

# Laser Light-scattering Study of Polyacrylamides With and Without Hydrolyzation in 0.35M KH<sub>2</sub>PO<sub>4</sub> Aqueous Solution

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**ABSTRACT:** Both the hydrolyzed and unhydrolyzed polyacrylamides with different molar masses were characterized in 0.35M KH<sub>2</sub>PO<sub>4</sub> aqueous solution at 25°C by laser light scattering (LLS). The Laplace inversion of precisely measured intensity-intensity time correlation function leads to an estimate of the characteristic line-width distribution  $G(\Gamma)$  which can be further reduced to a translational diffusion coefficient distribution  $G(D)$ . A combination of the measured weight-average molar mass  $M_w$  and  $G(D)$  enables us to establish a calibration of  $D$  (cm<sup>2</sup>/s) =  $(4.46 \pm 0.02) \times 10^{-5} M^{0.50 \pm 0.003}$ . Using this calibration, we convert each  $G(D)$  into a corresponding molar mass distribution. The calculated  $M_w$  from such a molar mass distribution is reasonably close to the measured  $M_w$  from static LLS. Most important is that when 0.35M KH<sub>2</sub>PO<sub>4</sub> aqueous solution is used as solvent, both the hydrolysed and unhydrolysed polyacrylamides can be represented by an identical calibration; namely, in 0.35M KH<sub>2</sub>PO<sub>4</sub> aqueous solution, the polyelectrolytes effect in the hydrolysed polyacrylamides has been suppressed. Therefore, the hydrolysed polyacrylamides can be characterized as a normal neutral polymer in 0.35M KH<sub>2</sub>PO<sub>4</sub> aqueous solution, which makes a routine characterization of the hydrolysed polyacrylamides much easier. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* 63: 1755–1760, 1997

**Key words:** laser light scattering; characterization of polyacrylamides; polyelectrolytes effect

## INTRODUCTION

Polyacrylamide contains both carbonyl and amides groups along its hydrophobic backbone. Polyacrylamide and its various anionic or cationic copolymers and derivatives form one of the most important series of water-soluble polymers in various industrial applications. Linear polyacrylamides with a high molar mass are particularly useful in the applications of flocculation and enhanced oil recovery.

The average molar mass of polyacrylamide are

usually determined by either viscosity measurement or size-exclusion chromatography (SEC).<sup>1-4</sup> It is known that the molar mass estimated from viscosity has a large uncertainty because of the errors associated with the Mark-Houwink-Sakurada parameters. As for SEC, a proper calibration of the SEC columns requires a series of narrowly distributed polyacrylamides standards, which is rather difficult to obtained in practice. Moreover, a normal SEC is not able to characterize a sample with an average molar mass higher than  $\sim 5 \times 10^6$ .

Dynamic laser light scattering (LLS) has been used in the characterization of macromolecules, such as poly(tetrafluoroethylene),<sup>5</sup> branched epoxy polymer,<sup>6</sup> poly(ethylene),<sup>7</sup> and dextrane.<sup>8</sup> Recently, a complementary method of combining static and dynamic LLS has been developed to

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characterize special macromolecules, such as phenolphthalein poly(ether ketone) or poly(ether sulfone),<sup>9-11</sup> poly(sulfoalkyl methacrylate),<sup>12</sup> and hydroxyethyl cellulose acetate.<sup>13</sup>

After the hydrolyzation, polyacrylamide becomes polyelectrolytes in aqueous solution, and its characterization becomes problematic.<sup>14</sup> In this study, we found that when 0.35M KH<sub>2</sub>PO<sub>4</sub> aqueous solution is used as solvent, the polyelectrolytes effect is suppressed so that the hydrolysed polyacrylamide can be characterized as a neutral polymer.

