Electrophoretic Behavior of Ampholytic Polymers and Nanogels[†]

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Polyampholyte gel particles with hydrodynamic radii (R_h) 132 to 87 nm at an isoelectric point were synthesized by aqueous redox polymerization in the presence of sodium dodecylbenzene sulfonate as a surfactant. Acrylic acid and 1-vinylimidazole were respectively used as anionic and cationic monomers, both of which were incorporated into the network of *N*-isopropylacrylamide cross-linked with *N,N′*-methylenebisacrylamide (BIS). Potentiometric titration gave the following contents (in mol %) of anions (A) and cations (C) in the nanogels: A = 3 and C = 13 for nanogel G(1/4); and A = 14 and C = 12 for nanogel G(1/1). Ampholytic terpolymers with $R_h = 23-20$ nm, the monomer compositions of which are very close to the corresponding nanogel, were also synthesized without use of cross-linker (BIS). Electrophoretic mobility was measured by electrophoretic light scattering at 25 °C as a function of pH and KCl concentration. Dynamic light scattering was performed to determine R_h at the same condition as used in electrophoresis. It was found that the mobilities of the nanogels agree with those of the terpolymers, although there is a big difference in their sizes as well as in their molar masses. A detailed comparison of experimental mobilities with theoretical calculations was made in terms of three different models: free draining model, charged surface model, and Henry's model. It became apparent that the free draining model explains the electrophoretic behavior not only of amphoteric terpolymers but also of polyampholyte nanogels.

Introduction

Electrophoresis of polyelectrolytes was studied theoretically in the 1950s by Hermans and Fujita,[1] Overbeek and Stigter,[2] and Hermans[3] and experimentally in 1960s by Noda et al.[4] The conclusion both from theories and from experiments was at first sight surprising; that is, a macromolecular coil with charges, which behaves in sedimentation or diffusion as impermeable, should behave in electrophoresis as if it were free draining. Thus, the electrophoretic behavior of polyions is different from that of colloid particles generally treated by Smoluchowski's model[5] as well as of proteins by Henry's model.[6]

The free draining model has led to renewed interest in electrophoresis of ionic microgel particles with diameters in the range of tens to hundreds of nanometers, often referred to as "nanogels." Pelton et al.[7] have studied, in collaboration with Rowell, the electrophoretic behavior of microgels consisting of a lightly cross-linked polymer of *N*-isopropylacrylamide (NIPA). Charges of the gel particle arise from ionic polymerization initiators bound to many of the end groups of NIPA chains. This microgel undergoes a marked diameter change as temperature is increased, so that the mobility varies depending on temperature. Thus, Pelton et al. analyzed their mobility data by two models: free draining model for polyelectrolytes and charged surface model established by themselves. In their model the following assumptions were made: (i) all the charges are located on the exterior surface of the microgel; (ii) the charge density is related to the potential by the Helmholtz equation; (iii) the surface potential equals the ζ potential; (iv) the electrophoretic mobility is related to the ζ potential by the Smoluchowski equation. The theoretical curves based on both

models showed similar behaviors, in reasonable agreement with experimental results. In particular, the free draining model showed the closest agreement, but neither model predicted a rapid mobility change, which was observed in the vicinity of the volume-phase transition temperature (T_V; ca. 32 °C) of NIPA gels.

Another interesting sort of microgel is a nanoparticle consisting of a hard core whose surface is covered with hair-like polymer chains or a thin gel layer. The electrophoresis of such a gel particle has been studied using both theory and experiment by Ohshima et al.[8] They presented a numerical formula (i.e., Ohshima equation) that becomes equivalent to the Smoluchowski equation[5] when the effect of the hair chains is negligible, and to Hermans-Fujita equation[1] when there is no effect of the hard core. The Ohshima equation well predicted electrophoretic mobilities of a NIPA-based nanogel (styrene-NIPA copolymer core with the surface of NIPA gel layer) as a function of ionic strength at temperatures below and above T_V of NIPA gels.

