Light Scattering Study of Semiflexible Polymer Solutions III. Multicomponent Solutions

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ABSTRACT: The Rayleigh ratio R_θ for multicomponent solutions containing stiff-polymer and small-molecular components of arbitrary concentrations is formulated using the scaled particle theory for wormlike spherocylinders combined with the generalized Ornstein–Zernike integral equation. The general expression for R_θ obtained is applied to the following specific cases: (1) ternary solutions consisting of two homologous polymer species and a solvent, (2) solutions of polydisperse polymer samples, and (3) ternary solutions containing two solutes of different chemical species (*e.g.*, one polymer dissolved in a mixed solvent). The result for the case of (1) is compared with experimental data for dilute through semidilute solutions containing two different molecular-weight samples of poly(*n*-hexyl isocyanate), a semiflexible polymer.
    KEY WORDS   Light Scattering / Multicomponent Solution / Semiflexible Polymer / Structure Factor / Wormlike Cylinder Model / Poly(*n*-hexyl isocyanate) /

Light scattering is a useful technique to characterize polymer molecules and their intermolecular interactions in solution. When applying this technique to multicomponent polymer solutions, one has to take into account some special effects inherent to multicomponent systems.[1,2] In order to consider these effects, light scattering theories for multicomponent polymer solutions were proposed by many authors.[3-8] These theories are mainly concerned with dilute polymer solutions, and give us recipes to determine the true molecular weight, second virial coefficient, and radius of gyration of polymers.

In Part II of this series of papers,[9] we formulated the Rayleigh ratio R_θ or the light-scattering structure factor for isotropic solutions of monodisperse wormlike spherocylinders of arbitrary concentrations, by the scaled particle theory combined with the generalized Ornstein–Zernike integral equation. The formulated R_θ was shown to be favorably compared with experimental data for dilute through semidilute solutions of a semiflexible polymer, poly(*n*-hexyl isocyanate).

In the present study, we have extended the previous formulation to multicomponent polymer solutions containing macromolecular and small-molecular components to obtain R_θ valid at arbitrary concentrations. While the present theory is not applicable to solutions of flexible polymers due to approximations used in the formulation, it is utilized to analyze light-scattering data for concentrated multicomponent solutions containing stiff-chain polymers, which include important information to characterize intermolecular interactions among solute components.[10]

FORMULATION

Rayleigh Ratio at the Zero-Scattering Angle
    Consider a solution consisting of r macromolecular and small-molecular species (solutes) and a primary solvent, and suppose that the solute species s ($=1$, $2, \cdots, r$) is composed of $N_{0,s}$ identical isotropic scattering (monomer) units; for small-molecular species, the whole molecule is regarded as one scattering unit with $N_{0,s} = 1$. By fluctuation theories of light scattering, the excess Rayleigh ratio R_0 (for vertically polarized incident light) of this multicomponent solution over that of the primary solvent at the zero-scattering angle is related to thermodynamic properties of the solution by[2,11]

$$R_0 = (2\pi/\lambda)^4 \alpha \mu^{-1} \alpha^{\mathrm{T}} \qquad (1)$$

where λ is the wavelength of light in vacuum, α is the r-dimensional row vector whose element α_s ($s = 1, 2, \cdots, r$) is the excess polarizability of the monomer unit of species s, the superscript T represents the transpose of the row vector α, and μ is the symmetric matrix whose element is given by

$$
\mu_{st} \equiv \left(\frac{\partial^2 \mathscr{F}/k_{\mathrm{B}}T}{\partial c_{0,s}' \partial c_{0,t}'} \right)_{T,\mu^\circ,c_{0,u}'}
$$
$$
= \frac{1}{N_{0,s} N_{0,t}} \left[\frac{\partial}{\partial c_t'} \left(\frac{\mu_s}{k_{\mathrm{B}}T} \right) \right]_{T,\mu^\circ,c_{0,u}'} \qquad (2)
$$

with the free energy density $\mathscr{F}$ and the chemical potential μ_s of species s; $k_{\mathrm{B}}T$ is the Boltzmann constant multiplied by the absolute temperature. In eq 2, $c_{0,s}'$ and c_s' are the monomer and polymer number concentrations of species s, respectively, and μ° is the chemical potential of the primary solvent. (If species s is a small-molecular component, $c_{0,s}' = c_s'$.) Strictly speaking, the above equations are valid for multicomponent solutions which are in a dyalitic equilibrium with the pure primary solvent under the osmotic pressure depending on the composition of the solutions.*[1,11] Here we neglect the pressure dependence of μ_s to apply the equations to multicomponent solutions under a constant pressure.

