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Correction of Collision-Induced Polarizabilities to the Depolarized Rayleigh Scattering by Dilute Solutions of Oligomers and Polymers

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It is shown that the correction of collision-induced polarizabilities to the depolarized Rayleigh scattering intensity may be made using a usual light-scattering photometer with a mercury lamp as a light source if its spectral distribution is narrow.

During the past decade, we have made a theoretical study of equilibrium and dynamic properties of dilute solutions of flexible polymers on the basis of the helical worm-like (HW) chain,[1)] which is considered to mimic the conformational behavior of real chains on the bond length or somewhat longer scales. Very recently, we have started an experiment to determine the mean-square optical anisotropy $\langle\Gamma^2\rangle$ of atactic polystyrene over a wide range of molecular weight including the oligomer region. This is a first step in examining whether the HW model can give a self-consistent explanation of experimental results for solution properties of flexible chains.[2,3)] The quantity $\langle\Gamma^2\rangle$ is proportional to the component R_{Hv} of the reduced scattering intensity which is determined experimentally as the ratio of the intensity of the horizontal component of scattered light per unit volume to the intensity of vertically polarized incident light. It is known that R_{Hv} consists of the intrinsic molecular contribution $R_{Hv,mol}$ and collision-induced one $R_{Hv,col}$.[4)] Since theoretical expressions for $\langle\Gamma^2\rangle$ or R_{Hv} are obtained without taking account of $R_{Hv,col}$, a proper correction to experimental data is necessary in order to separate $R_{Hv,mol}$ from the apparently observed R_{Hv}.

A correction procedure has already been proposed by Carlson and Flory,[5)] who have shown that it can deduce reasonable values of the desired $R_{Hv,mol}$ from experimental data measured on a special light-scattering photometer with a He-Ne laser as a light source and with narrow bandpass interference filters. In principle, their procedure may be applied to the case for which a high pressure vapor mercury lamp is used in place of laser as the light source, if its distribution is narrow. In this paper, we report that $R_{Hv,mol}$ may also be deduced from data measured on a Fica automatic light-scattering photometer with the mercury lamp, which has been improved to be suitable for measurements of this kind.

First, we modify their basic equations for an analysis of experimental data in order to take account of the spectral distribution $\mathscr{I}_i^0(k_i)$ of vertically polarized incident light. It is given by

$$\mathcal{I}_i^0(k_i) = I_i^0 f_i(k_i - k_i^0) \tag{1}$$

where I_i^0 is the total intensity of incident light, and f_i is the spectral distribution normalized with respect to the wave number k_i with k_i^0 its center wave number. Note that f_i may be regarded as the Dirac delta function if laser is used as the light source. Let $\mathcal{I}_{mol}(k_f|k_i)$ and $\mathcal{I}_{col}(k_f|k_i)$ be the intensities of the intrinsic molecular and collision-induced horizontal components of scattered light of wave number k_f, respectively, due to the incident light of unit intensity and of wave number k_i. The spectral distribution $\mathcal{I}_{Hv}(k_f)$ of the horizontal component of scattered light is given by

$$\mathcal{I}_{Hv}(k_f) = \int_0^\infty [\mathcal{I}_{mol}(k_f|k_i) + \mathcal{I}_{col}(k_f|k_i)]\mathcal{I}_i^0(k_i)dk_i. \tag{2}$$

If the distribution of incident light is narrow, $\mathcal{I}_{mol}$ and $\mathcal{I}_{col}$ may be assumed to be independent of k_i and regarded as functions of $\Delta k = k_f - k_i$. Following Carlson and Flory, therefore, these functions may be assumed to be of the form,

$$\mathcal{I}_\alpha(\Delta k) = I_\alpha f_\alpha(\Delta k) \qquad (\alpha = \text{mol, col}), \tag{3}$$

where I_α is the total intensity of scattered light due to the incident light of unit intensity, which corresponds to the reduced component $R_{Hv,\alpha}$, and f_α is the normalized spectral distribution and is given by