## EXPERIMENTAL

### Sample Synthesis

Acrylamide monomer was recrystallized twice in benzene before its polymerization in highly purified deionized water. A proper amount of acrylamide was dissolved in a three-neck round bottom flask filled with a glass stirring rod with a Teflon™ pad, a reflux condenser, and a nitrogen bubbling tube. The polymerization was initiated by adding hydrogen peroxide, and the reaction temperature was kept at 56 ± 1°C. After the reaction, polyacrylamide was precipitated in methanol and dried under vacuum at 60 ± 1°C. Such obtained polyacrylamide was further fractionated in a methanol water mixture. Two polyacrylamide fractions and two hydrolysed polyacrylamides samples with a hydrolysis degree of ~ 25% were used in this study, which are labelled as PAM1, PAM2, PAM3, and PAM4 hereafter. For each fraction, five solutions with a concentration range of 5.40 × 10<sup>-5</sup>–2.72 × 10<sup>-4</sup> g/mL were prepared by dilution. All polymer solutions were clarified at room temperature using a 0.5 μm Millipore filter.

### Laser Light Scattering

A modified commercial light-scattering spectrometer (ALV/SP-125 equipped with an ALV-5000 multi-τ digital time correlator and a solid-state laser, ADLAS DPY 425II; output power ≈ 400 mW at λ = 532 nm) was used. The primary beam is vertically polarized with respect to the scattering plane (the optical table surface, in this case). The detail of the LLS instrumentation and theory can be found elsewhere.<sup>15,16</sup> All LLS measurements were carried out at 25 ± 0.1°C. In static LLS, the angular dependence of the excess absolute time-averaged scattered light intensities

(known as the excess Rayleigh ratio  $R_{90}(q)$ ) of a dilute polymer solution of different concentrations  $C$  (g/mL) at different scattering angles  $\theta$  were measured.  $R_{90}(q)$  is related to the weight average molar mass  $M_w$  as<sup>17</sup>

$$\frac{KC}{R_{90}(q)} \approx \frac{1}{M_w} \left( 1 + \frac{1}{3} \langle R_g^2 \rangle q^2 \right) + 2A_2C \quad (1)$$

where  $K = 4\pi^2 n^2 (dn/dC)^2 / (N_A \lambda_0^4)$  and  $q = (4\pi n / \lambda_0) \sin(\theta/2)$  with  $N_A$ ,  $dn/dC$ ,  $n$  and  $\lambda_0$  being the Avogadro number, the specific refractive index increment, the solvent refractive index, and the wavelength of the light *in vacuo*, respectively;  $A_2$  is the second virial coefficient; and  $\langle R_g^2 \rangle^{1/2}$  (or written as  $\langle R_g \rangle$ ) is the root-mean square  $z$ -average radius of gyration of the polymer chain in solution. After measuring the values of  $R_{90}(q)$ , we are able to determine  $M_w$ ,  $\langle R_g \rangle$ , and  $A_2$  from a Zimm plot which incorporate  $q$ - and  $C$ -extrapolation on a single grid. Equation (1) shows that a precise values of  $dn/dC$  is critically important in the determination of  $M_w$ . In this study, a novel and high precision differential refractometer was used.<sup>18</sup> It has been found that  $dn/dC = 0.176$  mL/g for the polyacrylamide samples in 0.35M KH<sub>2</sub>PO<sub>4</sub> aqueous solution at  $T = 25^\circ\text{C}$  and  $\lambda = 532$  nm.

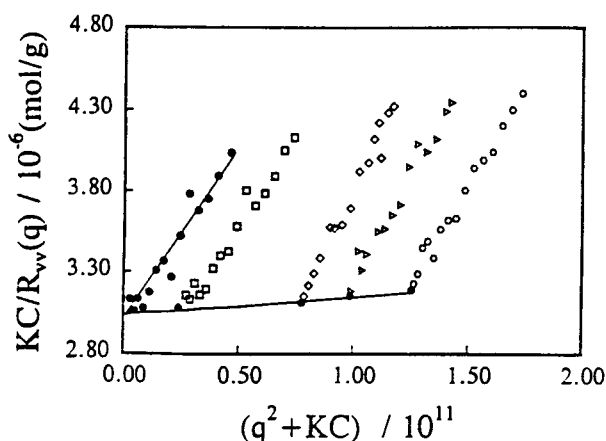
In dynamic LLS, precise intensity-intensity time correlation functions  $G^{(2)}(t, q)$  in the self-beating mode were measured, which has the following form:<sup>15,16</sup>

$$G^{(2)}(t, q) = \langle I(t, q)I(0, q) \rangle \\ = A[1 + \beta |g^{(1)}(t, q)|^2] \quad (2)$$

