Laser Light-Scattering Study of Poly(sulfoalkyl methacrylate)s in 0.1 M NaCl Aqueous Solution

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ABSTRACT: Poly(sulfoalkyl methacrylate)s (PSSRMA) with different alkyl side chain lengths in 0.1 M NaCl aqueous solution at 25 °C were studied by laser light scattering (LLS). In static LLS, the weight-average molecular weights, *z*-average radii of gyration, and second virial coefficients of the PSSRMA samples were determined. In dynamic LLS, the Laplace inversion of the precisely measured intensity−intensity time correlation function leads to an estimate of the characteristic line width distribution $G(\Gamma)$. The characteristic line width $\langle\Gamma\rangle$ increases rapidly when the polymer concentration is higher than $\sim 10^{-3}$ g/mL, which corresponds to a decrease in the surface tension. In the temperature range 25−47 °C, $\langle\Gamma\rangle$ increases with the temperature. All LLS results consistently indicate that poly(sulfoalkyl methacrylate)s with a longer alkyl side chain have a more compact chain conformation in 0.1 M NaCl aqueous solution. A combination of static and dynamic LLS results enables us to establish a scaling equation of D (cm²/s) $= k_D M^{-\alpha_D}$ with $\alpha_D \sim 0.56$ and k_D in the range of $(1.54 \times 10^{-4})-(2.07 \times 10^{-4})$ depending on the alkyl side chain length. With this calibration, we were able to calculate the PSSRMA's molecular weight distribution from $G(\Gamma)$.

Introduction

A series of sodium sulfoalkyl methacrylates with different alkyl side chain lengths have been synthesized.[1] The following structure diagram shows that these polymers contain alkyl side chains with end-attached negatively charged sulfonate groups. It is
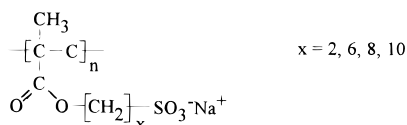
expected that such a structure will lead to a significant surface activity, and they can be used as a biocompatible material. The length of the alkyl side chain will certainly influence their surface properties and applications.[2] It is in the interest of both basic research and application to study these polymers in a fluid close to the conditions of the human body.

The ion-containing polymers are receiving increasing attention year by year. Kessaissia *et al.* grafted different alkyl chain lengths onto silica gel and reported that the contact angle for water increases with the carbon chain length.[3] Andrade *et al.* studied various charged copolymers of methacrylic acid, methyl methacrylate, and trimethylaminoethyl methacrylate and the influence of surface charge and side chain length.[4] Chen *et al.*[1] found that the surface tension of aqueous salt solution of poly(sulfoalkyl methacrylate) monomers and homopolymers decreases as the alkyl side chain length increases; their study of the surface characteristics of coated hydroxyethyl methacrylate−sodium sulfoalkyl methacrylate copolymer films showed that the contact angle hysteresis increases with increasing the alkyl side chain length, while the receding angle decreases. X-ray

photoelectron spectroscopy (XPS) analysis of the copolymer surfaces showed a striking enrichment of the sulfonate groups on the surface.[1]

In comparison, the aqueous solution properties of poly(sulfoalkyl methacrylate), such as conformation and other molecular parameters, have not been systematically studied. In this work, laser light scattering has been used to study a series of poly(sodium sulfoalkyl methacrylate) (PSSRMA) homopolymers in 0.1 M NaCl aqueous solution. Research interests are in the conformational changes of PSSRMA molecules in the solution and the influence of the alkyl side chain length.