After the above two publications, Nabzar et al.[9] measured electrophoretic mobilities as a function of electrolyte concentration for cationic colloid particles (latexes) composed of a polystyrene core with shell of copolymer of NIPA with aminoethyl methacrylate, and claimed that Ohshima's theory[8] did not predict their results. Ito et al.[10] studied NIPA nanogels having acrylic acid (AAc) as an anionic monomer by using potentiometric titration and electrophoresis. It was demonstrated that the free draining model was better than the charged surface model in the estimation of charges per particle, but yet there was not a good agreement between the results calculated from the mobility and those obtained by titration. On the other hand, Pelton reported in his recent review[11] that there are no big differences among the temperature curves of mobilities for NIPA microgels calculated from the above three theories under the

assumption of a set of parameters and that the calculated curves are close to the observed results. It appears that these different conclusions are caused by uses of uncertain parameters in the calculations, because both the Hermans−Fujita equation[1] and the Ohshima equation[8] were based on a two-parameter model.

From the above it is clear that, solely in the gel system, the comparison of theories and experiments is insufficient. Therefore, an electrophoretic study using ionic nanogels and polyelectrolytes, both of which are extremely similar in chemical composition, should be required. Very recently we have succeeded in preparing ampholytic nanogels and terpolymers, which were composed of similar quantities of NIPA, AAc, and *N*-vinylimidazole (VI).[12] The purpose of this paper is to report their electrophoretic behavior as a function of pH and ionic strength and to make a detailed comparison with theories.

Theories

Our ampholytic terpolymers would be expected to behave as free-draining coils in electrophoresis at pH levels at which either carboxyl groups of AAc units or imidazole groups of VI units are fully ionized. The theoretical mobility was thus calculated using the Hermans−Fujita expression. Also, calculation using the Henry equation was made, because Noda et al.[4] have compared the calculated mobilities by both equations in the demonstration of free-draining behavior of AAc homopolymers. For the polyampholytic nanogels, the approach of Pelton et al.[7] was employed in the comparison of experimental and theoretical mobilities. The reason we did not adopt the Ohshima equation[8] is that a parameter relating to thickness of the hair chains (or dangling chains) on the nanogel surface cannot be determined experimentally. Even when our mobility data successfully fitted with a calculated curve obtained by choosing a set of two parameters in the Ohshima equation, several difficulties would arise in the discussion about whether their choice was reasonable.

Henry's Model. According to Noda et al.,[4] electrophoretic mobility (U_H) calculated using the Henry equation of a rigid nondraining sphere may be given by eq 1, under conditions where the ionic strength is high enough and the electric conductivity of the sphere is the same as that of the solvent.

$$U_H = \frac{S_{eff}}{6\pi\eta r(1 + \kappa r)} \tag{1}$$

Here S_{eff} is the effective charge uniformly distributed on the surface of the sphere of radius r, η is the viscosity coefficient of the solvent, and κ is the reciprocal thickness of ionic atmosphere defined by Debye and Hückel:

$$\kappa = \left(\frac{8\pi N_A e^2}{1000\epsilon k_B T}\right)^{1/2} I^{1/2} \tag{2}$$

where N_A is Avogadro's number, I is the ionic strength, e is the electronic charge, ϵ is the dielectric constant, and k_B is Boltzmann constant. As far as the nondraining model is concerned, S_{eff} may be taken as the net charge appearing on the surface of the sphere, i.e., the difference between the fixed charges on the polyion and the total charges of counterions and co-ions absorbed on the sphere. The concentrations of counterions and co-ions inside the sphere can be calculated from the Poisson−Boltzmann equation

$$\nabla^2\psi = \frac{4\pi e}{\epsilon}[n_C \exp(-e\psi/k_B T) - n_C \exp(e\psi/k_B T)] \tag{3}$$

where ψ is the electrostatic potential and n_C is the number concentration of both counterions and co-ions in the solvent. By solving eq 3 according to ref 13, we obtain

$$S_{eff} = \epsilon\frac{E_D}{2\kappa}(1 + \kappa r)\exp(-\kappa r)[(1 + \kappa r)\exp(-\kappa r) - $$
$$(1 - \kappa r)\exp(\kappa r)] \tag{4}$$

where

$$E_D = \frac{k_B T}{e}\ln\frac{1 + \sqrt{1 + \left(\frac{8\pi}{3}\frac{1}{Z}r^3 n_C\right)^2}}{\left(\frac{8\pi}{3}\frac{1}{Z}r^3 n_C\right)} \tag{5}$$

and Z is the number of fixed charges on the sphere.

