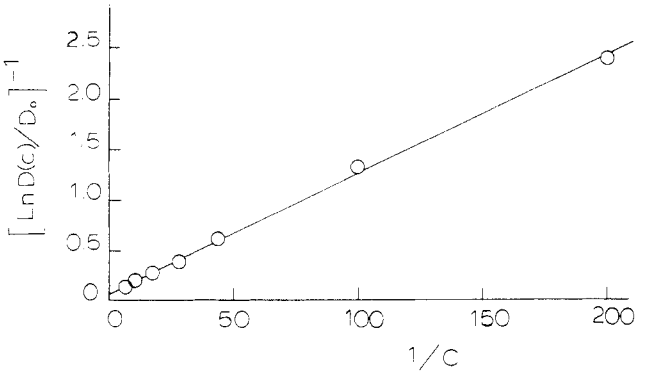

Figure 2. Plot of $1/[\ln D(C)/D_0]$ versus $1/C$. The intercept, $f(T,0)/B_d$, is 7.769×10^{-2}, and the slope, $[f(T,0)]^2/B_d\beta$, is 1.181×10^{-2}.

the volume fraction). Thus we write

$$f(T,C) = f(T,0) + \beta(T)\, C \tag{6}$$

where $f(T,0)$ represents the fractional free volume in the pure polymer and $\beta(T)$ is a parameter independent of concentration.

Substituting eq 6 into eq 5 and doing some algebra, one finds

$$\{\ln [D(C)/D_0]\}^{-1} = f(T,0)/B_d + [f(T,0)^2/B_d\beta(T)](1/C) \tag{7}$$

where $D(C)$ is the diffusion coefficient when the dye concentration is equal to C and D_0 is the diffusion coefficient in the limit of zero dye concentration. In Figure 2, we plot $1/\ln [D(C)/D_0]$ versus $1/C$; the linear plot confirms eq 7 and hence supports the free-volume theory of Fujita.[8] Using the assumption $f(T_g,0) = 0.025$, we have calculated $f(T = 127\ °C, 0)$ to be equal to 0.030, also assuming the thermal expansion coefficient at T_g to be $4.82 \times 10^4\ K^{-1}$, and this gives $B_d = 0.384$ and $\beta(T) = 0.128$. If eq 6 is expressed in terms of the volume fraction, B_d becomes 0.392 and $\beta(T) = 0.164$. These values are consistent with Fujita's results[8] and clearly show that the remarkable concentration dependence of the diffusion coefficient is due to the smallness of the $f(T,0)$ and $\beta(T)$ values.

One notes that even at 0.5% CQ concentration, D still has not reached the zero concentration self-diffusion limit, although the difference is about 6% in the present case. We expect that the difference increases as the temperature is brought toward T_g of the polymer. Thus, efforts must be taken to ascertain the dependence of D on the dye concentration when investigating the diffusion process in the vicinity of T_g. The presence of dye molecules tends to suppress the rapid change of D associated with the effect due to a large change in the chain motion that takes place in the vicinity of the glass transition region. To monitor the effect of the glass transition on the density fluctuation through the diffusion study, it is therefore essential to keep the dye concentration at a very small level.

Acknowledgment. We thank the ONR and the NSF Polymer Program (DMR 86-6884) for financial support.

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Registry No. PMMA, 9011-14-7; CQ, 465-29-2.

The Effective Interaction Coefficient Corresponding to Translational Diffusion of High Molecular Mass Polystyrene in Good Solvents

GYULA J. VANCSO*,[1]

University of Toronto, Department of Chemistry, 80 St. George Street, Toronto, Ontario M5S 1A1, Canada

MARTIN FORRER

Swiss Federal Institute of Technology, ETH-Zentrum, CH-8092 Zürich, Switzerland. *Received June 26, 1989; Revised Manuscript Received August 30, 1989*

