Macromolecules **1984**, *17*, 2629-2633

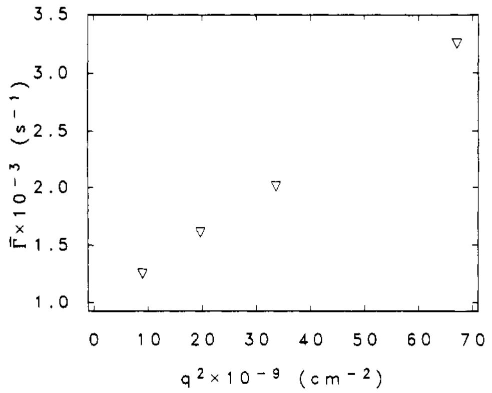

Figure 4. Average decay rate $\bar{\Gamma}$ for the depolarized (HV) Rayleigh scattering from solubilzed polyacetylene in toluene plotted against q^2. The slope yields the translational self-diffusion coefficient ($D_0 = 3.45 \times 10^{-8}$ cm^2/s) and the intercept is equal to 6 times the rotational diffusion coefficient ($\Theta = 153$ s^{-1}).

but as we will see below, it may not fully reflect the geometric size of the PA part of the particle.

Initial studies of the dynamic light scattering under the same conditions revealed a large change in the shape of the relaxation function with angle. At low q the long-time part of the decay changed as q^2, but the first cumulant became nearly independent of angle. This suggested that depolarized scattering was important. The VV relaxation function is a sum of the relaxation function due to the scalar part, which decays as D_0q^2, and the relaxation function due to the anisotropic part, which decays as $D_0q^2 + 6\Theta$. The first cumulant yields the average decay constant which is dominated by the 6Θ part, while the long-time decay is dominated by the D_0q^2 part. The HV relaxation function was easily measurable for the PA polymer. The large excess depolarized scattering is very unusual and suggests strongly that there is substantial orientation correlation between the PA subunits in the particle. The depolarized (HV) relaxation function did not change shape with angle and the second cumulant remained small. The average decay rate $\bar{\Gamma}$ is plotted against q^2 in Figure 4. The results behave as expected from eq 4. The translational self-diffusion coefficient is calculated to be 3.45×10^{-8} cm^2/s. The hydrodynamic radius of the particle is calculated to be 1050 ± 200 Å. This is very much larger than the carrier polymer and much larger than the characteristic length deduced from the angular dependence of the intensity. For a dense sphere the hydrodynamic radius is 50% larger than the radius of gyration, and the hydrodynamic radius is for the whole particle, including the carrier polymer. Even so, it must be concluded that 350 Å is only a persistence length for the correlation in orientation of the PA subunits in the particle. The rotational diffusion coefficient is calculated to be $\Theta = 153 \pm 20$ s^{-1}. The hydrodynamic volume is calculated to be 7.5×10^9 Å.^{3} The radius of the equivalent sphere based on this volume is 1200 Å, which is within experimental error of the hydrodynamic radius. If we assume that the particle can be represented as an ellipsoid of revolution with major axis a and minor axis b, then the Perrin[9,10] equations can be used to estimate the axial ratio $\rho = b/a$. The present values for D_0 and Θ yield $a = 1800$ Å and $\rho = 0.4$. The oblate solution does not give a reasonable value for a. The limits of uncertainty on ρ are large (20%), but it is reasonable to conclude that the particles are prolate in shape with approximately a 1:2 axial ratio. In any case the average size of the particles giving rise to the light scattering is very much larger than any single graft copolymer molecule. This suggests that the molecules aggregate in solution to form a micellar particle with an average radius near 1050 Å. Within the aggregate there must be a high degree of orientation correlation between neighboring PA subunits.

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Dynamic Light Scattering of Polymer Solutions. 4. Semidilute Solutions of Polystyrenes and Their Binary Blends in Benzene

Norio Nemoto,* Yutaka Makita, Yoshisuke Tsunashima, and Michio Kurata

Institute for Chemical Research, Kyoto University, Uji, Kyoto 611, Japan.