Charged Surface Model. According to Pelton et al.,[7] the electrophoretic mobility (U_C) of a sphere with a charged surface (i.e., hydrodynamically equivalent sphere with the surface on which all the charges are located) can be given by

$$U_C = \frac{-Ne}{4\pi\eta\kappa r^2} \tag{6}$$

Here, N is the total number of charges per particle and identical to Z in eq 5. Note that eq 6 can be obtained under assumptions i−iv mentioned in the Introduction.

Free Draining Model. When charges are distributed throughout the volume of a particle and the particle behaves in electrophoresis as if it were free draining, the mobility (U_F) may be given by the following Hermans and Fujita expression:[1]

$$U_F = \frac{-e}{6\pi\eta r_S}\left(\frac{3\kappa^3 + 3\kappa^2 b + 2\kappa b^2 + b^3}{3\kappa^3 + 3\kappa^2 b}\right) \tag{7}$$

where $b = (6\pi r_S N_S)^{1/2}$, r_S is the hydrodynamic radius of a segment in the particle (or polymer), and N_S is the number of the segments per unit volume. Equation 7 may also be employed in the calculation of mobility for ampholytic terpolymers.

Experimental Section

Materials. All chemicals were obtained from commercial sources: NIPA from Kojin Chemical Co. (Tokyo, Japan); AAc, *N*,*N*′-methylenebisacrylamide (BIS, cross-linker), and ammonium persulfate (APS; initiator) from Wako Pure Chemical Co. (Osaka, Japan); VI and sodium dodecylbenzenesulfonate (NaDBS; surfactant) from Tokyo Chemical Industry Co. (Tokyo, Japan). The monomers (NIPA, AAc and VI) were purified according to the usual methods. All pregel solutions were prepared with distilled water passed through a Milli-Q filter.

Polymerization. We adopted here an oil-free aqueous redox polymerization initiated by APS because this enabled us to prepare NIPA-based anionic and cationic polyelectrolyte nanogels.[10] The polymerization was carried out using an aqueous 0.01 M NaDBS solution (300 mL) containing the desired quantities of the monomers. The O₂-free monomer solution was placed in the usual separable flask (500 mL) equipped with a cooler and a magnetic stirrer and maintained at a desired temperature with stirring (200 rpm). To remove oxygen well, nitrogen gas was continuously supplied above the surface of the solution for 1 h before the reaction. The polymerization reaction was initiated by adding 1 mL of aqueous O₂-free solution of APS (7.5 w/w %), allowed to continue for 2 h, and terminated by blowing oxygen through the reactor. After that, residual monomers and NaDBS were removed from the resulting

TABLE 1: Characterstics of Polyampholytic Nanogels and Terpolymers[a]

	charge density (mmol/g of dry weight)		$10^{-5} M_W$	R_h		ρ^b
sample	carboxyl	imidazole	(g/mol)	(nm)	R_g/R_h	(g/cm³)
G(1/4)	0.31	1.15	524	132	0.81	0.0091
G(1/1)	1.36	1.12	149	87	0.93	0.0090
P(1/4)	0.31	1.16	1.92	20	1.40	0.0096
P(1/1)	1.40	1.16	2.97	23	1.96	0.0097

[a] Measurements of weight-average molecular weight (M_W), hydrodynamic radius (R_h), and radius gyration (R_g) were carried out in 100 mM KCl solution at 25 °C and at isoelectric points: pH 6.5 for G(1/4) and P(1/4); pH 5.3 for G(1/1) and P(1/1). [b] Estimated by a relation $\rho = (f/f_{min})(3/4\pi)(M_W/N_A)(1/R_h^3)$, where f represents the actual frictional coefficient and f_{min} is the minimum frictional coefficient for a hypothetical sphere. Note that $f/f_{min} \sim 1$ was assumed.

reaction mixture by an alkaline dialysis method[10] using a Spectra/Por CLC500 tube with a molecular weight cut off of 100 000. Further purification was carried out by passing the dialyzed solution through a mixed bed of anion and cation-exchange resins. The purified nanogel suspension and polymer solution were then lyophilized for 3 days. The yield was more than 85% in all the preparations.

