

## Evidence for Polyelectrolyte/Ionomer Behavior in the Collapse of Polycationic Gels

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**ABSTRACT:** The interaction of slightly cross-linked positively charged gels of poly(diallyldimethylammonium chloride) (PDADMACl) with sodium salts of chloride, bromide, iodide, and acetate in aqueous media has been investigated. At the critical concentration of sodium iodide, a phase transition of the network to the collapsed state was observed. A wide hysteresis accompanied this transition. The presence of other salts did not initiate the network collapse in the investigated concentration range. A decrease in the charge density of the cationic network by copolymerization of DADMACl with acrylamide resulted in the disappearance of the phase transition. In this case, the usual contraction of polyelectrolyte gels in the presence of the mentioned salts was observed. The rate of volume change increased sharply with increasing concentration of sodium iodide. For some cases, two well distinct regions in the kinetic behavior were observed: a region of fast polyelectrolyte contraction and a region of slow collapse which, to our knowledge, had not been observed previously. The experimental results can be explained by the formation of ion pairs and multiplets (ionomer effect) for the sufficiently charged networks in the collapsed state. As a result, the collapsed ionomeric state of the network becomes competitive with the swollen polyelectrolyte state at high enough fractions of the ion-containing segments because of the tendency of the ion pairs to associate. A potential barrier which separates the ionomeric and the polyelectrolyte states of the gel can be used to explain the two-step kinetics of the collapse.

### Introduction

The strongly swollen polymer networks in solution may undergo sharp, often discontinuous, conformational transitions with small changes of the experimental parameters such as temperature, composition of the medium, etc. This phenomenon was first demonstrated by Tanaka for slightly cross-linked poly(acrylamide) (PAAm) gels swollen in water–acetone mixtures. A very strong decrease of the gel volume was observed at a certain concentration of acetone (bad solvent for PAAm). In some cases the volume of the gels decreased in a jumpwise fashion by as much as hundreds of times when compared with the initial volume. This phenomenon is known as the polymer network collapse.<sup>1</sup>

The appearance of sharp volume changes of PAAm gels with variation of the acetone content (and also of the temperature and the pH value) is due to the uncontrolled hydrolysis of amide groups of PAAm resulting in a slight charging of the polymer chains.<sup>2,3</sup> To avoid this problem, charged groups were introduced into the PAAm networks by copolymerization of acrylamide (AAM) with sodium methacrylate (SMA)<sup>4</sup> and also with *N*-acryloylsuccinimide, which can be hydrolyzed easily in aqueous media.<sup>5</sup> The phenomenon of chain collapse was also studied for the networks of PAAm which contained cationic ammonium<sup>6–8</sup> and pyridinium groups.<sup>9</sup>

The gel collapse phenomenon was analyzed theoretically for neutral polymers,<sup>10</sup> polyelectrolyte networks with charges of one sign,<sup>2</sup> and polyampholyte networks with different amounts of positive and negative ions attached to the chains.<sup>11,12</sup> It was demonstrated that the main factor which could lead to a discontinuous phase transition in charged polymer networks was the

osmotic pressure of mobile counterions within the network (although electrostatic interactions can also be important for some cases.<sup>23</sup> Due to the condition of electroneutrality of the gel, the higher the concentration of charged groups attached to the cross-linked polymer chains (or the concentration of noncompensated charges for the case of polyampholyte networks), the higher the concentration of counterions, their osmotic pressure inside the network, the degree of swelling, and the amplitude of collapse. For gels with a larger charge density, the transition occurs at a higher content of a bad solvent. These theoretical predictions are in good agreement with observed experimental data.

Theoretical analysis<sup>12,13</sup> and experimental studies<sup>13</sup> have also shown that the swelling of polyelectrolyte gels can be decreased substantially if some low molecular weight salt is added to the external solution. This effect is due to the decrease in the osmotic pressure of counterions under these conditions. For poor enough solvents the addition of salt may even result in a jumpwise collapse of the gel. According to the analysis of refs 12 and 13, an increase in the fraction of charged monomer units always favored the swollen state of the gel.

The first theories of the gel collapse studied the slightly charged networks by varying the solvent quality. The experiments used slightly charged copolymers of AAM with SMA, swollen in mixtures of water with methanol, ethanol, and dioxane (and with the dielectric constant  $\epsilon$  changing from 34 to 2). A decrease in  $\epsilon$  resulted in a smaller amplitude of the phase transition and moved the transition point in the collapsed state to a lower bad solvent content.<sup>14</sup> These results were explained by the formation of ion pairs even for the networks with very low charge density, e.g., the network containing only 1.88 mol % of SMA groups. The formation of ion pairs should be more pronounced for solutions with a lower solvent dielectric constant. The decrease in  $\epsilon$  could lead to a very strong exponential

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growth of the fraction of ion pairs formed between the charges of the network and the counterions.