Quasielastic laser light scattering (QELS) experiments,[2,3] in conjunction with applications of new theoretical achievements involving scaling theories,[4,5] have opened up a new stage in studying polymer dynamics. Despite considerable progress there are still unanswered questions related to some scaling exponents. QELS of polymer solutions is usually studied by using the photon correlation spectroscopy (PCS) technique.[2] In a PCS experiment the time autocorrelation function (ACF) of the scattered light intensity is measured. The observed decay rate Γ of the ACF is related to diffusion phenomena. In dilute solutions Γ depends on concentration c and scattering angle θ [or scattering vector $\mathbf{q}$, where $|\mathbf{q}| = q = (4\pi/\lambda) \sin(\theta/2)$ and λ is the wavelength of light in the scattering medium]. The concentration dependence is caused by effective polymer segment–solvent molecule and segment–segment interactions while the $\mathbf{q}$ dependence is related to the influence of chain internal modes of motion. The product qR_h (with the R_h Stokes-effective hydrodynamic radius) is closely related to the characteristics of diffusional movement measured in the experiment.[3-5] If $qR_h < 0.4$–0.5, translational diffusion of the macromolecular center-of-mass (characterized by the corresponding D_t diffusion coefficient) dominates the ACF.[6,7] In this scattering vector regime both the effec-

0024-9297/90/2223-1220$02.50/0

tive measured value of the diffusion coefficient and the first-order correction of its concentration dependence are independent of the scattering angle. With increasing θ (or increasing molecular size), if $qR_h \gtrsim 0.4$–0.5, contributions from internal movements will also be reflected in the measured effective diffusion coefficient.[6,7] The c and q dependence of the reduced cumulant can be schematically written as[8]

$$\Gamma_m/q^2 = (\Gamma_0/q^2)\mathcal{F}(q)(1 + k_D c + ...) \quad (1)$$

where subscript m refers to the measured effective value, subscript 0 to the limiting case at $c \to 0$ and $q \to 0$, $\mathcal{F}(q)$ is some function of the scattering vector, and the parameter k_D, which describes the first order correction factor of the concentration dependence, is the effective interaction coefficient. If $qR_h < 0.4$–0.5, k_D does not depend on q (see ref 6, 7). In this case its value describes the molar mass dependent thermodynamic and hydrodynamic interactions[8,9] related to the translational movement of the center-of-mass of the whole macromolecule. If $qR_h \gtrsim 0.4$–0.5, the measured value of k_D decreases with increasing q due to contributions from segmental movements (intermolecular dynamics) to the measured ACF.[6,7] To emphasize the difference between the two scattering vector regimes, we denote hereinafter k_D by $k_{D,0}$ if $qR_h < 0.4$–0.5 and with $k_{D,eff}$ otherwise.

It has been shown for polystyrene in good solvents[9] that the relationship between $k_{D,0}$ and the weight-average molar mass $\bar{M}_w$ can be expressed by $k_{D,0} \propto (\bar{M}_w)^{\upsilon}$ where $\upsilon \approx 0.76$ if $\bar{M}_w \lesssim 4 \times 10^6$. A decrease in the magnitude of this exponent was reported for samples with higher molar masses,[9] but no theoretically based explanations have been given for this. In this note we want to point out that an interpretation for the change in the value of υ can be given without assuming intrinsic effects related to large molecular sizes. The apparent decrease of υ can be explained by the change in the experimentally observed diffusion regime due to the increased influence of chain-internal movements on the measured ACF at high molar masses.

Experimental Section

Measurements were carried out on eight PS standard samples. The sample specifications are given elsewhere[6,7] except PS9 (a product of Polymer Laboratories LTD) for which $\bar{M}_w = 9.3 \times 10^6$ g/mol and $\bar{M}_w/\bar{M}_n < 1.2$. Solutions were made with tetrahydrofuran (THF) (a good solvent for PS). Reagent grade THF was first dried with KOH and then freshly distilled from KOH under N_2 atmosphere. N_2 was kept over the distilled solvent prior to use, and the viscosity and refractive index were checked before making the solutions. PCS measurements were carried out at 40 and 45 °C by using a Spectraphysics Ar ion laser operating at 514.5 nm. Other details of the experimental setup are described elsewhere in detail.[10]

