Dynamic and Electrophoretic Light Scattering of Poly(dimethyldiallylammonium chloride) in Salt-Free Solutions

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SYNOPSIS

Dynamic and electrophoretic light scattering were used to study the diffusion and electrophoretic mobility of poly(dimethyldiallylammonium chloride) as a function of polymer molecular weight in salt-free solutions. Two relaxation modes characterized as fast diffusion (D_f) and slow diffusion (D_s) were obtained from dynamic light scattering. Although the slow diffusion coefficient D_s strongly depends on molecular weight (M_w), the fast diffusion coefficient D_f was found to be independent of M_w over the range in the study. The fast diffusion was considered as the diffusion of a part of the polymer chain; the slow diffusion was interpreted by multichain diffusion. Electrophoretic light scattering results in the salt-free solution show that the electrophoretic mobility of the polymer is independent of M_w.

Keywords: dynamic light scattering • electrophoretic light scattering • poly(dimethyldiallylammonium chloride) • salt-free solutions

INTRODUCTION

The translational diffusion of neutral polymers in dilute solutions has been extensively studied by dynamic light scattering (DLS). Both theoretical results and experimental studies in dilute solutions[1,2] show that the translational diffusion coefficient, D, is related to polymer molecular weight, M, by $D \propto M^{\alpha}$, with α ranging from -0.5 to -0.6. Recently, a growing focus in the field of dynamic light scattering of polymer solutions has been the semidilute and concentrated regimes, where autocorrelation functions usually show both fast and slow relaxation modes.[3-12] It was found that the fast mode diffusion coefficient is independent of molecular weight in the semidilute regime.[12] However, the slow mode diffusion coefficient[11,12] exhibits a scaling of $D \propto M^{\alpha}$ with a larger α value, around -2. This new phenomenon of the slow mode relaxation has been the subject of different interpretations. For examples, Chu and Nose[3] suggested that the slow mode relaxation is related to the translational diffusion of entangled polymer chains, whereas Nishio and Wada[6] attributed this relaxation to the diffusion of the whole polymer chain. Recently, Brown[12] studied the diffusion of poly(ethylene oxide) in semidilute solution by both dynamic light scattering and pulsed field gradient NMR. He found that the slow mode is one to two orders of magnitude slower than that of the corresponding self-diffusion. It was proposed, in accord with the suggestion of Chu and Nose, that the slow mode is due to the translational diffusion of intermolecularly entangled polymer chains. On the other hand, Wang[13] recently interpreted the slow relaxation in terms of osmotic pressure fluctuations and viscoelasticity.

DLS has also been applied to polyelectrolyte solutions. In contrast to neutral polymers in various solvents, polyelectrolytes are usually studied in electrolyte solutions because the polymer chain conformation strongly depends on the ionic strength.

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From dynamic light scattering measurements on poly(styrene sulfonate) (NaPSS) in sodium chloride solutions, Wang and Yu[14] concluded that the polymer behaves like a neutral polymer in a good solvent at high ionic strength. Schmidt and coworkers[16] found a bimodal distribution of decay times for quaternized poly(2-vinylpyridine) in aqueous solutions of $I \leq 0.0001$ M. The fast mode was interpreted according to a transient network model, and the slow mode was considered to be associated with long-range concentration fluctuations. Such bimodal behavior was also reported for poly(styrene sulfonate) in salt-free solutions by Amis and coworkers.[17,18] They attributed the fast mode to the coupled diffusion of the polyion and counterion, and the slow mode to the dynamics of large multichain domains. This bimodal phenomenon for polyelectrolytes in low-salt or salt-free systems has been referred to in the context of an "ordinary–extraordinary transition."[19-22] Similar transition-like behavior has been reported for the mobility, as measured by electrophoretic light scattering (ELS).[22,23] Indeed, various "transitions" have been reported, including discontinuities with respect to both polyelectrolyte concentration,[22] and with respect to the concentration of added salt,[19-22] based on both DLS and ELS. A discussion of the relationships among these transitions and the interpretation of these results may be found in ref. 24.