The strong influence of ion-pair formation on the state of polyelectrolyte chains in the solution or in the gel phase was confirmed by Klooster et al.<sup>15</sup> They investigated the influence of charge density, solvent dielectric constant, and the nature of counterions on the conformational state of a linear polyelectrolyte, poly(acrylic acid) (PAA) in methanol solutions. The initial increase in the degree of ionization caused by adding sodium methoxide to a methanol solution of PAA led to a strong polyelectrolyte swelling of the polymer chains. However, after the degree of ionization had reached  $\sim 0.1$ , a rapid collapse of the coils was observed. Most of the counterions were in the bound state in the collapsed coils. The nature of counterions had a strong influence on the state of PAA. For lithium methoxide ( $\text{CH}_3\text{OLi}$ ), after the initial polyelectrolyte swelling a monotonous transition to a more compact state was observed at the degree of ionization equal to  $\sim 0.2$ . The dimensions of shrunk coils in the presence of  $\text{CH}_3\text{OLi}$  were much larger than those of collapsed coils in the presence of  $\text{CH}_3\text{ONa}$ . One of the explanations for the collapse of PAA chains in the neutralization process by  $\text{CH}_3\text{ONa}$  was that the collapse was a result of the attraction between ion pairs formed between the carboxylate anions and the sodium cations.

Similar results were obtained by Morawetz and Wang<sup>16</sup> in a titration of solutions of PAA and poly(methacrylic acid) in methanol with  $\text{CH}_3\text{OLi}$ , by using potentiometric and viscosity measurements.<sup>16</sup> The authors observed nonmonotonous changes in viscosity with the degree of ionization for both acids. The shrinking of the coils after a certain degree of ionization, depending on the nature of polyelectrolyte, was explained by the "attraction between ion pairs formed by the counterion condensation".

The study of the rotational mobility of a spin label chemically attached to poly(4-vinylpyridine) (P-4-VP) partly alkylated by benzyl chloride<sup>17</sup> and the study of the viscosity and the critical concentration of salting out (CCS) of P-4-VP quaternized with halide alkyls<sup>18</sup> showed that all three parameters passed through a maximum value with increasing degree of quaternization. It was also demonstrated that the nature of monovalent anions could strongly influence the viscosity and the CCS. The decrease of the mentioned parameters at high degrees of ionization could be explained by the increase of attraction between ion pairs at high content of charged groups of the cationic polyelectrolyte.

A new theoretical approach to the problem of polymer gel collapse was developed in a recent publication.<sup>19</sup> The theory took into account the fact that the dielectric constant of the gel depended on the volume fraction of the polymer inside the gel and hence on the gel volume. Therefore, the amount of ion pairing inside the gel which could be controlled by the dielectric constant of the gel medium varied with the degree of swelling and should be much larger for the collapsed gels. The theory also took into account the formation of ionomer multiplets which resulted from strong attractions between ion pairs. In other respects the consideration followed the usual framework of the theory of polymer gel collapse.<sup>1,2,10-12</sup> The main results of the theory of ref 19 were as follows.

The formation of ion pairs inside the gel generally led (i) to a significant decrease of the osmotic pressure of counterions inside the gel and (ii) to the dipole-dipole

attraction between the ion pairs. Both factors favor a contraction of the gel. As a result, the region of stability for the collapsed state and the volume change at the transition point were larger in the theory of ref 19 than in the conventional theory. In many cases the mixed polyelectrolyte/ionomer behavior was predicted: in the swollen state most of the counterions were free (polyelectrolyte regime); in the collapsed gel, most counterions formed ion pairs with the charges on the gel chains. Ion pairs were in turn organized into multiplets (ionomer regime). It was shown in ref 19 that, for some cases, two states of a collapsed gel are possible: the normal collapsed state where there is enough water, so that the amount of ion pairs is not large, and the "supercollapsed" state. In this latter state the polymer volume fraction within the gel is so large (and the dielectric constant of the gel medium is so low) that numerous ions pairs form a well-defined ionomer multiplet structure. The supercollapsed state is usually separated from the slightly collapsed state by a potential barrier. To overcome this barrier, the following avalanche-type process should be induced: the polymer concentration in some part of the gel must occasionally (i.e., due to fluctuations) become so high and the dielectric constant so low that the amount of new ion pairs formed in this region induce further contraction of this part of the gel.

In this paper, the swelling and the collapse behavior of strongly charged networks of poly(diallyldimethylammonium chloride) (PDADMACl) upon addition of low molecular weight salts (sodium salts of chloride, bromide, iodide, and acetate) is presented. In particular, the addition of sodium iodide led to a jumpwise collapse of the gel which could be interpreted within the framework of the recent theory,<sup>19</sup> i.e., as a transition from the swollen polyelectrolyte regime to the supercollapsed ionomer regime of the gel.

