

The Gelation Studies of PAA Polyelectrolytes in Aqueous Media

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폴리 아크릴산 고분자 전해질의 수용액 속에서의 겔화에 관한 연구

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Abstract: Polyelectrolytes of various ionization degrees, which are prepared by neutralization of poly(acrylic acid) (PAA), were crosslinked by ethylene glycol diglycidyl ether(EGDE) in aqueous solution. C_{gel} , the minimum polymer concentration at which gelation occurs, was higher than expected. C_{gel} was comparable with that of neutral polymer. This is considered to be due to the size contraction of polyelectrolyte, which comes from ionic strength increase as polymer concentration is increased. C_{gel} is low when molecular weight of the sample becomes high. It reveals that polyelectrolyte is crosslinked in coil form not in extended rod form. This behavior is similar to the crosslinking of neutral polymers. Polyelectrolytes of partially ionized sample generally follow the behavior of fully ionized polyelectrolyte. Polyelectrolyte with added salt was also studied. Considering the pH dependence of EDGE reactivity it was difficult to compare the system which differs in pH significantly.

요 약: Polyacrylic acid를 NaOH와 NH₄OH로 중화시켜 중화도가 다른 polyelectrolyte를 만든 후, 수용액 상에서 ethylene glycol diglycidyl ether(EGDE)로 가교시켜 안정한 상태의 겔을 얻었다. 안정한 겔이 얻어지는 가장 작은 polyelectrolyte의 농도인 C_{gel} 은 polyelectrolyte의 extended form에도 불구하고 비슷한 분자량의 중성 고분자의 값과 비슷하였다. 전해질 고분자에 대한 scaling이론에 의하면 semi-dilute 영역에서의 전해질 고분자용액은 분자량 의존성이 없어야 함에도 불구하고 gelation 결과는 중성 고분자와 흡사한 분자량 의존성을 보이며 entanglement 농도인 C^* 와 비교했을 때에도 C_{gel} 은 훨씬 큰 값을 갖는다. 이는 고분자 전해질의 농도가 전해질수록 용액의 이온세기가 증가하여 extended form에서 coil form으로 변화되기 때문으로 보인다. 고분자 전해질의 중화도에 따른 gelation은 100% 중화된 시료의 C_{gel} 값과 분자량 의존성에 있어 거의 비슷한 경향을 보이며 이는 고분자 전해질의 conformation 변화가 이온세기에 상당히 민감함을 보여 준다. 고분자 전해질 수용액에 추가로 저분자량의 염을 가하면 고분자의 용액 속에서의 크기가 더욱 축소하여 더 큰 C_{gel} 값을 보인다.

1. Introduction

Interactions between polymer molecules in solu-

tion depend on solute concentration. When a solution is dilute, polymer chains are far apart each other so that no interactions occur. As a concentra-

tion becomes high, polymer chains begin to contact each other and an entanglement can occur. At a proper concentration C^* , the polymer coil overlaps as a whole and the solution becomes homogeneous [1]. Available experimental methods to identify C^* are viscometric method[2] and dynamic light scattering method[3]. In the previous paper, we proposed that C^* can be measured by a simple gelation experiment[4]. A dilute solution could not form a gel by the addition of a crosslinking agent since the chain density is not sufficiently high. It is found that the lowest gelation concentration of linear neutral polymer is quite close to C^* . In the case of polyelectrolyte, interactions become much more complex because of charges on the chain. De Gennes[5] and Odijk[6] divided the polyelectrolyte solution into four concentration regimes. They are the gas-like regime, ordered structure regime, overlap regime, and entangled regime. The borderline concentrations between two regimes are C_g , C^* , and C^{**} respectively. We adopt the Odijk's notation here. Although the notation C^* of polyelectrolyte is the same as C^* of neutral polymer, it is noted that they have quite different meaning.

Experimental supports of the above picture are presented by a few groups. Diffraction patterns satisfying the Bragg's condition were observed[7]. It shows the existence of internal order of polyelectrolyte solution. Slow diffusion mode which is due to the network motion is observed by dynamic light scattering[8]. However, such results are not satisfactory to prove the whole picture of Odijk. Ise proposed a new model for polyelectrolyte solution [9].

Various scattering methods are strong tools for the study of polyelectrolyte solutions. Other experimental technique, for example viscometry, is rather limited in use due to the complex nature of the polyelectrolyte solution. In this paper, a simple gelation experiment is adopted to study the behavior of polyelectrolyte solution. A special emphasis is put on the correlation between overlap concentration of polyelectrolyte and gelation concentration.