Experimental Section

Sample Preparation. Sodium sulfohexyl methacrylate (SSHMA), $CH_2=C(CH_3)COO(CH_2)_6SO_3Na$, sodium sulfooctyl methacrylate (SSOMA), $CH_2=C(CH_3)COO(CH_2)_8SO_3Na$, and sodium sulfodecyl methacrylate (SSDMA), $CH_2=C(CH_3)COO-(CH_2)_{10}SO_3Na$, with purity $>99\%$ were prepared in the Polymer Division, Chemistry Department, Peking University, China.[1] Sodium sulfoethyl methacrylate (SSEMA), $CH_2=C(CH_3)COO-(CH_2)_2SO_3Na$, was prepared from sulfoethyl methacrylate (Polyscience; 95%) through neutralization and purification.[1] Polymerization was carried out at 70 °C under nitrogen with 0.1% potassium persulfate as an initiator.[1] Hereafter, these poly(sulfoalkyl methacrylate)s will be referred to as PSSRMA. All PSSRMA solutions were prepared by dissolving a proper amount of polymer in 0.1 M NaCl aqueous solution. For each PSSRMA sample, five concentrations ranging from 5×10^{-5} to 1.0×10^{-3} g/mL were prepared by dilution. All PSSRMA solution for laser light scattering (LLS) were clarified by a 0.1, 0.22, or 0.5-μm Millipore filter depending on the polymer size.

LLS Instrumentation. The absolute scattered light intensities and intensity−intensity time correlation functions of PSSRMA in 0.1 M NaCl aqueous solution at different scattering angles (20−150°) were measured with a modified commercial LLS spectrometer (ALV/SP-125 equipped with an ALV-5000 multi-τ digital time correlator). A solid state laser (ADLAS DPY425II, output power = $\sim$400 mW at $\lambda = 532$ nm) was used as the light source. The incident beam was vertically polarized with respect to the scattering plane. The spatial coherence constant $\beta = \sim 0.9$, a rather high value for an LLS spectrometer capable of doing both static and dynamic LLS

Table 1. Summary of Static and Dynamic LLS Results of Four PSSRMA Samples[a]

polymers	dn/dc (mL/g)	$10^{-5}M_w$ (g/mol)	$\langle R_g \rangle$ (nm)	$10^4 A_2$ (mol mL/g²)	$10^8 \langle D \rangle$ (cm²/s)	$\langle R_h \rangle$ (nm)	$\langle R_g \rangle / \langle R_h \rangle$	$10^4 k_D$ (mL/g)	M_w/M_n	p (nm)
PSSEMA	0.135	3.06	43.3	6.41	12.2	20.1	2.16	1.54	1.5	4.2
PSSHMA	0.140	4.94	42.9	5.61	10.2	23.8	1.80	1.72	2.0	3.5
PSSOMA	0.149	7.01	40.9	2.03	10.0	24.5	1.67	1.99	1.8	2.1
PSSDMA	0.170	7.34	39.9	1.91	9.75	25.1	1.59	2.07	2.1	2.5

[a] Relative errors: dn/dc, ±1%; M_w, ±3%; $\langle R_g \rangle$, ±5%; A_2, ±10%; $\langle D \rangle$, ±1%; k_D, ±10%; and M_w/M_n, ±15%.

simultaneously. The detail of LLS instrumentation and theory can be found elsewhere.[5,6]

Results and Discussion

The angular dependence of the excess absolute time-averaged scattered intensity, known as the excess Rayleigh ratio ($R_{vv}(\theta)$), was measured. For a dilute polymer solution at a relatively low scattering angle (θ), $R_{vv}(\theta)$ can be expressed as[7]

$$\frac{KC}{R_{vv}\theta} \approx \frac{1}{M_w}\left(1 + \frac{1}{3}\langle R_g^2 \rangle q^2\right) + 2A_2 C \qquad (1)$$

where $K = 4\pi^2 n^2 (dn/dc)^2/(N_A\lambda_o^4)$ and $q = 4\pi n/\lambda_o \sin(\theta/2)$ with N_A, dn/dc, n, and λ_o being Avogadro number, the specific refractive index increment, the solvent refractive index, and the wavelength of light in vacuo, respectively. M_w is the weight-average molecular weight, A_2 is the second virial coefficient, and $\langle R_g^2 \rangle_z^{1/2}$ (or written as $\langle R_g \rangle$) is the root-mean square z-average radius of the polymer chain in solution. After measuring $R_{vv}(\theta)$ at a set of C and θ, we were able to determine M_w, $\langle R_g \rangle$, and A_2 from a Zimm plot which incorporates θ and C extrapolation on a single grid.