## Experimental Section

**1. Gel Preparation.** The gels were prepared by free-radical copolymerization of an aqueous solution of monomers in cylindrical glass tubing (inner diameter 1.07 mm and  $\sim 300$  mm long) or between two glass plates  $65 \times 100$  mm, separated by two ( $0.63 \pm 0.03$  mm thick) polyethylene spacers. The two separate spacers provided an inlet and an outlet so that the monomer solution could be injected between the glass plates from one side and the air inside the chamber could be forced out from the outlet side. The concentration of the monomers was 2.67 mol/L and the cross-linker [*N,N*-methylenebis(acrylamide)] was  $1/200$  of monomer units.

The initial mixture for gel formation containing 10 mL of the monomer solution was heated up to 35 °C, to which was added 5  $\mu\text{L}$  of *N,N,N,N*-tetramethylethylenediamine and 50  $\mu\text{L}$  of a 10% ammonium persulfate solution. The mixture was injected between the plates through a 0.22- $\mu\text{m}$  Millipore filter. Gelation was carried out at 22 °C for 22 h in a closed chamber in order to prevent evaporation.

After gelation, the upper glass plate was removed. First one piece of the gel (0.15–0.20 g) was quickly cut from near the center of the reaction chamber by using a razor blade, weighed on an analytical balance, and then washed with a large amount of distilled water for 3 weeks. The distilled water was changed every 1–2 days. This first piece of gel is referred to as the control gel. It was used to determine the degree of swelling of the initially prepared gels in pure water. Other parts of the gel (50  $\times$  80 mm) were also cut from the initial sheet, divided into smaller pieces, removed from the surface of the plate, and washed in the same way.

For the cylindrical reaction chamber, the glass tubing was cut into shorter pieces, each about 20 mm long, and then stored in the freezer compartment of a refrigerator for 1 week.

**Table 1. Fraction of Monomer Units in the Gel,  $Q$ , and the Pure Water Swelling Parameter,  $F$ , for Gels with Different Fractions of Cationic Links,  $G^a$** 

$G$ (mol %)	100	75	50	25	0
$F$	40.5	44.5	28.0	28.5	1.8
$Q$ (wt %)	29	56	59	90	>95

<sup>a</sup> Washing time 12–14 days with 8–10 changes of water.

Afterward, the pieces of gel were pressed out from the cylindrical glass tubes into a beaker filled with water and washed in the same manner as the gel in the sheet form.

**2. Determination of Swelling Ratio  $F$  and monomer units  $Q$ .** The prepared gels were characterized as follows. We first defined the swelling ratio of a control gel in pure water  $F = m_w/m_0$ , with  $m_w$  being the mass of the gel swollen to equilibrium in pure water and  $m_0$  the mass of the same gel sample just after polymerization.

We worked only with gel samples swollen to equilibrium either in pure water or in a salt solution of known concentration and avoided performing measurements with initial gels which rapidly changed their weight when exposed to the atmosphere. The swelling ratio,  $m/m_0$ , used in Figures 2–5 of this paper was calculated as follows:

$$m/m_0 = (m/m_w)F$$

where  $m$  is the mass of the gel (not the control gel) swollen to equilibrium at given experimental conditions, recalling  $F$  is the swelling ratio of the control gel exposed to pure water.

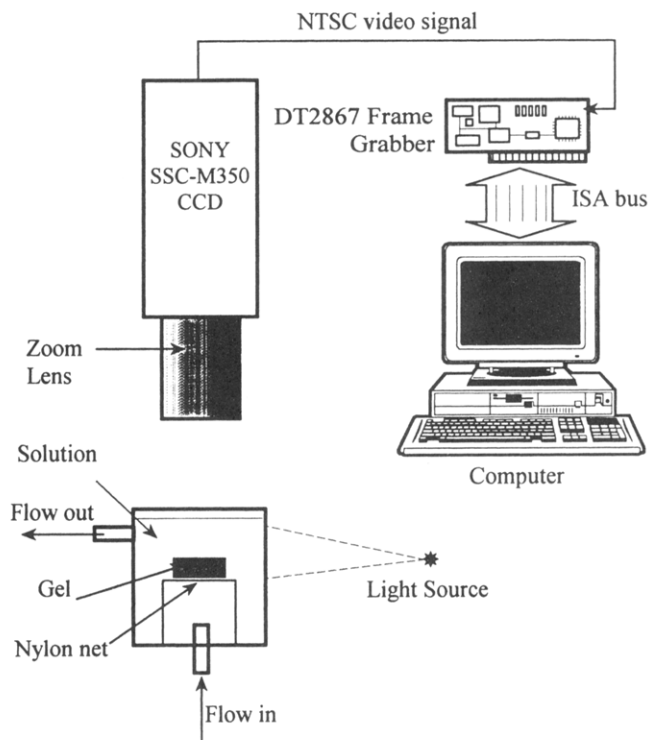
The initial gel contained the cross-linked polymer, the sols, unreacted monomers, and water. Therefore, an important quantity characterizing the initial gels is the fraction of monomer units constituting the gel,  $Q$ , which is defined as the ratio of the amount of cross-linked polymer to the amount of initial monomer. The value of  $Q$  was determined as follows. A piece of control gel with known initial mass,  $m_0$ , after equilibration with water was dried, and its mass,  $m_d$ , was measured. The ratio  $m_d/m_0$  gives the weight fraction of a polymer network in the gel after polymerization. The weight fraction of monomers in the polymerized mixture,  $W$ , is known. Thus, the parameter  $Q$  can be calculated using the formula:

$$Q = (m_d/m_0)/W$$

An acceptable procedure to determine the weight of the dry polymer was to heat the swollen gel for 12 h at 101–103 °C on an aluminum foil, which had been preheated for 1 h at the same temperature. The same result was obtained if the heating time was increased by a factor of 2 or more. The time between cooling the dried sample and measuring its weight was less than 2 min. This short transition time was used in order to minimize the fast absorption of moisture from the air. The weight of the swollen gel was measured after removing the solution from its surface with filter paper. These measurements needed some experience because the gels were very fragile and had a strong adhesion to plastic and metal surfaces.

Table 1 lists the values of  $F$  and  $Q$  for the prepared gels with a different fraction of cationic links,  $G$ . An increase in the AAm content could result in a significant increase in the fraction of monomer links which actually form the gel,  $Q$ . For PDADMACl (i.e., in the absence of AAm links in the initial monomer mixture) the weight concentration of the polymer gel after polymerization was only 11.7% (11.7% polymer, 28.3% monomer, and 60% water). Thus, cationic links have a much lower ability to enter polymerization reactions than neutral AAm links.

The gels were equilibrated with salt solutions of known concentrations. After equilibration, the washed gel contained the cross-linked polymer which was in equilibrium with the salt solution. The excess anions in the solution, in comparison with the amount of counterions in the polymer salt, were no less than 30 times the lowest salt concentration (0.005 M). For sodium acetate the initial solution was changed after a 1-week immersion because acetate anions had a weak affinity to the cations of the polymer network. After immersion of the gel in



**Figure 1.** Schematic diagram for studying the kinetics of gel collapse.

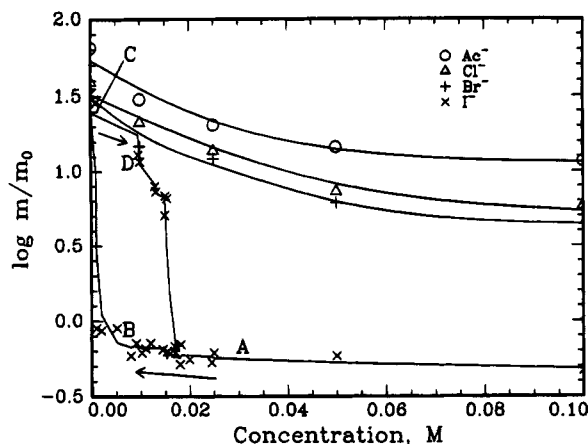
the salt solution for 2–3 weeks, the sample was weighed. The gravimetric results showed that the degree of ion exchange reached an estimated value of  $90 \pm 10\%$  (i.e., practically all the counterions were exchanged) within 4 h. The ratio between the mass of the gel at equilibrium with a salt solution and that of the gel after synthesis,  $m/m_0$ , depended on the salt concentration.

**3. Dynamics of Gel Collapse.** The dynamics of gel collapse was studied in two sets of experiments. In the first one samples (diameter  $5.0 \pm 0.4$  mm with a thickness of about  $1.6 \pm 0.1$  mm) were obtained from the PDADMACl flat gel. Then, each sample was immersed in the flask containing a 0.04 M, 0.02 M NaI, or 0.04 M NaCl solution for some specified time period, and its weight was determined afterward. In this way the weight of the gel as a function of time could be determined.

For the second set of experiments a special setup was designed (see Figure 1). The samples were placed on top of a small table in a tank containing approximately 75 mL of a salt solution. The table top was made of black nylon net, permitting free flow of solution. The solution flux was coming from underneath the table. The flux was approximately 1.5 mL/min through a cross section of about 5 cm<sup>2</sup>. The diameter of the flat samples and the diameter and the height of the cylindrical samples were measured by taking electronic pictures of the gel sample in the tank with a Sony SSC-M350 CCD camera and a Data Translation DT2867 frame grabber. The timing of the pictures was computer controlled. The cylindrical samples gave more precise information on the gel volume. In these experiments, the projected linear dimensions of a sample could be measured every 150–250 s, with the gel being flushed by a slow constant flux of an aqueous salt solution. The sample volume could be computed approximately from the diameter and the height of the cylinder. The volume was normalized to unity at time  $t = 0$ . The precision of our measurements was about 5%.