There have been relatively few studies of the MW dependence of DLS-based diffusivities in salt-free solution.[25] Some studies show that the fast diffusion coefficient is independent of MW, whereas the slow one strongly depends on MW.[17,25] As far as the mobility is concerned, it is generally understood that polyelectrolyte mobility in the presence of salt is MW independent; however, some MW effect has been reported.[23] We recognize that relatively few polyelectrolytes are available as well-characterized narrow MWD fractions; most studies have been done with NaPSS, or, to a lesser degree, with poly(methacrylic acid) (PMA). These two polymers, for one reason or another, may have linear charge densities of questionable consistency. In the case of NaPSS, the commercial "standards" have variable degrees of sulfonation, typically ranging around 85%,[26] and a major concern is whether the synthetic route gives rise to compositional polydispersity such that a significant portion of the material might be of considerably lower sulfonation. The observation that lower MW NaPSS standards exhibit relatively higher electrophoretic mobilities in 0.1*M* NaCl (26) is also suggestive of variable sulfonation. With regard to poly(methacrylic acid), the charge density is pH dependent, and, unless solutions are buffered, the pH in turn may depend on polymer concentration. For this reason, it is of interest to study the behavior of salt-free solutions of well-characterized narrow MWD fractions of polymers whose charge is independent of pH or the mode of preparation. Therefore, we measured the diffusion coefficients and electrophoretic mobility, in salt-free solution, of MW fractions of poly(dimethyldiallylammonium chloride) (PDMDAAC), a polymer in which each residue bears a positive charge regardless of pH. It is of interest to compare these results with those for the other polyelectrolytes noted above.

EXPERIMENTAL

Materials

Poly(dimethyldiallylammonium chloride), a commercial sample "Merquat 100" with nominal molecular weight of 2×10^5 and reported polydispersity of $M_w/M_n = 10$, was obtained from Calgon Corporation (Pittsburgh, PA). The commercial sample was fractionated via size-exclusion chromatography (SEC) prior to use. The fractionation of PDMDAAC was carried out using a mobile phase of 0.5*M* $NaNO_3$ buffered with 25 m*M* NaOAc of pH 6.5, which has been found to sufficiently repress adsorption effects. The polymer (40.0 mg) was applied to a Sephacryl S400 gel column via a 2.0-mL sample loop. The mobile phase was eluted through the column at a velocity of 2.0 mL/min, and the eluent was monitored using an R401 differential refractometer (Waters). The injected sample was separated into 30 fractions, collected at 4.8-mL intervals following the beginning of sample elution. The obtained fractions were then dialyzed against water for 2 days and lyophilized. Although the fractions obtained near the median of the distribution were abundant, the low/high MW fractions were not plentiful. For this reason, we were unable to carry out studies of concentration dependence, and nearly all the experiments were done at polymer concentrations of either 3 g/L (QELS) or 1 g/L (ELS). All salts used in the present work were AR grade and obtained from Sigma. Distilled and deionized water was used in all experiments.

To determine molecular weights of the PDMDAAC fractions, analytical SEC was carried out on an apparatus comprised of a Minipump (Milton Roy), a model 7012 injector (Rheodyne) equipped with a 100-μL sample loop, and an R401 differential refractometer (Waters). A Superose-6 column (30 × 1 cm od) (Pharmacia) was eluted at

0.34 mL/min. Column efficiency, determined with acetone, was at least 12,000 plates/m. Injections were performed in mobile phase of $0.5M$ NaCl and pH 6.5. The pH was maintained by $0.25M$ NaOAc buffer. Polymer samples (2.0 g/L) were filtered with Gelman 0.2-μm syringe filters before injection. Molecular weights, as given in Table I, were obtained from the SEC calibration curve for PDMDAAC based on fractions of this polymer that had been characterized by static light scattering.[27] The M_w/M_n values were in the range of 1.1 to 1.2.

Table I. Characteristics of PDMDAAC Fractions Obtained by SEC

Sample	M_w
PD4	1.3×10^6
PD8	5.9×10^5
PD12	2.9×10^5
PD16	2.0×10^5
PD20	9.4×10^4
PD22	6.4×10^4
PD26	2.8×10^4

Methods

Sample Preparation

Samples of polymer fraction samples were weighed and dissolved in deionized water with a resistivity of 18 MΩ cm. All solutions were made dust-free by filtering through Gelman 0.2-μm syringe filters. Concentrations of PDMDAAC were 1.0 and 3.0 g/L for electrophoretic light scattering and dynamic light scattering, respectively.

