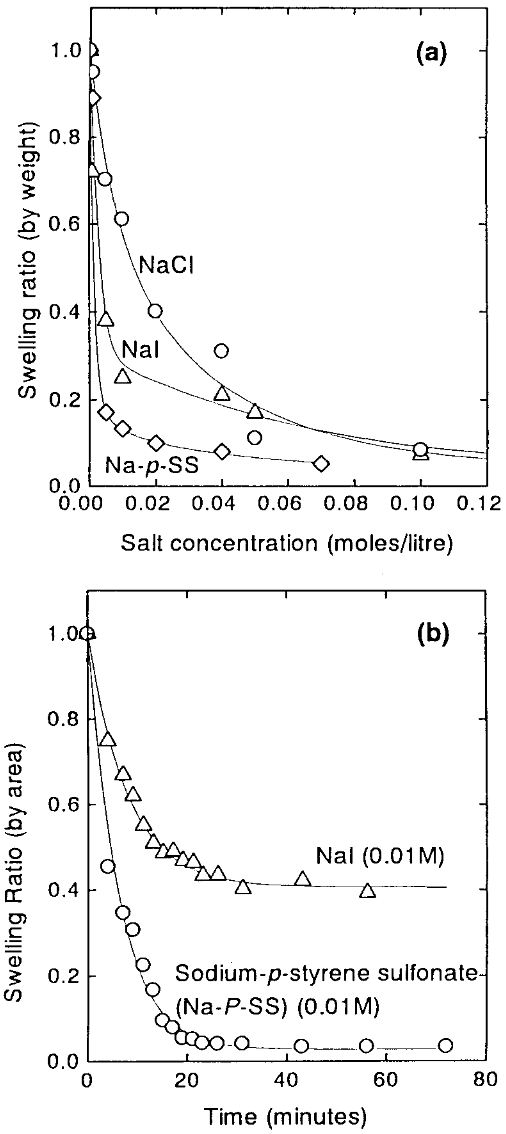

Figure 1. (a) Swelling profiles of PAAMHCl−GA (cross-linked with glutaraldehyde) gels when equilibrated at various salt concentrations for 1 week: sodium chloride (○), sodium iodide (△), and sodium *p*-styrenesulfonate (◇). The initial concentration of the gels used in the present paper is 0.14 g/g, and gels were prepared at pH 4.5 unless otherwise specified. (b) Swelling profiles of PAAMHCl−GA gels in salt solutions (0.01 M) as a function of time: sodium iodide (△) and sodium *p*-styrenesulfonate (○).

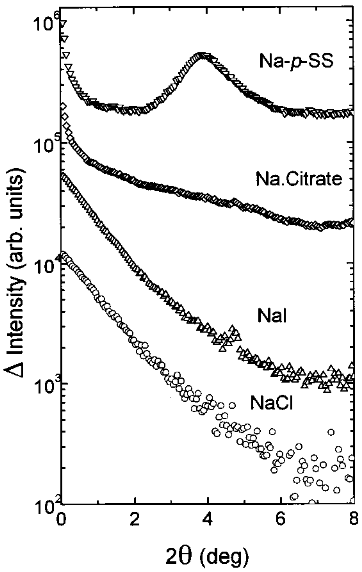

Figure 2. SAXS profiles of PAAMHCl−GA gels in various salt solutions (0.07 M): sodium chloride (○), sodium iodide (△), sodium citrate (◇), and sodium *p*-styrenesulfonate (▽).

the gel collapsed by 90−95% of its initial weight. The collapsed gel was stable, and extensive washing with water did not result in swelling of the gels. Such collapse of the gels was also observed when the swollen PAAM-HCl gels were equilibrated with sodium citrate, benzoate, benzenesulfonate, *p*-ethylbenzenesulfonate, and 2-naphthalenesulfonate.