It is quite important to determine the existence of un-cross-linked and dissolved polymers in nanogel dispersions. However, this is a rather difficult problem with respect to experimental techniques and was usually ignored in previous studies. To overcome this difficulty, we employed here an analytical method based on a combination of dialysis and colloid titration because (i) the terpolymer is permeable into the outer solution through the dialysis membrane with a molecular weight cut off 1 000 000, and (ii) a very slight amount (less than 0.005 w/v %) of permeated terpolymers is detectable by colloid titration.[14] As a result, it was found that our nanogel samples are free from un-cross-linked and dissolved terpolymers after the purification.

Measurements. The overall contents of acidic and basic groups were determined by pH titration at 25 °C and in 0.5 M KCl solution with HCl and KOH (0.1 M each) as the standard titrant. Hydrodynamic diameter (d_h) and weight-average molecular weight (M_W) were determined by laser light scattering techniques, using an Otsuka DLS-7000 apparatus equipped with a 75 mW argon ion laser (NEC model GLG-3112). Electrophoretic mobility was measured by electrophoretic light scattering (ELS) using an Otsuka ELS-6000 apparatus.

Results

Table 1 shows several characteristics of the ampholyte nanogels and terpolymers used in our electrophoretic measurements. There is a big difference in M_W as well as in R_h between the nanogel and terpolymer. However, overall charges of the nanogel were very close to those of the terpolymer. Therefore, a comparison of electrophoretic mobilities between the nanogel and the terpolymer would be possible.

Figure 1 shows electrophoretic mobilities of nanogel G(1/4) and terpolymer P(1/4) as a function of pH at ionic strength (I) 0.01. Also shown in Figure 2 is the effect of ionic strength on the mobilities of G(1/4) and P(1/4) at pH 3. There is a good agreement in the mobilities between the gel and the polymer. The same conclusion was obtained by comparing G(1/1) with P(1/1) (data are not shown). When considering the free draining behavior of polyelectrolytes, it is natural to conclude that our polyampholyte nanogels behave as a free draining "network"
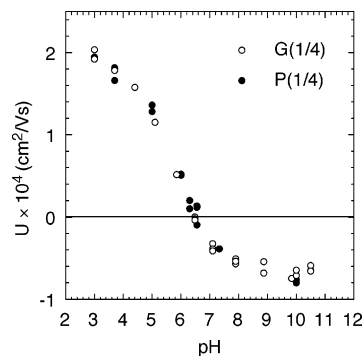
Figure 1. Dependence of electrophoretic mobility (U) on pH for G(1/4) and P(1/4) at ionic strength 0.01 (KCl) and at 25 °C.
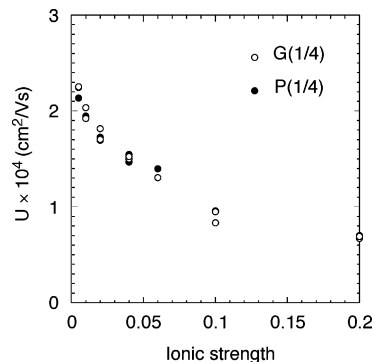
Figure 2. Dependence of electrophoretic mobility (U) on ionic strength for G(1/4) and P(1/4) at pH 3 and 25 °C.

in electrophoresis, at least, under pH conditions where either carboxyl groups or imidazole groups are in complete ionization state.

Discussion

It is of importance to compare the experimentally and theoretically obtained mobilities, to confirm the above conclusion. For this purpose, it is required to determine charges per polymer or nanogel particle as well as to estimate the size of a segment and the number of segments per unit volume. Then, we must consider effects of counterions on electrophoretic mobility, as pointed by Buscall et al.[15] Before comparing the experimental and theoretical mobilities, therefore, our discussion was focused not only on the determination of Z in eq 5, which is equivalent to N in eq 6, but also the estimation of r_S and N_S in eq 7.