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ABSTRACT: Dynamic light scattering (DLS) measurements have been made on solutions of polystyrenes and their binary blends in benzene in the semidilute concentration range. The cooperative diffusion coefficient D_{coop} estimated from the gel mode has been shown to be independent of molecular weight M for homogeneous solutions as well as M of components for blends. The hydrodynamic screening length (or the blob size), ξ_H, has been found to be in proportion to the radius ξ_e of the tube formed by entanglements. The magnitude of ξ_e has been found to be about 5 times larger than ξ_H. The slow mode has been found for a solution of the binary blend of component polymers with $M = 42800$ and 775000. Forced Rayleigh scattering measurements on a binary blend with about the same concentrations and molecular weights have shown that D_{slow} estimated from the slow mode observed by DLS does not represent the self-diffusion of the lower molecular weight component of the blend.

Introduction

Scaling theory based on the blob and the reptation models[1] has given a new guide for studying equilibrium as well as nonequilibrium properties of polymer solutions in the range of polymer concentration which is higher than the critical overlapping concentration c^*. According to the

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theory, dynamic light scattering (DLS) detects, in principle, two different types of dynamical process, the gel mode and the reptation mode. The former mode is related to the cooperative motion of polymer chains giving rise to local concentration fluctuation and is characterized by the blob size (or hydrodynamic screening length) ξ_H. The latter mode is related to the self-diffusion of a single chain through the tube formed by other chains and is characterized by the entanglement spacing as tube diameter $2\xi_e$. The proportionality of ξ_e to ξ_H was originally suggested by de Gennes. The two quantities have been assumed to be identical a priori in most literature dealing with experimental data.[2-4] However, ξ_H is a quantity definable for entangled and unentangled polymer–solvent systems if $c \gg c^*$, whereas ξ_e is a quantity definable only for entangled systems. Further ξ_H decreases at sufficiently high c to a short length corresponding to several monomer units, whereas ξ_e decreases only to a larger length which is related to the entanglement molecular weight $M_{e,0}$ in the bulk state. Therefore the equality $\xi_e = \xi_H$ may not be correct, and the proportionality relation between these two ξ needs to be reexamined experimentally.

Another problem still unsettled is concerned with the slow mode observed on several polymer–solvent systems.[5-24] Amis and Han[5] have made DLS measurements on semidilute solutions of polystyrenes (PS) in tetrahydrofuran and cyclohexane. They have identified the diffusion coefficient D_{slow} obtained from the slow mode as the self-diffusion coefficient D_s on grounds that dependences of their D_{slow} values on molecular weight (MW) and c have been in good agreement with the theoretical prediction for D_s. Absolute values of D_{slow}, however, have been found to be smaller than those of D_s obtained from forced Rayleigh scattering measurements on PS–benzene systems[11] by about one order of magnitude. Similar discrepancies between D_{slow} and D_s have been also reported for aqueous solutions of gelatin[10,12] and aqueous solutions of poly(ethylene oxide).[25] Mathiez et al.[8] have suggested that knots of higher concentration in polymer solutions give rise to the slow diffusion process. Their conjecture is, however, based on the result of molecular weight independent D_{slow}, which disagrees with Amis and Han's data.

In this article we present an attempt to solve the above-mentioned two problems. Semidilute solutions of PS and their binary blends in benzene have been chosen as test solutions for this purpose because (1) dilute solution properties of this system have been studied in great detail,[13,14] (2) benzene is a very good solvent for PS without specific interaction, (3) the self-diffusion of a lower MW component through a matrix formed by polymer molecules of a higher MW component may be observable if the slow mode is due to the reptation motion of single chain, and (4) the applicability of the scaling theory to binary blends has not been studied in detail so far.

Experimental Section

Materials. Five samples of narrow-distribution molecular weight polystyrenes (M = 42 800, 186 000, 422 000, 775 000, and 8 420 000, Toyo Soda) were used for the present study. The two higher MW samples were used as polymers for preparation of semidilute solutions of homogeneous polymers (PS78 and PS84 series) and as the higher MW component for solutions of binary blends. The three lower MW samples were used as the lower MW components of the blend solutions. Spectrograde benzene (Nakarai Chemicals) was used as solvent without further purification. Solutions with $c < 0.02$ g/g were prepared by dissolving the polymer into dust-free benzene and made optically clean by filtering with a Millipore filter (nominal pore size, 0.5 μm). Solutions with $c > 0.02$ g/g were prepared by evaporating benzene slowly from 2% solutions. Concentrations of homogeneous and blending solutions were determined by weighing and are listed in Table I.