Dynamic Light Scattering (DLS)

DLS measurements were made at scattering angles from 30° to 150° with a Brookhaven (Holtsville, NY) 264-channel BI-2030 AT digital Correlator and using a Spectra-Physics 2020 Ar^+ laser operating at 200 mW. A 200-μm pinhole aperture was used for the EMI photomultiplier tube, and decahydronaphthalene (Decalin) was used as the refractive index matching fluid to reduce stray light. We obtain the homodyne intensity–intensity correlation function $G(q, t)$, with q, the amplitude of the scattering vector, given by $q = (4\pi n/\lambda)\sin(\theta/2)$, where n is the refractive index of the medium, λ is the wavelength of the excitation light in a vacuum, and θ is the scattering angle. For a Gaussian distribution of intensity profile of the scattered light, $G(q, t)$ is related to the electric field correlation function $g(q, t)$ by:

$$G(q, t) = A(1 + bg(q, t)^2) \tag{1}$$

where A is the experimental baseline and b is a constant, which depends on the number of coherence areas that generates the signal ($0 < b < 1$). The quality of the measurements was verified by determining that the difference between the measured value of A and the calculated one was less than 1%. The electric field correlation function depends on the Fourier transform of the fluctuating number density of particles or molecules. For the center of mass diffusion of identical particles the following simple relation holds:

$$g(q, t) = e^{-t/\tau}$$
$$\frac{1}{\tau} = Dq^2 \tag{2}$$

where τ is decay time and D is diffusion coefficient. More detailed discussions of DLS data analysis may be found in refs. 28 and 29.

For polydisperse systems the correlation function $g(q, t)$ can be expressed as an integral of the exponential decays weighted over the distribution of relaxation times $\rho(\tau)$:

$$g(t) = \int_0^{\infty} e^{-t/\tau}\rho(\tau)\, d\tau. \tag{3}$$

In principle, it is possible to obtain the distribution $\rho(\tau)$ by integral transformation of the experimental $[G(t)/A - 1]^{1/2}$, but in practice this presents a formidable problem for numerical analysis, because taking the inverse Laplace transform is numerically an ill-posed problem. Several numerical methods developed so far are devoted to calculating $\rho(\tau)$. In the present work, we analyze the autocorrelation functions by using the CONTIN program, which employs the constrained regularization method.[30]

From eq. (3), the mean relaxation time, $\langle\tau\rangle$, defined as the area of $g(t)$, is given by

$$\langle\tau\rangle = \int_0^{\infty} g(t)\, dt = \int_0^{\infty} \tau\rho(\tau)\, d\tau \Big/ \int_0^{\infty} \rho(\tau)\, d\tau. \tag{4}$$

This $\langle\tau\rangle$ value can be resolved from each of the distribution modes of $\rho(\tau)$, as the first moment of the normalized relaxation spectrum. Therefore, the diffusion coefficient, which corresponds to each value of $\langle\tau\rangle$, can be calculated using

$$D = \frac{\lambda^2}{16\pi^2\sin^2(\theta/2)\langle\tau\rangle}. \tag{5}$$

Electrophoretic Light Scattering (ELS)

ELS measurements were made at four scattering angles (8.7°, 17.4°, 26°, and 34.7°), using a Coulter (Hialeah, FL) DELSA 440 apparatus. The light source was a 5-mW He-Ne laser (λ = 632.8 nm). The total volume of sample chamber is about 1 mL. A rectangular channel runs through a 5-mm thickness of the insert, connecting the hemispherical cavities in each electrode. The electric field was applied at a constant current of 0.4 mA. The temperature of the thermostated chamber was maintained at 25°C. Electro-osmotic corrections were determined by measuring the spatial flow profile in the chamber and taking the mobility readings at a distance 16% of the rectangular length from the respective walls of the chamber. This procedure was verified by using the DELSA electrophoretic mobility standard.

In ELS, the photon-counting heterodyne correlation function for a solution with an electrophoretically monodisperse solute can be written as[31]:

$$C(\tau) = \beta_0\delta(\tau) + \alpha_0 + \alpha_1\exp(-2Dq^2\tau) + \alpha_2\exp(-Dq^2\tau)\cos(\Delta\omega\tau) \tag{6}$$

where β_0, α_0, α_1, and α_2 are constants independent of correlation time, τ, and $\delta(\tau)$ is the delta function. D is the diffusion coefficient. The cosine term is due to simultaneous electrophoresis and diffusion.