Polyacrylic acid (PAA) is a weak electrolyte. It behaves more like a neutral polymer in moderate concentration range. When it is neutralized by NaOH or NH_4OH , it becomes a strong polyelectrolyte. Aqueous solution of PAANa and PAANH₄ was crosslinked by ethylene glycol diglycidyl ether (EGDE).

2. Experimental

2.1. Polymerization[10]

200ml of acrylic acid was mixed with 1800ml of deionized water in a 2000ml four neck kettle equipped with a mechanical stirrer. Then a redox initiator of 1:1 sodium persulfate ($\text{Na}_2\text{S}_2\text{O}_8$) and sodium pyrosulfite ($\text{Na}_2\text{S}_2\text{O}_5$) were added to the monomer solution. The mixture was purged under N_2 atmosphere and polymerized by heating to 60°C for 5hrs. After the reaction, the prepared PAA solution was freeze dried. Six samples of different molecular weight were chosen from many batches prepared by the same procedure differing only in the amount of initiator.

Molecular weight of prepared sample was determined in the form of PAANa. Intrinsic viscosities of PAANa's are measured in 1.25M NaSCN solution at 30°C (theta condition). Molecular weights are calculated by the following equation[11].

$$[\eta] = 1.54 \times 10^{-3} M^{0.5}$$

2.2. Preparation of Polyelectrolyte

PAANa and PAANH₄ were prepared from PAA by adding NaOH and NH_4OH . In the case of PAANa, 10N of NaOH solution was added slowly to 20g/dl of PAA solution until pH of the solution became 10. The solution was then cooled to 5°C in a refrigerator and precipitated in methanol at 5°C . To remove the residual NaOH, the precipitate was dissolved in water again and the solution was precipitated to 5°C methanol. This operation was repeated two times[12]. Final precipitate was dissolved in water and freeze dried.

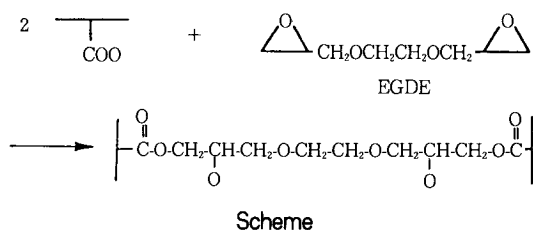
In case of PAANH₄, 25wt% of NH_4OH was

added slowly to 20g/dl of PAA solution until pH of the solution became 10. The solution was then cooled and precipitated to 5°C acetone. The precipitate obtained as above was dissolved in water and freeze dried.

Polyelectrolytes of partially ionized samples were prepared by adding calculated amounts of NaOH and NH₄OH. In the pH titration experiment of PAA, it is found that neutralization proceeds as the amount of bases is increased. Therefore, the ionization degree is the same as the neutralization degree.

2. 3. Gelation

In the test tubes of 1.5cm diameter, 1ml of polymer solutions which have gradual difference in concentration were pipetted to each tube. Then 35 μ l (2.25 \times 10⁻⁴mole) of ethyleneglycol diglycidyl ether (EGDE) was added to each tube and mixed thoroughly. After this, the tubes were sealed and left at 80°C for 1.5hrs. Crosslinking reaction between polymer and EGDE is shown in the following Scheme [13].



Solutions which do not form gels flow when the tubes are tilted. When a metastable gel is formed, it does not flow. When we take it out of the tube, it does not maintain its shape. We identified a gel as a stable sample which maintains its shape when we took it out of the tube. The lowest gel forming concentration is taken as the gelation concentration of the sample, C_{gel} .

3. Results and Discussion

3. 1. pH Dependence of Gelation

A 100% neutralized 0.1g/dl aqueous PAANA is

a basic solution of pH=9.20. This is because the ionic species in solution hydrolyze water. PAANA's of different neutralization degree show pH difference in aqueous solution. When PAA is neutralized by NH₄OH, the pH increase is much more diminished. The pH of 100% neutralized 0.1g/dl aqueous PAANH₄ solution is 7.20.

Gelation is conducted with various kinds of samples. All the samples of different neutralization degree except for a parent PAA reacted with EGDE and became gel under proper condition. It seems that a small amount of -COO⁻ group is required for the activation of EGDE.