Results and Discussion

The reduced concentration dependence of PS in THF, $1 + k_{D,eff}c$, measured at different scattering angles at 45 °C, of two samples with $\bar{M}_w = 1.29 \times 10^6$ g/mol (PS5) and $\bar{M}_w = 4.47 \times 10^6$ g/mol (PS7) are plotted in parts a and b of Figure 1, respectively. The displayed values were calculated by using eq 1 from data used for dynamic Zimm plots published elsewhere.[6,7] $\mathcal{F}(q)$ was determined by extrapolating the value of Γ_m/q^2 to $c \to 0$. According to the plotted data, $k_{D,eff}$ for PS5 does not depend on q if $\theta \lesssim 60°$. This is illustrated in Figure 1a by three undistinguisably matching fitted lines at the highest slope for $\theta = 35°$, 50°, and 60°. For the sample PS7 (with significantly higher molar mass) the fitted lines of the reduced concentration dependence only approximately match for $\theta = 27°$ and 35°. For PS7 a further decrease of the scattering angle was unreasonable due to increasing experimental problems arising from stray light effects. For the sample PS7 we expect therefore a contribution of internal modes of movement to the ACF even at $\theta = 27°$. We attribute this effect mainly to the high molar mass tail of the molar mass distribution (MMD) function. For the sample PS9 the convergence of the k_D values was even poorer. The decreasing value of $k_{D,eff}$ (i.e. the decreasing slope of the fitted lines) in parts a and b of Figure 1 at increasing scattering angles refers to an influence of segmental movement since at the corresponding q values internal parts of the molecules are already "seen" in the scattering experiments. In Table I we summarize some characteristics of three samples with the highest molar mass and the qR_h values for the smallest θ values of the corresponding measurements.

Figure 2 displays the molar mass dependence of k_D for eight different PS samples in THF measured at 40 °C. Open circles correspond to $k_{D,0}$, and filled triangles to $k_{D,eff}$. The open circle at the highest molar mass represents the data obtained on PS5. For the two samples

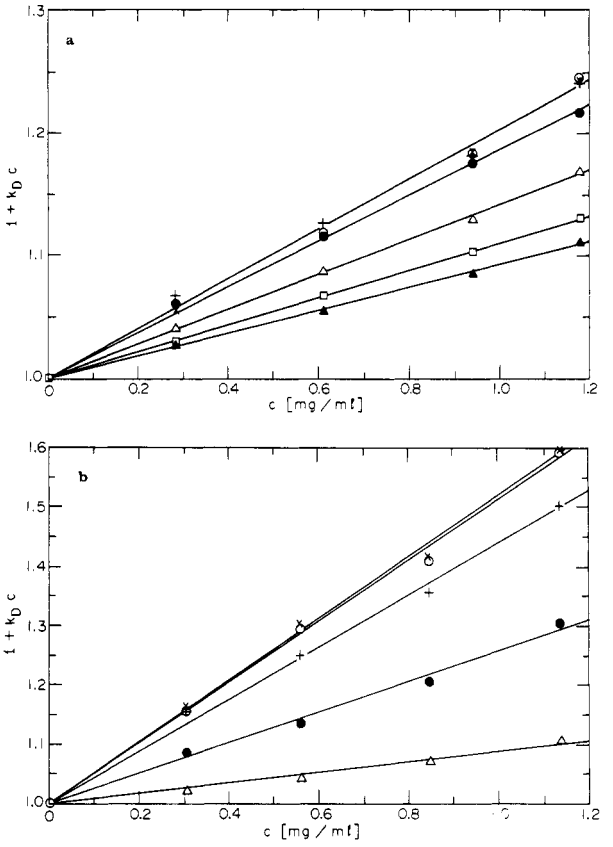

Figure 1. a. Reduced concentration dependence of the effective diffusion coefficient of the sample PS5 ($\bar{M}_w = 1.29 \times 10^6$ g/mol) measured at different scattering angles: (○) 35°; (×) 50°; (+) 60°; (●) 75°; (△) 90°; (□) 110°; (▲) 130°. b. Reduced concentration dependence of the effective diffusion coefficient of the sample PS7 ($\bar{M}_w = 4.47 \times 10^6$ g/mol) measured at different scattering angles: (○) 27°; (×) 32°; (+) 50°; (●) 65°; (△) 90°.

Table I
Some Experimental Characteristics and Parameters of the Samples with the Three Highest Molar Masses

sample	PS5	PS7	PS9
$10^{-6}\bar{M}_w$, g/mol	1.3	4.5	9.3
θ(min), deg	31	27	31
qR_h	0.3	0.45	1.0

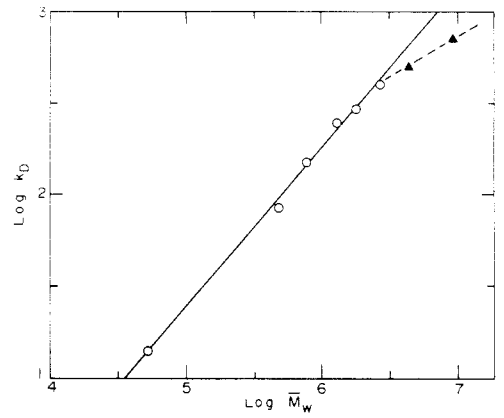

Figure 2. log–log plot of the effective interaction coefficient $k_{D,eff}$ of PS measured at 40 °C in THF as a function of the weight average molar mass ($\bar{M}_w$ in g/mol; $k_{D,eff}$ in mL/g; symbol ▲ and dashed line: for explanation see text).

