

Characterization of an Unknown Polymer Using Static and Dynamic Light Scattering

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In this investigation, the effective diameter, polydispersity and average molecular weight of an unknown polymer in the solution phase is characterized using static and dynamic light scattering. Light scattering experiments were conducted at 5 concentrations. Static light scattering data resulted in Zimm plots with a parabolic shape that were fit using both linear and 2nd order polynomial forms to extrapolate Kc/R_{90} to zero scattering angle. The linear extrapolation resulted in a molecular weight of $(1.88 \pm 0.28) \times 10^6$ g and the quadratic extrapolation resulted in a molecular weight of $(6.19 \pm 0.82) \times 10^5$ g with a 67.1% difference between the two values. Dynamic light scattering gave an average effective diameter of 113.0 ± 9.9 nm and an average polydispersity of 1.222 ± 0.013 . Future experiments using these techniques should filter solvents to reduce excess scattering due to dust contamination.

INTRODUCTION

One important method for the characterization of particles in the solution phase involves scattering visible light in the solution. The theory behind light scattering in gases was first proposed by Rayleigh in the late 1800's, and Smoluchowski and Einstein extended light scattering theory to liquids in 1908 and 1910 respectively¹. These two scientists proposed that the patterns of light scattered from a pure liquid are caused by irregularities in the medium due to random thermal motion.¹ In a solvent/solute system, light scattering is also caused by small variations in the solute concentration.¹

Static and dynamic light scattering are two different experimental methods for measuring the patterns of light scattered from a solvent/solute system. Static light scattering measures light intensity as a function of scattering angle and solute concentration. This allows the determination of average molecular weight, radius of gyration, and shape information for the solute. Dynamic light scattering (DLS) is an experimental method which uses the intensity and polarization of light scattered from a solution to characterize the size, shape, and interactions of the particles in a solution.¹ Photon correlation spectroscopy is the most common way to analyze dynamic light scattering data.¹

Static and dynamic light scattering give complementary pieces of information, and for this reason they are commonly used in tandem for characterization of polymer solutions.^{2,3,4} In this experiment, static and dynamic light scattering will be used to characterize the polydispersity, effective

diameter and average molecular weight of an unknown polymer.

THEORY

Static light scattering measures the intensity of light scattered off of a solution at a single time. In 1948, Zimm derived the relationship between the concentration and the intensity of the scattered light

$$K \frac{c}{I} = \frac{1}{MP(\theta)} + 2A_2c \quad (1)$$

where c is the concentration, M is the solute molecular weight, $P(\theta)$ is the particle scattering function that depends on particle shape, and I is the intensity of scattered light.⁵ The constant K is defined to be

$$K = 4\pi^2 n^2 \left(\frac{dn}{dc} \right)^2 N_A \lambda_0^{-4} \quad (4)$$

where n is the index of refraction, dn/dc is the refractive index increment, and λ_0 is the wavelength of the incident light.² Zimm then proposed the use of a special graphing technique, now called a Zimm plot, to use equation 1 to extract useful information from the experimental data.⁵ A Zimm plot graphs the concentration over the intensity vs $\sin^2(\theta/2)$.⁵

Before constructing a Zimm plot, counts per second must be converted to reduced Rayleigh ratios using the expression

$$R_{\theta} = R_c(90^\circ) \cdot (\sin \theta) \cdot \frac{I_{\theta}}{I_c} \quad (2)$$

where $R_c(90^\circ)$ is the absolute scattering intensity of toluene, I_{θ} is the experimental intensity corrected by the Brookhaven software, and I_c is the corrected

experimental intensity of toluene at 90° .⁶ In this experiment, Zimm plots are fit using both linear and quadratic functions⁴ of c/R_\square vs scattering vector q^2 . These fits are used to extrapolate c/R_\square to zero scattering angle to get a value c/R_0 . The average molecular weight (M_w) is then determined using a virial expansion

$$\frac{Kc}{R_{\square=0} M_w} = \frac{1}{M_w} (1 + 2A_2 M_w c + 3A_3 M_w c^2 + \dots) \quad (3)$$

where all of the virial coefficients (A_2 , A_3 etc) higher than second order are ignored to give a linear relationship.³