where  $q$  is the scattering vector;  $\beta$ , a parameter depending on the detection coherence;  $t$ , the delay time;  $g^{(1)}(t, q)$ , a normalized first-order electric field time correlation function; and  $A$ , a measured base line. It should be stated that  $A$  is not treated as an adjustable parameter in this study. Instead, we insisted on the agreement between  $A$  and the calculated baseline within 0.1%, which requires a careful (dust free) solution preparation. For a polydisperse sample,  $g^{(1)}(t, \theta)$  is related to the line-width distribution  $G(\Gamma)$  by

$$g^{(1)}(t, \theta) = \langle E(t, \theta)E^*(0, \theta) \rangle \\ = \int_0^\infty G(\Gamma)e^{-\Gamma t} d\Gamma \quad (3)$$

A Laplace inversion of  $g^{(1)}(t, q)$  can lead to  $G(\Gamma)$ .



**Figure 1** Typical Zimm plot for PAM1 in 0.35M  $\text{KH}_2\text{PO}_4$  at  $T = 25^\circ\text{C}$ , where  $C$  ranges from  $5.40 \times 10^{-5}$  to  $2.27 \times 10^{-4}$  g/mL.

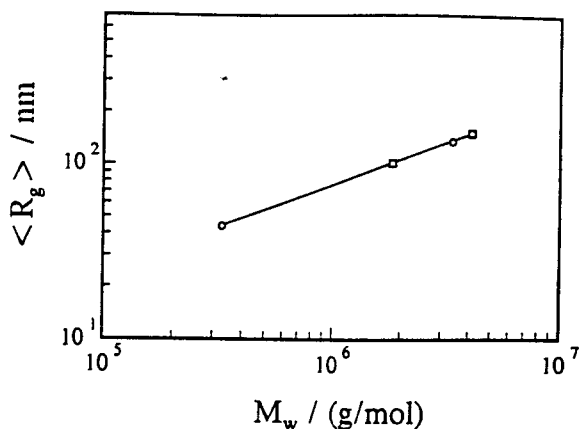
The line width  $\Gamma$  usually depends on both  $C$  and  $q$  as follows:<sup>19,20</sup>

$$\frac{\Gamma}{q^2} = D(1 + k_d C)(1 + f \langle R_g^2 \rangle q^2) \quad (4)$$

where  $D$  is the translational diffusion coefficient at  $C \rightarrow 0$ , and  $q \rightarrow 0$ ;  $k_d$ , the diffusion second virial coefficient; and  $f$ , a dimensionless parameter depending on the chain structure, solvent quality, and polydispersity. The value  $f$  generally increases as  $M_w$  decreases.

## RESULTS AND DISCUSSION

Figure 1 shows a typical Zimm plot of the unhydrolysed polyacrylamide (PAM1) in 0.35M  $\text{KH}_2\text{PO}_4$  aqueous solution at  $25^\circ\text{C}$ , where  $C$  ranges from  $5.40 \times 10^{-5}$  to  $2.72 \times 10^{-4}$  g/mL. On the basis of eq. (1), we determined  $M_w$ ,  $\langle R_g \rangle$ , and  $A_2$  from the extrapolations of  $[KC/R_{vv}(q)]_{q \rightarrow 0, C \rightarrow 0}$ ,  $[KC/R_{vv}(q)]_{C \rightarrow 0}$  versus  $q^2$ , and  $[KC/R_{vv}(q)]_{q \rightarrow 0}$  versus  $C$ , respectively. The results are listed in Table I. The positive values of  $A_2$  show that 0.35M



**Figure 2** Double logarithmic plot of  $\langle R_g \rangle$  versus  $M_w$  for polyacrylamide where (○) represents the data for the unhydrolysed and (□) represents the values for hydrolysed polyacrylamides, and the solid lines represent the least-squares fitting of  $\langle R_g \rangle$  (nm) =  $4.95 \times 10^{-2} M_w^{0.49}$ .

