Table III
Bond Conformational Probabilities Calculated for a PVDC Chain with $E = 2.0$ kcal mol^{-1}, $E_1 = 1.4$ kcal mol^{-1}, $\theta_1 = 112°$, $\theta_2 = 123°$

	Infinite D	$D = 2$
$p_g = 1 - p_t$	0.3501	0.3922
$p_{g^+g^+} = p_{g^-g^-}$	0.0307, 0.0053[a]	0.0457, 0.0086[a]
$p_{g^+g^-} = p_{g^-g^+}$	0.0307, 0	0.0127, 0
$p_{g^+t} = p_{tg^+}$	0.1138, 0.1698	0.1378, 0.1875
p_{tt}	0.4223, 0.3103	0.3323, 0.2328

[a] First figure for bond pairs flanking CH_2; second figure for pairs flanking CCl_2.

effect in PVDC is somewhat augmented by the inequality of the chain bond angles θ_1 and θ_2. The results for other choices of E, E_1, and θ_1 are qualitatively similar.

In conclusions, we may advise the reader to regard the above calculations with mild skepticism, in view of the recognized difficulties[16] of dealing with such highly substituted chains. It would be illuminating to study the PVDC chain with a more sophisticated model, such as that of Boyd and Breitling.[18]

Acknowledgment. We are very grateful to Dr. R. A. Wessling of the Dow Chemical Company for encouragement and valuable suggestions. This research was supported by the National Science Foundation.

References and Notes

(1) Supported by the National Science Foundation.

(2) R. A. Wessling, "Encyclopedia of Polymer Science and Technology", Vol. 14, Wiley, New York, N.Y., 1971, p 540.

(3) (a) C. S. Fuller, *Chem. Rev.*, **26**, 143 (1940); (b) P. DeSantis, E. Giglio, A. M. Liquori, and A. Ripamonti, *J. Polym. Sci., Part A*, **1**, 1383 (1963); (c) V. M. Coiro, P. DeSantis, A. M. Liquori, and A. Ripamonti, *Polym. Lett.*, **4**, 821 (1966).

(4) T. Miyazawa and Y. Ideguchi, *Polym. Lett.*, **3**, 541 (1965).

(5) M. Asahina, M. Sato, and T. Kobayashi, *Bull. Chem. Soc. Jpn.*, **35**, 630 (1962).

(6) M. L. Wallach, *Polym. Prepr.*, **10**, 1248 (1969).

(7) R. A. Wessling, *J. Appl. Polym. Sci.*, **14**, 1531 (1970).

(8) K. Matsuo and W. H. Stockmayer, *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.*, **15**, 527 (1974).

(9) P. J. Flory, "Principles of Polymer Chemistry", Cornell University Press, Ithaca, N.Y., 1953.

(10) W. H. Stockmayer and L. L. Chan, *J. Polym. Sci., Part A-2*, **4**, 437 (1966).

(11) H. Yamakawa, "Modern Theory of Polymer Solutions", Harper and Row, New York, N.Y., 1971, Chapter VII.

(12) J. Pouchlý and D. Patterson, *Macromolecules*, **6**, 465 (1973).

(13) T. A. Orofino and P. J. Flory, *J. Chem. Phys.*, **26**, 1067 (1957).

(14) K. J. Ivin, H. A. Ende, and G. Meyerhoff, *Polymer*, **3**, 129 (1962).

(15) S. Lifson and I. Oppenheim, *J. Chem. Phys.*, **33**, 109 (1960).

(16) P. J. Flory, "Statistical Mechanics of Chain Molecules", Interscience, New York, N.Y., 1969, pp 198–201.

(17) G. Allegra, E. Benedetti, and C. Pedone, *Macromolecules*, **3**, 727 (1970).

(18) R. H. Boyd and S. M. Breitling, *Macromolecules*, **5**, 1 (1972).

(19) C. A. J. Hoeve, *J. Chem. Phys.*, **32**, 888 (1960).

(20) L. Pauling, "The Nature of the Chemical Bond", Cornell University Press, Ithaca, N.Y., 1960; "The Chemical Bond", Cornell University Press, Ithaca, N.Y., 1967.

