

# Nonstoichiometric Polyelectrolyte Complex of Carboxymethylcellulose and *N*-Methylated Poly(2-vinylpyridine): Formation of a Gel-Like Structure

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**ABSTRACT:** The formation of polyelectrolyte complexes between carboxymethylcellulose and *N*-methylated poly(2-vinylpyridine), at a nonstoichiometric mixing ratio, was studied. Various methods, such as viscometry, turbidimetry, electrophoresis, and optical spectroscopy, were used to investigate the complexes with respect to their composition, structure, and stability in aqueous systems of different ionic strengths. A gel-like structure was proposed for the nonstoichiometric polyelectrolyte complexes. Two steps of complex formation—ionic bond formation followed by its rearrangement—were identified. The conformational change of the polyelectrolyte chains in the complexes, responsible for the slower and latter step, was followed by viscometry, and the results were interpreted on the basis of a model proposed for the kinetics of swelling of hydrogels. A similarity was found between the kinetics of diffusion of polymer segments responsible for the swelling of a macrogel of a nonionic polymer and the rearrangement of ionic bonds leading to the formation of a nonstoichiometric polyelectrolyte complex. © 2003 Wiley Periodicals, Inc. *J Polym Sci Part A: Polym Chem* 41: 2288–2295, 2003

**Keywords:** polyelectrolytes; nonstoichiometric complex; conformational rearrangement; gels; viscometry; networks

## INTRODUCTION

Intermacromolecular complexation caused by the attractive interaction of complementary polyelectrolytes (PEs) has been the focus of much attention during the last few decades.<sup>1–7</sup> As a result, a clear picture of the complexation process has emerged. A thorough understanding of the ther-

modynamic and kinetic aspects of polyelectrolyte complex (PEC) formation, the relevance of the characteristics of PECs, and the nature of the interacting systems has been well established. This knowledge has assisted in the understanding of the complex biological phenomenon<sup>8</sup> and self-assembly of molecules. Furthermore, PECs have been used in the development of new materials with potential industrial, pharmaceutical, biomedical, and biotechnological applications.<sup>9–12</sup>

In our earlier work,<sup>13</sup> the significance of the characteristics of the component PEs, such as the charge density, chain length, rigidity, and concentration, in the formation of PECs was reported; sodium salt of carboxymethylcellulose (NaCC), a rigid polyanion, and a few flexible-chain vinylic polycations were used. In that study, an observation of very high viscosity, in comparison with the

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additive viscosity of the individual PEs, was reported for an aqueous system of poly(2-vinyl-*N*-methylpyridinium iodide) (P2VPMI) and NaCC at certain mixing ratios. In this study, an attempt was made to understand the structure of the PECs causing the high-viscosity behavior. Various methods, such as viscometry, turbidimetry, electrophoresis, and optical spectroscopy, were used to investigate the formation of nonstoichiometric polyelectrolyte complexes (NPECs). A loose, gel-like structure was proposed for NPECs, based on evidence from different experiments. The conformational changes in the PE chains caused by the rearrangement of the ionic crosslinks leading to the proposed structure of NPECs was studied on a timescale of several hours.

## EXPERIMENTAL

### Materials

NaCC (BDH, United Kingdom) and methyl iodide (Sisco, India) were used as received. 2-Vinylpyridine (Merck) was distilled twice under reduced pressure before use. Methyl orange (MO; BDH) was purified by recrystallization from ethanol. All other reagents were reagent-grade and were used as received. The preparation of poly(2-vinyl-*N*-methylpyridinium iodide) with a low degree of substitution (P2VPMI-LDS) and the characterization of the polymer samples used in this work were reported elsewhere.<sup>13</sup> The degree of substitution and the viscosity-average molecular weight of the NaCC sample were 0.73 and  $4.3 \times 10^5$ , respectively. The corresponding values for P2VPMI-LDS were 0.40 and  $2.3 \times 10^4$ , respectively.