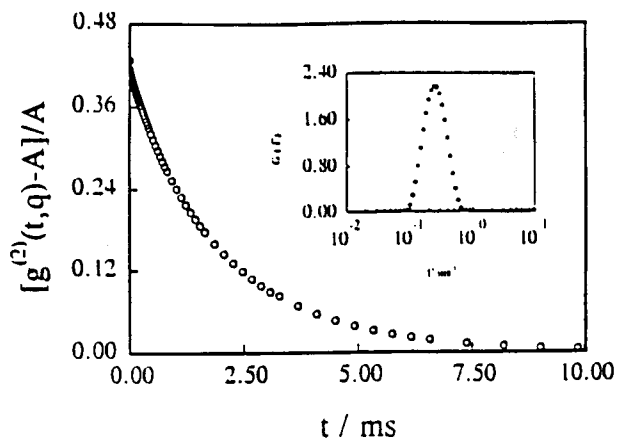
$\text{KH}_2\text{PO}_4$  aqueous solution is a reasonably good solvent for both the hydrolysed and unhydrolysed polyacrylamides. As expected,  $\langle R_g \rangle$  increases as  $M_w$  increases.

Figure 2 shows a double logarithmic plot of  $\langle R_g \rangle$  versus  $M_w$  for polyacrylamide in 0.35M  $\text{KH}_2\text{PO}_4$  aqueous solution at  $25^\circ\text{C}$ . The solid line represents the least-squares fitting of  $\langle R_g \rangle$  (nm) =  $4.95 \times 10^{-2} M_w^{0.49}$ . It shows that both the hydrolysed and unhydrolysed polyacrylamides have a very similar molar mass dependence of the chain dimension. The exponent value of  $\sim 0.5$  indicates that the polyacrylamide chains have a unperturbed random-coil conformation in 0.35M  $\text{KH}_2\text{PO}_4$  aqueous solution at  $25^\circ\text{C}$ .

Figure 3 shows a typical plot of the measured intensity-intensity time correlation function for the unhydrolysed polyacrylamide (PAM1) in 0.35M  $\text{KH}_2\text{PO}_4$  aqueous solution at  $\theta = 20^\circ$  and  $T = 25^\circ\text{C}$ . The insert shows a typical line width distribution  $G(\Gamma)$  calculated from the Laplace inversion of  $G^{(2)}(t, q)$ , using a CONTIN<sup>21,22</sup> program equipped with ALV-5000 digital correlator.

**Table I** Summary of LLS Results of Polyacrylamides in 0.35M  $\text{KH}_2\text{PO}_4$  Aqueous Solution at  $25^\circ\text{C}$

Fractions	$10^{-6} M_w$ (g/mol)	$\langle R_g \rangle$ (nm)	$10^4 A_2$ (mol · mL/g <sup>2</sup> )	$10^6 \langle D \rangle$ (cm <sup>2</sup> /s)	$\langle R_h \rangle$ (nm)	$k_d$ (mL/g)	$f$	$\langle R_g \rangle / \langle R_h \rangle$	$10^{-6} (M_w)_{\text{ruled}}$ (g/mol)	$(M_w / M_n)$
PAM1	0.33	44	3.40	7.70	31.7	195	0.11	1.4	0.32	1.63
PAM2	3.38	134	9.51	2.50	97.5	250	0.20	1.4	3.30	1.98
PAM3	1.84	101	1.98	3.20	76.2	200	0.11	1.3	2.06	1.87
PAM4	4.12	150	3.11	2.00	116	300	0.26	1.3	3.91	2.10

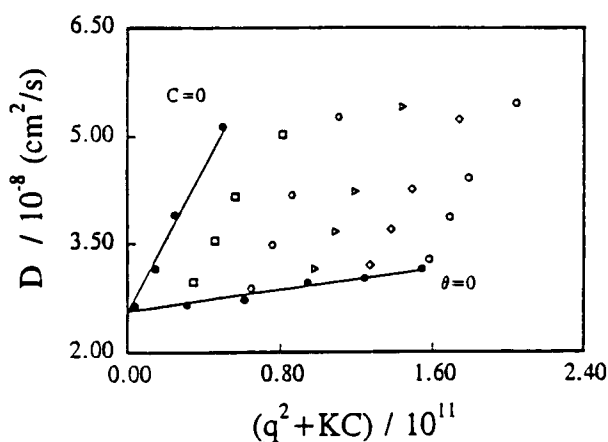


**Figure 3** Typical measured intensity-intensity time correlation function  $G^{(2)}(q, t)$  for PAM1 in  $0.35M$   $\text{KH}_2\text{PO}_4$  at  $\theta = 20^\circ$  and  $T = 25^\circ\text{C}$ . The insert shows the line-width distribution  $G(\Gamma)$  calculated from the Laplace inversion of  $G^{(2)}(q, t)$ .

