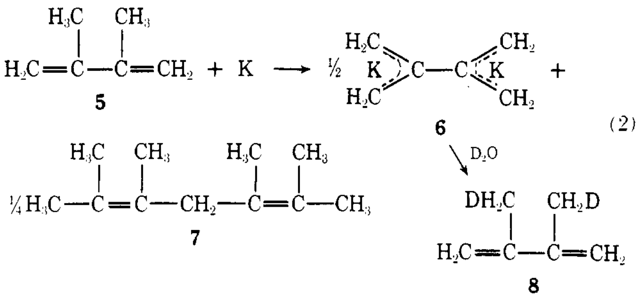
2,3,6,7-tetramethyl-2,6-octadiene (7),[4] $C_{12}H_{22}$; yield, 50%.



(2)

The nmr spectrum of 6 shows a single peak at δ 1.4 ppm and the deuteriolysis of 6 with D_2O gave 2,3-dimethylenebutane-*1,4-d*$_2$ (8)[5] in a quantitative yield. These results can be interpreted by assigning the symmetrical structure, which is represented in eq 2, for 6.

The polymerization of 5 was carried out in tetrahydrofuran at 30° with 6 or metallic potassium as a catalyst. Quite similar results were obtained with both catalysts (Table I). These results are also in good agreement with those reported by Schué.[6] Thus, the initiation reaction in the polymerization of 5 with metallic potassium is considered to be the formation of 6 and the polymerization proceeds *via* 6 with the dianionic active species.

(4) The structure of 7 is supported by following data: ir 1636 (ν(C=C)) 889 (trans δ(CH) of —CH=CH—); nmr δ 1.50 (s, 9 H, CH_3—) 1.98 (s, 2 H, —CH_2—C=); *Anal.* Found; 166 (mol wt by ms). Calcd for $C_{12}H_{22}$: 166.

(5) The structure of 8 is supported by the following data: δ 1.30 (s, 4 H, —CH_2D) 4.46 (s, 4 H, CH_2=); *Anal.* Found: 84 (mol wt by ms). Calcd for $C_6H_8D_2$: 84.

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Hajime Yasuda, Akio Yasuhara, and Hisaya Tani*
Department of Polymer Science
Faculty of Science, Osaka University
Toyonaka, Osaka 560, Japan

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Quasielastic Light Scattering from Nonideal Solutions

According to current quasielastic light-scattering theories on infinitely dilute solutions of macromolecules, internal relaxation modes can be observed for sufficiently large molecules.[1-4] These internal molecular relaxation terms, however, are coupled to the center-of-mass translational diffusion term. Therefore, the slowest relaxation time obtainable from light scattered by these macromolecules is predicted to be due to pure diffusion. Recent experimental results of quasielastic light scattering from solutions of DNA[5,6] and polyacrylamide[7] do not conform to this theoretical prediction. In these systems, two relaxation times differing by a factor of ~20–50 have the predicted K^2 dependence for translational diffusion. The presence of two modes of translational diffusion is assumed to be due to the highly nonideal nature of the solution in which molecular motions are strongly affected by neighboring molecules.

The subject of the present communication is the development of a general form for the autocorrelation function of the phototube current resulting from light scattered by nonideal solutions.[8] The phototube current autocorrelation function $\langle I(0)I(\tau)\rangle$ is related to the K-space polarizability of the sample $\alpha(\mathbf{K},\tau)$ by

$$\langle I(0)I(\tau)\rangle = A\langle\alpha^*(\mathbf{K},0)\alpha(\mathbf{K},0)\alpha^*(\mathbf{K},\tau)\alpha(\mathbf{K},\tau)\rangle \quad (1)$$

where A is a proportionality constant, τ is the time delay, and the angular brackets denote the ensemble average. Restricting the development to center-of-mass motions, we write the excess polarizability of the scattering volume centered about the point defined by the vector $\mathbf{r}$ in an arbitrary reference frame as

$$\alpha(\mathbf{r},t) = \alpha\sum_J \delta[\mathbf{R}_J(t) - \mathbf{r}] \quad (2)$$

where $\mathbf{R}_J(t)$ locates the center-of-mass of the Jth particle at time t and $\delta(x)$ is the Dirac delta function. All particles are assumed to have the same polarizability α.

The Fourier transform of eq 2 is the K-space polarizability

$$\alpha(\mathbf{K},t) = \alpha\sum_J \exp[-i\mathbf{K}\cdot\mathbf{R}_J(t)] \quad (3)$$

Substitution of eq 3 into eq 1 gives the expression

$$\langle I(0)I(\tau)\rangle = A\alpha^4\sum_G\sum_H\sum_I\sum_J\langle\exp[-i\mathbf{K}\cdot(\mathbf{R}_G(0) - \mathbf{R}_H(0) + \mathbf{R}_I(\tau) - \mathbf{R}_J(\tau))]\rangle \quad (4)$$