The theory of dynamic light scattering has been extensively reviewed elsewhere.⁵ The experimentally determined intensity autocorrelation function $C(\square)$ can be converted to an electric field autocorrelation function $g_1(\square)$ through the Siegert relation

$$C(\square) = B(1 + f^2 |g_1(\square)|^2) \quad (5)$$

where B and f are constants dependent on experimental conditions.⁷ The cumulant expansion

$$|g_1(\square)| = \exp(-\square) \cdot \left[\frac{\square}{1} + \frac{\square^2}{2!} \frac{\square_2}{\square} + \frac{\square^3}{3!} \frac{\square_3}{\square^2} + \dots \right] \quad (6)$$

is then used to extract useful information from $g_1(\square)$.⁷ \square is the relaxation rate, which is equal to Dq^2 . Particle size is given by the diffusion constant D ¹

$$D = \frac{k_B T}{\square} = \frac{k_B T}{6 \square \square r} \quad (7)$$

and polydispersity (u) is given by the reduced second cumulant through⁷

$$\frac{\square_2}{\square^2} = u(1 + u) \quad (8)$$

EXPERIMENT

Static and dynamic experiments were conducted using a Brookhaven goniometer with monochromatic, high intensity light provided by a Melles-Griot HeNe laser. The sample cell was temperature controlled at 24.9°C and immersed in naphthalene that is filtered to remove dust. Initial data analysis was conducted on a Dell Dimension XPS R400 with an internal correlator board using Brookhaven Goniometer Alignment Software 9kistw v.2.07 (static) and Brookhaven Dynamic Light Scattering Software 9kdls w v.2.20 (dynamic). Further analysis was conducted using Igor Pro v.4.05 Carbon.

Samples of the unknown polymer were prepared in tetrahydrofuran (THF) in 5 dilutions: 0.0174g/ml, 0.00684g/ml, 0.00116g/ml, 0.000581g/ml, and 0.000291g/ml. For the 0.0174 g/ml and 0.00684 g/ml dilutions approximately 3mL of polymer/ THF solution was placed in a 12x75 mm glass culture tube and the tube was sealed with a cork covered with pipe thread seal tape. The culture tube was then centered in the 20ml sample cell and secured using thin plastic wedges. The extra space in the sample cell was filled with naphthalene to prevent refraction of light. For the

remaining dilutions, 15ml of polymer/THF was placed directly in the glass sample cell.

For static light scattering, light scattered from all dilutions was detected at scattering angles ranging between 30° and 150° in 10° increments. Light was collected for one second during each repeat and 10 repeats were taken for each angle. Scattering from pure THF solution at all angles was taken to control for scattering from the solvent. A noise rejection ratio of 1.33 was used for scattering off of pure solvents and 3.00 for polymer solutions. Counts per second detected by the photomultiplier were corrected automatically by the Brookhaven software to account for noise in the detector, reflection, and the volume of the cell. Data were analyzed using the index of refraction of THF ($n=1.405$)⁹ and the refractive index increment for polystyrene in THF ($dn/dc=0.185\text{ml/g}$)⁸. Reduced scattering intensities were calculated in Igor using equation 2.

Dynamic light scattering data were taken for all 5 dilutions. Data for the 0.0174 g/ml dilution were taken at scattering angles between 30° and 90° at 10° intervals. Data for the 0.00684 dilution were taken at 90° , 70° and 50° scattering angles. Data for the remaining dilutions were taken only at 90° . The sampling time for each dilution was adjusted to allow sufficient statistics for cumulant fits. For the 0.0174g/ml and 0.00684g/ml dilutions the correlator was run for 15 minutes for each sample. The 0.00116g/ml dilution was run for 80 minutes, the 0.000581g/ml dilution was run for 75 minutes, and the 0.000291g/ml dilution was run for 3 hours.

ANALYSIS AND INTERPRETATION

Data for all five dilutions are given in Figures 1 and 2. Calculated values for C/R_\square were plotted against the square of the scattering vector q (equation 6), which is the graphical approach taken by Normula and Cooper. While conventional Zimm plots are linear, the data in Figures 1 and 2 are clearly parabolic, and all of the dilutions except 0.000581 g/ml show an increase in C/R_\square at small scattering angles. Because of the unusual form of the Zimm plots, data could not be extrapolated to both zero scattering angle and zero concentration as in conventional static light scattering analysis (see Zimm, 1948). Figure 1 shows the scattering data extrapolated to zero scattering angle using the polynomial expression

$$\frac{c}{R_\square} = \frac{a_0}{K} + \frac{a_1}{K} q^2 + \frac{a_2}{K} q^4 \quad (9)$$