We measured C_{gel} 's of PAANA of different neutralization degree, α . As mentioned previously, samples of different neutralization degree show different pH values. In Fig. 1, we plotted C_{gel} 's of PAANA of molecular weight 396,000 as a function of various pH values. We notice in Fig. 1 that C_{gel} is minimum at pH=6.27, which corresponds to neutralization degree $\alpha=0.5$. When the solution becomes more acidic or basic, C_{gel} becomes higher.

Such C_{gel} variation with regard to α or pH is considered in two ways. It may be due to chain conformation change caused by the variation of neutralization degree. Another possibility is that the reac-

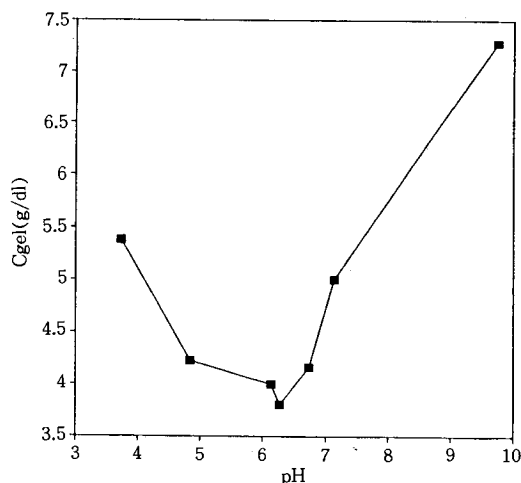


Fig. 1. The pH dependence of C_{gel} of molecular weight 396,000 PAANA. Samples of different pH have different neutralization degree, α .

tivity of EGDE crosslinking agent is dependent on pH. It is known that two reactions of EGDE compete in $-\text{COO}^-/-\text{COOH}$ mixture, which are esterification(crosslinking) and self hydrolysis. An NMR study showed that esterification is predominant in near neutral condition, and the self hydrolysis to diol is dominant in acidic or basic condition[14].

What is the major factor of these two? To answer the question, gelations of both PAANa and PAANH_4 of $\alpha=1$ is compared. These two polyelectrolytes are the same charge density and therefore believed to be the same conformation in aqueous solution. On the other hand, pH's of PAANa and PAANH_4 are 9.00 and 7.20, respectively. If C_{gel} 's of PAANa and PAANH_4 differ significantly, we would conclude that the difference is due to pH difference. Experimental results of C_{gel} 's of PAANa and PAANH_4 are 8.41g/dl and 4.61g/dl, respectively for molecular weight 396,000 sample. Such discrepancy of the two different type polyelectrolytes appear in other molecular weight samples as well as partially neutralized samples. This point will be discussed later.

The above consideration shows that the C_{gel} variation with regard to α or pH is mainly due to the pH effect on EGDE reactivity. In acidic or basic condition, no effective gelation progresses since EGDE is wasted by self hydrolysis.

3. 2. Gelation of PAANH_4

A 100% neutralized PAANH_4 is neutral in aqueous solution. We choose it for the gelation study of polyelectrolyte, since EGDE could be used for gelation with minimum loss.

De Gennes[5] and Odijk[6] independently predict the overlap concentrations of polyelectrolyte in salt free condition as follows:

$$C^* = (M_0/N_A)(16\pi QAl)^{-1} \quad (1)$$

$$C^{**} = 0.04(M_0/N_A)(4\pi Q^2 A)^{-1} \quad (2)$$

where M_0 is the molecular weight of polyelectrolyte repeating unit, and N_A is the Avogadro number. Q

is the Bjerrum length which is 7.13 Å in 25°C water. A is the distance between charges. It has 2.54 Å in acrylic monomer. l is the contour length of the chain.

C^* is the concentration at which rodlike polyelectrolyte molecule starts to bend owing to mutual charge interaction. C^{**} is the concentration of penetration between chains to start. The beginning of semi-dilute regime of polyelectrolyte is considered to be C^{**} [6]. To crosslink polymer by using small EDGE molecules, a proper chain density in solution is needed. Thus we adopt the semi-dilute C^{**} as the theoretical concentration at which gelation can be possible.

Experimentally determined C_{gel} of PAANH_4 in fact appeared much higher than both C^* and C^{**} . In Table 1, we showed C_{gel} 's of various molecular weight of PAANH_4 and the calculated values of C^* and C^{**} by using eqn. (1) and (2), respectively. C_{gel} is 10^3 fold higher than C^* and 10 fold than C^{**} .