### Methods

#### *NPEC Formation and Measurements*

An NPEC of the composition  $[p^+]/[p^-] = 0.25$  {or  $[p^-]/([p^+] + [p^-]) = 0.8$ ; NPEC-25} was made by the addition of an appropriate amount of a P2VPMI-LDS solution (concentration of the ionic groups =  $8.0 \times 10^{-3}$  mol dm<sup>-3</sup>) to a solution of NaCC of identical concentration in an Ubbelohde viscometer. The relative viscosity ( $\eta_r$ ) of the mixture was measured as a function of time by the measurement of the rate of flow. The intrinsic viscosity ( $[\eta]$ ) of the solution at a given time was calculated from the corresponding  $\eta_r$  value with

the following empirical relation:<sup>14</sup>  $[\eta] = 2(\eta_{sp} - \ln \eta_r)^{0.5}/C$ , where  $\eta_{sp}$  and  $C$  are the specific viscosity and the total concentration of the polymer (g/dL), respectively.

#### *Dye-Release Measurements*

The formation of NPEC-25 was followed in a separate experiment by the recording of ultraviolet-visible (UV-vis) spectra of P2VPMI-LDS and MO systems ( $[p^+]/[\text{dye}] = 1.0$  and  $[\text{MO}] = 3.33 \times 10^{-5}$  mol dm<sup>-3</sup>) before and immediately after the addition of NaCC, which led to the formation of NPEC-25. A UV-vis spectrometer (Hitachi U 3400) was used.

#### *Electrophoresis*

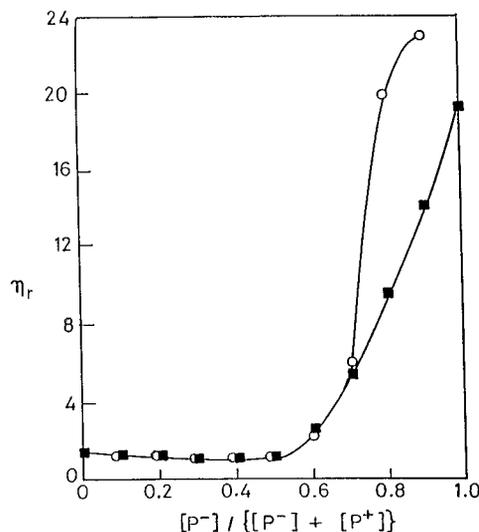
An equilibrium solution of NPEC-25 was electrophoresed on a 0.3% agarose gel matrix in a phosphate buffer (0.05 mol dm<sup>-3</sup>, pH 7–8) under a steady electric field. The NPEC-25 and P2VPMI-LDS solutions (0.15 mL) were loaded into adjacent sample wells created at the center of the gel. The samples were allowed to move under a potential drop of 1 V/cm maintained across the electrophoretic cell with a regulated direct-current power supply (Digireg 133, Digitronics, India). After 2 h, the gel was removed and stained in an iodine chamber. The polymer bands appeared as brown streaks. The stained gel was photographed.

#### *Turbidity Measurements*

The stability of NPECs toward the low molecular weight electrolytes was determined by the measurement of the transmittance of an equilibrium solution of NPEC-25 as a function of the ionic strength of the medium at a wavelength of 420 nm with a Hitachi U3400 spectrometer. The ionic strength was varied by the addition of the appropriate amounts of NaCl solutions to PEC mixtures.

## RESULTS AND DISCUSSION

A viscometric study of a system of NaCC and *N*-methylated poly(2-vinylpyridine) of a low (40%) degree of substitution (P2VPMI-LDS), reported earlier,<sup>13</sup> is presented again in Figure 1. It is evident from the figure that the PEC composition was stoichiometric in the range  $[p^-]/([p^+] + [p^-]) = 0-0.7$ , as shown by the good agreement be-