It is vital in static light scattering to have a precise value of the differential refractive index increment (dn/dC) because the measured M_w is proportional to (dn/dC)$^{-2}$. A novel and high-precision differential refractometer was incorporated into the light scattering spectrometer,[8] which enables us to measure dn/dC and the scattered light intensity under identical experimental conditions, so that the wavelength correlation was eliminated.

The measured dn/dC values for four PSSRMA samples are listed in Table 1. The dn/dC value increases with the alkyl side chain length, which indicates that the PSSRMA chain density in 0.1 M NaCl aqueous solution increases with the alkyl side chain length since for a given polymer the refractive index increment increases with density.[9] In other words, the PSSRMA sample with a longer alkyl side chain has a more compact conformation in the solution.

Figure 1 shows a typical Zimm plot of PSSHMA in 0.1 M NaCl aqueous solution at 25 °C, where a 0.22-μm filter was used and C ranges from 2.16 × 10^{-4} to 1.08 × 10^{-3} g/mL. On the basis of eq 1, we have the values of M_w, $\langle R_g \rangle$, and A_2, respectively, from [KC/$R_{vv}(\theta)$]$_{\theta\to0,c\to0}$, [KC/$R_{vv}(\theta)$]$_{c\to0}$ vs q^2, and [KC/$R_{vv}(\theta)$]$_{\theta\to0}$ vs C. The static LLS results of four PSSRMA samples are summarized in Table 1. The positive values of A_2 indicate that 0.1 M NaCl aqueous solution is a good solvent for poly(sulfoalkyl methacrylate) at 25 °C, but the decrease of A_2 indicates that the solvent quality becomes poorer with increasing alkyl side chain length. A comparison of the values of M_w and $\langle R_g \rangle$ also shows that the PSSRMA sample with a longer alkyl side chain has a more compacted conformation in the solution.

Flory[10] has shown that there is a simple relationship between the persistence length (p), the characteristic
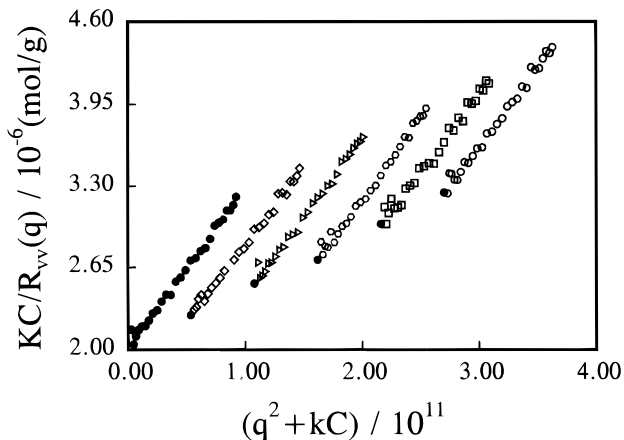
Figure 1. Typical Zimm plot of PSSHMA in 0.1 M NaCl aqueous solution at $T = 25$ °C, where C ranges from 2.16 × 10^{-4} to 1.08 × 10^{-3} g/mL and the solutions were clarified with a 0.22-μm filter.

