The function $\rho(\mathbf{r})$ is related to the Ursell-Mayer cluster functions used by Albrecht[2] and Yamakawa,[3] but the present formulation leaves off here in the treatment of intermolecular interactions. The coefficient of the first term in eq 9 is $[2/mn(mn-1)]mn(n-1)/2$, whereas that of the second term is $[2/mn(mn-1)]n^2m(m-1)/2$; for a polydisperse system $\langle P_1(\Theta)\rangle$ and $\langle F^2(\Theta)\rangle$ must be defined so as to be compatible with these coefficients.

The molecular structure factor for the linear chain will be calculated for illustration. (It should be recalled that the power of the generalized inverse is in its application to molecules with circuits, for which it is not easy to do calculations by other methods.) The four-condition inverse is required, and has elements given by

$$k_{ii}^{-1} = [i(i-1) + (n-i)(n-i+1) - n^2/3 + \tfrac{1}{3}]/2n \qquad (11)$$

which can be obtained from the three-condition inverse[5,8,9] by adding the constant term $-(n^2-1)/6n$, so that

$$\sum_{j=1}^{n} k_{ij}^{-1} = 0$$

Upon replacing the sum in eq 10 by an integral and dropping terms of $0(1/n)$ from eq 11, one obtains

$$F_k(\Theta) = \pi^{1/2} \exp(-u/12)\, \mathrm{erf}(u^{1/2}/2)/u^{1/2} \qquad (12)$$

where

$$u = (8\pi^2\langle r_k^2\rangle/3\lambda^2) \sin^2 \Theta/2 = \mu^2\langle s_k^2\rangle \qquad (13)$$

is the Debye variable, and $\mathrm{erf}(x)$ is the error function. Here, $\langle r_k^2\rangle = n_k\langle l^2\rangle = 6\langle s_k^2\rangle$, as usual. [If the chain is labeled with atoms of various cross sections, group structure factors f_i will multiply the exponential function in eq 10.] It may be noted that eq 12 defines a monotonic function which decreases from 1.0 at $u = 0.0$ to 0.535 at $u = 4.0$. It was first obtained in a different context by Benoit and Goldstein[10] and has also been encountered in dynamic scattering theory.[11,12] It is slightly different from the corresponding function calculated by Flory and Bueche.[13] Equation 9 with eq 12 might be useful for analysis of radiation scattered by concentrated polymer solutions.[14]

Equation 8 may be applied to a pair of linear chains separated by a distance r. This illustration might find application to scattering from denatured duplex DNA prior to diffusive strand separation,[15] provided that the molecules are not correlated and hence adopt Gaussian statistics within times short compared with the rate of strand separation. An alternative application could be made to flash photolytic scission of a long polymer chain at its midpoint. For these cases, $m = 2$, $n - 1 \approx n$, $P_1(\Theta)$ is the Debye function, $F(\Theta)$ is given by eq 12, and $\exp(i\mathbf{r}\cdot\mu)$ is rotationally averaged to give

$$P(\Theta) = P_1(\Theta)/2 + (\pi/2u) \exp(-u/6)[\mathrm{erf}(u^{1/2}/2)]^2 \sin(u^{1/2}\xi)/u^{1/2}\xi \qquad (14)$$

where u is defined by eq 13, and $\xi = r/\langle s^2\rangle^{1/2}$. If the scattered radiation is observed at an angle Θ_1 such that $u = 1$, for example, eq 14 gives

$$P(\Theta_1) = 0.368 + 0.360(\sin \xi)/\xi$$

the derivative $\mathrm{d}P(\Theta_1)/\mathrm{d}t$ will give the rate of strand separation.

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References and Notes

(1) B. H. Zimm, *J. Chem. Phys.*, **16**, 1093 (1948).
(2) A. C. Albrecht, *J. Chem. Phys.*, **27**, 1014 (1957).
(3) H. Yamakawa, *J. Chem. Phys.*, **46**, 973 (1967).
(4) H. Yamakawa, "Modern Theory of Polymer Solutions", Harper and Row, New York, N.Y., 1971, Chapter 5.
(5) B. E. Eichinger, *Macromolecules*, **11**, 432 (1978).
(6) H. Benoit et al., *Macromolecules*, **8**, 451 (1975).
(7) D. S. Pearson, *Macromolecules*, **10**, 696 (1977).
(8) S. Aronowitz and B. E. Eichinger, *J. Math. Phys. (N.Y.)*, **16**, 1278 (1975).
(9) A. Ben-Israel and T. N. E. Greville, "Generalized Inverses: Theory and Applications", Wiley-Interscience, New York, N.Y., 1974.
(10) H. Benoit and M. Goldstein, *J. Chem. Phys.*, **21**, 947 (1953).
(11) R. Pecora, *J. Chem. Phys.*, **49**, 1032 (1968).
(12) B. J. Berne and R. Pecora, "Dynamic Light Scattering", Wiley, New York, N.Y., 1976, p 187.
(13) P. J. Flory and A. M. Bueche, *J. Polym. Sci.*, **27**, 219 (1958).
(14) M. Daoud et al., *Macromolecules*, **8**, 804 (1975).
(15) This problem was suggested to me by Professor Hyuk Yu.