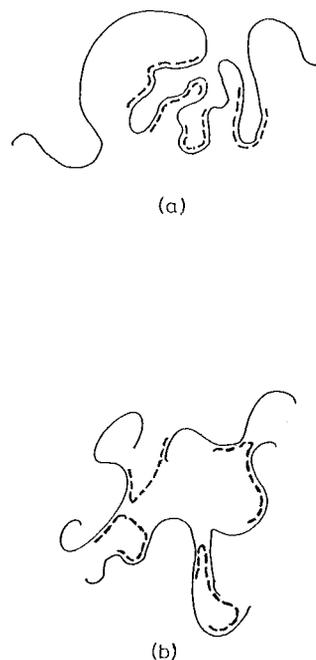
**Figure 1.**  $\eta_r$  versus the solution composition at various mixing ratios for (○) a mixture of NaCC and P2VPMI-LDS and (■) a control solution containing only the excess PE and NaI expected to be released on the formation of 1:1 PEC.

tween the  $\eta_r$  values of the PEC solution and the control. This observation is typical for systems in which stoichiometric complexes precipitate out of solutions and, therefore, do not contribute to the viscosity of the mixture. At mixing ratios of  $[p^-]/([p^+] + [p^-]) > 0.7$ , where the concentration of a fixed negative charge ( $p^-$ ) in solution was in excess compared with the concentration of a fixed positive charge ( $p^+$ ), the PEC solutions showed distinctly high  $\eta_r$  values than the control  $\{[p^-]/([p^+] + [p^-]) = 0.8 \text{ and } 0.9\}$ . The viscosity in this region of the mixing ratio was much higher than the additive viscosity of the individual components. There are reports in the literature in which interpolymer complex systems show high-viscosity behavior because of the existence of nonstoichiometric complex species in the associated state.<sup>15,16</sup> The capacity of a particular system for association is determined by the structural parameters of the interacting components and the experimental conditions.<sup>4</sup> In this system, the component PEs differed, both in their chain length and charge density, by a large magnitude. The polyanion chains, which were of relatively longer lengths, acted as host polyelectrolytes (HPEs), in the generally used terminology, whereas the shorter polycation chains could be considered guest polyelectrolytes (GPEs). The rigidity of the NaCC chains and a large difference between the neighboring charges on the P2VPMI-

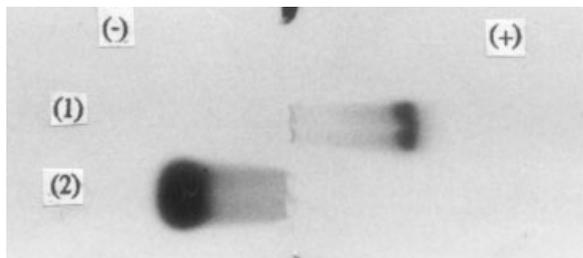
LDS and NaCC chains used here might have led to an inefficient complexation of the oppositely charged groups, hindering the regular arrangement of the GPE on the HPE as in a ladder-like structure of the PEC [Fig. 2(a)]. However, large complex species or microgels could be formed by the crosslinking of the HPE chains by the GPE chains [Fig. 2(b)]. This crosslinked gel-like structure could account for the high viscosity of the solution.

### Evidence for the Structure of NPECs

According to the mechanism of formation of NPECs at compositions with excess polyanions, the complexes are expected to have a net negative charge, stabilizing it in the solution. To test this hypothesis, we performed the electrophoresis of an NPEC solution at a mixing ratio of  $[p^+]/[p^-] = 0.25$  (NPEC-25) along with a pure polycation solution as a standard. In the photograph shown in Figure 3, the bands 1 and 2 correspond to NPEC-25 and the pure polycation solution, respectively, after the electrophoresis and exposure of the gel matrix to iodine vapor. Iodine stained only the polycation units (forming a charge-transfer complex with pyridine)<sup>17</sup> and not the nonaro-



**Figure 2.** Schematic representation of the possible structures of NPECs: (a) ladder-like and (b) gel-like. The solid lines represent NaCC chains, and the dotted lines represent P2VPMI-LDS chains.