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*[1] In eq 2, $\mathscr{F}$ is the characteristic function per unit volume V for systems under constant T, V, and μ°.

In part I of this series,[1,2] we calculated the osmotic compressibility or R_0 for monodisperse stiff polymer solutions by the scaled particle theory for wormlike spherocylinder solutions incorporated with intermolecular dispersion interactions as a thermodynamic perturbation. The thermodynamic quantities μ_{st} for multicomponent polymer solutions can be calculated by the same theory, as mentioned below.

Let us consider a solution of volume V containing r wormlike spherocylinder components; the component s has the contour length $L_{c,s}$ of the cylinder part, the hard-core diameter d_s, and the persistence length q_s, and the solution contains n_s molecules of the component s. Applying the previous result[*2] of the scaled particle theory[13] for μ_s, we have

$$\mu_{st} = \frac{1}{N_{0,s}N_{0,t}}\left(\frac{\delta_{st}}{c_s'} + \frac{2M_sM_t}{N_A}\Gamma_{st}\right) \quad (3)$$

where δ_{st} is Knonecker's delta, N_A is the Avogadro constant, M_s is the molecular weight of species s, and Γ_{st} is the apparent second virial coefficient between species s and t, which is defined by

$$\frac{2M_sM_t}{N_A}\Gamma_{st} \equiv \frac{1}{1-\bar{v}c'}\left[B_{st} + C_{st}\frac{c'}{1-\bar{v}c'} + D_{st}\left(\frac{c'}{1-\bar{v}c'}\right)^2\right.$$
$$\left. + E_{st}\left(\frac{c'}{1-\bar{v}c'}\right)^3\right] + \beta_{w,st} \quad (4)$$

In this equation, c' is the total number concentration of spherocylinders $(=\sum_{s=1}^{r} n_s/V)$, and

$$\bar{v} = \sum_{s=1}^{r} x_s v_s \quad (5)$$

$$B_{s,t} = 2b_{st}\rho_{st} + b_{st}^\circ + v_s + v_t \quad (6)$$

$$C_{st} = \sum_{u=1}^{r} x_u \left\{\frac{2}{3}\left[(c_{stu}\rho_{st} + c_{stu}^\circ) + (c_{ust}\rho_{us} + c_{ust}^\circ)\right.\right.$$
$$\left. + (c_{tus}\rho_{tu} + c_{tus}^\circ)\right] + v_s(2b_{tu} + b_{tu}^\circ)$$
$$\left. + v_t(2b_{us} + b_{us}^\circ)\right\} + v_sv_t \quad (7)$$

$$D_{st} = \sum_{u=1}^{r}\sum_{v=1}^{r} x_u x_v \left\{\frac{4}{3}\left[v_s(c_{tuv}\sigma_{tu} + c_{tuv}^\circ)\right.\right.$$
$$\left. + v_t(c_{suv}\rho_{su} + c_{suv}^\circ)\right]$$
$$+ \frac{2}{3}\left[v_s(c_{uvt}\rho_{uv} + c_{uvt}^\circ) + v_t(c_{uvs}\rho_{uv} + c_{uvs}^\circ)\right]$$
$$\left. + v_sv_t(2b_{uv} + b_{uv}^\circ)\right\} \quad (8)$$

and

$$E_{st} = \sum_{u=1}^{r}\sum_{v=1}^{r}\sum_{w=1}^{r} x_u x_v x_w[2v_sv_t(c_{uvw}\rho_{uv} + c_{uvw}^\circ)] \quad (9)$$

with the mole fraction x_s $(=n_s/\sum_{s=1}^{r} n_s)$ of the component s, the spherocylinder volume v_s $(=\frac{\pi}{4}L_{c,s}d_s^2 + \frac{\pi}{6}d_s^3)$ of the component s, and the parameters defined in Table I for the cases of homogeneous mixtures $(d_s = d$ for all $s)$ and heterogeneous mixtures. In eq 6—9, ρ_{st}

represents the reduction of the intermolecular excluded volume between the components s and t by the orientation defined by eq 11 of ref 13, and $\rho_{st} = 1$ in the isotropic state.

