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Light Scattering by Chain Molecules Composed of Anisotropic Units

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ABSTRACT: The theory of Rayleigh light scattering by independent isotropic systems composed of anisotropic units developed by Nagai is extended according to the rotational isomeric state model. Calculations for the polymethylene chain indicate that for molecules in the random-coil state in dilute solution the terms arising from the anisotropy of the units should be small in comparison to those arising from the scalar mean polarizability of the molecules. However, for molecules with a regular structure such as a helix or all-trans conformation the anisotropy of the units must be taken into account.

A theory of Rayleigh light scattering by independent isotropic systems composed of anisotropic units has been developed by Nagai.[1] In this paper we take the system to be a chain molecule with n skeletal bonds and assign a vector $\mathbf{l}_i$ to each main-chain bond and a polarizability tensor α_i to each unit of the chain composed of the skeletal bond and the preceding atom or group(s) attached to that atom.[2]

The intensity of Rayleigh scattering in the forward direction depends on the quantities[2]

$$\bar{\alpha}^2 = \sum_{i,j} \bar{\alpha}_i \bar{\alpha}_j \tag{1}$$

$$\langle \gamma^2 \rangle = \frac{3}{2} \sum_{i,j} \langle \hat{\boldsymbol{\alpha}}_i{}^{\mathrm{R}} \hat{\boldsymbol{\alpha}}_j{}^{\mathrm{C}} \rangle \tag{2}$$

where $\bar{\alpha}_i = (1/3)\mathrm{Tr}\alpha_i$ is the scalar mean polarizability of the ith unit, $\bar{\alpha}^2$ is the square of the molecular scalar mean polarizability, $\hat{\alpha}_i = \alpha_i - \bar{\alpha}_i \boldsymbol{E}_3$ is the anisotropy tensor of the ith unit, $\boldsymbol{E}_3$ is the identity matrix of order three, $\hat{\boldsymbol{\alpha}}_i{}^{\mathrm{R}}$ and $\hat{\boldsymbol{\alpha}}_i{}^{\mathrm{C}}$ are the row and column forms of $\hat{\boldsymbol{\alpha}}_i$, respectively, $\langle \gamma^2 \rangle$ is the mean-squared optical anisotropy, and the angular brackets denote an average over all configurations of the chain.

If the intensity of Rayleigh scattering as a function of angle is expanded in a power series in the quantity $\mu = 4\pi/\lambda \sin \theta/2$, where λ is the wavelength of light in the scattering medium and θ is the angle between the incident light and the scattered light in the scattering plane, then to terms of order μ^2 the intensity will also depend on the quantities[1] (see Appendix)

$$\langle Q_1 \rangle = \sum_{i<j} \langle \bar{\alpha}_i \bar{\alpha}_j r_{ij}{}^2 \rangle \tag{3}$$

$$\langle Q_2 \rangle = \sum_{i<j} \langle \bar{\alpha}_i \boldsymbol{r}_{ij}{}^{\mathrm{T}} \hat{\boldsymbol{\alpha}}_j \boldsymbol{r}_{ij} \rangle \tag{4}$$

$$\langle Q_3 \rangle = \sum_{i<j} \langle \boldsymbol{r}_{ij}{}^{\mathrm{T}} \hat{\boldsymbol{\alpha}}_i \boldsymbol{r}_{ij} \bar{\alpha}_j \rangle \tag{5}$$

$$\langle Q_4 \rangle = \sum_{i<j} \langle r_{ij}{}^2 \hat{\boldsymbol{\alpha}}_i{}^{\mathrm{R}} \hat{\boldsymbol{\alpha}}_j{}^{\mathrm{C}} \rangle \tag{6}$$

$$\langle Q_5 \rangle = \sum_{i<j} \langle \boldsymbol{r}_{ij}{}^{\mathrm{T}} \hat{\boldsymbol{\alpha}}_i \hat{\boldsymbol{\alpha}}_j \boldsymbol{r}_{ij} \rangle \tag{7}$$

where

$$\boldsymbol{r}_{ij} = \sum_{k=i+1}^{j} \boldsymbol{l}_k$$

is the vector from the ith unit to the jth unit and the superscript T denotes the transpose.