**Figure 3.** Photograph of the agarose gel stained with iodine after the electrophoresis: (1) NPEC-25 band and (2) P2VPMI-LDS band (standard).

matic polyanion, NaCC. The movement of the NPEC toward the positive electrode, in the direction opposite to the movement of the positively charged polycation, indicated the existence of a net negative charge on the NPEC. It also showed that the ionic bonds between the PEs in the NPEC were intact and that the structure did not break into individual components under the ionic environment of the solution ( $\mu = 0.05 \text{ mol dm}^{-3}$ ) used for electrophoresis. The limits of the ionic strength, which defined the stability of the ionic bonds in NPEC-25, were further determined by turbidity measurements.

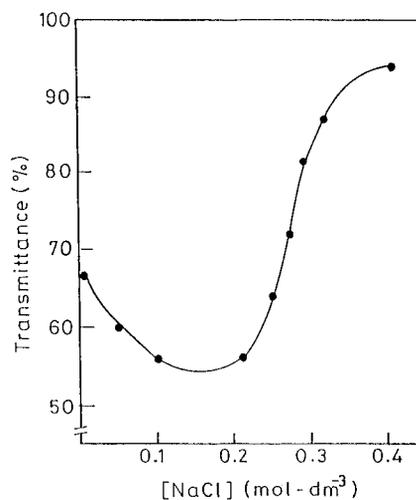
#### Stability of NPECs in Salt Solutions

In PEC systems, the strength of bonding between the oppositely charged PEs is determined by the ionic strength of the media. At high ionic strengths, the fixed charge on the PEs is screened by the free ions, reducing the strength of complexation. To study the stability of NPECs in aqueous media of high ionic strength, we measured the percentage transmission ( $T$ ) of an NPEC-25 solution at different ionic strengths (in terms of the concentration of NaCl  $C_1$ ) and plotted the results in Figure 4. The initial decrease in  $T$  with an increase in the ionic strength indicated contraction of the NPEC species due to screening of the excess charge on the NPEC particles by the free ions. This led to an increase in the density and refractive index of the particles, making the solution more turbid. At  $C_1 > 1.5 \times 10^{-1} \text{ mol dm}^{-3}$ ,  $T$  decreased as the PEC started breaking down into individual soluble components, and the solution finally became clear around  $C_1 = 3 \times 10^{-1} \text{ mol dm}^{-3}$ . This showed that the NPEC was stable at the ionic strength used for the electrophoresis experiment.

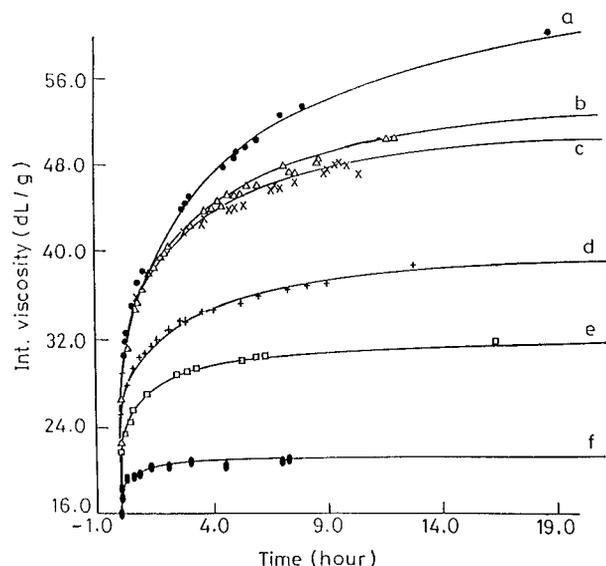
In comparison with NPECs, the properties of stoichiometric complexes will be distinctly different. The complete charge neutralization will make the latter electrically neutral and, therefore, will not move under the electrical potential on the electrophoretic gel. The high degree of coulombic interactions make the structures of stoichiometric complexes highly stable even in dilute salt solutions, and they do not undergo swelling or dissolution in the range of ionic strengths used here.