ratio (C_∞), and the main chain bond length (l), *i.e.*, $p = (C_\infty + 1)l/2$, where C_∞ is further related to the conformation (steric) factor σ [$=\langle R_g \rangle/(2Nl^2)$] by $C_\infty = 2\sigma^2$, with N being the number of bonds along the main backbone chain of the polymer. From PSSRMA, the C–C bond length l is 0.153 nm, and N can be estimated from M_w, so that p values for each sample can be obtained, which are listed in Table 1. The decrease of p with increasing alkyl side chain length indicates that PSSRMA with a longer alkyl side chain is more flexible in 0.1 M NaCl aqueous solution. Normally, a polymer with a larger side group will be less flexible due to the steric effect. This paradox can be explained after considering the polyelectrolyte nature of PSSRMA. For PSSRMA with a short alkyl side chain, the electrostatic repulsion between two neighboring charged groups will be stronger because they are closer, which extends the polymer chain and makes it less flexible. The steric interaction and electrostatic repulsion have opposite effects on the chain flexibility. When the alkyl side chain is short, the electrostatic repulsion is dominating; this is why PSSEMA has the longest persistence length. The increase of side chain length increases the steric effect but, at the same time, decreases the electrostatic repulsion, which leads to a point (PSSOMA) where the polymer chain reaches its highest flexibility (lowest p). Further increase of the side chain length will make the steric effect become dominating. This is why PSSDMA has a longer persistence length than PSSOMA. Practically, it has been found that the surface mobility properties of PSSOMA are best,[11] which may be due to its highest chain flexibility.

In dynamic LLS, the intensity–intensity time correlation function ($G^{(2)}(t,q)$) in the self-beating mode was measured. $G^{(2)}(t,q)$ is related to the normalized first-order electric field time correlation function ($g^{(1)}(t,q)$) as[5,6]

$$G^{(2)}(t,q) = \langle I(0)I(t) \rangle = A[1 + \beta|g^{(1)}(t,q)|^2] \qquad (2)$$
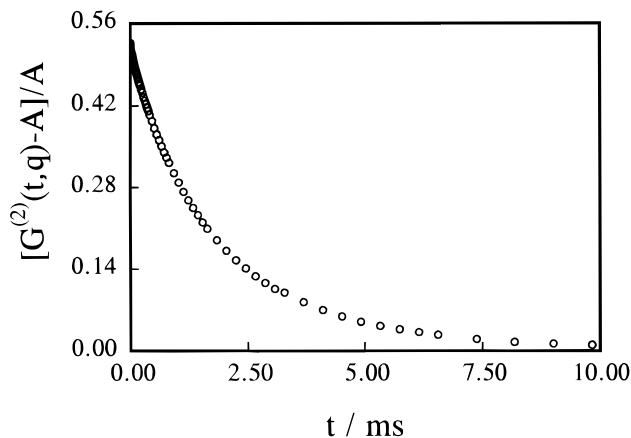
Figure 2. Typical measured intensity−intensity time correlation function of PSSHMA in 0.1 M NaCl aqueous solution at $\theta = 20°$ and $T = 25$ °C.

Figure 3. Translational diffusion coefficient distribution ($G(D)$) of PSSEMA (○), PSSHMA (◇), PSSOMA (△), and PSSDMA (□) in 0.1 M NaCl aqueous solution at $T = 25$ °C.

Where A is a measured baseline, β is, as stated before, a parameter depending on the coherence of the detection, and t is the delay time.

Figure 2 shows a typical plot of the measured intensity−intensity time correlation function of PSSHMA in 0.1 M NaCl aqueous solution at $\theta = 20°$ and $T = 25$ °C. For a polydisperse sample, $g^{(1)}(t,q)$ is related to the normalized characteristic line width distribution ($G(\Gamma)$) by

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

Using a Laplace inversion program (CONTIN[12]) equipped with the correlator, we were able to calculate $G(\Gamma)$ from $G^{(2)}(t,q)$.