We consider this discrepancy as follows. The solution at C^{**} is thought to be such that each chain is intermolecularly penetrated. It comes from the Odijk's condition of sufficiently large chain length [6]. Therefore, C^{**} has no chain length dependence in eqn(2). It is the value of high molecular weight limit. When the solution is much like this, EGDE can crosslink neighboring chains and gel can be formed. We call this chain-chain crosslinking. In this case, gelation concentration(in g/dl) should be the same for all different chain length polymers. It

Table 1. The Physical Data of PAANH_4 ($\alpha=1$) and PAAM.

PAANH ₄ ($\alpha=1$)					PAAM'	
M.W.	C_{gel} (g/dl)	C^* (g/dl) ^a	C^{**} (g/dl) ^b	l (mol/l) ^c	M.W.	C_{gel} (g/dl)
75,000	9.23	8.03×10^{-3}	0.38	0.184	35,000	22.70
126,000	6.42	4.78×10^{-3}	0.38	0.128	62,000	14.37
248,000	5.10	2.43×10^{-3}	0.38	0.102	145,000	7.28
396,000	4.61	1.52×10^{-3}	0.38	0.092	397,000	3.25
757,000	4.00	8.06×10^{-4}	0.38	0.079	615,000	2.99

^a Calculated by eqn (1) in the text.

^b Calculated by eqn (2) in the text.

^c Calculated by eqn (3) in the text.

is because the average chain density is dependent only on concentration of solute. We see in Table 1 that the limiting value C^{**} is constant. But as molecular weight of polymer increases, C_{gel} decreases to the limiting value C^{**} .

The decrease of C_{gel} with increasing molecular weight in Table 1 reveals that the gelation is not proceeded by the chain-chain crosslinking. It is viewed that polymer chain does not penetrate extensively and each molecule has its own domain like a coil of neutral polymer. Because of the ionic strength increase of solution, an extended conformation is not maintained as concentration becomes higher. In this case, EDGE can crosslink neighboring molecular coils. We call it molecule-molecule crosslinking. Under the picture of this kind, the molecular weight dependence of C_{gel} may be reduced to the case of neutral polymers, which will be discussed later.

It is interesting to check whether C_{gel} is a meaningful concentration in other experiments. Recently Park and Yu[15] observed that homogeneous regime begins at concentration much higher than C^{**} . In their dynamic light scattering experiment, the self diffusion constant of linear NaPSS (M.W. = 200,000) was constant up to 10wt% of NaPSS. The diffusion constant dropped significantly over this concentration. Although the concentration is somewhat higher than our gelation concentration of comparable molecular weight sample, it supports the fact that a meaningful concentration does exist over C^{**} .

As mentioned previously, the gelation of PAANH₄ is accomplished by molecule-molecule crosslinking. It is similar to the gelation of neutral polymer. We showed in the previous paper that polymer coil overlapped at C^* and at this concentration gelation proceeded by adding crosslinking agent. To compare the behavior of polyelectrolyte and neutral polymer, C_{gel} 's of polyacrylamide (PAAm)[4] are also shown in Table 1. Two points will be discussed. One point is that the C_{gel} 's of PAANH₄ are similar to those of PAAm in magnitude. The other is mo-

lecular weight dependence is not same for both polymers.

It is thought that the similarity in magnitude of C_{gel} compared to neutral polymer is due to the size contraction of polyelectrolyte. Le Bret[16] and Fixmann[17] predict independently that the radius of gyration of polyelectrolyte is contracted by increasing polymer concentration. The size contraction is due to the charge screening effect with increasing of ionic strength. Nierlich[18] confirmed this with small angle neutron scattering (SANS) experiment. As concentration becomes higher, counterion trapped inside the chain will come out. According to the counterion condensation theory, ionic strength of polyelectrolyte solution is as follows[19].

$$I = (1/2)(A/Q)C_m \quad (3)$$

where C_m is the concentration of charged repeating unit (in mol/l). Ionic strengths of PAANH₄ at C_{gel} 's are shown in Table 1. They appear from 0.184M for low molecular weight sample to 0.0079M for high molecular weight sample. These are the sufficient ionic strength to contract the polyelectrolyte to coil form. Intrinsic viscosities of the samples did not diverge in aqueous NaSCN solution when ionic strength is dropped to 0.0025M. It reveals that they are in coil form in this ionic strength range. In other experimental observation by dynamic light scattering, it is reported that a dimension of a polyelectrolyte at high concentration limit is the same as a neutral polymer[20].