#### Kinetics of the Formation of NPECs

During the preparation of NPEC-25, it was observed that immediately after the mixing of the solution of NaCC with the solution of P2VPMI-LDS in the viscometer, the mixture turned slightly turbid, and with the progress of time, it became clearer and clearer. This change was also accompanied by an increase in the viscosity (Fig. 5). The highest and relatively constant value of viscosity was attained after several hours. We assume that, during this period, the ionic bonds that instantaneously formed with the mixing of the PE components rearranged with the involvement of uncomplexed polyanion segments to form a more stable structure. This led to the formation of the swollen gel-like structure of the NPEC. Such rearrangement reactions or exchanges of salt bonds are known to be facilitated by the presence of microions in solution. Therefore, we followed the kinetics of swelling of the NPEC species by the measurement of the viscosity of the solu-



**Figure 4.** Transmittance (%) of NPEC-25 versus the concentration of NaCl.



**Figure 5.** Variation of  $[\eta]$  of NPEC-25 with time at different ionic strengths: (a) 0.0, (b)  $0.8 \times 10^{-3}$ , (c)  $1.6 \times 10^{-3}$ , (d)  $3.2 \times 10^{-3}$ , (e)  $5.2 \times 10^{-3}$ , and (f)  $1.0 \times 10^{-3}$  M NaCl.

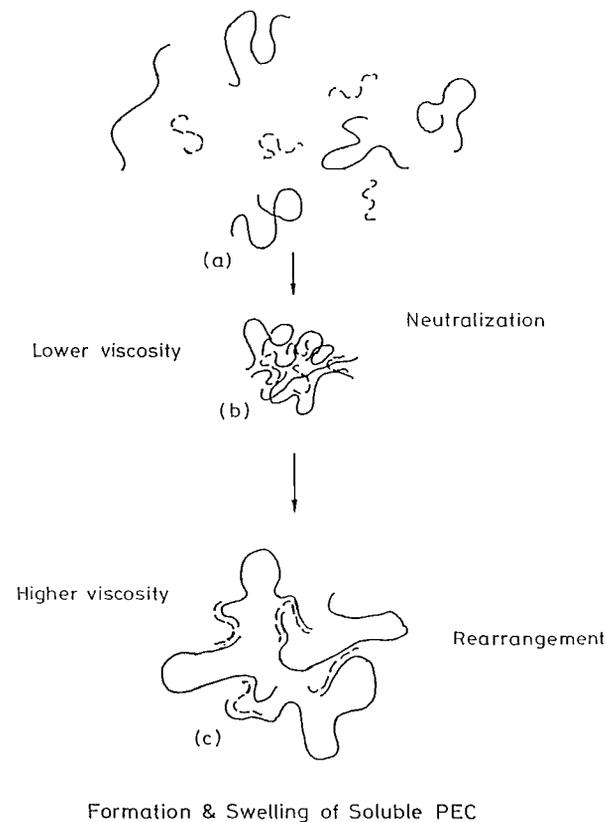
tion as a function of time at different ionic strength conditions maintained with externally added microsals. The formation of the swollen NPEC species is a two-step process (Fig. 6), as shown by earlier studies.<sup>18,19</sup> The faster first step involves the formation of ionic bonds between oppositely charged groups, the rate of which is controlled by the diffusion of the PE chains toward one another. In the slower second step, the PEC relaxes to a relatively more stable structure by the rearrangement of the ionic bonds and the conformational changes of the PE chains leading to the gel-like (swollen microgel) structure.

To establish that the first step occurs on a much shorter timescale than the second, we followed the release of an anionic counterion of the polycation on complexation with NaCC by spectrometry (Fig. 7). MO, an anionic dye molecule, exhibits metachromasy (a shift in the absorption frequency depending on its chemical environment); the molecule shows a substantial blueshift when it exists in an aggregated state.<sup>20</sup> When MO was added to the polycation solution at a concentration ratio of  $[p^+]/[MO] = 1$ , most of the dye molecules were bound to the polycation, and the absorption band appeared at a blueshifted position of 424 nm [Fig. 7(b)]. On the addition of NaCC for the formation of NPEC-25, the band shifted to 465 nm [Fig. 7(c)], indicating the release of the dye molecules from the polycations.