In general, Γ is a function of both C and q. As C increases, the interaction between polymer molecules will effect the diffusion process. On the other hand, as q increases, the internal molecular motion will influence Γ. This effect can be expressed in the form of[13,14]

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

where D is the translational diffusion coefficient at $c \to 0$ and $q \to 0$, k_d is the diffusion second virial coefficient, and f is a dimentionless number depending on the chain conformation, solvent, and internal motions. According to eq 4, D, f, and k_d can be calculated respectively from $(\Gamma/q^2)_{c\to0,q\to0}$, $(\Gamma/q^2)_{c\to0}$ vs q^2, and $(\Gamma/q^2)_{q\to0}$ vs C. Our results showed that $f \sim 0.2$ and $k_d \sim 210$ mL/g, which indicate that the corrections of both q and C are very small in this study. With pair values of k_d and f, $G(\Gamma)$ can be converted into $G(D)$.

Figure 3 shows translational diffusion coefficient distributions ($G(D)$) of four PSSRMA samples in 0.1 M NaCl aqueous solution at 25 °C, from which we were able to calculate the average translational diffusion coefficient ($\langle D \rangle$), defined as $\int_0^\infty G(D)D\, dD$, and the average hydrodynamic radius ($\langle R_h \rangle$), defined as $K_B T/(6\pi\eta\langle D \rangle)$, where K_B, T, and η are the Boltzmann constant, the absolute temperature, and solvent viscosity, respectively. The values of $\langle D \rangle$, $\langle R_h \rangle$, and $\langle R_g \rangle/\langle R_h \rangle$ of four PSSRMA samples are also listed in Table 1. The ratio of $\langle R_g \rangle/\langle R_h \rangle$ is an important parameter depending on the polymer architecture, chain conformation, and polydispersity. It is known that $\langle R_g \rangle/\langle R_h \rangle$ is $(3/5)^{1/2}$, ~ 1.8, and ~ 2 for a uniform sphere, a polydisperse linear coil, and a rodlike linear chain, respectively.[15−17] The decrease
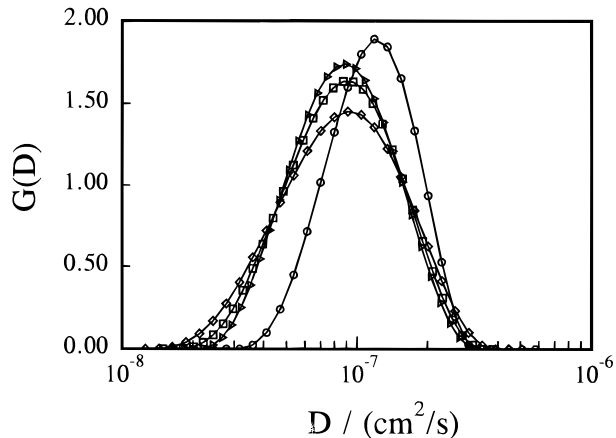
of $\langle R_g \rangle/\langle R_h \rangle$ from 2.16 to 1.59 further suggests that PSSEMA in 0.1 M NaCl solution is more stretched than PSSDMA, or in other words, PSSRMA with a long alkyl side chain has a more compact conformation in 0.1 M NaCl aqueous solution, which is also reflected by the values of $\langle D \rangle$ in Table 1. At $\theta = 0$ and $C = 0$, on the basis of eqs 1 and 3, we have

$$\int_0^\infty G(D)\, dD \propto \langle I \rangle \text{ and } \int_0^\infty F_w(M)M\, dM \propto \langle I \rangle \quad (5)$$

from static and dynamic LLS, respectively, which leads to

$$\int_0^\infty F_w(M)M^2\, d(lnM) \propto \int_0^\infty G(D)D\, d(lnD) \quad (6)$$