The Fourier transform of eq. (6) with respect to time, as stipulated by the Weiner-Khinchine theorem,[32] gives the power spectrum:

$$S(\omega) = \beta_0 + \alpha\delta(\omega) + \frac{2(\alpha_1/\pi)Dq^2}{\omega^2 + (2Dq^2)^2} + \frac{\alpha_2 Dq^2}{2\pi}\left[\frac{1}{(\omega + \Delta\omega)^2 + (Dq^2)^2} + \frac{1}{(\omega - \Delta\omega)^2 + (Dq^2)^2}\right] \tag{7}$$

where α is a constant independent of ω.

In both eqs. (6) and (7), $\Delta\omega$ is the difference between the angular frequency of the scattered light, ω_s, and that of the reference beam, ω_r, which is the same as that of the incident beam. Because the frequency of the incident beam is modulated in the scattered light by the amount of the Doppler shift frequency, $\Delta\omega$ is given by:

$$\Delta\omega = \frac{2\pi n}{\lambda} uE \sin\theta \tag{8}$$

where E (volts/cm) and u ((μm s^{-1})/(V cm^{-1})) are the applied electric field strength and electrophoretic mobility, respectively. Therefore, u can be directly evaluated from the power spectrum. The u values obtained in this work are repeatable within the error less than 10%.

RESULTS AND DISCUSSION

Figure 1 shows a typical normalized autocorrelation function for PD4 at θ = 90°. CONTIN fit of the autocorrelation function gives a bimodal distribution, from which the fast and slow diffusion coefficients of 9.8 × 10^{-7} and 3.7 × 10^{-9} cm^2/s, respectively, were obtained.

Figures 2a and b shows the angle dependence for the fast and the slow diffusion coefficients, respectively. Although D_f is independent of the angle, D_s displays a linear dependence on $\sin^2(\theta/2)$ (and thus on q^2). A similar angular dependence of the diffusion coefficient was also observed for other polyelectrolytes.[15-17] Sedlak et al.[15] attributed the slow mode diffusion of PMA to the diffusion of domains consisting of a large number of macromolecules. Förster et al.[16] interpreted the angular dependence of D_s for quaternized polyvinylpyridine on the basis of the polydispersity of the diffusing particles and the internal motion of large structures. They found that both D_s and the static scattering function are q dependent. They also suggested that the slow diffusion

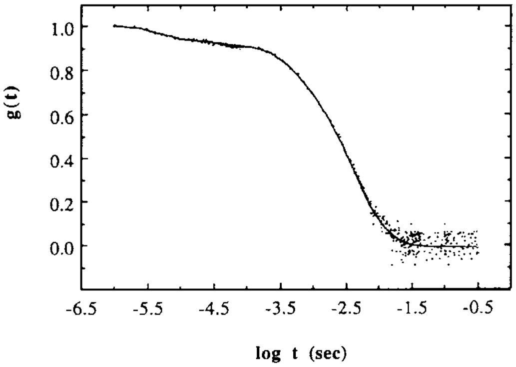

Figure 1. Typical normalized autocorrelation function obtained for PD4 at θ = 90°.

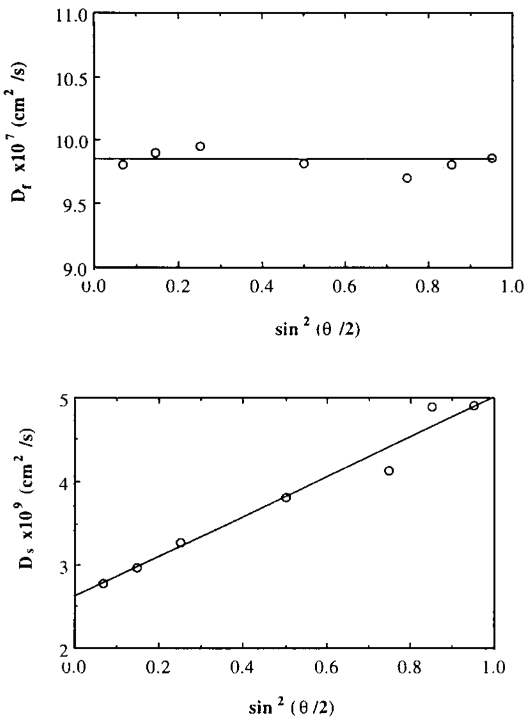

Figure 2. Dependence of diffusion coefficients D_f (a) and D_s (b) on scattering angle.

mode is caused by the motion of large domains because only relatively large particles yield the q dependence. Sedlak and Amis[17] estimated the magnitude of the large domains for NaPSS by measuring the apparent radius of gyration and concluded that these contain many molecules. In the present study, we observed q dependence for all the polymer fractions at a relative low concentration of 3.0 g/L, at which concentration chain entanglements[33] are unlikely. We also then conclude that multichain structures are responsible for D_s.