with the highest molar masses (PS7 and PS9), the condition $qR_h < 0.4$–0.5 was not fulfilled (see Table I). The corresponding $k_{D,eff}$ values in Figure 2 are labeled with ▲ and are connected by a dashed line. The exponent υ in the relationship $k_D \propto (\bar{M}_w)^{\upsilon}$ has a value of $\upsilon = 0.86$ if $qR_h < 0.4$ (solid line) and $\upsilon = 0.49$ for the two samples PS7 and PS9 (dashed line). This difference in the slopes clearly corresponds to the influence of the chain internal movements on the effective interaction coefficient for PS7 and PS9. A similar deviation toward smaller values of the exponent υ at high molar masses was reported by Tsunashima[9] in a thorough analysis of PCS results for PS in good solvents. A careful reanalysis of the data reported in ref 9 and, in particular, those of ref 11 and 12 shows that the four data points for k_D in ref 9, for which $\bar{M}_w > 5 \times 10^6$, are based on measurements where the magnitude of qR_h was close to or higher than 0.4. Correspondingly, the first-order correction factor of the concentration dependence discussed by Tsunashima[9] et al. represents at high molar masses $k_{D,eff}$ rather than $k_{D,0}$ values. This recognition led us to the conclusion that the previously published apparent decrease in the value of the exponent υ is associated with a contribution of the chain-internal dynamics to the measured time autocorrelation function at high molar masses rather than with an intrinsic effect.

Finally it is worthwhile to note that the use of synthetic polymers as model systems at high molar masses ($M \gtrsim 10^7$ g/mol) is affected by a serious problem arising from the polydispersity of the MMD function. Even if the relative polydispersity ratio $\bar{M}_w/\bar{M}_n$ is kept constant while the whole function is shifted toward higher M values, the absolute width of the distribution is increasing. This means that the influence of the polymer molecules at the high M tail of the distribution becomes more important in samples with similar polydispersity index but with high M. A possible way out of this dilemma might be the use of biopolymers as model systems[13] with strictly monodisperse MMD. Only a further decrease in the scattering angle to lower values, a significant improvement in the accuracy of polydispersity analyses of the measured ACF, and the use of monodisperse model polymers will allow one to obtain reliable information about the scaling of k_D and D_t with M of high molar mass polymers from PCS measurements.

Acknowledgment. Financial support by the Swiss Federal Institute of Technology and by the Ontario Centre for Materials Research is gratefully acknowledged. We are indebted to Dr. I. Tomka for many stimulating discussions and to V. Foyle for his valuable comments concerning the manuscript.

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Registry No. PS, 9003-53-6.

Neutron Scattering from Elastomeric Networks. 2. An Alternative Phantom Network Model

A. KLOCZKOWSKI* AND J. E. MARK

Department of Chemistry and the Polymer Research Center, The University of Cincinnati, Cincinnati, Ohio 45221

B. ERMAN

Polymer Research Center, Bogazici University, Bebek 80815, Istanbul, Turkey. *Received April 21, 1989; Revised Manuscript Received June 26, 1989*

Introduction

In our recent paper[1] an alternative treatment of fluctuations $\langle(\Delta r_{ij})^2\rangle$ of the distance $\mathbf{r}_{ij}$ between two points i and j on a chain has been proposed. In the classical theory of rubber elasticity[2,3] it is assumed that points on a chain are equivalent to bifunctional junctions. This assumption leads directly to the strain independence of fluctuations of these points, similar to the strain independence of fluctuations of multifunctional junctions in the network. The neutron scattering from a labeled, end-linked chain with the assumption of the strain independence of fluctuations has been studied by Pearson.[4] Recently we have generalized this result to the case of neutron scattering from a labeled, cross-linked path in a network[5] without the additional assumption[6] that different chains along the path are randomly oriented.

Theory

If only the multifunctional junctions ($\phi > 2$) are retained in the configurational function in the James–Guth theory[2,3] there would be no information on the behavior of points

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