In eq 4, the last term $\beta_{w,st}$ represents the binary cluster integral with respect to the soft dispersion interaction between species s and t, which is formulated in Appendix. The explicit form in the isotropic state is given in Table I, where $\delta_{1,st}$ (or δ_1 for homogeneous mixtures) represents the strength of the isotropic dispersion interaction between the components s and t. It is noted that $\beta_{w,st}$ in eq 4 is just the first thermodynamic perturbation term by the soft dispersion interaction and higher perturbation terms are neglected in eq 4.[12]

Angular Dependence of the Rayleigh Ratio

In order to formulate the angular dependence of the excess Rayleigh ratio R_θ, we have to refer the distribution-function theory of light scattering. In terms of the Fourier transforms $\hat{\omega}_s(k; i_1, j_1)$ of the intramolecular distribution function for the monomers i_1 and j_1 in the same polymer chain 1 of species s and the Fourier transforms $\hat{h}_{st}(k; i_1, i_2)$ of the intermolecular total correlation function for the monomers i_1 and i_2 in the different polymer chains 1 and 2 of species s and t, respectively, R_θ can be written by[2]

$$R_\theta = \left(\frac{2\pi}{\lambda}\right)^4 c_0'\left[\sum_{s=1}^{r} \alpha_s^2 x_{0,s}\hat{\omega}_s(k)\right.$$
$$\left. + c_0'\sum_{s,t=1}^{r} \alpha_s\alpha_t x_{0,s}x_{0,t}\hat{h}_{st}(k)\right] \quad (10)$$

Here c_0' is the number concentration of the total scattering units of all solute species, $x_{0,s}$ is the mole fraction of the scattering units of species s in the total units, and $\hat{\omega}_s(k)$ and $\hat{h}_{st}(k)$ are defined by

$$\hat{\omega}_s(k) \equiv \frac{1}{N_{0,s}}\sum_{i_1,j_1=1}^{N_{0,s}} \hat{\omega}_s(k; i_1, j_1) \quad (11)$$

and

$$\hat{h}_{st}(k) \equiv \frac{1}{N_{0,s}N_{0,t}}\sum_{i_1=1}^{N_{0,s}}\sum_{i_2=1}^{N_{0,t}} \hat{h}_{st}(k, i_1, i_2) \quad (12)$$

(k: the absolute value of the scattering vector). Equation 10 is conveniently written in the following matrix notation:

$$R_\theta = (2\pi/\lambda)^4 c_0'[\alpha\hat{S}(k)\alpha^T] \quad (13)$$

where $\hat{S}(k)$ is the $r \times r$ structure factor matrix defined by

$$\hat{S}(k) = \hat{\Omega}(k) + c_0'\hat{H}(k) \quad (14)$$

with two matrices, $\hat{\Omega}(k)$ and $\hat{H}(k)$, whose st elements are respectively given by

$$\hat{\Omega}_{st}(k) \equiv x_{0,s}\hat{\omega}_s(k)\delta_{st} \quad (15)$$

and

$$\hat{H}_{st}(k) \equiv x_{0,s}x_{0,t}\hat{h}_{s,t}(k) \quad (16)$$

The st element $\hat{S}_{st}(k)$ of $\hat{S}(k)$ is referred to as the partial structure factor for species s and t.

[*2] Equations 7 and 8 of ref 13 contain errors; B in eq 7 and $B_s'/2$ and $C_s'/3$ in eq 8 should be replaced by $B/2$, B_s, and C_s, respectively.

Several workers[14-18] calculated $\bar{\omega}_s(k)$ using the worm-like chain model. Among them, the calculation of Yo-shizaki and Yamakawa[18] is the most accurate in the k range of light scattering. In the following, we use their result for $\bar{\omega}_s(k)$.

The function $\hat{h}_{st}(k)$ may be calculated using the generalized Ornstein–Zernike (GOZ) integral equation.[19-24] In Part II,[9] we utilized this equation to formulate R_θ for monodisperse polymer solutions. The extension of the equation to multicomponent polymer solutions may be given by[23,24]

$$\hat{H}(k) = \hat{\Omega}(k)\hat{C}(k)\hat{\Omega}(k) + c_0'\hat{\Omega}(k)\hat{C}(k)\hat{H}(k) \qquad (17)$$

or

$$\hat{H}(k) = [I - c_0'\hat{\Omega}(k)\hat{C}(k)]^{-1}\hat{\Omega}(k)\hat{C}(k)\hat{\Omega}(k) \qquad (18)$$

where $\hat{C}(k)$ is the $r \times r$ matrix whose st element is the Fourier transform $\hat{C}_{st}(k)$ of the (average) direct correlation function between scattering units of species s and t, and I is the unit matrix.

As mentioned in Part II,[9] the GOZ integral equation includes the following approximations:

(1) It does not consider the intramolecular excluded-volume effect for polymer species, *i.e.*, the interaction between monomer units or interaction sites belonging to a same polymer chain (the self interaction).

(2) It takes into account all single-contact terms in $\hat{h}_{st}(k)$ for any sizes of interacting clusters, but neglects all multiple-contact terms for interacting clusters where at least a pair of polymer chains interact on more than one pair of interaction sites.