Figure 3 shows the molecular weight dependence of the fast diffusion coefficient D_f. Over the MW range studied, D_f is independent of molecular weight. This behavior has been considered a manifestation of coupled diffusion of polyions and counterions.[17] The coupling is a consequence of polymer concentration fluctuation induced by surrounding counterions. Qualitatively, the diffusion of polymer chains at a certain level is affected by the motion of counterion. The coupling diffusion coefficient (D_{cp}) may be expressed by:[19]

$$D_{cp}(q = 0, C_{\mathrm{add}} = 0) = \frac{(2 + Z_p)D_pD_c}{Z_pD_p + 2D_c} \qquad (9)$$

where D_p and D_c are the diffusion coefficients of the hypothetical uncharged polymer chain and the counterion, respectively; Z_p is the effective charge of the polyion; and C_{add} is the concentration of added salt. The factor of 2 arises because of the charge neutrality requirement, i.e.,

$$2C_c/C_p = Z_p \quad (C_{\mathrm{add}} = 0) \qquad (10)$$

where C_c and C_p are counterion and polymer concentrations, respectively. From eq. (9) the coupled diffusion coefficient is constant for $Z_pD_p \gg D_c$ (i.e., the macroion diffuses as fast as the counterion), but this is generally not valid. However, if we assume that the coupling is between a portion of the polymer chain and its counterions, the coupled diffusion coefficient would be a constant over a range of molecular weights. In this case, D_p in eq. (9) would correspond to the blob diffusion of polymers.[17] For PDMDAAC this portion of the polymer chain could be no larger than the size of the smallest fraction of this study, PD26 (i.e., about 200 repeat units). Förster et al.[16] interpreted the fast diffusion as thermal displacement fluctuations of polymer segments between entanglements because they observed it under conditions wherein polymer chains could overlap. However, we observed the fast diffusion at a relative low concentration of 3 g/L at molecular weights as low as 2.8 × 10^4. This is well below the overlap concentration, so it is unlikely that such entanglements take place.

Figure 4 shows a strong dependence of the slow diffusion coefficient D_s on molecular weight. This molecular weight dependence of the slow diffusion coefficient has been discussed in the context of a reptation model,[34] leading to the following relationship:

$$D \propto M_w^{-2}c^{-3} \qquad (11)$$

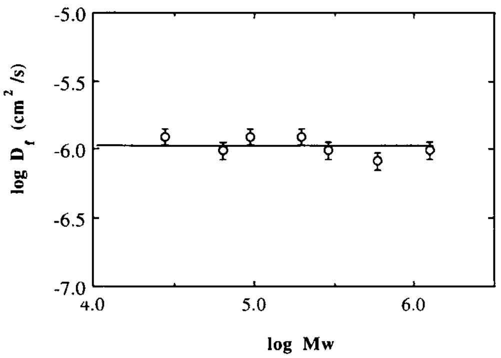

Figure 3. Dependence of fast diffusion coefficient D_f on molecular weight at θ = 90°.

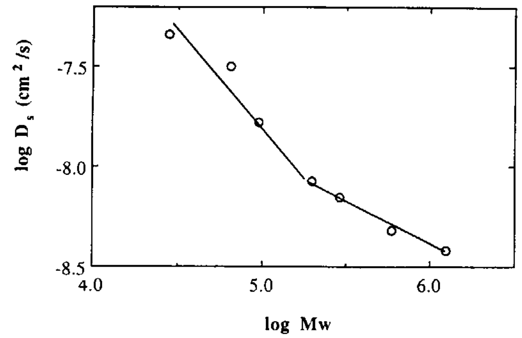

Figure 4. Dependence of slow diffusion coefficient D_s on molecular weight at $\theta = 90°$.

where c is the concentration of the polymer. In Figure 4, the slow diffusion coefficients show a discontinuity at $M_w = 2.0 \times 10^5$, where the slope of the dependence changes from -0.9 to -0.4. Obviously, the present results are not consistent with eq. (11). A similar discontinuity in the $D_s \sim M_w$ relationship was also reported for poly(styrene sulfonate) system,[17] for which the slope changed from -0.3 to -1.1. The discontinuity was discussed in terms of the molecular weight dependence of the apparent radius of gyration. However, no clear conclusion was obtained. In the present case, the situation is further complicated by the possibility of branching for $M_w > 2 \times 10^5$.[27] The slow diffusion at $M_w < 2.0 \times 10^5$ follows a scaling law close to $D \sim M_w^{-1}$, which is typical for neutral rodlike polymers.[1,2] This may suggest that the slow diffusion is due to the diffusion of the stretched PDMDAAC chain. However, this hypothesis would not agree with the q dependence of D_s as seen in Figure 2b. At present, our analysis of the molecular weight dependence of D_s is not conclusive.