SAXS studies were carried out to determine the structure of the gels. Figure 2 shows the SAXS profiles of the gels equilibrated with sodium chloride, iodide, citrate, and *p*-styrenesulfonate. Except for the sulfonate, the scattering profiles are monotonically decreasing function of 2θ, where 2θ is the angle between incident X-ray and scattered X-ray. A single broad peak was observed in the collapsed gels with sodium *p*-styrenesulfonate (Na-*p*-SS) as counterions. Yoshikawa et al. have observed a single broad peak for dilute poly(allylamine hydrochloride) solutions and interpreted that the peak was due to the presence of an ordered arrangement of macroions in the solutions.[17] The strong peak observed in the collapsed gels in the present study indicates that there exists an ordering in the collapsed *p*-styrenesulfonate gels. The maximum in the SAXS patterns of the collapsed gel is reproduced even after 3 months of aging. It was suggested that the electrostatic interactions were responsible for the formation of collapsed gels, and the ordering in the collapsed gels was due to both electrostatic and hydrophobic interactions. The ordered structure observed in the present study may be similar to that of polyelectrolyte gel−surfactant complexes, where both electrostatic and hydrophobic interactions are operating, and the correlation length of the complex was approximately equal to twice the length of counterion. A schematic of the PAAM−*p*-styrenesulfonate complex is shown in Figure 3. Elemental analysis of the collapsed gels (prepared at pH 4.5) showed that the polymer cations and the sulfonate anions were present in a 1:0.85 molar ratio.

Though the gels were fully collapsed in sodium citrate similarly to the sulfonate solutions, no maximum was observed in their SAXS patterns. Citrate is a highly polar and trivalent anion, and hence by replacing the chloride ions, the concentration of the mobile counterions in the gel network was decreased to 1/3 and resulted in a decrease in osmotic pressure and hence the gel collapsed. The absence of hydrophobic interaction among the citrate groups might have inhibited the formation of an ordered structure.

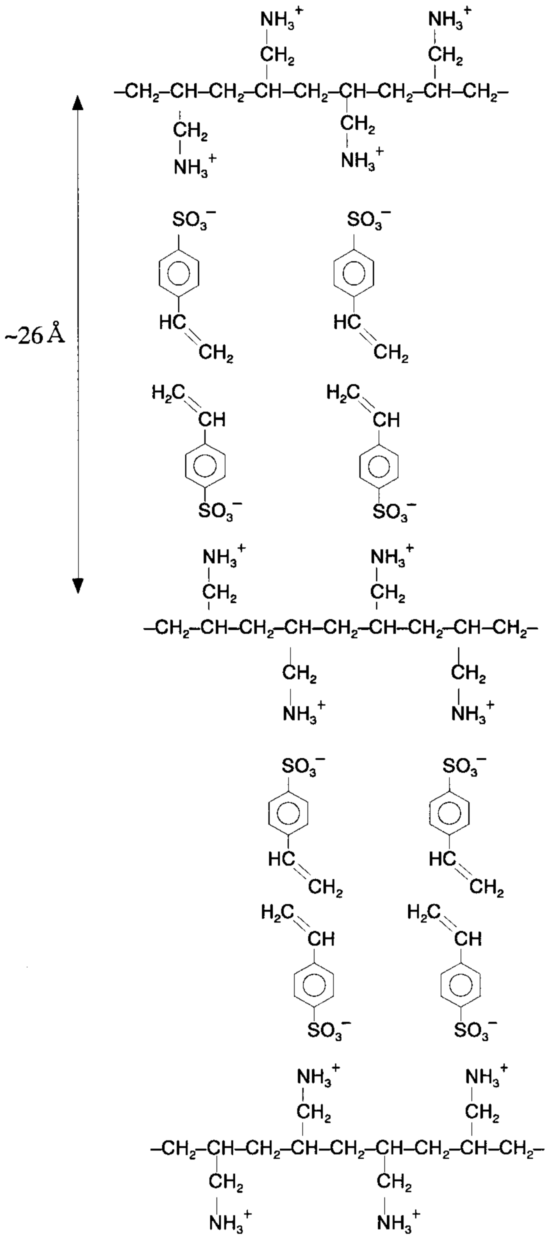

Figure 3. Schematic representation of structure of the PAAM−*p*-styrenesulfonate complex.