## Experimental Results

After having immersed the samples of the PDADMAC network, initially swollen in pure water, into the solution of sodium iodide, bromide, chloride, or acetate (Ac), the gel contraction was observed. Figure 2 illustrates



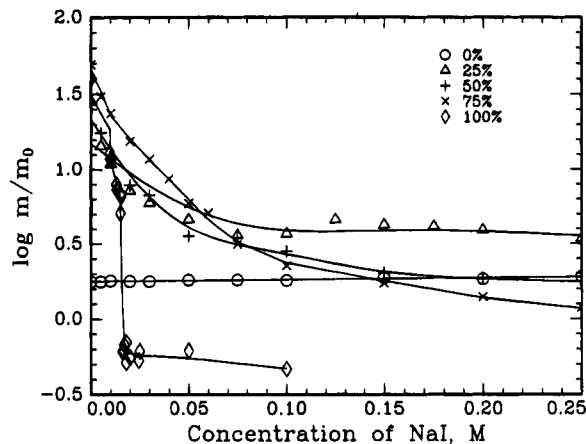
**Figure 2.** Plot of  $\log(m/m_0)$  versus salt concentration of sodium acetate (○), chloride (Δ), bromide (+), and iodide (×).  $T = 21 \pm 1$  °C. Symbols × show the direct and reverse transition in  $m/m_0$  versus the NaI concentration.

the dependence of the relative mass ( $m/m_0$ ) of the cationic gel on the salt concentration. For Ac, Cl, and Br counterions, an increase in the salt content resulted in a decrease of the osmotic pressure in the charged network and in a monotonic lowering of the degree of swelling of the gel, in general agreement with the theory of ref 12. However, the nature of the anions influenced the degree of swelling; i.e., at the same salt concentration, the volume of the network decreased in the order  $\text{Ac} > \text{Cl} > \text{Br}$ . This effect, which was not described in the theory of ref 12, could be explained by the formation of ion pairs between the cations of the network and the counterions. The anions of bromide are known to have the greatest polarizability and to form more ion pairs than chloride or acetate ions. Thus the osmotic pressure in the gel was lower for bromide anions, and the degree of swelling was smaller.

An increase in the radius (and polarizability) of anions qualitatively resulted in a qualitatively new behavior of the network-counterion system. For sodium iodide, at some critical concentration (in our case at 0.016 M), a jumpwise transition to the collapsed state was observed (Figure 2).

Analogous results could be found in the literature. For example, in aqueous media, the addition of sodium iodide resulted in a jumpwise collapse of the cationic gels of *N*-*n*-butyl-*N,N*-dimethyl-4-vinylbenzylammonium bromide,<sup>20</sup> *N*-*n*-butyl-4-vinylpyridinium bromide, and *N*-*n*-butyl-*N,N*-dimethyl-4-vinylanilinium bromide.<sup>21</sup> The authors explained the gel collapse by a strong binding of iodide anions to the cationic charges of the networks and also by hydrophobic interactions between the polymer segments.

There is a small hysteresis near the phase transition point of slightly charged gels in a bad solvent.<sup>22</sup> For the collapse transition studied in the present work, the hysteresis effects were much more substantial. The hysteresis effect was studied for two samples, which were collapsed in a 0.02 M solution of NaI and then equilibrated with solutions at a lower salt concentration for 1 week. The results are shown in Figure 2. It can be seen that the region of hysteresis is very wide. The gel collapse was reversed only in a 0.001 M solution of NaI. The expansion of the gel could also be initiated if the samples were immersed in a 0.1 M solution of sodium acetate. In the latter case the exchange of counterions destroyed the structures which were formed in the collapsed gel.



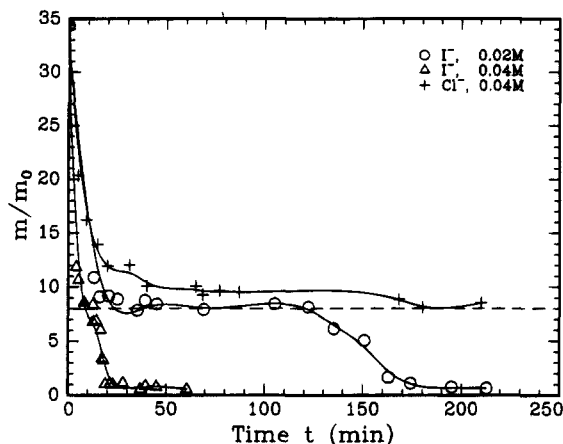
**Figure 3.** Plot of  $\log(m/m_0)$  versus NaI concentration for PAAm with 0% charged groups and for polymer networks containing 25, 50, 75, and 100% of charged groups.

The collapse of the PDADMACl gel in the presence of sodium iodide seemed analogous to the ordinary collapse of slightly charged gels in a poor solvent due to the decrease of the osmotic pressure of counterions in the presence of salt. The increase of the ionic strength of the medium could result in a jumpwise collapse of the gel.<sup>13</sup> However, if our situation were analogous to that of ref 13, the phase transition should depend strongly on the charge density of the network; i.e., the higher the charge density was, the higher should be the salt concentration required to induce the collapse.