For a random flight chain, all the above five invariants are zero, except the first. Nagai has evaluated these averages for the Porod-Kratky chain model.[1] In this paper we evaluate the above quantities according to the rotational isomeric state model[2] and carry out calculations for the polymethylene chain.

Theoretical

A cartesian coordinate system is chosen for each unit with the x_i axis along the ith skeletal bond, the z_i axis perpendicular to the plane defined by bonds i and $i - 1$, and the y_i axis chosen to complete a right-handed coordinate system. A vector expressed in the frame of reference of bond $i + 1$ can be transformed into the coordinate system of bond i by the orthogonal matrix

$$\boldsymbol{T}_i = \begin{bmatrix} \cos\theta & \sin\theta & 0 \\ \sin\theta\cos\varphi & -\cos\theta\cos\varphi & \sin\varphi \\ \sin\theta\sin\varphi & -\cos\theta\sin\varphi & -\cos\varphi \end{bmatrix} \tag{8}$$

where θ_i is the angle between vectors $\mathbf{l}_{i+1}$ and $\mathbf{l}_i$ (the supplement of the normal valence angle) and φ_i is the angle of rotation of bond $i + 1$ around bond i relative to bond $i - 1$, measured from the trans state for which $\varphi = 0°$.

The quantity of $\bar{\alpha}^2$ depends only on the scalars $\bar{\alpha}_i$ and $\bar{\alpha}_j$ so that no averaging is required. The evaluation of the mean-squared optical anisotropy has been developed elsewhere,[3] but is reproduced here for illustration before proceeding to the more complex averages.

Initially a particular configuration is considered, so that all $\boldsymbol{T}_i$'s are specified. The sum is arranged so that the factors in each element of the sum are ordered with respect to the indices, and all the vectors and tensors are expressed in a common frame of reference.

$$\gamma^2 = \frac{3}{2}\Big[\sum_{i=j}\hat{\alpha}_i{}^2 + 2\sum_{i<j}\hat{\boldsymbol{\alpha}}_i{}^{\mathrm{R}}(\boldsymbol{T}\times\boldsymbol{T})_i{}^{(j-i)}\hat{\boldsymbol{\alpha}}_j{}^{\mathrm{C}}\Big] \tag{9}$$

where $\hat{\alpha}_i{}^2 = \hat{\boldsymbol{\alpha}}_i{}^{\mathrm{R}}\hat{\boldsymbol{\alpha}}_i{}^{\mathrm{C}}$, $(\boldsymbol{T}\times\boldsymbol{T})$ is the self-direct product of $\boldsymbol{T}$, and $(\boldsymbol{T}\times\boldsymbol{T})_i{}^{(j-i)}$ denotes the serial product commencing with $(\boldsymbol{T}\times\boldsymbol{T})_i$ and comprising $j-i$ factors. The above sum can be executed by serial multiplication of matrices.[4]

$$\gamma^2 = \mathrm{C}_{11}{}^*\boldsymbol{P}_i{}^{(n)}\mathrm{C}_{11} \tag{10}$$

where

$$\mathrm{C}_{11}{}^* = (1\ 0\ \ldots .\ 0) \tag{11}$$

$$\boldsymbol{P}_i = \begin{bmatrix} 1 & 2\hat{\boldsymbol{\alpha}}^{\mathrm{R}}(\boldsymbol{T}\times\boldsymbol{T}) & (3/2)\hat{\alpha}^2 \\ 0 & (\boldsymbol{T}\times\boldsymbol{T}) & (3/2)\hat{\boldsymbol{\alpha}}^{\mathrm{C}} \\ 0 & 0 & 1 \end{bmatrix}_i \tag{12}$$

$$\mathrm{C}_{11} = \mathrm{col}(0\ 0\ \ldots .\ 0\ 1) \tag{13}$$

In order to obtain the averaged quantity $\langle\gamma^2\rangle$, the configuration partition function Z must be obtained.[2]

$$Z = \mathrm{J}^*\boldsymbol{U}_1{}^{(n)}\mathrm{J} \tag{14}$$

where the $\boldsymbol{U}$ are statistical weight matrices, and

$$\mathrm{J}^* = (1\ 0\ \ldots .\ 0) \tag{15}$$

$$\mathrm{J} = \mathrm{col}(1\ 1\ \ldots ..\ 1) \tag{16}$$

The order of $\boldsymbol{U}$ and hence J^* and J is determined by the number of rotational states for each bond.