Table I
Concentrations of Sample Solutions[a]

	$c \times 10^2$, g/g					
sample	F842	F80	F4	F20	F40	total
PS78		4.84				4.84
		4.90				4.90
		5.62				5.62
		6.35				6.35
		8.02				8.02
PS7804		4.18	2.58			6.76
PS7820		4.19		2.60		6.79
PS84	0.394					0.394
	0.599					0.599
	1.68					1.68
	2.31					2.31
PS8404	1.75		1.45			3.20
PS8420	0.389			0.138		0.527
	0.718			0.254		0.972
	1.67			0.560		2.23
PS8440	1.68				0.224	1.91
	2.28				0.304	2.59

[a] Molecular weights of F4, F20, F40, F80, and F842 are 42 800, 186 000, 422 000, 775 000 and 8 420 000, respectively.

Methods. The dynamic light scattering instrument used has been described elsewhere.[15]

The intensity autocorrelation function of solutions was measured at 25.0 ± 0.02° by either a time interval method or a shift register method of homodyne photon correlation spectroscopy. Data analysis was made with the histogram method.[16]

Results

Semidilute Solutions of Homogeneous PS (PS78 and PS84 Series). Since the gel mode and the slow mode should appear at separated time scale, the intensity autocorrelation function $A(\tau)$ of the solutions was first measured by choosing a sampling interval, $\Delta\tau$, suitable for the detection of the gel mode and then measured by using a longer interval, $(10\text{–}30)\Delta\tau$, to detect the slow mode. The latter $A(\tau)$ data decayed within a few sampling intervals and gave a flat line identical with the calculated base line to an accuracy of 0.3%. Thus the slow mode with a relative amplitude of more than a few percent does not exist for the solutions tested. The first cumulant Γ_e was calculated by integration of the distribution function of the decay rate, $G(\Gamma)$, obtained by histogram analysis of the former data. Dependences of Γ_e on the scattering vector q are shown for four solutions with c = 0.00394 and 0.0168 g/g (PS84 series) and c = 0.0484 and 0.0635 g/g (PS78 series) in Figure 1. Since Γ_e of the PS84 solution with $c = 0.00394 \simeq 4c^* = 3M/\pi R_G^3 N_A \rho$ showed a q dependence steeper than q^2, D_{coop} was estimated from the Γ_e value at a scattering angle of 10° as $D_{coop} = (\Gamma_e/q^2)_{\theta=10°}$. For other solutions, Γ_e was proportional to q^2 and D_{coop} $(=\Gamma_e/q^2)$ was estimated within an accuracy of 5%. It may be noted that $G(\Gamma)$ of PS84 series solutions was much broader than $G(\Gamma)$ of PS78 series. The concentration dependence of D_{coop} is shown in Figure 2 and the least-squares fitting gave the solid line expressed by

$$D_{coop} = 5.74 \times 10^{-6} c^{0.67} \qquad (1)$$

Our data are in excellent agreement with the results on the same system reported by Adam and Delsanti.[17]

Semidilute Solutions of Binary Blends. Among the eight solutions tested, the slow mode in addition to the gel mode was found for the sample PS7804 as is shown in Figure 3. Γ from the slow mode of the solution and Γ_e