Scattering studies were performed on the collapsed gels obtained for various aromatic sulfonates and benzoate and are presented in Figure 4. All the samples showed a maximum in their SAXS patterns and indicate the presence of ordering in the collapsed gels. Among the aromatic counterions employed in the present study, the approximate axial lengths (from the polymer chain to other end of the counterion) of benzoate, benzenesulfonate, 2-naphthalenesulfonate, *p*-styrenesulfonate, and *p*-ethylbenzenesulfonate were 9, 9, 12, 13, and 13 Å, respectively, and the correlation lengths of their collapsed gels obtained from the SAXS patterns were 18, 19, 23, 23, and 25 Å, respectively. It seems that the peak position in the SAXS patterns shifts toward smaller angles with increasing length of the counterions.

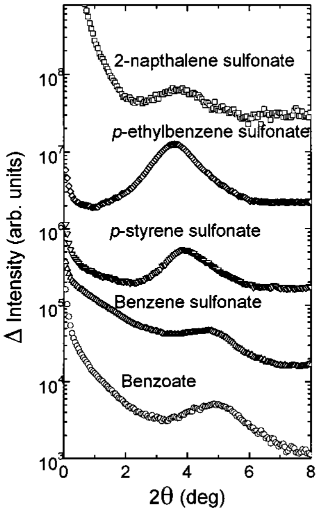

Figure 4. SAXS patterns of collapsed PAAMHCl−GA gels in various aromatic sodium salt solutions (0.07 M): benzoate (○), benzenesulfonate (△), *p*-styrenesulfonate (▽), *p*-ethylbenzenesulfonate (◇), and 2-naphthalenesulfonate (□).

The aromatic counterions used in the present study are known as hydrotropes.[18] It was reported that, above a certain minimum hydrotrope concentration (MHC), these aromatic ions will aggregate to form liquid crystalline structures or open layer assemblies.[19,20] Even though the concentration of aromatic ions used in the present study (0.07 M) was lower than the MHC (∼0.3 M), the concentration of aromatic counterions might have exceeded the MHC inside the collapsed gel. The structure-forming ability of these aromatic ions might have driven the gel to an ordered state. The wide-angle X-ray scattering data for the PAAM−*p*-styrenesulfonate complex showed a single strong broad peak at a *d* spacing of 4.53 Å which might indicate that the complex has a highly distorted ordered arrangement. On the other hand, such behavior was not observed for chloride, iodide, and citrate ions.

The structure of the collapsed gels was disturbed in the presence of salt and resulted in swelling of the gels. The absence of a peak in the presence of salt confirms the dissociation of the ordered structure as shown in Figure 5. In the present study, the collapsed gels were reswollen in the presence of sodium chloride, bromide, and iodide when salt concentration was in excess to that of polymer concentration.

Gels of various polymer concentrations were prepared and treated with sodium *p*-styrenesulfonate. The SAXS patterns of the collapsed gels are presented in Figure 6. There was no change in the position of the most intense peak with variation in the concentration of the gels. Since the volume decrease by collapse of the gel was around 90−95% and we took excess amount of counterions, the final volume fraction of the polymer in the collapsed gel was almost the same irrespective of initial concentrations even though the starting concentrations of the gel were different. This explains the observed scattering behavior.

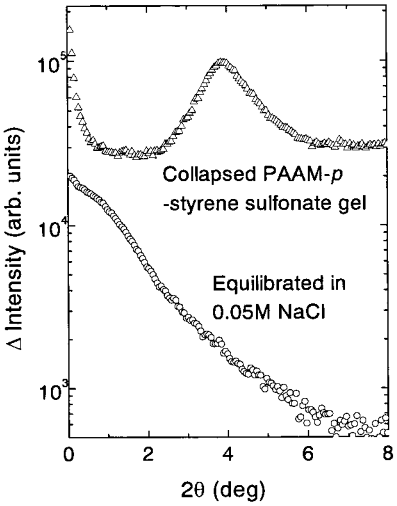

Figure 5. SAXS patterns of collapsed *p*-styrenesulfonate−GA gel (△) and collapsed gel when equilibrated with 0.05 M NaCl (○).