The mean-squared optical anisotropy $\langle\gamma^2\rangle$ is then given by[4]

$$\langle\gamma^2\rangle = Z^{-1}\hat{\mathrm{J}}^*\hat{\boldsymbol{P}}_1{}^{(n)}\hat{\mathrm{J}} \tag{17}$$

where

$$\hat{\boldsymbol{P}}_i = [(\boldsymbol{U}\times\boldsymbol{E}_{11})\,||\boldsymbol{P}||\,]_i \tag{18}$$

$||\boldsymbol{P}||_i$ denotes the pseudo-diagonal matrix consisting of "elements" $\boldsymbol{P}_i(1)$, $\boldsymbol{P}_i(2)$, $\ldots\boldsymbol{P}_i(\nu)$ for the respective rotational states 1 to ν in diagonal array, $\boldsymbol{E}_{11}$ is the identity matrix of order eleven, and

$$\hat{\mathrm{J}}^* = \mathrm{J}^*\times\mathrm{C}_{11}{}^* \tag{19}$$

$$\hat{\mathrm{J}} = \mathrm{J}\times\mathrm{C}_{11} \tag{20}$$

The basic procedure outlined for the mean-squared optical anisotropy is followed for each of the more complex averages. The first sum Q_1 can be expressed as

$$Q_1 = \sum_{i<j}\bar{\alpha}_i\Big[\sum_{i+1\leq h=k\leq j} l_h{}^2 + 2\sum_{i+1\leq h<k\leq j}\mathbf{l}_h{}^{\mathrm{T}}(\boldsymbol{T})_h{}^{(k-h)}\mathbf{l}_k\Big]\bar{\alpha}_j \tag{21}$$

This sum can be executed by serial multiplication of matrices

$$Q_1 = \mathbf{C}_{15}{}^*\boldsymbol{M}_1{}^{(n)}\mathbf{C}_{15} \tag{22}$$

where

$$\boldsymbol{M}_i = \begin{bmatrix} 1 & \bar{\alpha} & 0 & 0 & 0 \\ 0 & 1 & 2\mathbf{l}^{\mathrm{T}}\boldsymbol{T} & l^2 & l^2\bar{\alpha} \\ 0 & 0 & \boldsymbol{T} & \mathbf{l} & \mathbf{l}\bar{\alpha} \\ 0 & 0 & 0 & 1 & \bar{\alpha} \\ 0 & 0 & 0 & 0 & 1 \end{bmatrix}_i \tag{23}$$

The average is given by

$$\langle Q_1\rangle = Z^{-1}\hat{\mathrm{J}}^*\hat{\boldsymbol{M}}_1{}^{(n)}\hat{\mathrm{J}} \tag{24}$$

where

$$\hat{\mathrm{J}}^* = \mathrm{J}^*\times\mathrm{C}_{15}{}^* \tag{25}$$

$$\hat{\boldsymbol{M}}_i = [(\boldsymbol{U}\times\boldsymbol{E}_{15})\,||\boldsymbol{M}||\,]_i \tag{26}$$

and

$$\hat{\mathrm{J}} = \mathrm{J}\times\mathbf{C}_{15} \tag{27}$$

The procedure for obtaining the averaged quantity for all the other invariants is entirely analogous and will be omitted henceforth.

For a chain composed of identical subunits, $\langle Q_1\rangle$ reduces to $n^2\bar{\alpha}_i{}^2\langle s^2\rangle$ where $\langle s^2\rangle$ is the mean-squared radius of gyration.[1]

The quantity Q_2 is given by

$$Q_2 = \sum_{i<j}\bar{\alpha}_i\Big[\sum_{i+1\leq h=k\leq j}(\mathbf{l}_h{}^{\mathrm{T}}\times\mathbf{l}_h{}^{\mathrm{T}})(\boldsymbol{T}\times\boldsymbol{T})_h{}^{(j-h)} + 2\sum_{i+1\leq h<k\leq j}\mathbf{l}_h{}^{\mathrm{T}}(\boldsymbol{T})_h{}^{(k-h)}(\boldsymbol{E}_3\times\mathbf{l}_k{}^{\mathrm{T}})(\boldsymbol{T}\times\boldsymbol{T})_k{}^{(j-k)}\Big]\hat{\boldsymbol{\alpha}}_j{}^{\mathrm{C}} \tag{28}$$