According to the scaling theory of neutral polymer, the plot of $\log(\text{molecular weight})$ vs. $\log(C^*)$ is linear[1]. The plot of $\log(\text{molecular weight})$ vs. $\log(C_{gel})$ is also linear[4] as shown in Fig. 2. In polyelectrolyte system, the plots of $\log(\text{molecular weight})$ vs. $\log(C_{gel})$ deviate somewhat from linearity as shown in Fig. 2. We see that the deviation is large for high molecular weight sample. It is thought that the size contraction by ionic strength increase is more effective for low molecular weight than for high molecular weight sample.

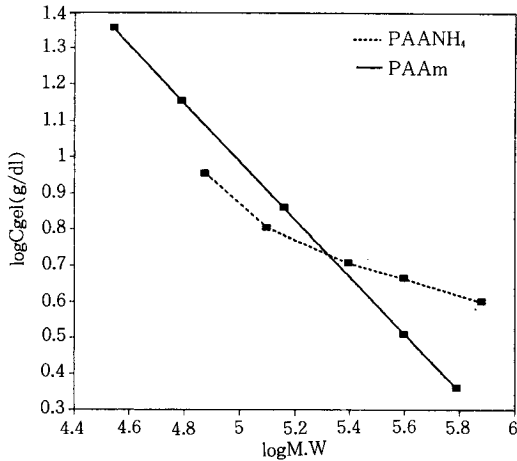


Fig. 2. Molecular weight dependence of C_{gel} of $PAANH_4$. The curved line is for $\alpha=1$ $PAANH_4$. The straight line of neutral PAAm is also plotted for comparison.

Table 2. The C_{gel} 's of Variously Neutralized PAANa and $PAANH_4$.

M.W.	PAANa			PAANH ₄		
	$\alpha=0.1$ pH=4.30	$\alpha=0.5$ pH=6.27	$\alpha=1$ pH=9.00	$\alpha=0.1$ pH=3.36	$\alpha=0.5$ pH=5.38	$\alpha=1$ pH=7.20
75,000	10.53	6.67	22.15	10.4	6.11	9.00
126,000	7.65	5.38	15.38	7.83	5.33	6.42
248,000	5.71	4.58	10.00	5.16	4.55	5.10
396,000	5.00	4.00	8.41	4.67	4.00	4.64
757,000	4.61	3.40	8.18	4.00	3.75	4.00

3. 3. Gelation of Partially Ionized Polyelectrolyte

Previously we partly discussed the gelation of partially ionized polyelectrolytes. Now here, molecular weight dependence of C_{gel} of the sample of $\alpha=0.1, 0.5,$ and 1 will be discussed. The gelation data are shown in Table 2. We see that C_{gel} of $\alpha=0.5$ PAANa is two or three times higher than $\alpha=1$ PAANa for all molecular weights. $PAANH_4$ samples, however, do not show such a large difference between the sample of different ionization degrees. When we stand on the maximum EGDE reactivity point at $pH=6.25$, it becomes clear that the gelation data show consistent pH dependence of EGDE. The large difference of C_{gel} 's for PAANa is due to the

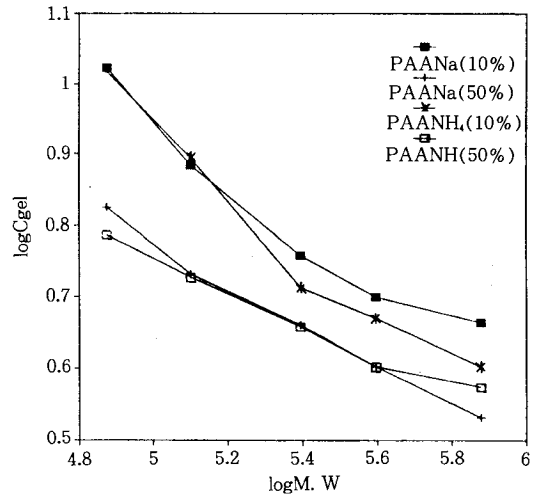


Fig. 3. Molecular weight dependence of C_{gel} for partially neutralized PAANa and $PAANH_4$.

large pH difference from $pH=6.25$. The pH's of $\alpha=0.1$ and 1 PAANa are 4.30 and 9.00, respectively. The pH's of $\alpha=0.1$ and 1 $PAANH_4$ are 3.36 and 7.20, respectively. They show rather small difference in pH compared with PAANa and show small difference in C_{gel} . We now conclude that the C_{gel} difference of partially ionized polyelectrolyte is mainly due to the pH effect not to the ionization degree effect.