Evidence Specifying the Origin of the NMR Doublet of Water in Oriented Macromolecular Systems

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A doublet has been consistently observed as part of the NMR spectrum of water absorbed by a variety of macromolecular systems.[1-6] The usual explanation is that the splitting arises due to the dipole-dipole interaction, but it has been suggested that such a splitting may be due to a diamagnetic susceptibility effect.[7,8]

If the splitting is dipolar in origin, its magnitude should be independent of the strength of the magnetic field in which the NMR experiment is performed.[9,10] On the other hand, splitting due to a diamagnetic susceptibility effect should be proportional to the field strength.[11,12] We obtained room temperature ^{1}H NMR spectra for samples of oriented (parallel to H_0) Fortisan (a highly oriented and highly crystalline rayon formed by the saponification of acetate), equilibrated at 65% relative humidity (about 9% moisture content), at two frequencies (and correspondingly, different field strengths): 15.1 and 56.4 MHz. In each case

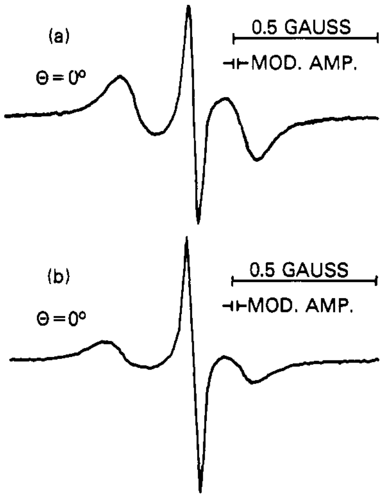

Figure 1. ^{1}H NMR spectra obtained using oriented Fortisan rayon fiber equilibrated at 65% relative humidity. Spectra were made at 15.1 MHz (a) and 56.4 MHz (b) with the fiber parallel to the magnetic field. The temperature was about 28 °C; the sweep frequency was 80 Hz, and the modulation amplitude was 17 mg.

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the spectrum consisted of a doublet and a singlet shifted slightly upfield from the doublet center (see Figure 1).

The doublet separation was the same in each case, ruling out, for this system at least, an explanation based on diamagnetic susceptibility. The method, of course, is equally applicable to other systems.

References and Notes

(1) H. J. C. Berendsen, *J. Chem. Phys.*, **36**, 3297–3305 (1962).
(2) C. Migchelsen and H. J. C. Berendsen, *J. Chem. Phys.*, **59**, 296–305 (1973).
(3) R. E. Dehl, *J. Chem. Phys.*, **48**, 831–835 (1968).
(4) B. M. Fung, *Science*, **190**, 800 and 801 (1975).
(5) P. Ducros, *Bull. Soc. F. Mineral. Cristallogr.*, **83**, 85–112 (1960).
(6) J. Hougardy, W. E. E. Stone, and J. J. Fripiat, *J. Chem. Phys.*, **64**, 3840–3851 (1976).
(7) M. P. Klein, and D. E. Phelps, *Nature (London)*, **224**, 70 and 71 (1967).
(8) G. Chapman and K. A. McLauchlan, *Nature (London)*, **215**, 391 and 392 (1969).
(9) G. E. Pake, *J. Chem. Phys.*, **16**, 327–336 (1948).
(10) H. S. Gutowsky and G. E. Pake, *J. Chem. Phys.*, 18, 162–170 (1950).
(11) M. Shporer, A. J. Vega, and *J.*, A. Frommer, *J. Polym. Sci.*, **12**, 645–653 (1974).
(12) A. Abragam, "The Principles of Nuclear Magnetism", Oxford University Press, London, 1967.