The generator matrix N_i is

$$\boldsymbol{N}_i = \begin{bmatrix} 1 & \bar{\alpha} & 0 & 0 & 0 \\ 0 & 1 & 2\mathbf{l}^{\mathrm{T}}\boldsymbol{T} & (\mathbf{l}^{\mathrm{T}}\times\mathbf{l}^{\mathrm{T}})(\boldsymbol{T}\times\boldsymbol{T}) & (\mathbf{l}^{\mathrm{T}}\times\mathbf{l}^{\mathrm{T}})\hat{\boldsymbol{\alpha}}^{\mathrm{C}} \\ 0 & 0 & \boldsymbol{T} & (\boldsymbol{E}_3\times\mathbf{l}^{\mathrm{T}})(\boldsymbol{T}\times\boldsymbol{T}) & (\boldsymbol{E}_3\times\mathbf{l}^{\mathrm{T}})\hat{\boldsymbol{\alpha}}^{\mathrm{C}} \\ 0 & 0 & 0 & (\boldsymbol{T}\times\boldsymbol{T}) & \hat{\boldsymbol{\alpha}}^{\mathrm{C}} \\ 0 & 0 & 0 & 0 & 1 \end{bmatrix}_i \tag{29}$$

The evaluation of Q_3 is formally similar to that for Q_2 and the generator matrix $\boldsymbol{R}_i$ is given by

$$\boldsymbol{R}_i = \begin{bmatrix} 1 & \hat{\boldsymbol{\alpha}}^{\mathrm{R}}(\boldsymbol{T}\times\boldsymbol{T}) & 0 & 0 & 0 \\ 0 & (\boldsymbol{T}\times\boldsymbol{T}) & 2(\mathbf{l}\times\boldsymbol{E}_3)\boldsymbol{T} & (\mathbf{l}\times\mathbf{l}) & (\mathbf{l}\times\mathbf{l})\bar{\alpha} \\ 0 & 0 & \boldsymbol{T} & \mathbf{l} & \mathbf{l}\bar{\alpha} \\ 0 & 0 & 0 & 1 & \bar{\alpha} \\ 0 & 0 & 0 & 0 & 1 \end{bmatrix}_i \tag{30}$$

The quantity $r_{ij}{}^2$ is given by[4]

$$r_{ij}{}^2 = \mathrm{C}_5{}^*\boldsymbol{G}_{i+1}{}^{(j-1)}\mathrm{C}_5 \tag{31}$$

where

$$G_i = \begin{bmatrix} 1 & 21^{\mathrm{T}}\boldsymbol{T} & l^2 \\ 0 & \boldsymbol{T} & 1 \\ 0 & 0 & 1 \end{bmatrix}_i \tag{32}$$

Thus Q_4 can be expressed as

$$Q_4 = \sum_{i<j}[\mathbf{C}_5{}^* \times (\hat{\boldsymbol{\alpha}}^{\mathrm{R}}(\boldsymbol{T} \times \boldsymbol{T}))]_i \times [\boldsymbol{G} \times \boldsymbol{T} \times \boldsymbol{T}]_{i+1}{}^{(j-i-1)}[\boldsymbol{G}\mathbf{C} \times \hat{\boldsymbol{\alpha}}^{\mathrm{C}}]_j \tag{33}$$

and the generator matrix $\boldsymbol{S}_i$ as

$$\boldsymbol{S}_i = \begin{bmatrix} 1 & [\mathbf{C}_5{}^* \times (\hat{\boldsymbol{\alpha}}^{\mathrm{R}}(\boldsymbol{T} \times \boldsymbol{T}))] & 0 \\ 0 & [\boldsymbol{G} \times \boldsymbol{T} \times \boldsymbol{T}] & [\boldsymbol{G}\mathbf{C} \times \hat{\boldsymbol{\alpha}}^{\mathrm{C}}] \\ 0 & 0 & 1 \end{bmatrix} \tag{34}$$