(3) In eq 17 and 18, the Fourier transforms of the polymer–polymer and polymer–small-molecule direct correlation functions are replaced by ones $\hat{C}_{st}(k)$ averaged along the chain contours. That is, the equations neglect the dependence of those direct correlation functions on the position of the interacting monomer-units along the polymer chains.

Although the self-interaction and the multiple contact in polymer chains play important roles in light scattering behavior of flexible polymer–good solvent systems,[2] their importance may be much reduced with increasing the polymer chain stiffness.[9] It is well known that polymer chains with sufficient stiffness take unperturbed conformations even in good solvent.[25] Therefore, the above approximations (1) and (2) may be good for such stiff-chain polymer solutions. Furthermore, if the polymer chain is homogeneous and long enough, the averaging process of the Fourier transforms of the direct correlation functions along the polymer chain contour may not substantially affect the final result of the integral equation.

In addition to the above, we have used the following approximation in eq 17 and 18:

(4) Each small molecular component is regarded as a semiflexible spherocylinder in the scaled particle theory to formulate R_0 above, so that the direct correlation function concerned with the small molecular component has to be regarded as an orientation-dependent quantity.[26] To obtain eq 17 and 18, however, those direct correlation functions have been preaveraged isotropically with respect to the orientation of small molecular

components, and the orientational dependence has not been explicitly considered.

This approximation is expected not to affect the (isotropic) Rayleigh ratio within the light scattering k region.

Combining eq 14 and 18, we have

$$\hat{S}(k)^{-1} = \Omega(k)^{-1} - c_0'\hat{C}(k) \qquad (19)$$

Thus we can calculate the partial structure factor $\hat{S}_{st}(k)$, if we know $\hat{C}_{st}(k)$. The direct correlation function has a nature of taking non-zero values only when two scattering units (or interaction sites) concerned approach within their interaction ranges. If we choose monomer units of polymer species and whole small molecules as scattering units or interaction sites, their interaction ranges are too short to detect by light scattering experiments; *i.e.*, the interaction ranges multiplied by the light scattering k are all much smaller than unity. In such a condition, $\hat{C}_{st}(k)$ can be approximated by $\hat{C}_{st}(0)$.

Comparing eq 1 with eq 13, we have the relation

$$\mu = [c_0'\hat{S}(0)]^{-1} = c_0'^{-1}\Omega(0)^{-1} - \hat{C}(0) \qquad (20)$$

where the second equation is obtained using eq 19. Inserting eq 3 and 15 into eq 20, we can relate the quantity $\hat{C}_{st}(0)$ to the apparent second virial coefficient Γ_{st} by

$$\hat{C}_{st}(0) = -\frac{2M_{0,s}M_{0,t}}{N_A}\Gamma_{st} \qquad (21)$$

where $M_{0,s}$ is the molecular weight of the monomer unit of species s. (It is noted that $\bar{\omega}_s(k)$ is equal to $N_{0,s}$ at $k = 0$.) Therefore, eq 13, 19, and 21 give us the final expression of R_θ.

At the end of this section, we should refer to other theories dealing with the same problem. Schweizer and Curro[23,24] calculated the structure factor for polymer mixtures from the GOZ equation using the closure procedure based on "the mean spherical approximation." Their method may be more rigorous than ours mentioned above, but it needs an involved numerical analysis to solve the integral equation, and the structure factor cannot be expressed in an analytical form. Benoit and Benmouna[27] also calculated R_θ for solutions of polymer mixtures with arbitrary concentrations by the GOZ integral equation. In their formulation, interactions among monomer units were represented in terms of excluded-volume parameters (ϑ_A, ϑ_B, ϑ_{AB}), which are not explicitly specified from the molecular level but treated just as phenomenological parameters. (In fact, their excluded-volume parameters are concentration dependent, though the original authors did not argue their dependence.)

APPLICATIONS TO SOME SPECIFIC SYSTEMS

Ternary Solutions with Two Homologous Polymer Species

Let us consider first a solution of two stiff-polymer samples (components 1 and 2) of the same kind but with different molecular weights, dissolved in a solvent. These polymer samples have the identical hard-core diameter d, the persistence length q, the dispersion interaction parameter δ, the excess polarizability α, and the monomer molecular weight M_0. From eq 13, 19, and 21, we have

$$\frac{Kc}{R_\theta} = \frac{[1 + 2cw_1M_1P_1(k)\Gamma_{11}][1 + 2cw_2M_2P_2(k)\Gamma_{22}] - 4c^2w_1w_2M_1M_2P_1(k)P_2(k)\Gamma_{12}^2}{w_1M_1P_1(k) + w_2M_2P_2(k) + 2cw_1w_2M_1M_2P_1(k)P_2(k)[\Gamma_{11} + \Gamma_{22} - 2\Gamma_{12}]} \qquad (22)$$

where c is the total polymer mass concentration, w_s, M_s, and $P_s(k)$ are the weight fraction (in the total polymer), the molecular weight, and the intramolecular interference factor ($\equiv \hat{\omega}_s(k)/N_{0,s}$) of polymer species s, respectively, K is the optical constant defined by

$$K \equiv (4\pi^2 n^2/N_A\lambda^4)(\partial n/\partial c)^2 \qquad (23)$$

with the refractive index n of the solution, and Γ_{st} is the apparent second virial coefficient for species s and t, given by eq 4.