$$f_{mol}(\Delta k) = a/\pi[(\Delta k)^2 + a^2], \tag{4}$$

$$\begin{aligned} f_{col}(\Delta k) &= C(12b/7)^{12/7}e^{-12/7} && (|\Delta k| \leq 12b/7) \\ &= C|\Delta k|^{12/7}\exp(-|\Delta k|/b) && (|\Delta k| > 12b/7) \end{aligned} \tag{5}$$

with C the normalizing constant. The intrinsic molecular spectral distribution f_{mol} corresponds to the spectral density of depolarized Rayleigh scattering by a cylindrically symmetric molecule, and the half-linewidth a of the Lorentzian is proportional to its rotatory diffusion coefficient.$^{7)}$ The collision-induced spectral distribution f_{col} is an approximate one proposed by Bucaro and Litobitz,$^{4)}$ and the parameter b indicates its width.

Suppose that we measure the scattered component $\mathcal{I}_{Hv}$ through a narrow bandpass interference filter, whose transmittance curve T may be approximated by a Gaussian distribution,

$$T(k;\sigma) = T_{max}\exp[-(k-k_0)^2/\sigma^2] \tag{6}$$

with T_{max} the peak transmittance, k_0 the center wave number, and σ the parameter representing the band width. Then the observed total intensity $I_{Hv}(\sigma)$ may be written in the form,

$$I_{Hv}(\sigma) = T_{max}I_i^0[A(\sigma)I_{mol} + B(\sigma)I_{col}], \tag{7}$$

where $A(\sigma)$ and $B(\sigma)$ are coefficients defined by

$$A(\sigma) = T_{max}^{-1}\int_0^{\infty}dk_i\int_0^{\infty}dk_f f_{mol}(k_f-k_i)T(k_f;\sigma)f_i(k_i-k_i^0), \tag{8}$$

$$B(\sigma) = T_{max}^{-1}\int_0^{\infty}dk_i\int_0^{\infty}dk_f f_{col}(k_f-k_i)T(k_f;\sigma)f_i(k_i-k_i^0). \tag{9}$$

Note that Eqs. 7-9 give the same results that Carlson and Flory derived if $f_i(k_i)$ is the delta function. From the results obtained with two bandpass filters having different band widths σ, we may estimate I_{mol} and I_{col}, and therefore $R_{Hv,mol}$, from Eq. 7, which becomes a set of simultaneous linear equations for I_{mol} and I_{col}.

Next, we give a short sketch of improvements in the light-scattering photometer. Incident light of 435.8 nm wave length is made to be more monochromatic by the use of a narrow bandpass interference filter of 0.9 nm full width of half maximum (FMHW). Narrow bandpass filters of 0.9 and 2.5 nm FWHM are also placed in the scattered beam in order to permit the estimation of the collision-induced contribution. The values of σ are 28 and 79 cm^{-1} for the filters of 0.9 and 2.5 nm FWHM, respectively. Glan-Thompson prisms whose extinction ratios are smaller than 10^{-5}, are used as a polarizer and an analyzer in order to reduce those extinction ratios.

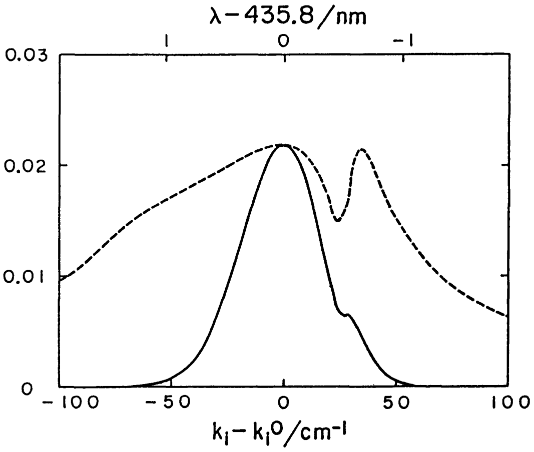

Fig. 1. Spectral distribution of the incident light (full curve) and the mercury lamp (broken curve).