(21) J. E. Mark, *J. Chem. Phys.*, **56**, 451 (1972).

Analysis of Polydispersity in Polymer Solutions by Inelastic Laser Light Scattering

Gary A. Brehm and Victor A. Bloomfield*

Department of Biochemistry, University of Minnesota, St. Paul, Minnesota 55108.

Received February 4, 1975

ABSTRACT: The autocorrelation function of light inelastically scattered from a polymer solution may be analyzed to determine the diffusion coefficient of the polymer. If the solution is polydisperse, the measured diffusion coefficient will be an average over all species. Koppel showed that if the autocorrelation function is analyzed in terms of its cumulants, the diffusion coefficient will be a *z* average. If the particle dimensions are not small compared with the wavelength of light, however, this conclusion will hold only in the limit of zero scattering angle, since at higher angles the form factors of the larger particles decrease their contributions relative to the smaller particles. We show how the slopes and intercepts of plots of K_1/K^2 and K_2/K^4 (where K_1 and K_2 are the first and second cumulants, and K is the scattering vector, $(4\pi/\lambda) \sin(\theta/2)$) can be analyzed to yield four *z* averages of the polymer radius distribution function: $\langle R^{-1} \rangle$, $\langle R^{-2} \rangle$, $\langle R \rangle$, and $\langle R^2 \rangle$. The experimental behavior of the angular dependence of K_1/K^2 for synthetic mixtures of polystyrene latex spheres gives good agreement with theory.

Polymer solutions are often polydisperse. Attempts to use inelastic laser light scattering to analyze such polydispersity or, conversely, to estimate the complicating effects of polydispersity on scattering measurements are common in the recent literature. These attempts have generally concentrated on data analysis at a single scattering angle, and have characterized polydispersity effects in terms of deviations from a simple Lorentzian line shape or a simple exponential decay, depending on whether spectral or autocorrelation analysis is employed. In recent work, autocorrelation analysis has been particularly prominent.[1-5]

In this paper we show that a more detailed analysis of polydispersity is possible if autocorrelation functions are obtained at several scattering angles, and if the scattering particles are large enough that intramolecular interference effects are significant. Our treatment is an extension of the cumulant expansion technique introduced by Koppel.[1]

Theory

The electric field autocorrelation function of light scattered from a polydisperse solution of spherical particles is

$$g^{(1)}(\tau) = \frac{\sum_i M_i W(M_i) P(K,M_i) e^{-K^2 D_i \tau}}{\sum_i M_i W(M_i) P(K,M_i)} \qquad (1)$$

where $W(M_i)$ is the weight fraction of species i with molecular weight M_i, diffusion coefficient D_i, and scattering form factor $P(K,M_i)$. K is the scattering vector, whose magnitude is $(4\pi/\lambda) \sin(\theta/2)$, where λ is the wavelength of light in the scattering medium and θ is the scattering angle.

The first and second cumulants of the autocorrelation function are, when written as combinations of moments about the mean

$$K_1 = \left(\frac{\partial g^{(1)}(\tau)}{\partial(-\tau)}\right)_{-\tau=0} = K^2\langle DP(K)\rangle/\langle P(K)\rangle \qquad (2)$$

and

$$K_2 = \left(\frac{\partial^2 g^{(1)}(\tau)}{\partial(-\tau)^2}\right)_{-\tau=0} - \left[\left(\frac{\partial g^{(1)}(\tau)}{\partial(-\tau)}\right)_{-\tau=0}\right]^2 = K^4\left[\frac{\langle D^2P(K)\rangle}{\langle P(K)\rangle} - \frac{\langle DP(K)\rangle^2}{\langle P(K)\rangle^2}\right] \qquad (3)$$

where the angular brackets define a z average

$$\langle f\rangle = \textstyle\sum_i f_i M_i W_i(M_i)/\sum_i M_i W(M_i)$$

Equation 2 has been obtained previously by Brown et al.[5]

The form factor for a spherical particle at low angles can be written in the Guinier[6] approximation as

$$P(K,M_i) = e^{-\alpha R_i^2 K^2} \qquad (4)$$

where R_i is the radius of particle i and α depends on the radial density profile. (For a solid sphere, $\alpha = \frac{1}{5}$. In that case, eq 4 agrees with the exact form factor to within 5% up to $KR \leq 2$.) Higher order corrections to the form factor could easily be included in the theory. However, these would introduce curvature into plots such as Figure 1 which would be difficult to analyze with sufficient statistical reliability. The Guinier approximation suffices to analyze the limiting slope at low angles.