Solutions of Polydisperse Polymer Samples

If L_s/d is much larger than unity for all s, Γ_{st} defined by eq 4 are independent of s and t, being written as

$$\Gamma_{2,st} = \Gamma_2 \equiv \frac{\pi dN_A}{4M_L^2} \left\{ \frac{1}{1 - \bar{v}c'} \left[1 + 4\frac{\bar{v}c'}{1 - \bar{v}c'} \right. \right.$$
$$\left. \left. + 5\left(\frac{\bar{v}c'}{1 - \bar{v}c'}\right)^2 + 2\left(\frac{\bar{v}c'}{1 - \bar{v}c'}\right)^3 \right] + \frac{\delta}{d} \right\} \qquad (24)$$

where M_L is the molar mass per unit contour length of polymer. In such a case, the inverse of the structure factor matrix $\hat{S}(k)^{-1}$ can be simplified, and eq 13, 19, and 21 finally yield

$$Kc/R_\theta = (M_wP(k)_z)^{-1} + 2\Gamma_2 c \qquad (25)$$

where M_w is the weight average molecular weight and $P(k)_z$ is the z-average intramolecular interference factor defined by

$$P(k)_z = \frac{1}{M_w} \sum_{s=1}^r w_sM_sP_s(k) \qquad (26)$$

At $\theta = 0$, where $P(k)_z = 1$, the above equation gives Kc/R_0 identical with that for a monodisperse polymer solution with the molecular weight equal to M_w and

volume fraction equal to $\bar{v}c'$. Thus polydispersity in molecular weight does not change the form of the equation for Kc/R_0, if the solution contains only sufficiently high molecular weight stiff-polymer components. The same conclusion was previously obtained for the equation for the concentration gradient in polydisperse stiff-polymer solutions in sedimentation equilibrium experiments.[10] On the other hand, the angular dependence of Kc/R_θ is strongly affected by polydispersity through $P(k)_z$.

When the total polymer concentration c' of a polydisperse polymer solution is sufficiently low, we can use the second virial approximation. Expanding each element $[\hat{S}(k)^{-1}]_{st}$ with respect to c' and omitting the higher virial terms, we obtain[11]

$$\frac{Kc}{R_\theta} = \frac{1}{M_wP(k)_z} + 2c\frac{\displaystyle\sum_{s,t=1}^r w_sw_tM_sM_tP_s(k)P_t(k)A_{2,st}}{[M_wP(k)_z]^2} \qquad (27)$$

where $A_{2,st}$ is the second virial coefficient for the components s and t given by

$$A_{2,st} = (\Gamma_{st})_{c=0} = \frac{N_A}{2M_sM_t}(B_{st} + \beta_{w,st}) \qquad (28)$$

with B_{st} and $\beta_{w,st}$ given by eq 6 and in Table I, respectively.

Ternary Solution with Two Solutes of Different Chemical Species

Next consider a solution contains two different kind solute components 1 and 2, each of which is a stiff-polymer or a small molecule. In general, the two solute components have different light-scattering powers, which can be expressed in terms of the refractive index increments $\gamma_s \equiv \partial n/\partial c_s$. Equations 13, 19, and 21 gives the Rayleigh ratio for this system as

$$\frac{R_\theta}{K'} = \frac{c_1M_1P_1(k)\gamma_1^2 + c_2M_2P_2(k)\gamma_2^2 + 2c_1c_2M_1M_2P_1(k)P_2(k)(\gamma_2^2\Gamma_{11} - 2\gamma_1\gamma_2\Gamma_{12} + \gamma_1^2\Gamma_{22})}{[1 + 2c_1M_1P_1(k)\Gamma_{11}][1 + 2c_2M_2P_2(k)\Gamma_{22}] - 4c_1c_2M_1M_2P_1(k)P_2(k)\Gamma_{12}^2} \qquad (29)$$

where $K' \equiv 4\pi^2 n^2/N_A\lambda^4$ and Γ_{st} is given by eq 4.

