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

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ABSTRACT: Poly(sulfoalkyl methacrylate) (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(Γ). The characteristic line width (Γ) increases rapidly when the polymer concentration is higher than 10−3 g/mL, which corresponds to a decrease in the surface tension. In the temperature range 25–47 °C, (Γ) increases with the temperature. All LLS results consistently indicate that poly(sulfoalkyl methacrylates) 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) = kD M−α with α0 ~ 0.56 and kD in the range of (1.54 × 10−3) – (2.07 × 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(Γ).

Introduction

A series of sodium sulfoalkyl methacrylates with different alkyl side chain lengths have been synthesized.† 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.‡ 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. Andrade et al. studied various charged copolymers of methacrylic acid, methyl methacrylate, and trimethylamine methacrylate and the influence of surface charge and side chain length.‡ Chen et al. 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.§

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), CH2=C(CH3)COO(CH2)6SO3Na, sodium sulfoctyl methacrylate (SSOMA), CH2=C(CH3)COO(CH2)8SO3Na, and sodium sulfodecyl methacrylate (SSDMA), CH2=C(CH3)COO(CH2)10SO3Na, were prepared from sodium methacrylate (Poly-science; 95%) through neutralization and purification. Polymerization was carried out at 70 °C under nitrogen with 0.1% potassium persulfate as an initiator. Hereafter, these poly(sulfoalkyl methacrylates) 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 × 10−4 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-γ digital time correlator). A solid state dye laser (ADLAS DPY425II, output power = ~400 mW at λ = 532 nm) was used as the light source. The incident beam was vertically polarized with respect to the scattering plane. The spatial coherence constant β = 0.9, a rather high value for an LLS spectrometer capable of doing both static and dynamic LLS measurements.
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 \( R_{\text{vv}}(\theta) \), was measured. For a dilute polymer solution at a relatively low scattering angle \( \theta \), \( R_{\text{vv}}(\theta) \) can be expressed as

\[
\frac{KC}{R_{\text{vv}}(\theta)} \approx \frac{1}{M_w} \left[ 1 + \frac{1}{3} (R_g q^2) + 2A_2 C \right]
\] (1)

where \( K = 4\pi^2 n^2 (dn/dc)^2 / (N_A \lambda_0^2) \) and \( q = 4\pi n / \lambda_0 \sin(\theta/2) \) with \( N_A \), \( dn/dc \), \( n \), and \( \lambda_0 \) 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 \( (R_g)^2 \) (or written as \( R_g \)) is the root-mean square z-average radius of the polymer chain in solution. After measuring \( R_{\text{vv}}(\theta) \) at a set of \( C \) and \( \theta \), we were able to determine \( M_w \) and \( A_2 \) from a Zimm plot which incorporates \( \theta \) 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)^-1. 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.5 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 \( C \) ranges from 2.16 × 10^-4 to 1.08 × 10^-3 g/mL and the solutions were clarified with a 0.22-μm filter.

![Figure 1. Typical Zimm plot of PSSHMA in 0.1 M NaCl aqueous solution at 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.](image.png)

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

<table>
<thead>
<tr>
<th>Polymers</th>
<th>dn/dc (mL/g)</th>
<th>( 10^{-3}M_w ) (g/mol)</th>
<th>( R_g ) (nm)</th>
<th>( 10^4A_2 ) (mol/mL/g^2)</th>
<th>( 10^9D ) (cm^2/s)</th>
<th>( R_g ) (nm)</th>
<th>( 10^{10}K_0 ) (mL/g)</th>
<th>( M_w/M_n )</th>
<th>p (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PSSEMA</td>
<td>0.135</td>
<td>3.06</td>
<td>43.3</td>
<td>6.41</td>
<td>12.2</td>
<td>20.1</td>
<td>1.5</td>
<td>1.5</td>
<td>4.2</td>
</tr>
<tr>
<td>PSSHMA</td>
<td>0.140</td>
<td>4.94</td>
<td>42.9</td>
<td>5.61</td>
<td>10.2</td>
<td>23.8</td>
<td>1.8</td>
<td>1.7</td>
<td>3.5</td>
</tr>
<tr>
<td>PSSOMA</td>
<td>0.149</td>
<td>7.01</td>
<td>40.9</td>
<td>2.03</td>
<td>10.0</td>
<td>24.5</td>
<td>1.67</td>
<td>1.99</td>
<td>2.1</td>
</tr>
<tr>
<td>PSSDMA</td>
<td>0.170</td>
<td>7.34</td>
<td>39.9</td>
<td>1.91</td>
<td>9.75</td>
<td>25.1</td>
<td>1.59</td>
<td>2.07</td>
<td>2.1</td>
</tr>
</tbody>
</table>

* Relative errors: dn/dc, ±1%; M_w, ±3%; \( R_g \), ±5%; A_2, ±10%; (D), ±1%; K_0, ±10% and \( M_w/M_n \), ±15%.