The final quantity Q_5 is more complicated. It is given by

$$\begin{aligned} Q_5 = \sum_{i<j} \hat{\boldsymbol{\alpha}}_i{}^R \Bigg[\sum_{i+1 \leq h=k \leq j} & (\boldsymbol{T} \times \boldsymbol{T})_i{}^{(h-i)}(\mathbf{1}_h{}^{\mathrm{T}} \times \boldsymbol{E}_3 \times \mathbf{1}_h) \cdot \\ (\boldsymbol{T} \times \boldsymbol{T})_h{}^{(j-h)} + \sum_{i+1 \leq h<k \leq j} & (\boldsymbol{T} \times \boldsymbol{T})_i{}^{(h-i)}(\boldsymbol{E}_9 \times \mathbf{1}_h{}^{\mathrm{T}})(\boldsymbol{T} \times \\ \boldsymbol{T} \times \boldsymbol{T})_h{}^{(k-h)}(\mathbf{1}_k \times \boldsymbol{E}_9) \cdot (\boldsymbol{T} \times \boldsymbol{T})_k{}^{(j-k)} + & \sum_{i+1 \leq k<h \leq j} (\boldsymbol{T} \times \\ \boldsymbol{T})_i{}^{(k-i)}(\mathbf{1}_k \times \boldsymbol{E}_3)(\boldsymbol{T})_k{}^{(h-k)}(\boldsymbol{E}_3 \times & \mathbf{1}_h{}^{\mathrm{T}})(\boldsymbol{T} \times \boldsymbol{T})_h{}^{(j-h)} \Bigg] \hat{\boldsymbol{\alpha}}_j{}^{\mathrm{C}} \end{aligned} \tag{35}$$

and the generator matrix $\boldsymbol{W}_i$ by

$$W_i = \begin{bmatrix} 1 & \hat{\boldsymbol{\alpha}}^{\mathrm{R}}(\boldsymbol{T} \times \boldsymbol{T}) & 0 & 0 & 0 & 0 \\ 0 & (\boldsymbol{T} \times \boldsymbol{T}) & (\boldsymbol{E}_9 \times 1^{\mathrm{T}}\boldsymbol{T})(\boldsymbol{T} \times \boldsymbol{T} \times \boldsymbol{T}) & (1 \times \boldsymbol{E}_3)\boldsymbol{T} & (1^{\mathrm{T}} \times \boldsymbol{E}_3 \times 1)(\boldsymbol{T} \times \boldsymbol{T}) & (1^{\mathrm{T}} \times \boldsymbol{E}_3 \times 1)\hat{\boldsymbol{\alpha}}^{\mathrm{C}} \\ 0 & 0 & (\boldsymbol{T} \times \boldsymbol{T} \times \boldsymbol{T}) & 0 & (1 \times \boldsymbol{E}_9)(\boldsymbol{T} \times \boldsymbol{T}) & (1 \times \boldsymbol{E}_9)\hat{\boldsymbol{\alpha}}^{\mathrm{C}} \\ 0 & 0 & 0 & \boldsymbol{T} & (\boldsymbol{E}_3 \times 1^{\mathrm{T}})(\boldsymbol{T} \times \boldsymbol{T}) & (\boldsymbol{E}_3 \times 1^{\mathrm{T}})\hat{\boldsymbol{\alpha}}^{\mathrm{C}} \\ 0 & 0 & 0 & 0 & (\boldsymbol{T} \times \boldsymbol{T}) & \hat{\boldsymbol{\alpha}}^{\mathrm{C}} \\ 0 & 0 & 0 & 0 & 0 & 1 \end{bmatrix} \tag{36}$$

Model Chain Calculations

Preliminary calculations were carried out on a model chain composed of n identical units. A vector of unit length was assigned to each skeletal bond. A cylindrically symmetric polarizability tensor was chosen for each unit of the form

$$\alpha_i = \bar{\alpha}\boldsymbol{E}_3 + \Delta\alpha \begin{pmatrix} 2/3 & 0 & 0 \\ 0 & -1/3 & 0 \\ 0 & 0 & -1/3 \end{pmatrix} \tag{37}$$

with mean scalar polarizability $\bar{\alpha}_i = 1$ and $\Delta\alpha = 1$.