Estimation of N and Z. We may easily determine the value of N (or Z) from our experimental data (i.e., charge density and M_W) shown in Table 1, when effects of counterions are ignored. However, it is well-known that electrophoretic mobility is greatly influenced by binding and/or condensation of counterions.[16,17] Thus, we considered the degree of shielding (d_S)[18] of polymer-fixed charges by counterions to estimate Z (or N) from charge density (D_C in mol/g) and M_W (g/mol) by

$$Z \sim N = (1 - d_S)D_C M_W \alpha_i \qquad (8)$$

where α_i is the degree of ionization and $\alpha_i = 1$ at pH = 3 or pH = 10 (see Figure 1). For d_S, unfortunately, we have no data for our samples; therefore we were forced to look for alternative data. There has been little attempt to measure d_S due to experimental difficulties. In our calculations by eq 8, we thus used data of Huizenga et al.[19] who succeeded in a direct measurement of d_S using partially neutralized sodium poly-

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(acrylic acid) and showed $d_S = 0.65$ under a complete neutralization. Note that effects of Cl^- ions on the polymer-bound imidazole cations is assumed to be identical to those of Na^+ ions on the polymer-bound carboxylate anions.

Estimation of r_s and N_s. To calculate U_F by eq 7, we have to estimate r_S and N_S. For this, it is necessary to obtain information about the structure of a segment, which may be defined as a "string-connection" of neutral monomer units plus one ionic monomer unit with either negative or positive charge. Thus, we gave the number of monomer units per segment as

$$n_s^+ = \frac{1}{\alpha_i(1-d_S)}\left(\frac{n_{NIPA} + n_{VI} + n_{AAc}}{n_{VI}}\right) \quad (9a)$$

$$n_s^- = \frac{1}{\alpha_i(1-d_S)}\left(\frac{n_{NIPA} + n_{VI} + n_{AAc}}{n_{AAc}}\right) \quad (9b)$$

Here, the superscript denotes a distinction between positively and negatively charged segments. Moreover, n_{NIPA}, n_{VI}, and n_{AAc} are the number of monomer units per polymer or gel particle and each subscript shows the sort of monomer. These can be obtained by

$$n_{NIPA} = (M_W - n_{VI}M_{VI}^\circ - n_{AAc}M_{AAc}^\circ)/M_{NIPA}^\circ \quad (10a)$$

$$n_{VI} = M_W D_C^{VI} \quad (10b)$$

$$n_{AAc} = M_W D_C^{AAc} \quad (10c)$$

where M_{NIPA}°, M_{VI}°, and M_{AAc}° are molecular weight of each monomer shown by the subscript and D_C^{VI} and D_C^{AAc} are charge density (mol/g) based on VI and AAc, respectively.

To study the chemical structure of the segment at the molecular level, we used a classical ball-and-stick model without the use of computer (Figure 3), from which the following two features can be seen: (i) A "center core" is made of a connection of hydrogen bonds between $-NH$ of a NIPA unit and $C=O$ of the neighboring NIPA unit, and (ii) the core is covered with a repeated $-CH-CH_2-$ main chain backbone and with regularly assembled $(CH_3)_2CH-$ side groups. Such a rodlike configuration is maintained even when about 20 units of NIPA are combined as well as when less than 5 units of nonionized VI and/or AAc are randomly joined with 15 units of NIPA. Therefore, we handled such a segment as a long rod and determined its length (L_S) and cross sectional radius (R_S) through a direct measurement from the model in Figure 3: i.e., $R_S \sim 4.25$ (Å) in all the case, and $L_S \sim 2.6n_s^+$ (Å) or $2.6n_s^-$ (Å) (see ref 20). For such long rod segments, it is reasonable to calculate r_S by[21]