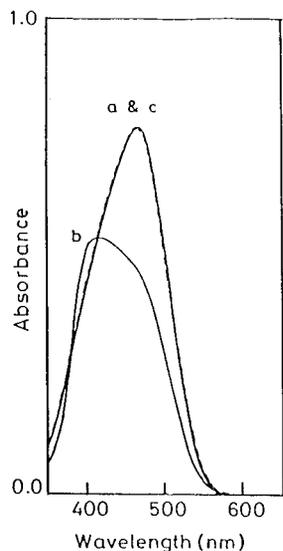
This change was observed to be immediate (few seconds), unlike the slow second step, which was followed for a period of 10–12 h. Therefore, it can be assumed that the initial step of complexation of NaCC with P2VMPI-LDS for the formation of NPEC-25 did not kinetically couple with the second step of the configurational rearrangement of the complex. In this work, this second step was studied in detail by viscometry.

### Kinetics of the Rearrangement

The NPEC particles in this system could be considered as swelled microgels dispersed in an aqueous medium. The increase in the viscosity of the NPEC solution could be related to the increase in the size of the particles with the change in the swellability of the microgels. From this point of view, the theory of swelling of macroscopic gels, developed by Tanaka et al. [Tanaka–Hockes–Benedek (THB) theory],<sup>21,22</sup> was applied to understand the kinetics of the rearrangement.



**Figure 6.** Schematic representation of the formation of NPEC. The solid lines represent NaCC chains, and the dotted lines represent P2VMPI-LDS chains.



**Figure 7.** Absorption spectra of MO under different conditions: (a) free dye (solid line), (b) in the presence of P2VPMI-LDS, and (c) with the formation of NPEC-25 (dotted line).

The THB theory relates the time dependence of swelling of a spherical gel to the diffusion coefficient ( $D$ ) of the gel network, rather than that of the fluid molecules. According to this theory, the equation of motion of the gel considers the displacement vector  $\mathbf{u}(\mathbf{r}, t)$  to represent the displacement of a point in the gel network as a function of space and time from its final equilibrium position in the fully swelled gel. The magnitude of the displacement obeys the following equation:

$$\frac{\delta u}{\delta t} = D \frac{\delta}{\delta r} \left[ \frac{1}{r^2} \cdot \frac{\delta}{\delta r} (r^2 u) \right] \quad (1)$$

The solution of this expression gives the change in the radius [ $\Delta a(t) = -u(a, t)$ ] of the gel during the swelling process:

$$\Delta a(t) = \Delta a_0 \left( \frac{6}{\pi^2} \right) \sum n^{-2} \exp(-n^2 D \cdot t/a^2) \quad (2)$$

where  $a$  is the final radius and  $\Delta a_0$  is the total change in the radius of the sphere in the entire process of swelling.

In the time domain of  $t \gg a^2/D$ , the higher order terms in eq 2 may be neglected, and the equation, in its logarithmic form, can be written as follows:

$$-\ln \frac{\Delta a(t)}{\Delta a_0} = -\ln \frac{6}{\pi^2} + \frac{D \cdot t}{a^2} \quad (3)$$

According to the Flory's equation,<sup>23</sup>  $[\eta]$  of a liquid containing spherical particles is directly proportional to the cube of the root-mean-square radius of gyration ( $S$ ) of the spheres. Therefore,  $[\eta]$  in this system may be related to the mean radius of the microgels:

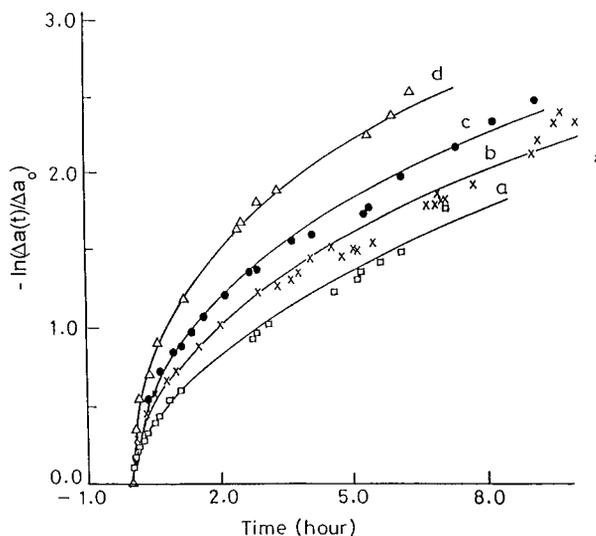
$$[\eta]^{1/3} \propto \langle S^2 \rangle^{1/2} \quad (4)$$