A three state rotation model was adopted with the trans state at $\phi_{\mathrm{t}} = 0°$ and two gauche states at $\phi_{\mathrm{g}} = \pm 120°$. The statistical weight matrix $\boldsymbol{U}_i$ takes the form

$$\boldsymbol{U}_i = \begin{bmatrix} 1 & \sigma & \sigma \\ 1 & \sigma & \sigma\omega \\ 1 & \sigma\omega & \sigma \end{bmatrix} \tag{38}$$

where $\sigma = \exp[-E_\sigma/RT]$ is the statistical weight of a gauche state and E_σ is the energy difference between the trans and gauche states. For successive rotations $g^\pm g^\mp$ an additional energy E_ω is incurred due to steric overlap; $\omega = \exp[-E_\omega/RT]$ is the statistical weight associated with this state.

These calculations were used to establish the chain-length dependence of the five invariants and to investigate the characteristic signs and magnitudes of the quantities.

The quantity $\bar{\alpha}^2$ increases as n^2 and $\langle\gamma^2\rangle$ as n so that for long chains the mean-squared optical anisotropy becomes small relative to the squared scalar mean polarizability. The quantity $\langle Q_1\rangle$ is proportional to n^3 for long chains, $\langle Q_2\rangle$ and $\langle Q_3\rangle$ to n^2, and $\langle Q_4\rangle$ and $\langle Q_5\rangle$ to n. Thus the last four invariants become small relative to $\langle Q_1\rangle$ in the limit of long chains. When the above fact is considered in the light that the $\langle Q\rangle$ invariants become important only for long chains, it is realized that the last four invariants result in a small correction to the already relatively insignificant $\langle\gamma^2\rangle$ term in the expression for the scattered intensity. However, if the chains are not in the random coil state but adopt a regular repeating conformation such as a helix or an all-trans state, then all the $\langle Q\rangle$ invariants will be important for long chains.

The quantity $\langle Q_1\rangle$ for the model chain is given by $n^2\bar{\alpha}_l{}^2\langle s^2\rangle$ as noted above. Hence it must be positive. The other four invariants may be either positive or negative depending on the values of E_σ and E_ω. Also, for $\langle Q_2\rangle$ and $\langle Q_3\rangle$, the sign could be changed by letting $\Delta\alpha = -1$ instead of 1. The relative magnitudes are in the order $\langle Q_1\rangle > \langle Q_2\rangle > \langle Q_3\rangle > \langle Q_4\rangle > \langle Q_5\rangle$.

Polymethylene Calculations

Calculations of the above five invariants were carried out using values of θ, ϕ, E_ω, l_{CC}, $\bar{\alpha}_{\mathrm{CC}}$, $\bar{\alpha}_{\mathrm{CH}}$, $\Delta\alpha_{\mathrm{CC}}$, and $\Delta\alpha_{\mathrm{CH}}$ determined previously.[2,5] The supplement of the valence angle θ was fixed at 68° and the rotation angle for the gauche states set at 120°. The rotational state energies E_σ and E_ω were taken to be 500 and 2500 cal mol^{-1}, respectively. The carbon—carbon distance is 1.53 Å. The scalar mean polarizabilities of the carbon—carbon and carbon—hydrogen bonds are $\bar{\alpha}_{\mathrm{CC}} = 0.64$ Å and $\bar{\alpha}_{\mathrm{CH}} = 0.65$ Å. And the two bond anisotropies were taken to be $\Delta\alpha_{\mathrm{CC}} = 0.95$ Å^3 and $\Delta\alpha_{\mathrm{CH}} = 0.21$ Å^3.

The values of $\langle Q_1\rangle/n^3$, $\langle Q_2\rangle/n^2$, $\langle Q_3\rangle/n^2$, $\langle Q_4\rangle/n$, and $\langle Q_5\rangle/n$ for polymethylene are plotted *vs.* n in Figure 1.