Since $P(K,M_i)$ approaches unity as K approaches zero, eq 2 and 3 yield

$$\lim_{K\to 0} K_1/K^2 = \langle D\rangle \qquad (5)$$

$$\lim_{K\to 0} K_2/K^4 = \langle D^2\rangle - \langle D^2\rangle \qquad (6)$$

By substituting eq 4 into eq 2 and 3, the limiting slopes of the cumulants may also be obtained.

$$\lim_{K\to 0}\frac{\partial(K_1/K^2)}{\partial K^2} = \alpha[\langle D\rangle\langle R^2\rangle - \langle DR^2\rangle] \qquad (7)$$

$$\lim_{K\to 0}\frac{(K_2/K^4)}{\partial K^2} = \alpha[\langle D^2\rangle\langle R^2\rangle - \langle D^2R^2\rangle - 2\langle D\rangle^2\langle R^2\rangle + 2\langle D\rangle\langle DR^2\rangle] \qquad (8)$$

The diffusion coefficient is generally inversely proportional to radius,

$$D_1 = \beta R_1^{-1} \qquad (9)$$

where for solid spheres, $\beta = kT/6\pi\eta_0$ with k equal to Boltzmann's constant, T temperature, and η_0 solvent viscosiy. Then the preceding expressions for the limiting intercepts and slopes become

$$\lim_{K\to 0} K_1/K^2 = \beta\langle R^{-1}\rangle \qquad (10)$$

$$\lim_{K\to 0} K_2/K^4 = \beta^2[\langle R^{-2}\rangle - \langle R^{-1}\rangle^2] \qquad (11)$$

$$\lim_{K\to 0}\frac{\partial(K_1/K^2)}{\partial K^2} = \alpha\beta[\langle R^{-1}\rangle\langle R^2\rangle - \langle R\rangle] \qquad (12)$$

$$\lim_{K\to 0}\frac{\partial K_2/K^4}{\partial K^2} = \alpha\beta^2[\langle R^{-2}\rangle\langle R^2\rangle - 1 - 2\langle R^{-1}\rangle^2\langle R^2\rangle + 2\langle R^{-1}\rangle\langle R\rangle] \qquad (13)$$

Thus, if the first and second cumulants can be measured as a function of angle, four z average moments of the radius distribution can be obtained: $\langle R^{-1}\rangle$, $\langle R^{-2}\rangle$, $\langle R\rangle$, and $\langle R^2\rangle$. These moments could also be expressed in terms of moments of the molecular weight distribution, since $R_i = \gamma M_i^{\delta}$. For a solid sphere, $\delta = \frac{1}{3}$; for a spherical shell of constant thickness, or for a random-coil polymer in a Θ solvent, $\delta = \frac{1}{2}$.

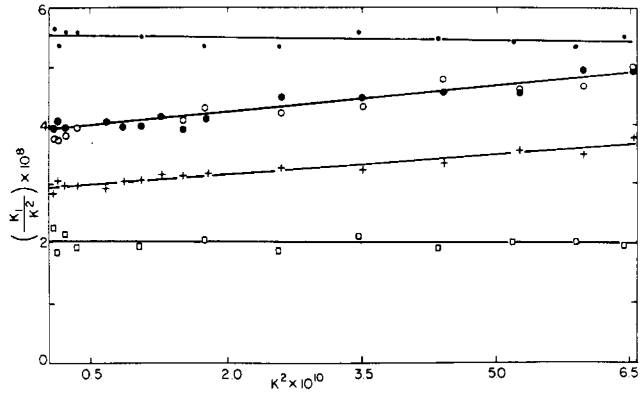

Figure 1. K_1/K^2 as a function of K^2 for polystyrene latex spheres with diameters 91 nm (●) and 234 nm (□), and for 95/5 (● and ○) and 75/25 (+) w/w mixtures.