$$r_S = L_S\left[2\ln\left(\frac{L_S}{R_S}\right) - 0.19 - \frac{8.24}{\ln(L_S/R_S)} + \frac{12}{\{\ln(L_S/R_S)\}^2}\right]^{-1} \quad (11)$$
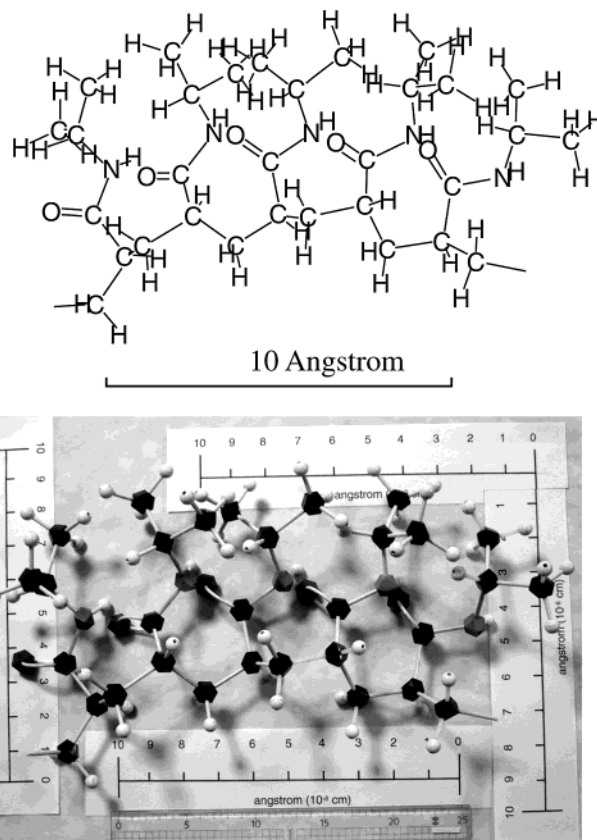
In addition, because $N_S = Z(3/4\pi R_h^3)$ (where R_h, hydrodynamic radius of terpolymer or nanogel), we obtain

$$b = (6\pi r_S N_S)^{1/2} = \left(\frac{9}{2}\frac{r_S}{R_h^3}Z\right)^{1/2} \quad (12)$$

As a result, we may calculate U_F of terpolymers and nanogels by eq 7.

Comparison of Experimental and Theoretical Mobilities. In Table 2 the mobilities of the nanogels and the terpolymers were compared with the calculated values. Although we

Figure 3. Configuration of NIPA pentamer. Hydrogen bonds would be formed between NH and O=C in two adjoining NIPA units. A center core composed of hydrogen-bonded NH and O=C groups is covered with $-CH-CH_2-$ backbone and N-isopropyl groups.

measured the mobility as a function of pH at ionic strengths (I) 0.01 and 0.1, there is the uncertainty in the pH dependence of d_S. Therefore, we chose the pH levels at which $\alpha_i \sim 1$ (a complete ionization state). Then, our calculations were made under conditions of $d_S \sim 0$ (no effect of counterion) and $d_S \sim 0.65$ (65% shielding of polyion charges).

The significant observations from Table 2 are as follows: (i) For both the nanogel and the terpolymer, the experimental results (U_{obsd}) at $I = 0.01$ (low ionic strength) and at $I = 0.1$ (high ionic strength) are close to the mobilities (U_F) calculated under the condition of $d_S \sim 0$ and of $d_S \sim 0.65$, respectively; the theory underestimated the experimental results by 3−37%, except for both G(1/4) and P(1/4) with a low COOH content. (ii) There is a lack of agreement between U_{obsd} and U_H, even at the high ionic strength ($I = 0.1$). (iii) U_{obsd} values for the nanogel at ionic strengths 0.01 and 0.1 are somewhat in agreement with U_C calculated under $d_S \sim 0.65$, but not with U_C under $d_S \sim 0$. (iv) In the case of the polymer, however, U_{obsd} is close to U_C under $d_S \sim 0$.

In our calculations of U_F (free draining model), the assumption of $d_S \neq function(I)$ was made; however, this would not be correct. In practice, it is natural to consider that d_S will increase with increasing ionic strength. Taking this into account, we may say from result (i) that the free draining model could account for the electrophoretic behavior of terpolymers P(1/1) and P(1/4) as well as of nanogels G(1/1) and G(1/4).