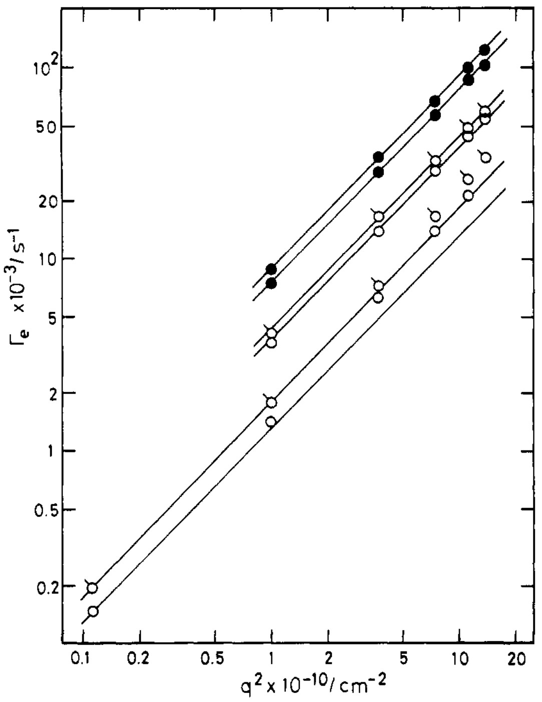

Figure 1. q dependence of the first cumulant Γ_e for six solutions. Symbols are as follows: (●) PS78 series, from the top, c = 0.0635 and 0.0484 g/g; (○) PS84 series, from the top, c = 0.0168 and 0.00394; (ŏ) solutions of a binary blend with F842 and F20, from the top, c of F842 = 0.0167 and 0.00389 and c of F20 = 0.0056 and 0.00138, respectively.

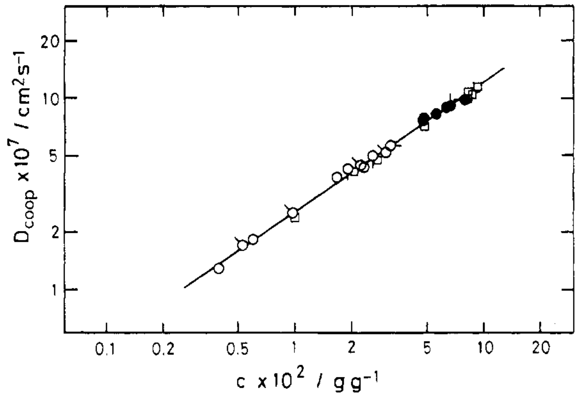

Figure 2. Concentration dependence of D_{coop}. Symbols are as follows: (●) PS78 series; (-●) PS7804 series; (●̍) PS7820 series; (○) PS84 series; (○-) PS8404 series; (ŏ) PS8420 series; (ọ) PS8440 series; (□) Adam et al.[17]

were estimated with the histogram method and both were found to be proportional to q^2. D_{coop} and D_{slow} were then obtained as 9.19×10^{-7} and 7.39×10^{-8} cm^2 s^{-1}, respectively. The relative amplitude of the slow mode was 0.125 ± 0.02 independent of the scattering angle. This indicates that the motion of dust particles is not responsible for the slow mode. $A(\tau)$ of other solutions showed no slow mode and indicated only the presence of the gel mode. The deviation from q^2 dependence for Γ_e at high θ was observed for the blend PS8420 with c of F842 = 0.00389 and c of F20 = 0.00138 g/g as is shown in Figure 1. D_{coop} of this sample was estimated from the q^2-dependent portion of the Γ_e vs. q^2 plot at lower θ. Γ_e of other blends was proportional to q^2. D_{coop} of blends is plotted against total polymer concentration c in Figure 2. Clearly, the data are located on the line given by eq 1. This agrees with the prediction of the scaling theory that D_{coop} is a function of only concentration and independent of molecular weight distribution in the semidilute region.

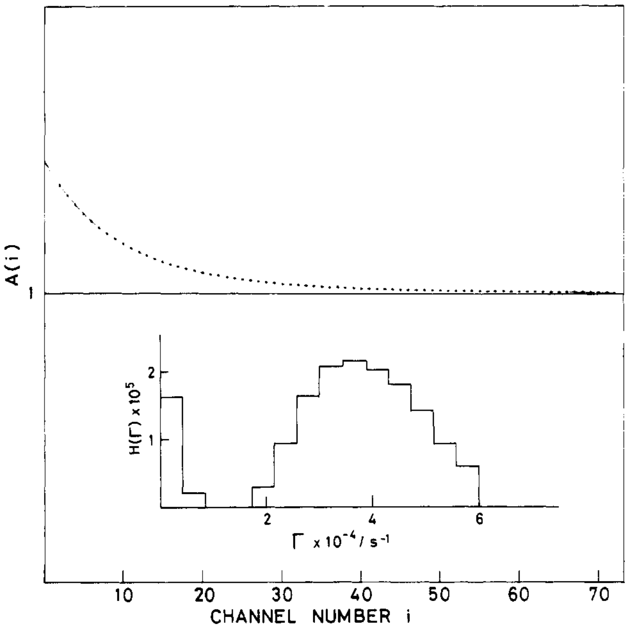

Figure 3. Intensity autocorrleation function $A(i\Delta\tau)$ of the sample PS7804. Scattering angle, 60°; sampling interval, 1.5 µs. The solid curve is fitted one which is calculated by using the distribution of decay rate $G(\Gamma)$, shown in the insert of the figure, obtained with the histogram analysis on the $A(i\Delta\tau)$ curve.