Experimental Methods and Results

Homodyne inelastic laser light scattering was performed using a Spectra-Physics 125A He-Ne laser, whose wavelength in water is λ 474.4 nm. The scattering cell was thermostated at 25.0°, and the scattering angle ranged from 150 to 9°. Aqueous solutions containing Dow polystyrene latex spheres, of diameter 91, 176, and 234 nm, either singly or in binary mixtures of known proportions, were prepared just prior to use. The photocurrent autocorrelation functions were obtained with a Saicor 42A correlator, read out on punched tape, and fit to a second-order polynomial in $(-\tau)$ to obtain the cumulants.

Data were analyzed using either weighted or unweighted least-squares fitting. In the former case, the weighting factors were proportional to the square of the signal intensity at each time point. The reduced second cumulants, K_2/K_1^2 which are often taken as measures of polydispersity, were in the range 0.01 to 0.02 for monodisperse samples, and in the range 0.05 to 0.08 for typical mixtures, indicating that second cumulant analysis using weighted data is sensitive to polydispersity.[2-4] When data were unweighted, K_2/K_1^2 typically ranged between 0.06 and 0.13 for both monodisperse samples and mixtures.

Figure 1 shows the first cumulant as a function of K^2 for monodisperse solutions of the latex spheres with diameters 91 and 234 nm, and for 95/5 and 75/25 (w/w) mixtures of the two. The slopes and intercepts of these plots, and for a mixture of 91 and 176 nm spheres, are tabulated and compared with expectations in Table I. It will be seen that in all cases, theory and experiment agree satisfactorily. These results were obtained using unweighted data; weighted least-square determinations of K_1 give essentially identical results. However, such weighting may underestimate the contribution of the long-time part of the autocorrelation function, in which the curvature associated with polydispersity is most manifest.

Discussion

In a monodisperse polymer solution, a plot of the autocorrelation function decay constant, K^2D, vs. K^2 gives a straight line whose slope is D, the diffusion coefficient of the polymeric solute. In a polydisperse solution, in which the dimensions of the polymeric species are not negligible compared with the wavelength of light, such a plot will be concave upwards. This is because the larger particles have form factors $P(K,M_i)$ which decrease more rapidly with increasing scattering angle; since they also have smaller diffusion coefficients, the average diffusion coefficient increases with angle. Such behavior is illustrated in Figure 1.

Extrapolation of K_1/K^2 to $K^2 = 0$ yields the z average diffusion coefficient. This agrees with the result of Koppel,[1] who analyzed the case in which all form factors are unity (or identical). However, we have shown that the slope of this plot also yields useful information about the distribution of particle sizes.

Table I
Intercepts and Slopes of Plots of K_1/K^2 for Mixtures of Polystyrene Latex Spheres

Diameters, nm	Relative composition (w/w)	Intercept $\times 10^8$		Slope $\times 10^{19}$	
		Exptl	Theory (eq 10)	Exptl	Theory (eq 12)
91		5.49 ± 0.04^a	5.39	-0.091 ± 0.12^a	0
176		2.72 ± 0.05	2.79	0.017 ± 0.12	0
234		2.06 ± 0.06	2.09	-0.076 ± 0.16	0
91/234	95/5	3.86 ± 0.03	3.84	1.55 ± 0.10	1.89
91/234	75/25	2.96 ± 0.03	3.04	1.11 ± 0.09	1.00
91/176	83/17	4.08 ± 0.06	4.03	0.76 ± 0.15	0.73

[a] Uncertainty is taken equal to one standard deviation.