EXPERIMENTAL TEST OF EQUATION 22

In order to test the validity of the above derived equation 22 of R_θ for ternary solutions containing two different molecular weight samples of a homologous polymer, we made light scattering measurements for isotropic dichloromethane (DCM) solutions with two fractionated poly(n-hexyl isocyanate) (PHIC) samples. We have chosen two PHIC samples, K-3 [$M_w = 1.11 \times 10^5$; $\langle S^2\rangle_2^{1/2}$ (the root-mean-square radius of gyration) = 26.6 nm] and V-1-2 [$M_w = 1.06 \times 10^6$; $\langle S^2\rangle_2^{1/2} = 97.9$ nm], previously used for light scattering study of binary solutions.[12] DCM solutions of each PHIC sample, separately prepared, were filtrated by Millipore filters

directly into a light scattering cell to prepare a ternary solution with a given composition. Light scattering experiment was made at 20°C in the same procedure as in the previous study.[12]

Figure 1 shows the plots of Kc/R_θ vs. k^2 for DCM solutions containing the two PHIC samples with three different mixing ratios, which are expressed by $\zeta_2 \equiv w_2M_{w,2}/(w_1M_{w,1} + w_2M_{w,2})$ where the subscripts 1 and 2 indicate the lower and higher molecular weight samples, K-3 and V-1-2, respectively. The angular dependence of Kc/R_θ becomes stronger with increasing ζ_2, but is almost independent of the total polymer concentration c.

Equation 22 contains the following molecular parameters: L_1, L_2, q, d, and δ_1. Among them, L_1 and L_2 can be calculated from $M_{w,1}$ and $M_{w,2}$ with the molar

Table I. Parameters appearing in eq 4 and 6—9

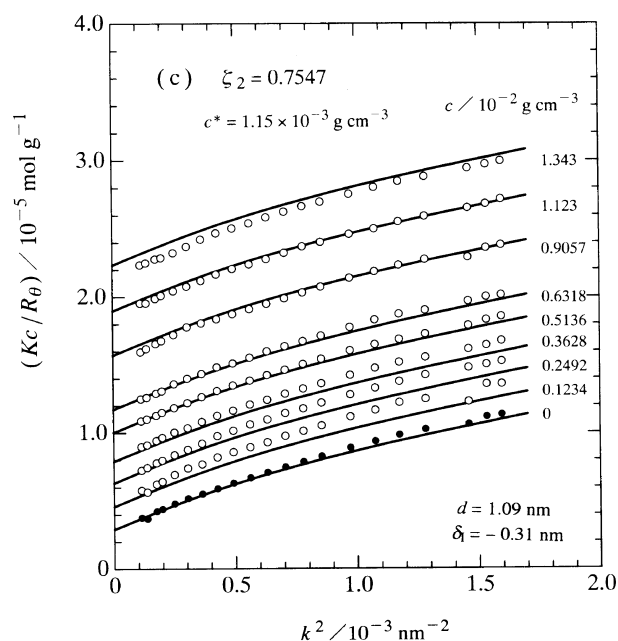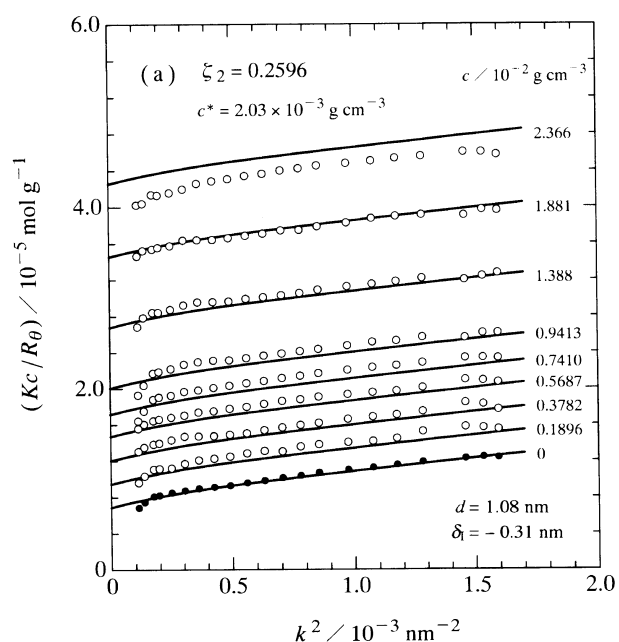| Parameter	Homogeneous mixture	Heterogeneous mixture
b_{st}	$\dfrac{\pi}{4} L_{c,s} L_{c,t} d$	$\dfrac{\pi}{8} L_{c,s} L_{c,t} (d_s + d_t)$
b_{st}°	$3(v_s + v_t)$	$\dfrac{\pi}{4}[d_s^2(L_{c,t} + 2d_t) + d_t^2(L_{c,s} + 2d_s) + 2d_s d_t(L_{c,s} + L_{c,t})]$
c_{stu}	$2\left(v_u + \dfrac{\pi}{12} d^3\right) b_{st}$	$\dfrac{\pi^2}{8} d_s d_t d_u (L_{c,u} + d_u) L_{c,s} L_{c,t}$
c_{stu}°	$2\left(v_u + \dfrac{\pi}{12} d^3\right)\left(v_s + v_t - \dfrac{\pi}{12} d^3\right)$	$\dfrac{\pi^2}{8} d_s d_t d_u (L_{c,u} + d_u)(L_{c,s} d_t + L_{c,t} d_s + d_s d_t)$
$\beta_{w,st}$	$2\left[b_{st} + 4(v_s + v_t) + \dfrac{2\pi}{3} d^3\right]\dfrac{\delta_1}{d}$	$\dfrac{\pi}{2}[L_{c,s} L_{c,t} + 2(L_{c,s} + L_{c,t})(d_s + d_t) + 2(d_s + d_t)^2]\delta_{1,st}$.