Discussion

Gel Mode. In the good solvent limit, scaling theory gives eq 2 for D_{coop}

$$D_{coop} = D_0(c/c^*)^{0.75} \tag{2}$$

Here, D_0 is the translational diffusion coefficient at infinite dilution. The exponent 0.75 is appreciably different from the experimental value 0.67. According to irreversible thermodynamics, the mutual diffusion coefficient D_m is exactly expressed by

$$D_m = \frac{1-\phi_p}{B_f}\left(\frac{\partial \Pi}{\partial c}\right)_{\mu_1,T} \tag{3}$$

where B_f is the friction coefficient per unit volume at the solvent-fixed frame of reference, ϕ_p the polymer volume fraction, Π the osmotic pressure of the solution, and μ_1 the chemical potential of the solvent. In scaling arguments, the term $B_f^{-1}(\partial\Pi/\partial c)_{\mu_1,T}$ has been considered and the term $(1 - \phi_p)$ has been neglected. When $D_{coop}/(1 - \phi_p)$ is plotted against c by taking into account the correction factor $(1 - \phi_p)$, the exponent becomes 0.69, which is still smaller than the theoretical value. Adam and Delsanti[17] have shown that, if the empirical relationship $D_0 \propto M^{-0.55}$ is used instead of $D_0 \propto M^{-0.6}$, the exponent becomes 0.69, in good agreement with their and also our experiments. However, this type of argument allows the presence of two parameters for spatial scaling, one being the radius of gyration for the static scaling and the other the hydrodynamic radius for the dynamic scaling. Then the fundamental simplicity of the scaling theory seems to have been lost.

It is often overlooked that the concept of the semidilute solution permits the use of the solvent viscosity η_s independent of c in the expression for the friction coefficient. This is an assumption and may be inapplicable for real polymer solutions. Indeed, the tracer diffusion coefficient D_{tr} of a dye molecule, methyl red, decreased from 1.60×10^{-5} cm^2 s^{-1} in pure THF to 9.09×10^{-6} cm^2 s^{-1} in a 20% solution of PS in THF.[18] Since methyl red is a small molecule, the decrease of about 40% may be largely attributed to the increase of the effective viscosity η_{eff} $(\geq\eta_s)$

Table II
D_{coop} and ξ_H[a]

sample	$c \times 10^2$, g/g	$D_{coop} \times 10^7$, cm^2/s	$\xi_H \times 10^7$, cm
PS78	4.84	7.68	4.54
	4.90	7.81	4.46
	5.62	8.36	4.14
	6.35	9.00	3.82
	8.02	9.88	3.43
PS7804	6.76	9.19	3.73
PS7820	6.79	9.28	3.69
PS84	0.394	1.30	27.8
	0.599	1.85	19.5
	1.68	3.89	9.18
	2.31	4.42	8.05
PS8404	3.20	5.02	6.20
PS8420	0.527	1.71	21.1
	0.972	2.55	14.1
	2.23	4.53	7.86
PS8440	1.91	4.31	8.29
	2.59	5.22	7.07

[a] ϕ_p is calculated from the weight fraction c with $\rho_s = 0.873$ and $\rho_p = 1.09$ g cm^{-3}.

accompanied with the change of the medium surrounding the dye molecule. At present, the size of the unit of the fundamental molecular motion for PS is not known but may be larger than the molecular size of methyl red. Thus the increase in η_{eff} with increasing polymer concentration may be larger for the unit of PS than that for methyl red. If we assume that η_{eff} increases about 15% with increasing c from 0.01 to 0.1 g cm^{-3}, the exponent decreases from 0.75 of eq 2 to 0.69. Experiments with extremely high molecular weight polymers in the range of c less than 1% may be necessary for the critical test of the theory.