Therefore, the LHS of eq 3 can be obtained from the following equation:

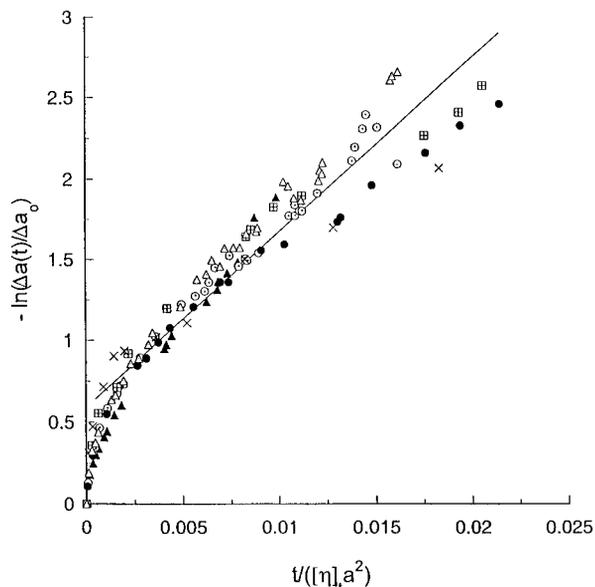
$$-\ln \frac{\Delta a(t)}{\Delta a_0} = -\ln \left( \frac{[\eta]_{\infty}^{1/3} - [\eta]_t^{1/3}}{[\eta]_{\infty}^{1/3} - [\eta]_0^{1/3}} \right) \quad (5)$$

where  $[\eta]_0$ ,  $[\eta]_{\infty}$ , and  $[\eta]_t$  are the intrinsic viscosities of the NPEC solution at time = 0, time =  $\infty$  and time =  $t$ , respectively.

Plots of  $-\ln [\Delta a(t)/\Delta a_0]$  versus  $t$ , for different ionic strengths of the medium, are shown in Figure 8. The nonlinear curves show that the systems did not follow eq 3, with  $D$  as a constant; the slope  $D/a^2$  decreased with time. This was due to the fundamental difference between the gel in this system and the macroscopic gels for which the THB theory was developed. In this system, the swelling of the microgel was limited not by the diffusion of the polymer chains but by the rate of the exchange reaction between the segments of the oppositely charged polymers. Therefore, the diffusion constant  $D$  actually represented the rate



**Figure 8.** Plot of  $-\ln [\Delta a(t)/\Delta a_0]$  versus time for NPEC-25 with (a) 0.0, (b)  $1.6 \times 10^{-3}$ , (c)  $3.2 \times 10^{-3}$ , and (d)  $5.2 \times 10^{-3}$  M NaCl.



**Figure 9.** Plot of  $-\ln [\Delta a(t)/\Delta a_0]$  versus  $t/(a^2[\eta]_t)$  at different concentrations of NaCl: (▲) 0, (△)  $8 \times 10^{-3}$ , (⊙)  $1.6 \times 10^{-3}$ , (●)  $3.0 \times 10^{-3}$ , (⊠)  $5.2 \times 10^{-3}$ , and (×)  $1.0 \times 10^{-3}$  M.