Comparing both sides of eq 6, we have

$$F_w(M) \propto \frac{G(D)D}{M^2} \quad (7)$$

For transforming $G(D)$ to a differential weight distribution ($f_w(M)$),[18] we have to establish a calibration between D and M, i.e., $D = k_D M^{-\alpha_D}$, where k_D and α_D are two scaling constants. The previous viscosity study[19] showed that $\alpha_\eta \sim 0.68$ in the scaling relation of $[\eta] \propto M_w^{\alpha_\eta}$, where $[\eta]$ is the intrinsic viscosity. According to Flory's prediction,[20] α_D and α_η for a polymer coil are related by $\alpha_D = (1 + \alpha_\eta)/3$, which leads to $\alpha_D \sim 0.56$ for PSSRMA in 0.1 M NaCl aqueous solution at 25 °C. Using this value of α_D, we were able to calculate k_D for each PSSRMA sample by combining eq 7 with $M_w = \int_0^\infty F_w(M)M\, dM/\int_0^\infty f_w(M)\, dM$ and $D = k_D M^{-\alpha_D}$, i.e.,[16]

$$M_w = \frac{k_D^{1/\alpha_D} \int_0^\infty G(D)\, dD}{\int_0^\infty G(D)D^{1/\alpha_D}\, dD} \quad (8)$$

where M_w and $G(D)$ are respectively from static and dynamic LLS. The calculated values of k_D are listed in Table 1. The increase of k_D with the alkyl side chain length further indicates that for a comparable molecular weight the PSSRMA sample with a longer alkyl side chain has a higher diffusivity, i.e., a smaller hydrodynamic volume or a more compact conformation.

With the known values of k_D and α_D, we were able to convert $G(D)$ into $f_w(M)$ on the basis of eq 7. Figure 4 shows differential weight distributions of four PSSRMA samples. From each $f_w(M)$, we were able to calculate
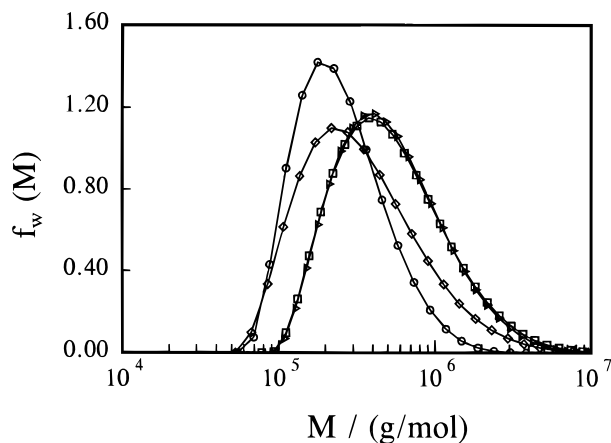
Figure 4. Differential weight distributions ($f_w(M)$) of PSSE-MA (O), PSSHMA ($\diamond$), PSSOMA ($\triangle$), and PSSDMA ($\square$).
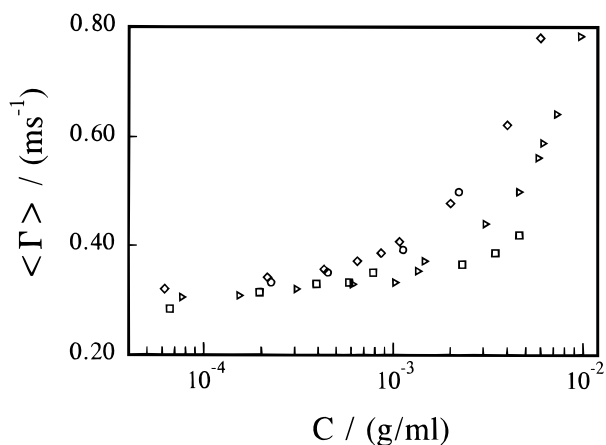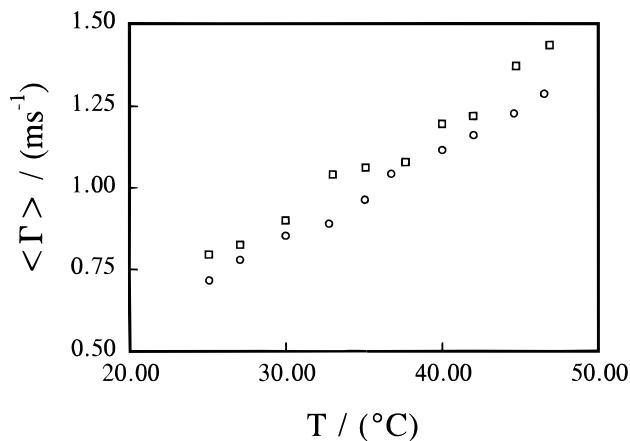