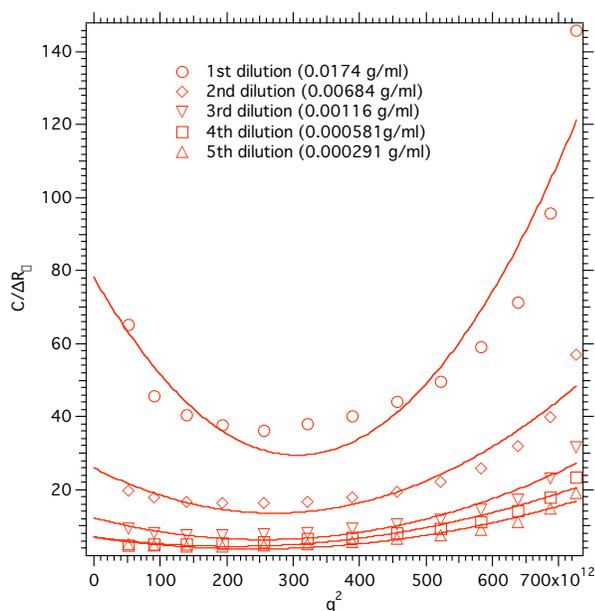


FIG. 1. Polynomial fits for the static light scattering data taken for all five dilutions.

Zimm plots were also extrapolated to zero scattering angle using a linear fit excluding q^2 values above 550 and below 150. These fits are shown in Figure 2.

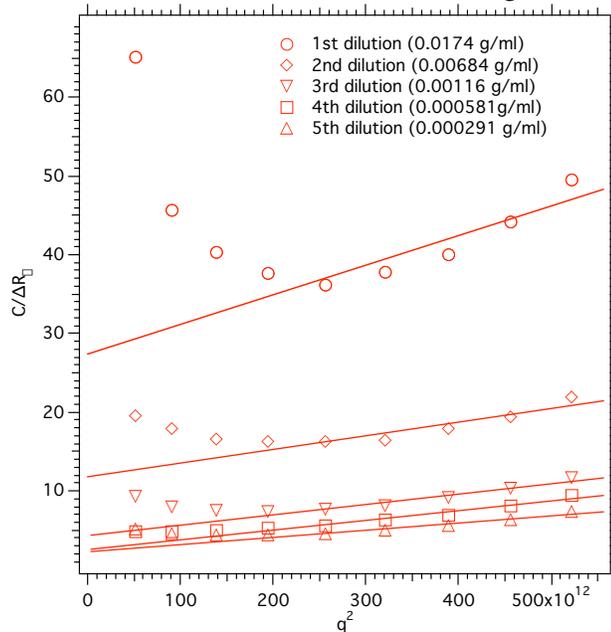


FIG. 2. Linear fits excluding wide angles for the static light scattering data taken for all 5 dilutions. Only data between $q^2 = 150$ -550 were used to develop the linear extrapolations.

The C/R_0 values extrapolated to zero scattering angle for each concentration were then graphed against concentration. Linear fits of both sets of data are shown in Figure 3. The y-intercept of the KC/R_0 graph gives the inverse of the average molecular weight. Using polynomial extrapolation methods, the average molecular weight was calculated to be $(6.19 \pm 0.82) \times 10^5$ g. This is a percent error of 13.3%.

Using the linear extrapolation of the Zimm plots gives an average molecular weight of $(1.88 \pm 0.28) \times 10^6$ g. This corresponds to a percent error of 15.1%. The average molecular weight values for the two methods have a percent difference of 67.1%.

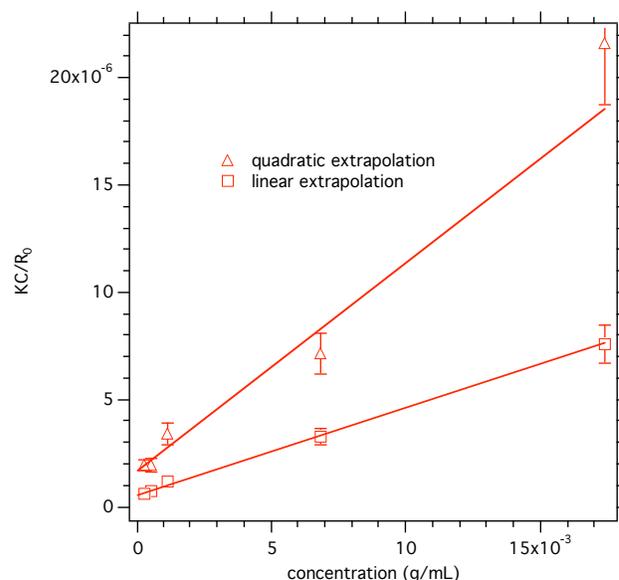


FIG. 3. Concentration dependence of KC/R_0 using both linear and quadratic methods to extrapolate the Zimm plot to zero scattering angle. The y-intercept of the line is the M_w^{-1} .