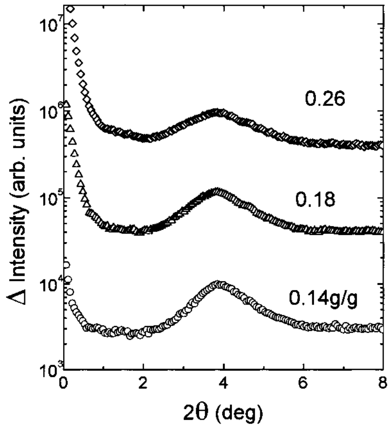

Figure 6. SAXS patterns of collapsed PAAM−*p*-styrenesulfonate GA gels at various polymer concentrations: 0.14 (○), 0.18 (△), and 0.26 g/g (◇).

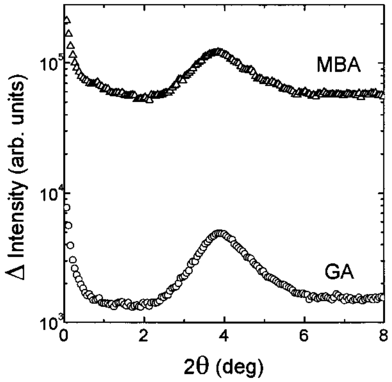

Figure 7. SAXS patterns of collapsed PAAM−*p*-styrenesulfonate gels with two different cross-linking agents: MBA (*N*,*N*′-methylenebis(acrylamide)) (△) and GA (glutaraldehyde) (○).

To study the effect of the charge density, the gels were prepared at various pH values, viz., 10.5, 8.9, 7.2, and 4.5. Since GA does not undergo cross-linking at higher pH values, the gels were prepared using MBA as a cross-linking agent. Figure 7 shows the SAXS patterns of collapsed gels prepared with GA and MBA as cross-linking agents, and the peak position was not influenced. The difference in cross-linking agents is not important under the present experimental conditions.

SAXS patterns of the collapsed gels prepared at various pH values are presented in Figure 8. The pK_a value of PAAM is 9.67,[21] and hence the degree of neutralizations of the polymer was 26, 72, 99, and 100% at pH values of 10.5, 8.9, 7.2, and 4.5, respectively. With increase in degree of neutralization, in other words, with

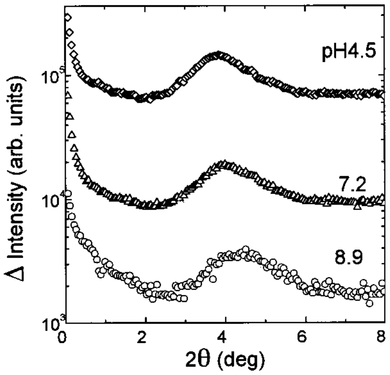

Figure 8. SAXS profiles of collapsed PAAM−*p*-styrenesulfonate gels (MBA) prepared at various pH values 4.5 (◇), 7.2 (△), and 8.9 (○).

increase in charge density, the peak positions in the SAXS patterns shifted to lower angles, though slightly. The gel prepared at pH 10.5 did not collapse. It was reported that the gels with higher charge density collapse more easily due to enhanced formation of ion pairs.[22] Elemental analysis of the collapsed gels revealed that the molar ratio of *p*-styrenesulfonate to monomer unit is 0.9 for the gels prepared at pH 4.5 and 7.2 (degree of neutralizations are 100 and 99%, respectively) and 0.6 for pH 8.9 (degree of neutralization is 72%), which indicates that the cationic polymer and anionic counterion formed nearly a 1:1 stoichiometric complex. The decrease in correlation length of the complex with decrease in charge density can be attributed to the decrease in the amount of the organic counterion.

Conclusions

Gradual volume transitions were observed for PAAM-HCl gels in sodium chloride and iodide solutions, whereas sharp jump-wise transitions were observed in organic salts such as sodium benzoate, *p*-styrenesulfonate, etc. Small-angle X-ray scattering (SAXS) studies on the collapsed gels showed a strong maximum, whereas this was not the case for the gels in the inorganic salts. The strong maximum in the SAXS patterns was attributed to the presence of ordered structures in the collapsed gels. Both electrostatic and hydrophobic interactions were responsible for ordering in the collapsed gels. The correlation length of the complex was increased with increasing length of the counterion. The amount of counterions in the complex was decreased with decrease in charge density of the polymer and resulted in smaller correlation lengths.

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