One may argue the use of the charged surface model in calculation of the mobilities of our terpolymers P(1/1) and P(1/4). Indeed, no attempt has been made to predict electrophoretic mobility of a polyion coil by the charged surface model. As shown in result iii, however, this model somewhat predicted

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TABLE 2: Comparison of Experimental and Theoretical Mobilities under Different Conditions of the Shielding Degree (d_s) of Polyion Charges with Counterions (25 °C)

pH	I	sample	$R_h{}^a$ (nm)	$10^4 U_{obsd}$ (cm²/Vs)	$10^4 U_{cald}(d_S = 0)^b$ (cm²/Vs)			$10^4 U_{cald}(d_S = 0.65)^b$ (cm²/Vs)		
					U_F	U_H	U_C	U_F	U_H	U_C
3	0.01	G(1/1)	136	1.82	1.37	0.043	3.93	0.58	0.015	1.38
3	0.01	P(1/1)	26	1.80	1.48	0.114	2.22	0.67	0.040	0.78
3	0.01	G(1/4)	191	1.96	1.37	0.056	7.20	0.65	0.020	2.52
3	0.01	P(1/4)	25	1.95	1.48	0.083	1.55	0.69	0.036	0.54
3	0.1	G(1/1)	100	0.79	1.16	0.011	2.30	0.54	0.004	0.80
3	0.1	P(1/1)	25	0.85	1.14	0.014	0.76	0.55	0.005	0.27
3	0.1	G(1/4)	145	0.90	1.23	0.013	3.95	0.60	0.005	1.38
3	0.1	P(1/4)	22	0.95	1.23	0.013	0.64	0.60	0.005	0.22
10	0.01	G(1/1)	120	−2.06	−1.68	−0.076	−6.13	−0.70	−0.027	−2.15
10	0.01	P(1/1)	26	−2.11	−1.91	−0.137	−2.68	−0.78	−0.049	−0.94
10	0.01	G(1/4)	135	−0.68	−0.66	−0.043	−3.88	−0.32	−0.015	−1.36
10	0.01	P(1/4)	21	−0.78	−0.67	−0.037	−0.59	−0.32	−0.013	−0.21
10	0.1	G(1/1)	93	−0.97	−1.48	−0.017	−3.23	−0.63	−0.006	−1.13
10	0.1	P(1/1)	25	−1.00	−1.49	−0.017	−0.92	−0.63	−0.006	−0.32
10	0.1	G(1/4)	133	−0.18	−0.54	−0.005	−1.26	−0.28	−0.002	−0.44
10	0.1	P(1/4)	20	−0.17	−0.55	−0.005	−0.21	−0.28	−0.002	−0.07

[a] Determined by dynamic light scattering. *[b]* Used eqs 1, 6, and 7 in calculations of U_H, U_C, and U_F, respectively.

the mobilities of our nanogel particles under a consideration of counterion effect ($d_S \sim 0.65$). This would suggest that the charged surface model should be useful for the terpolymer because there was little difference of ρ between the polymer and the gel. Nevertheless, a contradiction was observed from results iii and iv. Thus, the free draining model seems to be better than the charged surface model, at least, for our nanogel system.

Conclusions

It was demonstrated from our experiments that electrophoretic mobilities of the nanogels agree with those of the terpolymers, although there is a big difference in the size as well as in the molar masses between the gel and the polymer. The experimental mobilities were compared with theoretical mobilities calculated on the basis of the free draining model by of Hermans and Fujita and upon the charged surface model of Pelton et al.,[7] both of which have been employed in the analysis of mobility data for NIPA-based ionic nanogel networks. In addition to these models, we also used Henry's model because this was employed by Noda et al.[4] to compare it with the free draining model. In calculations of mobilities on the free draining model, the size of a segment was carefully estimated using a molecular model. Because the hydrodynamic radius was determined by dynamic light scattering and the charge density by potentiometric titration, all the parameters, other than the shielding degree of polyion charges by counterions, were experimental values and not adjustable with assumptions. As a result, we may say that the free draining model explains the electrophoretic behavior not only of amphoteric terpolymers, but also of polyampholyte nanogel networks, although uncertainty remained in the dependence of the shielding degree on ionic strength.

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