Communications to the Editor

Exactly Soluble Model for High-Frequency Viscoelastic Behavior of Polymer Solutions

Experimental data[1,2] for the high-frequency viscoelastic behavior of polymer solutions display a departure from predicted Rouse–Zimm behavior with a plateau region, $[\eta]_\infty$, in the viscosity occurring around 10^5–10^6 Hz for solvents with viscosities $\eta_0 \sim 10^1$–10^2 P. The observed $[\eta]_\infty$ is independent of molecular weight for long enough chains (e.g., polystyrene and $M \gtrsim 2 \times 10^4$). Values of $[\eta]_\infty$ are roughly 1–2 orders of magnitude smaller than the zero-frequency values $[\eta]$ (depending on M), and $[\eta]_\infty$ is correlated to the degree of side-chain flexibility. The experimental data were originally fit[1] to the phenomenological Cerf–Peterlin theory[3] of internal viscosity with a particular choice of its mode dependence, but recent calculations[2] with exact Rouse–Zimm eigenvalues do not reproduce the observed results. It will be of interest to determine a phenomenological form for the internal viscosity (with different mode dependence and, perhaps, frequency dependence[4]) which can satisfactorily explain the data.

Theoretical calculations of $[\eta]_\infty$ with models involving fixed bond lengths and possibly fixed bond angles give values 1.5 orders of magnitude too small,[4-6] so these constraints cannot be responsible for the $[\eta]_\infty$. Recent Monte-Carlo calculations by Fixman[7] for Rouse chains with fixed bond lengths and angles as well as with hindered bond rotations demonstrate that the latter feature can produce an $[\eta]_\infty$ of the correct qualitative form.

In an attempt to further understand the molecular origins of this perplexing $[\eta]_\infty$, we have introduced an exactly solvable model of polymer chain dynamics with the following important features: Side group motions are explicitly incorporated through the use of additional Rouse units. Hindered rotational potentials are simulated by side group–side group interactions. Constraints on bond lengths and angles are ignored consistent with their minor influence on $[\eta]_\infty$. Our model is one of a Rouse chain of units of type B with Kuhn length σ_B. Attached to each B unit is an A unit representing the side group, and the A–B Kuhn length is σ_A. The model differs from Kästner's model[8] of a Rouse comblike chain by having an interaction between successive A–B bond vectors, $\mathbf{y}_i - \mathbf{x}_i$, which is proportional to $(\mathbf{y}_i - \mathbf{x}_i)\cdot(\mathbf{y}_{i\pm1} - \mathbf{x}_{i\pm1})$, thereby providing hindered rotation potentials. The model is represented in Figure 1. In the absence of the hindering rotation interaction, the A units would move in three dimensions, harmonically bound about its B unit, but the interaction tends to align the A–B bonds in syndiotactic configurations. The model can be generalized to include a preferred

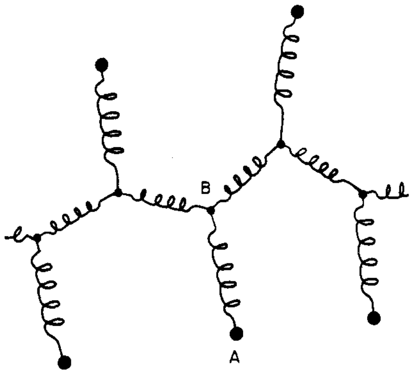

Figure 1. Schematic representation of the model. The B units correspond to an ordinary Rouse chain, while the A units (side groups) convert the chain into a comblike polymer. Interactions between neighboring AB bonds lead to hindered rotational potentials.

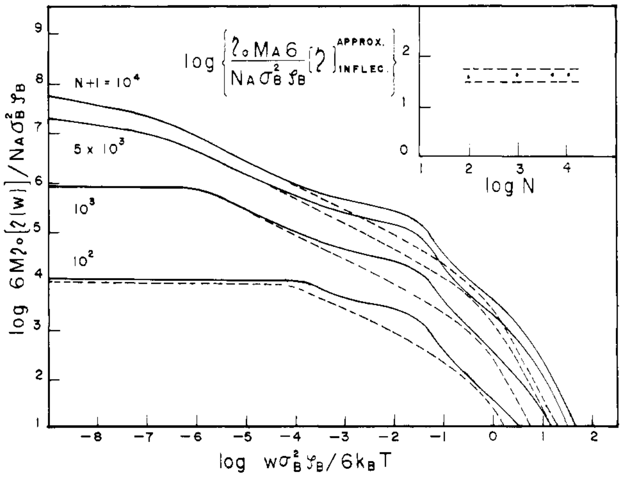

Figure 2. Plot of log $[\eta(\omega)]$ vs. log ω for the model (solid lines) and for a pure Rouse chain (dashed lines) where single units C_i replace a pair of A_i–B_i units. The parameters are $\gamma = 0.22$, $\epsilon_2 = 2\epsilon_3$, $\epsilon_3 = 0.125$. The curves are given for various chain lengths (N), and the insert shows that the $[\eta]_\infty$ is roughly independent of N. The dashed lines indicate approximate uncertainty in choice of $[\eta]_{\text{inflection}}{}^{\text{approx}}$.