The influence of the charge density on the phase transition was studied by comparing the results obtained for the copolymers with different amounts of DADMACl groups swollen in NaI solutions. Figure 3 plots the degree of swelling in a salt solution ( $m/m_0$ ) versus the NaI concentration for polymer networks with a different content of cationic groups and also for a neutral PAAm gel (Table 1). As expected, the addition of salt did not practically influence the degree of swelling in the neutral gel. For the networks with lower concentrations of cationic groups the usual polyelectrolyte deswelling without any collapse transition was observed. Only for the pure PDADMACl, the addition of NaI resulted in an abrupt transition to the collapsed state. Thus, an important difference in comparison with the experiments reported in ref 13 was observed. For our case, the higher the charge density was, the easier the transition to the collapsed state became.

The other feature of the data, as shown in Figure 3, was that in NaI solutions with concentrations higher than 0.07–0.08 M the increase of the charge density of the network resulted in a decrease in  $m/m_0$ . For the network with 75% charged groups the degree of swelling became even lower than that for the neutral PAAm gel.

The experimental data are in reasonable agreement with the theory of ref 19. Iodide anions are characterized by the highest polarizability, and therefore the amount of ion pairing of the counterions to the co-ions of the polymer chains should be the largest. The fact that the network containing 75% charged groups is less swollen than the neutral gel is not surprising: for these gels the attraction caused by the fact that charged monomer units form ion pairs with counterions is more important than the osmotic pressure exerted by the remaining free counterions. Moreover, at 100% charged groups the amount of ion pairs can be so large that an abrupt transition to the supercollapsed state described in ref 19 (see the Introduction) becomes possible. A



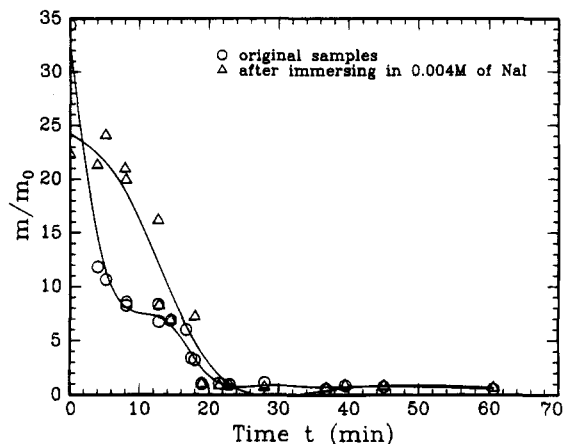
**Figure 4.** Plots of degree of swelling  $m/m_0$  versus time for PDADMACl gels in 0.04 and 0.02 M sodium iodide and 0.04 M sodium chloride. The dashed line indicates a volume of the gel sample after being immersed in 0.04 M NaCl solution for 2 days.

natural interpretation of the abrupt collapse for 100% charged gels in NaI could be attributed to the presence of the supercollapsed state.

To justify further that the process observed is due to the association of ion pairs, let us discuss the kinetics of the collapse of PDADMACl gels. Two methods were used in this work for the description of the process. The gravimetric data do not depend on the shape of the samples and on their possible distortion in the course of shrinking, but the process of weighing can easily damage the sample or at least subject the gel to an additional mechanical strain. That is the reason why each sample was used for one measurement only. Continuous automatic measurements of the linear dimensions of the gel are much better for studying the gel volume changes as a function of such factors as salt concentration, temperature, etc., and consequently for observing the dynamics of the gel collapse.

Figure 4 illustrates the change of mass of PDADMACl gels with time at two NaI concentrations: 0.04 and 0.02 M. The analogous dependence for the 0.04 M NaCl solution is also shown for comparison. It can be seen that at least for 0.02 M NaI the collapse process could be divided into three stages: the initial process was a fast decrease of the gel volume, then the volume remained practically constant for some time, and at later times another process was observed where the shrinking of the gel strongly depended both on the nature of the anions in the salt and its concentration. In 0.04 M NaI solutions, the first fast drop in the gel mass changed to a slower process and then again to a fast process of gel shrinking (Figure 4), although the second stage was much less pronounced than for 0.02 M NaI. In a 0.016 M NaI solution the final collapse was observed after 2 days. In the NaCl solution after the fast decrease of the gel volume, no subsequent collapse of the gel was observed.

The first fast decrease in the mass of the gel could be explained by the decrease of the osmotic pressure of counterions in the gel phase due to the addition of salt in the system. This decrease was controlled by the fast diffusion of counterions from the gel. As can be seen from Figure 4, this process took about 20 min. The second decrease in the gel volume (which might be related to the collapse state, with the mass changes being more than 10 times its initial value) required a much more complex description. In this paper, for



**Figure 5.** Plot of  $m/m_0$  versus collapse time for PDADMACl gel in a 0.04 M solution of sodium iodide and the values of  $m/m_0$  after having immersed the same samples for 1 week in 0.004 M NaI solutions.

simplicity, we will characterize it by one parameter only, namely, the characteristic time  $\tau$ , which is a time when the maximum rate of volume change is observed for this process.