We comment one thing in relation to the counterion condensation theory. According to eqn (3), ionic strength is constant for all partially ionized polyelectrolytes. When charged unit (C_m) increases, the spacing between charge (A) becomes small. It means that increased charges on a chain cause high field strength around chain. So counterions are more strongly trapped. In the case of $PAANH_4$, which shows narrower pH range between variously ionized samples, C_{gel} 's are almost the same for all ionization degrees as shown in Table 2 when we take into account the pH effect of EGDE.

Molecular weight dependence of C_{gel} is plotted for partially ionized samples in Fig. 3. The shape of the curves for PAANa is very similar to that of $PAANH_4$. Judging from the magnitude of C_{gel} 's and molecular weight dependence of C_{gel} , partially ion-

ized samples are thought to be crosslinked by molecule-molecule crosslinking.

3. 4. Gelation of PAANA with Added Salt

Until now, we discussed polyelectrolyte solution without salt. From now on we consider the system in which NaCl is added. It is known that diffusion coefficients increase for all concentration regions when salt is added[21]. It means that the size contraction of polyelectrolyte results from the addition of salt.

To see the salt effect, we added NaCl to a 100% ionized PAANA of molecular weight 757,000. The result is shown in Fig. 4. The minimum point in C_{gel} emerges as NaCl concentration increases. It was out of our expectation. When polymer size is contracted by salt, C_{gel} should be increased monotonically.

We also found that the pH of solution decreases with adding NaCl. The same pH fall is also found in small molecule analog. It seems that the activity coefficient of H^+ increased as ionic strength increased. As can be seen in Fig. 4, pH of the minimum point of C_{gel} is 6.25 which is the pH value of the maximum reactivity of EGDE. The decrease of C_{gel} to the minimum point is considered as follows. There are two factors which influence C_{gel} coun-

teractively when salt is added. They are the lowering of pH to 6.25 and the size contraction of polyelectrolyte. Since the ionic strength of polyelectrolyte solution without salt is sufficiently high around C_{gel} , additional small amount of salt gives little effect on the size contraction. Thus the lowering of pH to 6.25 activates EGDE and C_{gel} decreases. The increase of C_{gel} after minimum point by further addition of salt is as follows. Further decrease of pH from 6.25 deactivates EGDE, and polyelectrolyte contracts at the same time by further increase of ionic strength. The two factors combined to increase C_{gel} .

4. Conclusion

From the result of the simple gelation experiment so far, we conclude here:

1. A 100% neutralized $PAANH_4$ did not crosslink at C^* , which is the theoretical overlap concentration of infinitely large molecular weight polyelectrolyte. The gelation concentration measured is higher than C^* and it was almost in the same order as that of neutral polymer. The reason for this is thought to be the size contraction of $PAANH_4$ due to its salt nature.

2. Molecular weight dependence of C_{gel} for the gelation of $PAANH_4$ reveals that the crosslinking is proceeded by molecule-molecule crosslinking, which is similar to neutral polymers. But the molecular weight dependence of C_{gel} was not exactly the same as neutral polymers probably due to the charge effect of the polyelectrolyte.

3. Polyelectrolytes of different neutralization degree show different C_{gel} . It is found that the major reason is due to the reactivity difference of EGDE in various pH conditions. The conformation difference of differently neutralized samples does not seem to affect seriously.

The gelation phenomena of partially neutralized samples were very similar to a 100% neutralized polyelectrolyte.

4. Polyelectrolyte with added salt shows high C_{gel}

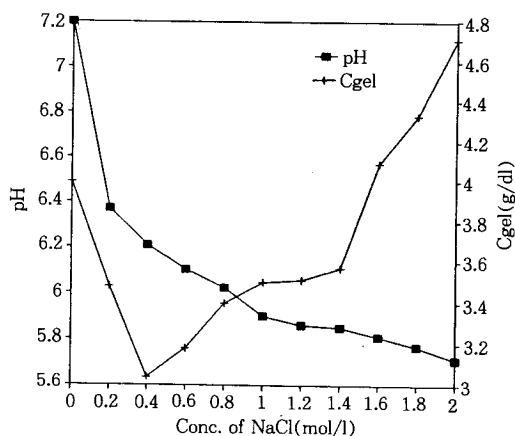


Fig. 4. Added salt effect on C_{gel} PAANA of molecular weight 757,000 ($\alpha=1$) is used. The points of the pH curve are pH's at C_{gel} 's of each salt concentration.

on account of the size contraction effect due to the ionic strength increase. The initial decrease of C_{gel} is due to the lowering of pH toward 6.25 with the addition of salt.

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