

Studies on Diffusion of Rhodamine B Labeled Polystyrene in Dilute and Semidilute Solutions by Fluorescence Correlation Spectroscopy

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1. Introduction

Our understanding of polymer dynamics has greatly improved due to the reptation model and the scaling ideas. [1] According to scaling and reptation theory, the diffusion coefficient in semidilute or concentrated regimes is related to the molar mass and polymer concentration by $D \sim M^2 c^{-1.75}$ and $D \sim M^2 c^{-3}$ for good-solvent and θ -solvent conditions, respectively. In a limited range of polymer concentration, these relationships are supported by experimental data. [2-5]

Fluorescence correlation spectroscopy (FCS) can be used to study the dynamics in a wide concentration range. However, the application of FCS in polymer science has almost entirely been limited to the area of biomacromolecules and aqueous media [6,7] and the application of FCS in organic media is rarely reported. [8]

In this work, the diffusion of Rhodamine B labeled polystyrene (PS) chains in dilute and semidilute toluene solutions was studied by FCS.

2. Results and Discussion

The FCS correlation function of freely diffusing monodisperse and uniformly fluorescent particles is defined by, [9]

$$G(\tau) - 1 = \frac{1}{N(1 + \tau/\tau_D)(1 + (\omega_1/\omega_2)^2(\tau/\tau_D))^{1/2}} \quad (1)$$

where N is the average number of particles in the observation volume, ω_1 and ω_2 define two characteristic sizes: the radius of the focused beam spot and the focal depth the direction of the laser beam, respectively. τ_D is the characteristic decay time for the diffusion process. For known ω_1 , the diffusion coefficient D of fluorescent species can be determined by, [9]

$$\tau_D = \omega_1^2 / 4D \quad (2)$$

In this work, ω_1 was calibrated by dynamic light scattering (DLS) by highly diluted solution of labeled PS in toluene.

Figure 1 shows the normalized FCS correlation functions of the labeled PS ($M_w = 3.9 \times 10^5$ g/mol,

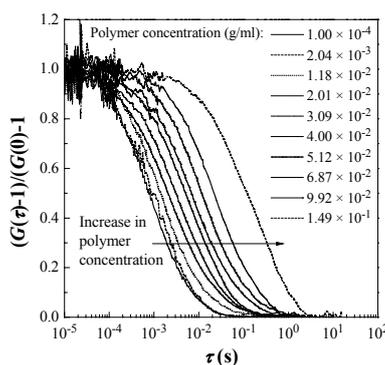


Fig. 1: Normalized FCS correlation function of labeled PS in different polystyrene solutions.

$M_w/M_n < 1.10$, 1×10^{-4} g/ml) in toluene solutions with different matrix PS concentration ($M_w = 3.35 \times 10^5$ g/mol, $M_w/M_n = 2.1$). The results show that the characteristic diffusion time of the labeled PS increases with increasing polymer concentration, by fitting of the correlation functions by Eq. 1 in combination with Eq. 2. The self-diffusion coefficient D_s of labeled PS was obtained. The results are shown in Figure 2 in double-log format. The error bar in the figure indicates the deviation of the results for 15-20 independent measurements. It turns out that D_s is fairly constant if the concentration is lower than the overlap concentration c^* (dilute regime). Above c^* , D_s decreases markedly with increasing concentration of matrix PS. In the range of 0.02 to 0.10 g/ml, D_s of labeled PS chains depends on the matrix PS concentration as $D_s \sim c^{-1.7 \pm 0.1}$ (solid line in Fig. 2). The result is in a good agreement with the theoretical prediction of scaling and reptation theory in good solvent cases: $D_s \sim c^{-1.75}$ (dotted line in Fig. 2).[1]

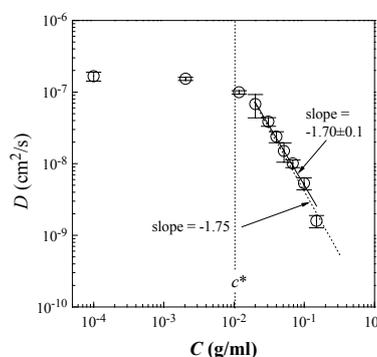


Fig. 2: D_s of labeled PS as a function of polymer concentration.

3. Conclusion

Rhodamine B labeled polystyrene was used as probe molecules to study the diffusion process of polystyrene in dilute and semidilute solutions by FCS. The self-diffusion coefficient of labeled polystyrene chain decreases with increasing polymer concentration of the matrix. In the semidilute regime, the self-diffusion coefficient of single labeled chains relates to the matrix polystyrene concentration as $D_s \sim c^{-1.7 \pm 0.1}$, in good agreement with the prediction of scaling and reptation theory.

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