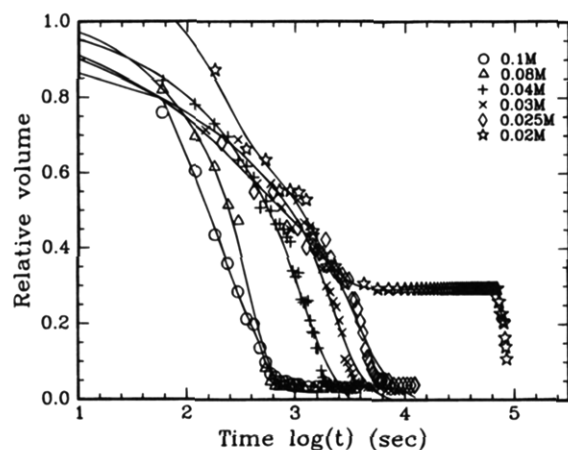
The second stage of the gel collapse started with a significant delay after the sample was immersed into the solution. This raises the question whether there are any structural changes in the sample during this latent time. To clarify this point, the following experiment was performed. A part of the samples was immersed for varying times into 0.04 M NaI solutions and then weighed. The weighed samples were placed into the NaI solution with a concentration of 0.004 M, which was within the concentration range where the hysteresis occurs. After 1 week the samples were weighed again. The results are shown in Figure 5. It can be seen that the samples, which did not collapse beyond a certain degree, expanded again in the solution of lower salt concentration. On the other hand, samples remained collapsed once they reached this state. The networks expanded from a collapsed state did not reach the volume, which they would have if they had been initially immersed in a 0.004 M NaI solution. These results clearly show that the gel expanded from a partially collapsed state (e.g., from A to B in Figure 2) had a structure distinct from the gel directly placed in a solvent with the same salt concentration (e.g., from C to D in Figure 2). The new structure elements which were formed in the gel had a long lifetime and did not disappear for at least 1 week.

The kinetics of the gel collapse is presented in the second set of experiments. Figure 6 illustrates the volume changes of the cylindrical gels with time at different concentrations of NaI. At high concentrations, a fast transition of the gel to the collapsed state was observed. A decrease in the salt concentration could result in the appearance of the previously mentioned latent period for the time of the collapse.

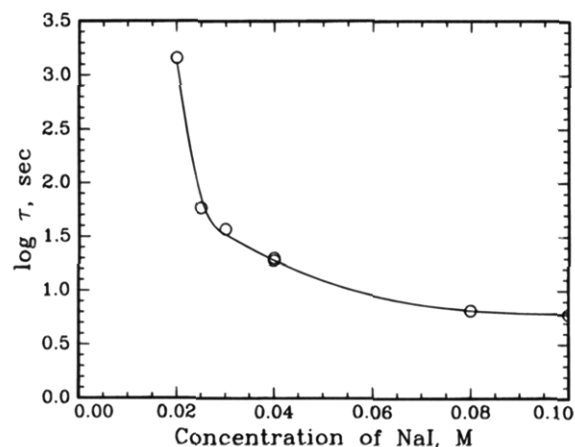
Figure 7 shows a plot of the characteristic time for the collapse to a final state,  $\tau$ , as a function of the NaI concentration. At high NaI concentrations the value of  $\tau$  depended only slightly on the salt concentration. In 0.08–0.1 M, the collapse proceeded in parallel with polyelectrolyte deswelling. The decrease in the NaI concentration resulted in a very fast rise of  $\tau$  at lower NaI concentrations ( $[NaI] < 0.03$  M).

Let us consider what is happening during the collapse process in the region of low NaI concentrations. Figure





**Figure 6.** Plots of relative volume as a function of time for PDADMACI gels in NaI solutions.



**Figure 7.** Plot of  $\log(\tau)$  versus NaI concentration.

8 illustrates the appearance of the gels during the phase transition. At first, the usual gel shrinking due to polyelectrolyte deswelling in the presence of salt was