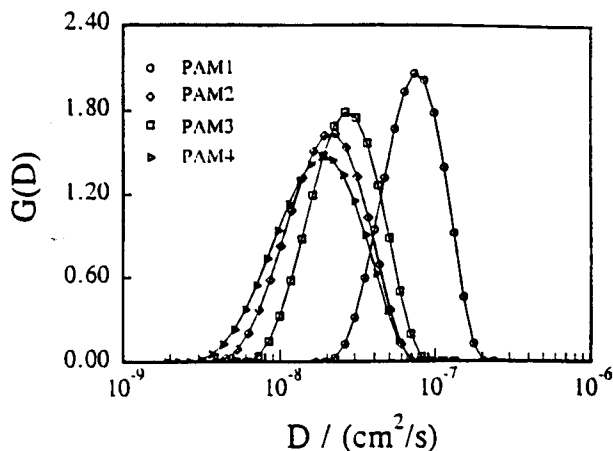
After measuring each polyacrylamide sample at a set of concentrations and scattering angles, we are able to determine the translational diffusion coefficient  $D$ .

Figure 4 shows a typical dynamic Zimm plot for the unhydrolysed polyacrylamide (PAM2) in  $0.35M$   $\text{KH}_2\text{PO}_4$  aqueous solution at  $25^\circ\text{C}$ . On the basis of Eq. (4),  $D$ ,  $f$ , and  $k_{\text{tr}}$  can be calculated, respectively, from  $(\Gamma/q^2)_{c \rightarrow 0, q \rightarrow 0}$ ,  $(\Gamma/q^2)_{c \rightarrow 0}$  versus  $q^2$ , and  $(\Gamma/q^2)_{q \rightarrow 0}$  versus  $C$ . The results are also summarized in Table I, where  $\langle \rangle$  means that the values obtained are averaged ones. With a pair of  $k_{\text{tr}}$  and  $f$ ,  $G(\Gamma)$  in Figure 3 can be converted into  $G(D)$ .

Figure 5 shows the translational diffusion coefficient distributions  $G(D)$  for both the hydrolysed



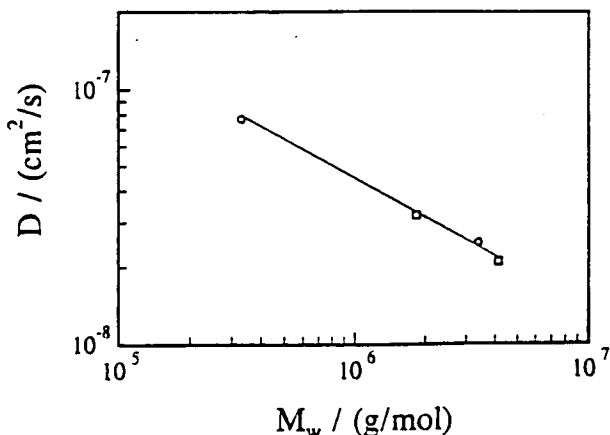
**Figure 4** Typical dynamic Zimm plot for PAM2 in  $0.35M$   $\text{KH}_2\text{PO}_4$  at  $T = 25^\circ\text{C}$ .