Figure 5. Concentration dependence of the average characteristic line width ($\langle\Gamma\rangle$) of PSSEMA (O), PSSHMA ($\diamond$), PSSOMA ($\triangle$), and PSSDMA ($\square$) in 0.1 M NaCl aqueous solution at $T = 25$ °C.

the corresponding number- and weight-average molecular weights and then the polydispersity index (M_w/M_n), which is also listed in Table 1.

Previously, the surface active properties of both the SSOMA monomer and the PSSOMA homopolymer in 0.1 M NaCl aqueous solution were studied by using surface tension method.[11] The surface tension (σ) decreases as the PSSOMA concentration (C) increases. The plot of σ vs C bends at $C = 1.30 \times 10^{-3}$ g/mL, which was attributed to the micelle formation.

Figure 5 shows the concentration dependence of the average characteristic line width ($\langle\Gamma\rangle$) for four PSSRMA samples in 0.1 M NaCl aqueous solution at 25 °C. $\langle\Gamma\rangle$ increases with C, which shows that no micelle was formed in this concentration range; otherwise, we would have observed a decrease of $\langle\Gamma\rangle$. Our results demonstrate that the decrease of the surface tension cannot be attributed to the micelle formation. A possible explanation for the decrease of surface tension may be related to the hydrophobic interaction. At higher PSS-RMA concentrations, the hydrophobic portion of the PSSRMA has tendency to come together toward the center of the polymer coil, and at the same time, the hydrophilic groups of SO_3^- remain at the coil surface toward the surrounding water, which leads to a decrease in the hydrodynamic volume and surface tension. PSS-DMA cannot completely dissolve when C is higher than 5×10^{-3} g/mL. A simple calculation shows that the overlap concentration (C^*) $[\sim M/N_A(2R_g)^3]$ of PSSRMA

Figure 6. Temperature dependence of the average characteristic line width ($\langle\Gamma\rangle$) of PSSOMA at $C = 9.73 \times 10^{-4}$ g/mL (O) and $C = 9.73 \times 10^{-3}$ g/mL ($\square$) in 0.1 M NaCl aqueous solution.

is $\sim 10^{-3}$ g/mL, which corresponds to the upturn of $\langle\Gamma\rangle$ vs C. This means that at $C \sim 10^{-3}$ g/mL, the PSSRMA chains do start to overlap with each other.

Figure 6 shows the temperature dependence of the average characteristic line width ($\langle\Gamma\rangle$) at two different concentrations for PSSOMA sample in 0.1 M NaCl aqueous solution. $\langle\Gamma\rangle$ increases linearly with the temperature, which shows that at high temperature the hydrophilic interaction decreases and PSSOMA chain has a more compact conformation in 0.1 M NaCl aqueous solution. A moderate temperature dependence of the chain conformation around ~ 37 °C is important for using PSSRMA as a biocompatable material.

In summary, our LLS study of poly(sulfoalkyl methacrylate)s with different alkyl side chain lengths shows that PSSRMA with a long alkyl side chain has a more compact chain conformation in 0.1 M NaCl aqueous solution. Our results show that the opposite effect of the steric interaction between the alkyl side groups and electrostatic repulsion between the SO_3^- groups leads to the shortest persistence length for PSSOMA, which may be the reason for its best surface properties. The overlap concentration of PSSRMA in 0.1 M NaCl aqueous solution is $\sim 10^{-3}$ g/mL. The calibration between the translational diffusion coefficient (D) and molecular weight (M), *i.e.*, $D = k_D M^{-\alpha_D}$, together with the values of A_2, k_d, and f obtained in this study will be useful in the future to characterize M from D.

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