constant of the exchange reaction. Earlier studies<sup>19</sup> on solution-state reactions of PEs have revealed that such reactions follow second-order kinetic equation. Therefore, if second-order kinetics are assumed for the exchange reaction in the microgel particles, then  $D$  (which is equivalent to the first-order rate constant) will be proportional to the local concentration of charged groups in the particles. Now, in a single particle, the concentration is inversely proportional to the volume of the particle (i.e., to the cube of the radius) and, therefore, to  $[\eta]$  of the solution:

$$D \propto 1/[\eta]_t \quad (6)$$

Putting eq 6 in eq 3, we obtain

$$-\ln \frac{\Delta a(t)}{\Delta a_0} = -\ln \frac{6}{\pi^2} + \frac{D' \cdot t}{a^2[\eta]_t} \quad (7)$$

where  $D'$  is a constant independent of the local concentration of the charged groups and the final radius of the particle is  $a \propto [\eta]_\infty$ . A plot of  $-\ln [\Delta a(t)/\Delta a_0]$  versus  $t/(a^2[\eta]_t)$  shows roughly a linear relationship (Fig. 9) with a constant slope,  $D'$ , as predicted by eq 7. Therefore, the increase in the viscosity of the NPEC solutions can be explained in terms of the swelling of the NPEC due to a

second-order exchange reaction between the free anionic groups and the complexed regions in the NPEC. Moreover, all the sets of data points, corresponding to the solutions at different ionic strengths, could be fitted with a single straight line (correlation factor = 0.960). This indicates that the intrinsic rate constant for the exchange reaction was not affected much by the change in the ionic strength of the medium in the range used for this study. This may be surprising as the rate of the exchange reaction was expected to be higher at higher ionic strengths. However, the maximum concentration of the external salt used in the experiment was small compared with the local concentration of the ionic groups in the NPEC particles. Therefore, the effect of the ionic strength of the solution on the rate constant was not important. The observed decrease in the rate of change in the viscosity and its decrease with the decrease in the ionic strength were only due to the expansion of the NPEC particles, reducing the local concentration of the reacting groups in the particles.

It may be noted here that the THB theory, which is the basis for the aforementioned analysis, is applied to systems fundamentally very different from this one. Not only is the theory applied to macroscopic gels, in contrast to the microgels of NPEC particles, the rate of swelling of the conventional gels is determined by the rate of free diffusion of the polymer segments, whereas the rate in this system was determined by the rate of the exchange reaction. Nevertheless, this study shows that the exchange reaction, which resulted from a random exchange of the ionic groups, can be considered a diffusion-like redistribution of the ionic crosslinks between the oppositely charged PEs in the NPEC. Because the rate of exchange reaction was slow, the process in this system occurred at a much slower pace than what would be expected from a typical true diffusion-limited process.

The earlier reports on the structure of the NPEC indicated that the equilibrium situation would be a uniform distribution of the GPE chains on all the available HPE chains, leading to soluble species. The structure proposed in this article (Fig. 6) could be a nonequilibrium state of the system corresponding to a local minimum energy state. The system was observed to be in this nonequilibrium intermediate state for a relatively long period, which could be due to kinetic factors, that is, the low rate of exchange reactions due to the low mobility of the rigid NaCC chain seg-

ments. To understand if the NPEC system could move to a more stable equilibrium state, we need to measure the viscosity for a much longer period. The slow degradation of NaCC chains in aqueous solutions restricts the use of viscometry for such a study. Another study is planned with different methods.

## CONCLUSIONS

A PEC formed between NaCC and P2VPMI, in a nonstoichiometric mixing ratio, was studied. At a specific composition of the PEC, at which NaCC was in excess, a viscous solution of the NPEC was obtained in which the dispersed species was proposed to be swelled microgels with an excess negative charge. The swellability of the microgels, which could be related to the viscosity of the NPEC solution, was thought to be due to the distribution of the ionic crosslinks in the complex. The process of the rearrangement and redistribution of the ionic bonds as the complex reached a relatively stable state, which could be a local minimum energy state, was observed to follow diffusion-like kinetics. This parallel between the kinetics of swelling of the NPEC and the macrogels of nonionic polymers, for which the swelling is determined by the true diffusion of polymer segments, might be due to the random nature of the exchange reaction between the large number of ionic bonds. Because the free energy associated with the breaking of an ionic bond is large, the swelling of an NPEC is much slower; nevertheless, it follows the same mathematical rule.

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