**Figure 5** Translational diffusion coefficient distributions  $G(D)$  for two hydrolysed and two hydrolysed polyacrylamide fractions in  $0.35M$   $\text{KH}_2\text{PO}_4$  at  $T = 25^\circ\text{C}$ .

and unhydrolysed polyacrylamides in  $0.35M$   $\text{KH}_2\text{PO}_4$  aqueous solution at  $25^\circ\text{C}$ . From each  $G(D)$ , we can calculate a hydrodynamic radius distribution  $f(R_h)$  and the average hydrodynamic radius  $\langle R_h \rangle = \int_0^\infty f(R_h) R_h dR_h$  using the Stokes-Einstein equation  $D = k_B T / (6\pi\eta R_h)$ , where  $k_B$ ,  $T$ , and  $\eta$ , are the Boltzmann constant, the absolute temperature, and solvent viscosity, respectively. The values of  $\langle R_z \rangle / \langle R_h \rangle$  are also listed in Table I. It is known that the value of  $\langle R_z \rangle / \langle R_h \rangle$  reflects the chain conformation. The values of  $\langle R_z \rangle / \langle R_h \rangle \sim 1.3-1.4$  indicate that the polyacrylamide chains have a flexible coil conformation in  $0.35M$   $\text{KH}_2\text{PO}_4$  aqueous solution at room temperature.

Figure 6 shows a double logarithmic plot of  $\langle D \rangle$



**Figure 6** Double logarithmic plots of  $\langle D \rangle$  versus  $M_w$  for Polyacrylamides, where the symbols are the same as in Figure 2, and the solid lines represent the least-squares fittings of  $\langle D \rangle$  ( $\text{cm}^2/\text{s}$ ) =  $(4.44 \times 10^{-5}) M_w^{0.501}$ .

versus  $M_w$ . The solid line represents a least-squares fitting of  $\langle D \rangle = \langle k_D \rangle M^{-\langle \alpha_D \rangle}$  with  $\langle k_D \rangle = 4.44 \times 10^{-5}$  and  $\langle \alpha_D \rangle = 0.50$  for the polyacrylamides in 0.35M  $\text{KH}_2\text{PO}_4$  aqueous solution at 25°C, where  $\langle \rangle$  means that the values of  $\langle k_D \rangle$  and  $\langle \alpha_D \rangle$  were obtained from  $\langle D \rangle$  and  $M_w$  rather than from  $D$  and  $M$  for monodisperse species. The value of  $\langle \alpha_D \rangle \sim 0.5$  further indicates the polyacrylamide chains have a unperturbed random coil conformation in 0.35M  $\text{KH}_2\text{PO}_4$  aqueous solution at 25°C. Theoretically, with these calibrations,  $G(D)$  can be transformed into a molar mass distribution, e.g., a differential weight distribution of molar mass  $f_w(M)$ . For the convenience of discussion, the principle is outlined as follows. In static LLS, when  $C \rightarrow 0$  and  $q \rightarrow 0$ ,

$$R_{vv}(\theta) \propto \langle I \rangle \propto \int_0^\infty f_w(M) M dM \quad (5)$$

On the other hand, in dynamic LLS,

$$g^{(1)}(t \rightarrow 0) = \langle E(t) E^*(0) \rangle_{t \rightarrow 0} = \int_0^\infty G(\Gamma) d\Gamma \propto \langle I \rangle \quad (6)$$

A comparison of eqs. (5) and (6) leads to

$$\int_0^\infty G(\Gamma) d\Gamma \propto \int_0^\infty G(D) D dD \propto \int_0^\infty f_w(M) M dM \quad (7)$$

where  $G(\Gamma) \propto G(D)$ . Equation (7) can be rewritten as

$$\int_0^\infty G(D) D d(\ln D) \propto \int_0^\infty f_w(M) M^2 d(\ln M) \quad (8)$$

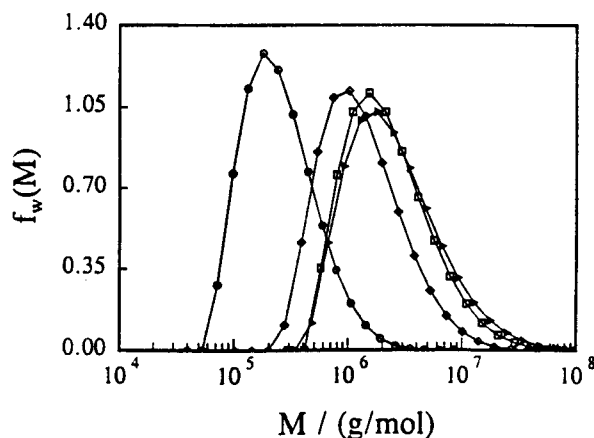
Since  $d(\ln D) \propto d(\ln M)$ , we have

$$f_w(M) M^2 \propto G(D) D \text{ or } f_w(M) \propto \frac{G(D) D}{M^2} \quad (9)$$