Relation between ξ_H and ξ_e. The hydrodynamic screening length or the blob size ξ_H has been calculated from D_{coop} by using eq 4, and the values are listed in Table II.

$$\xi_H = \frac{k_B T(1 - \phi_p)}{6\pi\eta_s D_{coop}} \qquad (4)$$

Its concentration dependence is well expressed by the solid line 1 in Figure 4 and is given by

$$\xi_H = 5.36 \times 10^{-8} c^{-0.69} \qquad (5)$$

ξ_e may be estimated by the use of results of stress relaxation measurements on semidilute solutions of high MW PS in Aroclor[19] as follows. It has been shown that in the range of concentration from 0.02 to 0.3 g cm^{-3}, the c dependence of molecular weight between entanglements M_e is expressed by

$$c^{1.4} M_e = 1.23 \times 10^4 \qquad (6)$$

If we convert the R_G–M_w relationship in the Θ state[20] to the ξ_e–M_e relation, we obtain

$$\xi_e^2 = 7.86 \times 10^{-18} M_e \qquad (7)$$

By combining eq 6 and 7 we obtain the ξ_e–c relation as

$$\xi_e = 3.11 \times 10^{-7} c^{-0.7} \qquad (8)$$

and eq 8 is shown by the solid line 2 in Figure 4. As is clear from the figure, ξ_e looks to be proportional to ξ_H as suggested by de Gennes, but the magnitude is about 5 times as large as ξ_H. This indicates that (1) the number of contact points between different chain molecules determines both the blob size and the entanglement spacing in semidilute solutions and (2) about 25 blobs must be connected to form one effective strand of the entanglement network.

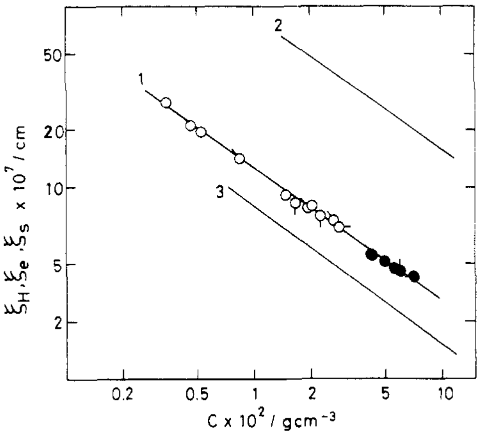

Figure 4. Concentration dependences of ξ_e, ξ_H, and ξ_s designated as the lines 2, 1, and 3, respectively.

It might be criticized that the proportionality between ξ_e and ξ_H has been derived by the use of the R_G–M_w relation for the unperturbed chain, which is inappropriate for the present polymer–good solvent system. If we use an R_G–M_w relation for PS in benzene at infinite dilution, ξ_e becomes much larger than the corresponding value given by eq 8 and the ratio ξ_e/ξ_H becomes larger. $\xi_e \simeq 5\xi_H$ is thus regarded as the lowest bound to ξ_e. Further, according to the blob concept, the excluded volume effect is fully developed only in each blob and the interaction between blobs is negligible. Therefore with the increase of the blob number n, $R_{G,n}$ of the chain consisting of n blobs may be described by using Gaussian statistics with an effective bond length ξ_H. Therefore eq 7 and 8 may still describe correct M_e and c dependences of ξ_e for $n \gg 1$.

In Figure 4 we also show the concentration dependence of the static screening length ξ_s by the solid line 3, which has been obtained by neutron scattering measurements on PS in carbon disulfide.[21] ξ_s values obtained by static light scattering measurements on PS in benzene are closely located on the line 3 for $c \geq 5 \times 10^{-3}$ g cm^{-3}.[22] ξ_s decreases with increasing c with an exponent of 0.75, a little larger than 0.69 for ξ_H, and the magnitude itself is smaller than ξ_H. It has been shown theoretically[23] that ξ_s is equal to ξ_H. We do not have any explanation for the substantial difference between these two quantities.