$L_{c,s} \equiv L_s - d_s.$
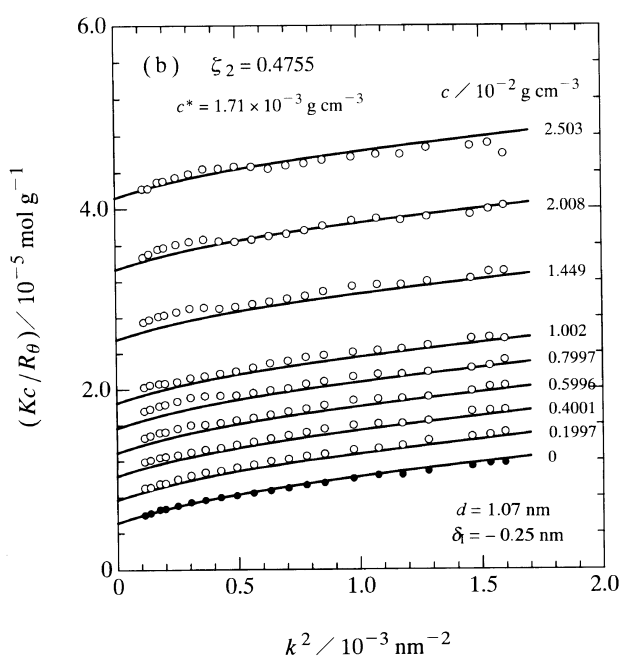
Figure 1. Angular dependence of Kc/R_θ for dichlorolomethane solutions containing two poly(n-hexyl isocyanate) samples of different molecular weights with three different mixing ratios; $\zeta_2 \equiv w_2 M_{w,2}/(w_1 M_{w,1} + w_2 M_{w,2})$ with $M_{w,1} = 1.11 \times 10^5$ and $M_{w,2} = 1.06 \times 10^6$; c^* (the overlap concentration) $= (3/4\pi N_A) \times [(\langle S^2 \rangle_1^{3/2}/M_1)w_1 + (\langle S^2 \rangle_2^{3/2}/M_2)w_2]^{-1}$ with $\langle S^2 \rangle_1^{1/2} = 26.6$ nm and $\langle S^2 \rangle_2^{1/2} = 97.9$ nm; solid curves, calculated from eq 22 with $M_L = 740$ nm^{-1}, $q = 21$ nm, and values of d and δ_1 given in each panel.