In principle, similar determination of the slope and intercept of a plot of K_2/K^4 vs. K^2 yields four simultaneous equations (eq 10–13) to be solved for the four z average moments of the size distribution, $\langle R^{-1} \rangle$, $\langle R^{-2} \rangle$, $\langle R \rangle$, and $\langle R^2 \rangle$. In practice, the second cumulant may not be determinable with sufficient precision to make such analysis feasible. If only the first cumulant can be measured with precision, then there are only two equations (eq 10 and 12) available to determine the three moments $\langle R^{-1} \rangle$, $\langle R \rangle$, and $\langle R^2 \rangle$. However, if there is reason to believe that the distribution of polymer sizes is adequately characterized by a two-parameter equation,[7] such as the Gaussian, log-normal, or Schulz–Zimm, then these parameters may be computed from the angular dependence of K_1 alone.

Our experimental study has been concerned with solid spherical polymers of constant density. However, the formalism developed here will apply as well to other spherical or quasi-spherical particles, such as random coiled polymers or spherical vesicles.

Acknowledgments. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to NIH Research Grant GM 17855, for partial support of this work. V.A.B. is a Research Career Development Awardee of NIH (GM 15583).

References and Notes

(1) D. E. Koppel, *J. Chem. Phys.*, **57**, 4814 (1972).
(2) S. P. Lee and B. Chu, *Appl. Phys. Lett.*, **24**, 575 (1974).
(3) C. B. Bargeron, *J. Chem. Phys.*, **60**, 2516 (1974).
(4) C. B. Bargeron, *J. Chem. Phys.*, **61**, 2134 (1974).
(5) J. C. Brown, P. N. Pusey, and R. Dietz, *J. Chem. Phys.*, **62**, 1136 (1975).
(6) A. Guinier, *Ann. Phys. (Leipzig)*, **12**, 161 (1939).
(7) L. H. Peebles, Jr., "Molecular Weight Distributions in Polymers", Interscience, New York, N.Y., 1971.

Relaxations in Cyano-Substituted Polypentenamers and Their Hydrogenated Derivatives

R. Neumann, K. Sanui, and W. J. MacKnight*

Chemistry Department, Polymer Science and Engineering Program and
Materials Research Laboratory, University of Massachusetts, Amherst, Massachusetts 01002.
Received March 18, 1975

ABSTRACT: Two series of cyano-substituted polypentenamers and their hydrogenated derivatives have been studied by dynamic mechanical and dielectric relaxation in the temperature range from −160 to 110°C and at frequencies from 3.5 Hz to 10 kHz. Series I contains 7.4 mol % cyano groups and series II contains 20 mol % cyano groups. The amorphous cyanopolypentenamers display one major mechanical and dielectric relaxation region associated with motions accompanying the glass transition and labeled β. A small secondary relaxation, labeled γ, is also discernible in the mechanical E'' results. The semicrystalline hydrogenated derivatives exhibit three relaxation regions labeled α, β, and γ in order of decreasing temperature. The α relaxation which occurs in both series I and II mechanically is resolvable by the dielectric technique only in annealed series I samples. The β and γ relaxations, on the other hand, are present both mechanically and dielectrically in all the derivatives. Enthalpies of fusion for the semicrystalline derivatives were determined using the diluent technique. It was found that the enthalpy of fusion depends on the concentration of the cyano substituents. Available evidence indicates some degree of incorporation of the cyano groups into the crystal lattice but this incorporation is considerably less than that occurring in chlorinated polyethylenes. The results indicate that the α relaxation arises from motions within the crystal phase, the β relaxation from motions accompanying the glass transition, and the γ relaxation from local motions in both the crystal and amorphous phases.

Previously we have reported on the mechanical relaxation behavior of polypentenamer and its hydrogenated derivatives.[1] It was found that the semicrystalline derivatives exhibit three relaxation regions between −150°C and the melting points at the frequencies employed (3.5, 11, and 110 Hz). These were labeled α, β, and γ in order of decreasing temperature. The α relaxation is associated with the crystalline phase being absent in the amorphous polypentenamer and the derivatives of low crystallinity. The β relaxation is associated with motions accompanying the glass transition. The γ relaxation is composite in nature, arising from local motions occurring in both the crystal and amor-