Slow Mode. In spite of efforts to find the slow mode for dust-free solutions of well-characterized polymer solutions, the slow mode has been only observed for a solution of the binary blend PS7804. The value of D_{slow}, 7.39 $\times 10^{-8}$ cm^2 s^{-1}, is much smaller than the translational diffusion coefficient of the low MW component at infinite dilution, 6.42 $\times 10^{-7}$ cm^2 s^{-1}, but appears to be larger than the self-diffusion coefficient of the high MW component at $c = 0.042$ g/g by about one order of magnitude.[11] Since the hydrodynamic radius R_H of the low MW component is comparable to the blob size ξ_H of the solution, we have first imagined that we are measuring the slow diffusive motion of the single free blob (the low MW component) through the medium consisting of connected blobs. However, forced Rayleigh scattering measurements on a THF solution of a binary blend whose composition is similar to that of PS7804 have shown that this conjecture is incorrect. The self-diffusion coefficient of dye-labeled PS with $M = 46000$ and $c = 0.0252$ g/g in a 3.59% solution of unlabeled PS with $M = 900000$ in THF has been measured by using an apparatus in Prof. Yu's laboratory at the University of Wisconsin. D_s has been estimated as

5.3×10^{-7} cm^2 s^{-1} within an experimental error of 10% from the linear plot of the relaxation time τ_s of the decay profile of the diffraction intensity vs. d^2, the square of the grating spacing. The value is larger than D_{slow} by a factor of about 5, even if we account for the difference in viscosity between THF and benzene. This kind of discrepancy has been found in the D_{slow} data of Amis and Han as mentioned already. At present we believe that the slow mode does not reflect the reptation motion of a single chain but does reflect coordinated motion of many polymer chains which gives rise to a long-lived concentration fluctuation.

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A Laser Light Scattering Study on Molecular Weight Distribution of Linear Polyethylene

John W. Pope and Benjamin Chu*

Department of Chemistry, State University of New York at Stony Brook,
Stony Brook, Long Island, New York 11794-3400.
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ABSTRACT: Time-average and time-dependent intensity of light scattered by linear polyethylene (LPE), Dutch State Mines sample L30-4-6, in a good organic solvent, 1,2,4-trichlorobenzene at 135 °C, was measured as a function of polymer concentration at scattering angles between 35 and 145°. Molecular properties determined were the *z*-average radius of gyration, $\langle R_g^2\rangle_z^{0.5} = 50$ nm, the *z*-average hydrodynamic radius, $\langle R_h^{-1}\rangle_z^{-1} = 27$ nm, the weight-average molecular weight, $\langle M\rangle_w = 570$, the weight distribution, $F_w(M)$, and the second virial coefficient, $A_2 = 1.5 \times 10^{-3}$ g^{-2} mL mol. The main purpose of this article was to determine $F_w(M)$ for a LPE based on $\langle M\rangle_w$, $\langle R_g^2\rangle_z$, A_2, and the characteristic line width distribution $G(\Gamma)$ computed from an inverse Laplace transform of the measured single-clipped time correlation function, $G_k^{(2)}(\tau)$. We have demonstrated this nonintrusive technique to be particularly useful in obtaining an approximate $F_w(M)$ for polydisperse synthetic high polymers which are difficult to characterize by more established analytical techniques such as gel permeation chromatography (GPC).

I. Introduction

1.1. Overview. Several studies[1,2] have attempted to determine the molecular weight distribution (MWD) of commercial linear polyethylene (LPE). It is also possible to extract the MWD of a polydisperse sample from combined measurements of static and dynamic light scattering.[3,4] The MWD is asscessible from light scattering due to the influence of the molecular weight distribution on dynamic measurements. For polydisperse samples, time correlation function (or power spectrum) profile analysis permits us to relate the distribution of translational diffusion coefficients with the molecular weight distribution provided we have taken into account interparticle interactions and molecular self-interference, i.e., virial coefficients and $P(K,R_g)$, respectively.

We approximate the power spectrum (or time correlation function) as a linear sum of basis functions with distinct characteristic decay times. Each characteristic decay time is related to a particular diffusion coefficient and, thus, to a particular molecular weight fraction. In addition to dynamic light scattering, we call upon static light scattering to determine the weight-average molecular weight, the *z*-average radius of gyration, and the second virial coefficient of the polymer–solvent system. The combination of both static and dynamic measurements allows a complete determination of the MWD.

This article will describe the combined dynamic and static light scattering experimental method used to characterize LPE. A yet more interesting problem is to investigate how LPE differs from long-chain branched polyethylene (BPE) of the same molecular weight. The present study is used to provide the experimental benchmark of LPE in order to begin the study of BPE, which is in progress.

The light scattering technique is similar to more established GPC by virtue of its use of the hydrodynamic radius

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