The slow diffusion mode has also been discussed in terms of the so-called "ordinary–extraordinary" transition[19-22] based on the observation of a bimodal diffusion coefficient for polyelectrolyte solutions at low salt concentration. The onset of the bimodal phenomenon was defined as the "ordinary–extraordinary" transition. This expression refers to the appearance of the slow diffusion mode; there is no actual phase transition involved. Unique behavior of the electrophoretic mobility at this "transition" point was also reported.[19,20] For example, molecular weight dependence of the electrophoretic mobility was observed for polylysine[19] in low salt concentration (ionic strength < 0.01*M*). Figure 5 shows a typical electrophoretic light scattering spectrum obtained at four different scattering angles for PD26 in salt-free solution, at a polymer concentration of 1.0 g/L. The measured mobility did not change when the concentration was reduced to 0.5 g/L, so we assume that the results essentially correspond to the limit of zero concentration. The average frequency of the spectrum gives a mobility of 3.2±0.3 μm-cm/V-s. The mobility obtained for different PDMDAAC fractions is plotted in Figure 6. In contrast to the results of ref. 23, the mobility data show no MW effect over the range of MW studied, even though dynamic light scattering displayed a bimodal distribution. The fact that the mobility data provide no evidence of the multichain assemblies inferred from the DLS data indicates that the mobility depends only the structure of the polymer unit, namely its charge to friction ratio. Therefore, neither MW, multichain association, nor branching (should it occur) affects the mobility.

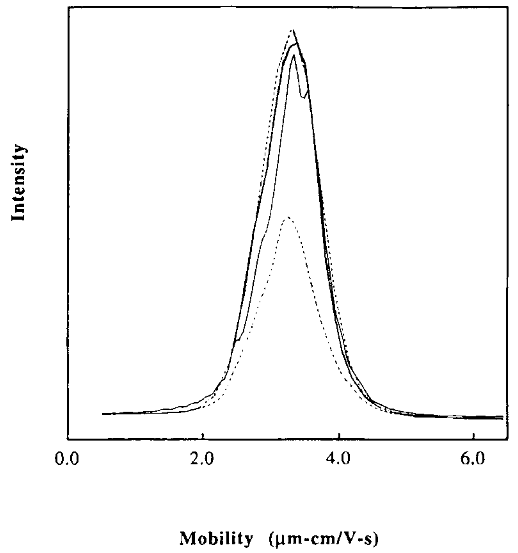

Figure 5. Typical electrophoretic light scattering spectrum obtained for PD26 at scattering angles of 8.7°, 17.4°, 26°, and 34.7°.

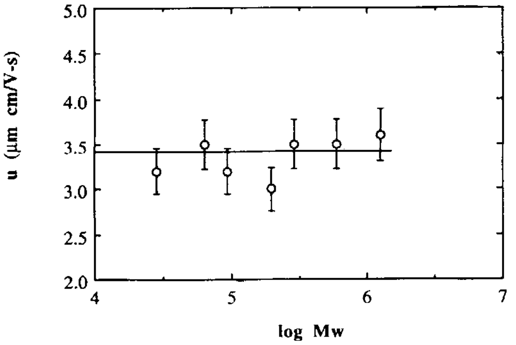

Figure 6. Dependence of electrophoretic mobility on molecular weight.

In summary, we studied PDMDAAC in salt-free solution by DLS and ELS. DLS results show a bimodal distribution of diffusional modes (i.e., D_f and D_s). D_f shows no angle or molecular weight dependence, whereas D_s strongly depends on both of these parameters. The q and MW dependence of diffusion coefficients for PDMDAAC is qualitatively similar to that seen for NaPSS. D_f may be interpreted as the coupled diffusion of the polyelectrolyte chain and counterions, whereas D_s can be explained by the diffusion of multichain assemblies. ELS results show constant mobility over the MW range studied.

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