With a pair of  $k_D$  and  $\alpha_D$ , we can convert  $D$  to  $M$  and  $G(D)$  to  $f_w(M)$ , respectively. One of the ways to verify such a molar mass distribution is to calculate its weight-average molar mass  $(M_w)_{\text{calcd}}$  and then compare it with  $M_w$  measured directly from static LLS. According to the definition of  $M_w$  and using eq. (9), we have

$$(M_w)_{\text{calcd}} = \frac{\int_0^\infty F_w(M) M dM}{\int_0^\infty F_w(M) dM} = \frac{k_D^{1/\alpha_D} \int_0^\infty G(D) dD}{\int_0^\infty G(D) D^{1/\alpha_D} dD} \quad (10)$$

We found that the weight-average molar masses calculated from  $G(D)$  using  $\langle k_D \rangle$  and  $\langle \alpha_D \rangle$  are 20% less than  $M_w$  measured directly from static LLS. This is expectable because we have used  $\langle k_D \rangle$  and  $\langle \alpha_D \rangle$  instead of  $k_D$  and  $\alpha_D$ . Therefore, we have to use a recently developed light-scattering method to find  $k_D$  and  $\alpha_D$  first, namely, a method of combining static and dynamic LLS results, i.e.,  $M_w$  and  $G(D)$ , obtained from two or more polyacrylamide fractions. The detail of this LLS method has already been reported elsewhere.<sup>23,24</sup> Using this method, we found that  $k_D = 5.52 \times 10^{-5}$  and  $\alpha_D = 0.514$  if using both the hydrolysed and unhydrolysed polyacrylamides;  $k_D = 5.31 \times 10^{-5}$  and  $\alpha_D = 0.509$  if using only two of the hydrolysed polyacrylamides; and  $k_D = 5.31 \times 10^{-5}$  and  $\alpha_D = 0.510$  if using only two of the unhydrolysed polyacrylamides. A comparison of these  $k_D$  and  $\alpha_D$  values shows that both the hydrolysed and unhydrolysed can be represented by the same calibration between  $D$  and  $M$ , namely  $D \text{ (cm}^2/\text{s)} = (5.4 \pm 0.1) \times 10^{-5} M^{-0.514 \pm 0.005}$ . This suggests that the polyelectrolytes effect has been suppressed in 0.35M  $\text{KH}_2\text{PO}_4$  aqueous solution. Using this cali-



**Figure 7** Differential weight distributions of molar mass for two hydrolysed and two unhydrolysed polyacrylamide fractions. The symbols are the same as in Figure 5.

bration, we converted each  $G(D)$  into a corresponding molar mass distribution.

Figure 7 shows differential weight distributions of molar mass  $f_w(M)$  of different fractions of polyacrylamides. From each  $f_w(M)$ , we can calculate the weight-average molar mass  $(M_w)_{\text{calcd}}$  and polydispersity index  $M_w/M_n$ , which are listed in Table I. The values of  $(M_w)_{\text{calcd}}$  agree reasonably with those measured directly from static LLS. The values of  $M_w/M_n$  shows that all fractions are moderately distributed.

## CONCLUSION

A combination of static and dynamic LLS results can be used to characterize both the hydrolysed and unhydrolysed polyacrylamides. Our result indicates that the polyelectrolytes effects can be suppressed in 0.35M  $\text{KH}_2\text{PO}_4$  aqueous solution, and the polyacrylamides behaves as a random coil. A calibration between the translational diffusion coefficient ( $D$ ) and molar mass ( $M$ ), namely,  $D(\text{cm}^2/\text{s}) = (5.40 \pm 0.1) \times 10^{-5} M^{-0.514-0.005}$ , has been established. Using this calibration, we obtained not only the weight-average molar mass  $M_w$  but also molar mass distribution in dynamic LLS. The established methodology and the calibration between  $D$  and  $M$  can be used in future to characterize polyacrylamides with an ultrahigh molar mass, which cannot be characterized by other conventional methods, such as SEC and viscometry.

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