The spectral distribution of the high pressure vapor mercury lamp (OSRAM, HBO 100W/2) near 435.8 nm wave length was measured using a Shimadzu GE-170 spectrometer. The measured values plotted against $k_i-k_i^0$ (or λ - 435.8 with λ the wave length) are shown in the broken curve in Fig. 1. Note that the intensity is expressed in arbitrary unit. In Fig. 1 are also shown the values of the normalized spectral distribution f_i of incident light in the full curve, which were evaluated by the use of the transmittance of the filter given by Eq. 6 with σ = 28 cm^{-1} and of the spectral distribution of the lamp. With these values, we estimate $A(\sigma)$ and $B(\sigma)$.

For solute molecules in dilute solution, it is known that the half width a of the Lorentzian f_{mol} ranges from 1 to 3 cm^{-1} for small, rapidly reorienting mole-

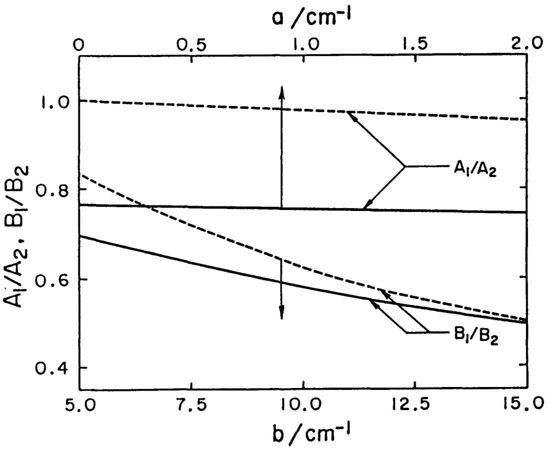

Fig. 2. Values of A_1/A_2 and B_1/B_2 plotted against a and b, respectively. The full and broken curves represent the values for the mercury lamp and laser, respectively.

cules, and is smaller than 0.001 cm^{-1} for polymer molecules. On the other hand, the parameter b appearing in Eq. 5 for the definition of f_{col} may be assumed to range from 12 to 18 cm^{-1}.5) The values of the ratios A_1/A_2 and B_1/B_2 plotted against a and b, respectively, in these ranges are shown in the full curves in Fig. 2, where A_1, A_2, B_1, and B_2 represent A(28 cm^{-1}), A(79 cm^{-1}), B(28 cm^{-1}), and B(79 cm^{-1}), respectively. For comparison, the values of the ratios for the case using laser as the light source are shown in the broken curves. The difference between these ratios determines the accuracy of the values of I_{mol} and I_{col} calculated from Eq. 7 with the observed values of $I_{Hv}(\sigma)$; the accuracy increases as the difference is increased. It is clear that this difference for laser is greater than that for the mercury lamp, and therefore the values of I_{mol} and I_{col} are more accurate for the former. However, the difference between the two cases in accuracy is rather small, so that I_{mol} and I_{col} may be determined with sufficient accuracy by the use of the mercury lamp.

Since the value of A_1/A_2 is almost independent of a in the range displayed in Fig. 2, we may use the values of A_1 and A_2 for a = 0 as done by Suter and Flory.6) On the other hand, the value of B_1/B_2 decreases with increasing b, and thus the ratio I_{col}/I_{mol} depends on the choice of b. Suter and Flory have determined this ratio for oligostyrenes, assuming that b = 12 cm^{-1}. Considering the fact that the functional form of f_{col} given by Eq. 5 is approximate, it is inadequate to use the same value of b for our case with the different light source. Thus we choose a value of b so that the ratio I_{col}/I_{mol} calculated from Eq. 7 with $I_{Hv}(\sigma)$ measured on our light-scattering photometer is identical with that determined by Suter and Flory for a solution of simple molecules.

Depolarized light scattering measurements on carbon tetrachloride solutions of cumene were carried out at 25.0 °C using the improved light-scattering photometer described above. Reagent grade carbon tetrachloride (Nakarai, 99% purity) and cumene (Wako, 98% purity) were used without further purification. It was found that the ratio above becomes identical with the one determined by Suter and Flory, if b is assigned a value of 7.5 cm^{-1}. The mean-square optical anisotropy $\langle\Gamma^2\rangle$ of atactic polystyrene will be determined with this value of b.

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