Since interference occurs only when quantities of opposite signs are paired, there are only four groups of time-dependent terms in eq 4; $G = J \neq H = I$, $G = I \neq J = H$, $G = J \neq H \neq I$, and $G \neq H \neq I \neq J$. That is, there are $N(N - 1)$ terms in the first two groups, $N(N - 1)(N - 2)$ terms in the third group, and $N(N - 1)(N - 2)(N - 3)$ terms in the fourth group. Thus, we define the time-dependent terms for the four groups by

$$C_1(\tau) \equiv \langle\exp[-i\mathbf{K}\cdot(\mathbf{R}_1(0) - \mathbf{R}_1(\tau))]\exp[-i\mathbf{K}\cdot(\mathbf{R}_2(\tau) - \mathbf{R}_2(0))]\rangle \quad (5a)$$

$$C_2(\tau) \equiv \langle\exp[-i\mathbf{K}\cdot(\mathbf{R}_1(0) - \mathbf{R}_2(\tau))]\exp[-i\mathbf{K}\cdot(\mathbf{R}_1(\tau) - \mathbf{R}_2(0))]\rangle \quad (5b)$$

$$C_3(\tau) \equiv \langle\exp[-i\vec{\mathbf{K}}\cdot(\mathbf{R}_1(0) - \mathbf{R}_1(\tau))]\exp[-i\mathbf{K}\cdot(\mathbf{R}_2(\tau) - \mathbf{R}_3(0))]\rangle \quad (5c)$$

$$C_4(\tau) \equiv \langle\exp[-i\vec{\mathbf{K}}\cdot(\mathbf{R}_1(0) - \mathbf{R}_2(\tau))]\exp[-i\mathbf{K}\cdot(\mathbf{R}_3(\tau) - \mathbf{R}_4(0))]\rangle \quad (5d)$$

where the subscripts 1, 2, 3, and 4 replace the alphabetic labels since the molecules are identical. The quantity $C_1(\tau)$ represents the correlation of two freely diffusing particles. In the infinite dilution case or Gaussian approximation, this term reduces to the square of the single particle correlation function

$$C_1(\tau) \longrightarrow D_1(\tau)D_1^*(\tau) \qquad \text{(infinite dilution)} \quad (6)$$

where

$$D_1(\tau) \equiv \langle\exp[-i\mathbf{K}\cdot(\mathbf{R}_1(0) - \mathbf{R}_1(\tau))]\rangle \quad (7)$$

and * denotes the complex conjugate. In more concentrated solutions or systems of very large particles, there may be a correlation between freely diffusing particles, such as an excluded volume effect. Therefore, $C_1(\tau)$ defined by eq

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(8) K. S. Schmitz, 165th National Meeting of the American Chemical Society, Dallas, Texas, April 8-13.

5a is the general form for the single particle correlation function. The $C_2(\tau)$ term represents the correlation of a single pair of molecules in the solution. This is, in effect, an *induced* or *perturbed* motion in one molecule by the presence of the second molecule. The *extreme limiting case* is dimerization, where the lifetime of the aggregate (dimer) is long compared to the duration of the experiment.

The quantity $C_3(\tau)$ represents the correlation of a freely diffusing particle with particles whose motions are coupled and, likewise, $C_4(\tau)$ correlates motions of two different pairs of particles. These processes can be schematically represented by a diagram resembling that of an activated complex reaction, *i.e.*

$$\underset{\substack{D_1(\tau)\\ \text{(infinite}}}{A} + \underset{\substack{D_1(\tau)\\ \text{dilution)}}}{A} \rightleftharpoons \underset{\substack{C_1(\tau)\\ \text{(free diffusion)}}}{2A} \rightleftharpoons \underset{\substack{C_2(\tau)\\ \text{(pair correlation)}}}{A_2} \qquad (8)$$

The term A_2 denotes coupled or perturbed motion and *not necessarily* dimerization. Similar diagrams can be written for $C_3(\tau)$ and $C_4(\tau)$.

The general form for the normalized phototube current autocorrelation function can be written as

$$\langle I(0)I(\tau)\rangle \simeq \frac{N^2(WC_1(\tau) + XC_2(\tau)) + N^3YC_3(\tau) + N^4ZC_4(\tau)}{N^2(W + X) + N^3Y + N^4Z} \qquad (9)$$

where W, X, Y, and Z are amplitudes that depend on the polymer dimensions and concentration. The functional dependence is inferred by the observation that the two diffusion modes of polyacrylamide merge to one mode at high salt concentration in reasonably concentrated polymer solutions because the molecular dimensions are greatly reduced.[7] The longest relaxation time in DNA, however, persists even at high salt concentration (2 M NaCl[5]) and dilute DNA concentration (6 μg/ml[6]). This difference in behavior could be explained by considering the dimensions of the molecule. Even at the most dilute concentration in the DNA system, the average distance between the molecules is the same order of magnitude as the molecular dimensions.[6] We assume, therefore, that $X \to 0$, $Y \to 0$, and $Z \to 0$ in the limit $\langle R_G\rangle/\langle L\rangle \to 0$, where $\langle R_G\rangle$ is the average radius of gyration and $\langle L\rangle$ is the average distance between the centers of mass of the particles.

The longest relaxation time in $C_1(\tau)$ and $C_3(\tau)$ is the single-particle diffusion time. Any slower relaxation modes observed by experiment can only come from $C_2(\tau)$ or $C_4(\tau)$. The shortest relaxation time in the DNA system is currently identified with single-particle translational diffusion[5,6] (*i.e.*, the $C_1(\tau)$ term). If this interpretation is correct, then the longest observation relaxation mode could conceivably come from the $C_2(\tau)$ term since it also depends on N^2. The data does not rule out the possibility, however, that the shorter relaxation time may be part of the $C_4(\tau)$ term since each of the four groups contain several relaxation modes in these systems of large particles.

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Kenneth S. Schmitz
Florida Atlantic University
Boca Raton, Florida 33432

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