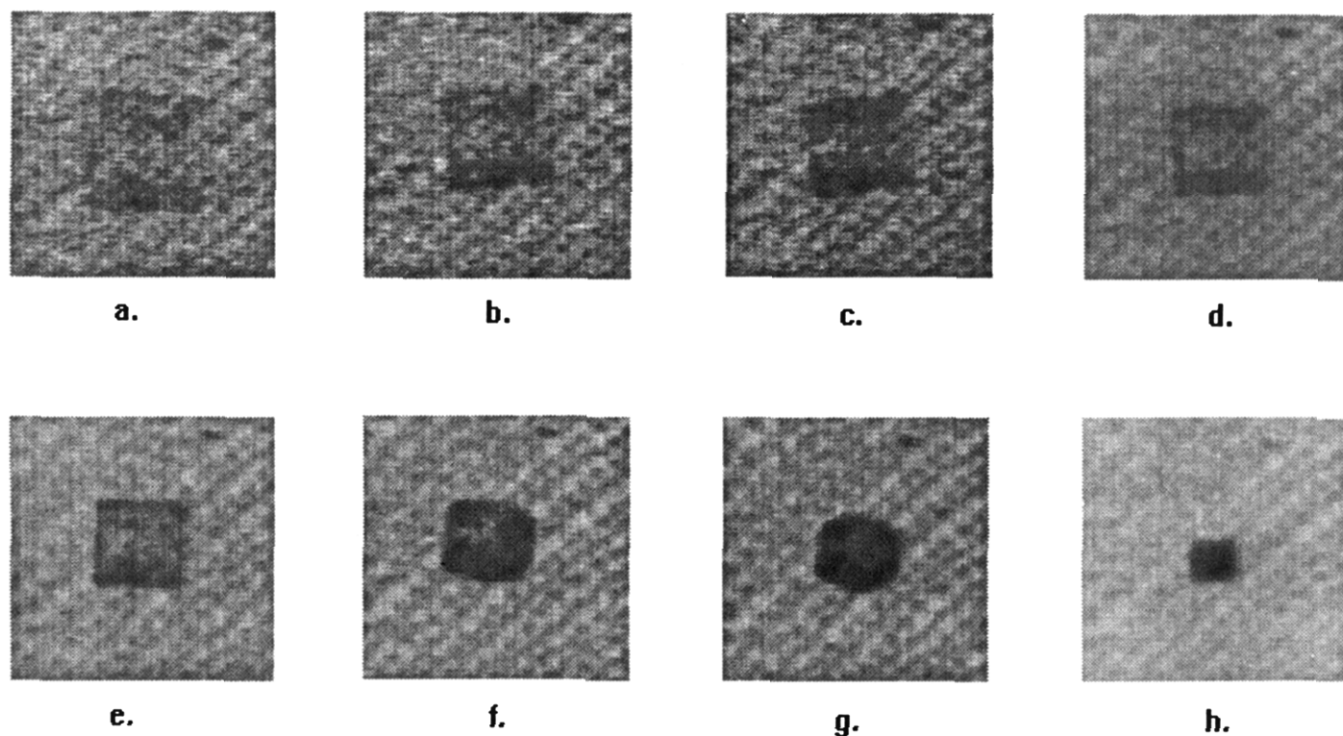
observed (Figure 8a–c); then no visible changes of the gel could be registered (Figure 8d,e). The next state of the collapsed region usually appeared near the corners of the cylinder (Figure 8f). As a result the cylindrical gels assumed the ellipsoidal form (Figure 8g). Finally, the completely collapsed gel returned to the initial cylindrical shape but with a greatly reduced volume (Figure 8h).

The results are in agreement with the concept of the transition to a supercollapsed state which is governed by the association of ion pairs into multiplets. Indeed, according to ref 19, this transition can take place only if some potential barrier is overcome (in contrast to the initial osmotic deswelling which has no barrier and is controlled by the diffusion of low molecular weight ions). Thus the collapse should occur via a nucleation and growth mechanism. The latent period which has been observed at sufficiently low NaI concentrations is a possible indicator for the mechanism: after the short period of initial osmotic deswelling, the system “waits” until a sufficiently large nucleus capable of growth appears. The pronounced hysteresis effects are also consistent with the picture described above.

The cylindrical shape of the gels makes it more likely that the initial nucleus is formed near the corners between the cross sections and side surface of the cylinders, and this is just what can be seen from the inspection of Figure 8. Indeed, the formation of a dense supercollapsed nucleus inside the gel would result in a great stress in its vicinity and thus requires high elastic energy which is unlikely. On the other hand, for the corner regions the elastic energy cost for nucleus formation should be much less. Thus, transition always starts from these regions, and once it is completed at the corners, it initiates collapse in the neighboring regions (Figure 8f).

### Conclusion

In this paper we have demonstrated that the formation of ion pairs (ionomer effect) is an important factor



**Figure 8.** Contraction of gel samples immersed in a 0.025 M NaI solution. The mesh background came from the nylon net. The expanded gel was very transparent, yielding a low contrast as shown in a.

in the collapse behavior of polycationic networks of poly-(diallyldimethylammonium chloride). The results are in general agreement with the predictions of ref 19 on the existence of a supercollapsed state of polyelectrolyte gels where the collapsed gel exhibits a characteristic ionomer behavior with multiplets formed by the attractions of ion pairs. A more detailed microscopic study of the structure of the collapsed gel is needed and will be the subject of one of the subsequent publications.

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