Because the extrapolation seems to fit a linear relation most accurately, it appears that dust contamination, not intermolecular interaction, is the cause of the nonlinear Zimm plots. Further evidence for the possible effect of dust contamination is the fact that after the pure THF sample was prepared, there were large flecks of dust that could be seen floating in the sample.

In future static light scattering experiments extreme care should be taken during sample preparation to prevent dust contamination. Ideally, the THF solvent should be filtered right before it is mixed with the polymer to ensure there is no contamination of the sample. Also, although the glass cells were washed with acetone before they were filled with the sample, excess dust or fingerprints on the outside of the glass might have skewed the scattering results. Future experimenters should clean the glass cells more thoroughly and always use gloves when handling the samples. Also, a more accurate knowledge of dn/dc could significantly decrease the uncertainty in K and consequently decrease the uncertainty in the average molecular weight.

Correlation functions calculated by the Brookhaven Dynamic Light Scattering software for the 5 dilutions are given in Figure 4. The uniformity in the shape of the curves suggests that there are not significant changes in the behavior of the polymer at different concentrations.

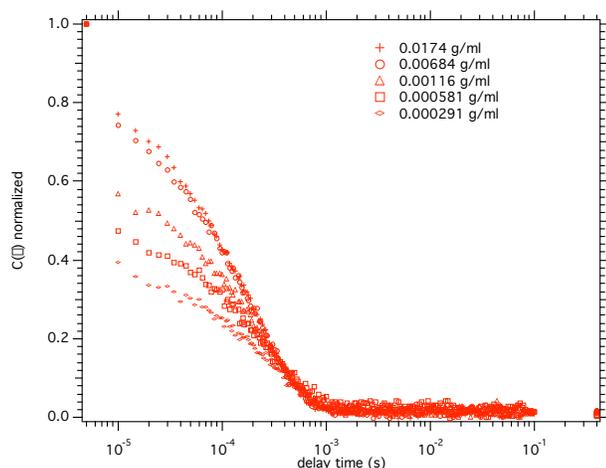


FIG.4. Normalized electric field autocorrelation functions of all five polymer dilutions in THF.

Table 1 gives the effective diameters and polydispersities for each dilution and scattering angle. Effective diameters from the 0.000581 g/ml dilution, all data from the 0.0174 g/ml sample at 30° and 40° and all data from the 0.000291 g/ml dilution were excluded from the analysis because they contained unreasonable values that probably resulted from insufficient statistics. Polydispersities appeared very consistent over all dilutions, with an average polydispersity (M_w/M_n) of 1.222 ± 0.013 . This suggests that there is significant variation in the molecular weights of the polymer particles. The polydisperse nature of the solvent/solute system may have contributed to the abnormal shape of the Zimm plots from the static data.

The effective diameter of the particles was found to increase slightly as concentration decreased (Table 1). This suggests that there is either swelling of the polymer at low concentrations or that not enough scattering statistics were taken at low concentrations to accurately reflect the system. The average effective diameter of the polymer particles was found to be 113 ± 9.9 nm.

TABLE 1. Parameters for the polymer solute as determined using photon correlation spectroscopy.

concentration (g/ml)	angle	effective diameter (nm)	polydispersity
0.0174	90	106.5	1.214
0.0174	80	108.0	1.214
0.0174	70	111.4	1.231
0.0174	60	109.0	
0.0174	50	109.9	1.197
0.00543	90	108.7	1.222
0.00543	70	112.2	1.231
0.00543	50	111.9	1.217
0.00116	90	131.2	1.233
0.00116	70	136.5	1.220
0.000291	86	159.6	1.246

CONCLUSIONS

In this experiment, both static and dynamic light scattering were used to characterize an unknown polymer in the solution phase. The resulting Zimm plots were then analyzed using both a 2nd order polynomial function and a linear function in order to extrapolate to zero scattering angle. Both of these methods gave similar average molecular weight values on the order of 1×10^6 grams, with a percent difference of 67.1% between the two extrapolation methods.

Dynamic light scattering provides additional data to describe the polymer in solution. The effective diameter of the polymer particles was found to be $113.0 \text{ nm} \pm 9.9 \text{ nm}$. Photon correlation spectroscopy also allowed the computation of an average polydispersity of 1.222 ± 0.013 for the sample, suggesting that there is significant variability in the molecular weights of the polymer particles.

One major obstacle in this experiment was dust contamination. Future experiments should filter the THF solvent in order to decrease dust contamination and improve the accuracy of both static and dynamic measurements.

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