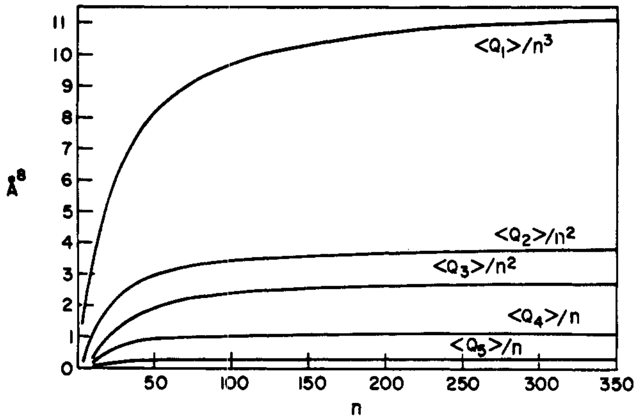

Figure 1. Plot of $\langle Q_1\rangle/n^3$, $\langle Q_2\rangle/n^2$, $\langle Q_3\rangle/n^2$, $\langle Q_4\rangle/n$, and $\langle Q_5\rangle/n$ *vs.* n for the polymethylene chain.

These results for polymethylene confirm the general conclusions reached for the model chain.

Conclusions

It should be remembered that the above calculations refer to the independent systems, and hence apply only in the limit of infinite dilution. At finite concentrations, correlations between the positions and orientations of pairs of molecules will alter the magnitudes and possibly even the signs of the quantities $\langle Q\rangle_{\text{effective}}$, where "effective" denotes the contribution per molecule at finite concentrations. However, for large molecules in the random-coil state and in the limit of infinite dilution, the contributions to the intensity due to the terms that arise from the optical anisotropy of the units should become small in comparison to the terms that arise from the isotropic scattering.

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Appendix

In order to relate the invariants in eq 1-7 to the excess Rayleigh ratios ΔR_{VV}, $\Delta R_{\text{HV}} = \Delta R_{\text{VH}}$, and ΔR_{HH}, we define

$$K = \frac{16\pi 4}{\lambda^4}\left(\frac{\tilde{n}^2 + 2}{3}\right)^2 \rho \qquad (39)$$

where λ is the wavelength of the incident light in a vacuum, $\tilde{n}$ is the refractive index of the medium, and ρ is the number density of scattering molecules; let the $\hat{\alpha}_i$ be taken as excess polarizability per unit; and assume that the solvent is isotropic so that the $\hat{\alpha}_i$ are the uncorrected molecular unit optical anisotropies. Then, to terms of order μ^2, the excess Rayleigh ratios at infinite dilution are given by[1]

$$\Delta R_{\text{VV}} = K\left[\left(\bar{\alpha}^2 + \frac{4}{45}\langle\gamma^2\rangle\right) - \left(\frac{\langle Q_1\rangle}{6} + C_1\right)\mu^2\right] \qquad (40)$$

$$\Delta R_{\text{HV}} = K\left[\frac{\langle\gamma^2\rangle}{15} - (C_2 + C_3 \cos\,\theta)\mu^2\right] \qquad (41)$$

$$\Delta R_{\text{HH}} = K\left[\frac{\langle\gamma^2\rangle}{15} + \left(\bar{\alpha}^2 + \frac{\langle\gamma^2\rangle}{45}\right)\cos^2\theta - \left(\frac{\langle Q_1\rangle}{6}\cos^2\theta + C_4 + C_5\cos\,\theta + C_6\cos^2\theta\right)\mu^2\right] \qquad (42)$$

where

$$C_1 = \frac{1}{105}[-7\langle Q_2\rangle - 7\langle Q_3\rangle + 6\langle Q_4\rangle - 4\langle Q_5\rangle] \qquad (43)$$

$$C_2 = \frac{1}{210}[8\langle Q_4\rangle - 3\langle Q_5\rangle] \qquad (44)$$

$$C_3 = \frac{1}{210}[-3\langle Q_4\rangle + 9\langle Q_5\rangle] \qquad (45)$$

$$C_4 = \frac{1}{210}[5\langle Q_4\rangle + 6\langle Q_5\rangle] \qquad (46)$$

$$C_5 = \frac{1}{210}[21\langle Q_2\rangle + 21\langle Q_3\rangle - 4\langle Q_4\rangle + 12\langle Q_5\rangle] \qquad (47)$$

$$C_6 = \frac{1}{210}[7\langle Q_2\rangle + 7\langle Q_3\rangle + 3\langle Q_4\rangle - 2\langle Q_5\rangle] \qquad (48)$$

Because of the number of variables and the complexity of these expressions, it is doubtful that all the $\langle Q\rangle$ invariants could be determined directly from the scattered intensities. However, calculation of these quantities can indicate when they will contribute significantly to the scattering.

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