In dynamic LLS, the 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

\[
G^{(2)}(t,q) = \langle I(0)I(t) \rangle = A[1 + \beta g^{(1)}(t,q)]^2
\] (2)
Where $A$ is a measured baseline, $\beta$ 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 $\theta = 20^\circ$ and $T = 25^\circ$ C. For a polydisperse sample, $g^{(2)}(t,q)$ is related to the normalized characteristic line width distribution ($G(\Gamma)$) by

$$g^{(2)}(t,q) = \langle E(0)E^*(t) \rangle = \int_0^\infty G(\Gamma) e^{-\Gamma t} d\Gamma$$

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, $\Gamma$ 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 $\Gamma$. This effect can be expressed in the form of $^{13,14}$

$$\frac{\Gamma}{q^2} = D(1 + k_dC)(1 + f(R_g^2,q^2)$$

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 dimensionless number depending on the chain conformation, solvent, and internal motions. According to eq 4, $D$, $f$, and $k_d$ can be calculated respectively from $(\Gamma/q^2)_{c \to 0,q \to 0}$, $(\Gamma/q^2)_{c \to 0}$ vs $q^2$, and $(\Gamma/q^2)_{c \to 0}$ 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 $^\circ$C, from which we were able to calculate the average translational diffusion coefficient ($\langle D \rangle$), defined as $\langle \int_0^\infty G(D) dD \rangle$, and the average hydrodynamic radius ($\langle R_h \rangle$), defined as $k_BT/(6\pi\eta \langle D \rangle)$, where $k_B$, $T$, and $\eta$ are the Boltzmann constant, the absolute temperature, and solvent viscosity, respectively. The values of $\langle D \rangle$, $\langle R_h \rangle$, and $\langle R_g/R_h \rangle$ of four PSSRMA samples are also listed in Table 1. The ratio of $\langle R_g/R_h \rangle$ is an important parameter depending on the polymer architecture, chain conformation, and polydispersity. It is known that $\langle R_g/R_h \rangle$ is $(3/5)^{1/2} \sim 1.8$, and $\sim 2$ for a uniform sphere, a polydisperse linear coil, and a rodlike linear chain, respectively. $^{15-17}$ The decrease of $\langle R_g/R_h \rangle$ from 2.16 to 1.59 further suggests that PSSRMA 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 ($D$) in Table 1. At $\theta = 0$ and $C = 0$, on the basis of eqs 1 and 3, we have

$$\int_0^\infty G(D) dD \propto \langle I \rangle$$

from static and dynamic LLS, respectively, which leads to

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

Comparing both sides of eq 6, we have

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

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., $D = k_0M^{-\alpha_D}$, where $k_0$ and $\alpha_D$ are two scaling constants. The previous viscosity study$^{19}$ showed that $\alpha_D \sim 0.68$ in the scaling relation of $[\eta] \propto M_w^{\alpha_D}$, where $[\eta]$ is the intrinsic viscosity. According to Flory's prediction,$^{20}$ $\alpha_D$ and $\alpha_w$ for a polymer coil are related by $\alpha_D = (1 + \alpha_w)/3$, which leads to $\alpha_D \sim 0.56$ for PSSRMA in 0.1 M NaCl aqueous solution at 25 $^\circ$C. Using this value of $\alpha_D$, we were able to convert $k_0$ 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 $D = k_0M^{-\alpha_D}$, i.e.,$^{16}$

$$M_w = \frac{k_0^{1+\alpha_D} \int_0^\infty G(D) dD}{\int_0^\infty G(D)^{1+\alpha_D} dD}$$

where $M_w$ and $G(D)$ are respectively from static and dynamic LLS. The calculated values of $k_0$ are listed in Table 1. The increase of $k_0$ 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 $k_0$ and $\alpha_D$, 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
The characteristic line width \( \Gamma \) of PSSOMA decreases as the PSSOMA concentration \( C \) increases. A possible explanation for the decrease of surface tension may be the micelle formation. A moderate temperature dependence of the chain conformation around \( \sim 37 ^\circ C \) is important for using PSSRMA as a biocompatible material.

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. The surface tension \( \sigma \) decreases as the PSSOMA concentration \( C \) increases. The plot of \( \sigma \) vs \( C \) bends at \( C \sim 0.1 \) g/mL, which is also listed in Table 1.

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