mass per unit contour length M_L. For PHIC in DCM at 20°C, $M_L = 740$ nm^{-1} and $q = 21$ nm, which were determined from the molecular weight dependence of the intrinsic viscosity and radius of gyration for PHIC in DCM.[12,28] Thus we use those parameter values and search for the interaction parameters d and δ_1 leading to the best fit of the Kc/R_θ data shown in Figure 1 to eq 22, where $P_1(k)$ and $P_2(k)$ are calculated by the theory of Yoshizaki and Yamakawa,[18,29] and Γ_{st} ($s, t = 1$ and 2) are estimated from eq 4 along with the parameters listed in Table I. The fitting results are shown by the solid curves in Figure 1, which are obtained by selecting d and δ_1 values given in each panel. The agreement between the theory and experiment is almost satisfactory. Furthermore, the values of d and δ_1 selected are close to those obtained previously from the concentration
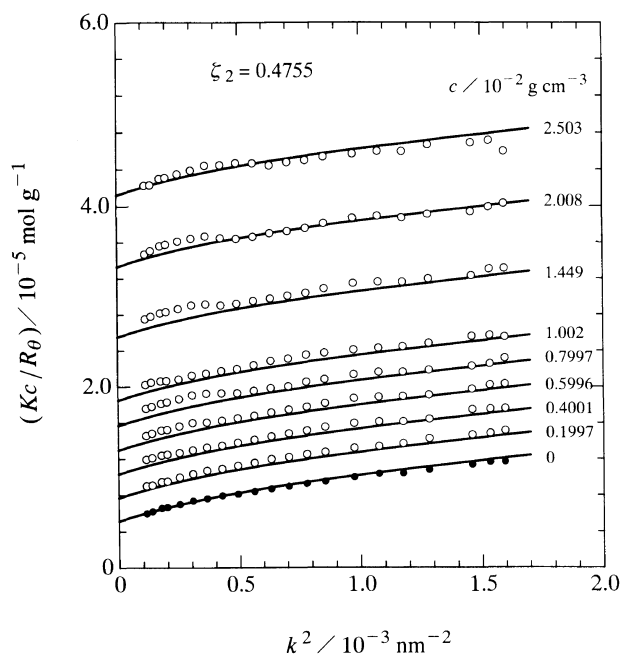
Figure 2. Comparisons of experimental results of Kc/R_θ for the ternary solutions of PHIC ($\zeta_2 = 0.4755$) with eq 25 and 26, using the molecular parameters same as in Figure 1b.
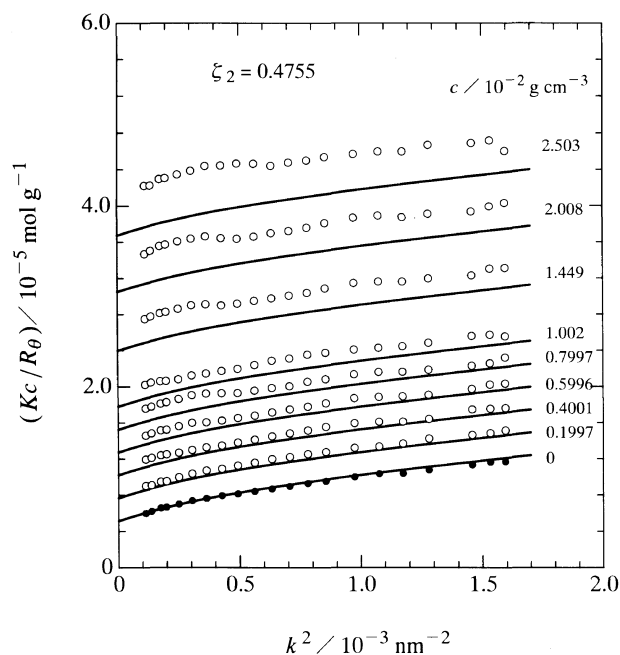

Figure 3. Comparisons of experimental results of Kc/R_θ for the ternary solutions of PHIC ($\zeta_2 = 0.4755$) with eq 27 and 28, using the molecular parameters same as in Figure 1b.

dependence of the osmotic compressibility for binary solutions of PHIC and DCM ($d = 1.07$ nm and $\delta_1 = -0.36$ nm).[12]

As mentioned in the previous section, if both L_1/d and L_2/d are sufficiently larger than unity, eq 22 can be approximated by a much simpler eq 25 with eq 24. Figure 2 compares the experimental results of Kc/R_θ for ternary PHIC solutions with $\zeta_2 = 0.4755$ with the values calculated from eq 25 and 24 with the molecular parameters same as in Figure 1b. The theoretical curves closely fit to the experimental data points; similar good fitting was obtained for ternary solutions with $\zeta_2 = 0.2596$ and 0.7547. Thus we can say that the polymer-end effect on Kc/R_θ is not important for the present ternary PHIC solutions. This effect was also unimportant on the second virial coefficient of PHIC in DCM.[10,12]

Figure 3 compares the same experimental data of Kc/R_θ with theoretical results calculated by eq 27 and 28 simplified using the second virial approximation. The agreement between experiment and theory is not good at high concentrations, demonstrating that the second virial approximation is not good for the present ternary PHIC solutions with c much higher than the overlap concentration c^* indicated in Figure 1b.

APPENDIX. FORMULATION OF THE SOFT DISPERSION INTERACTION

Let α_s be the local excess polarizability tensor per unit

length of a wormlike spherocylinder (WSC) of species s in a solvent with the dielectric permittivity ε. The tensor α_s is assumed to be cylindrically symmetric; $\alpha_{s,1}$ ($=\alpha_{s,2}$) and $\alpha_{s,3}$ denote the local excess polarizabilities parallel and perpendicular to the cylinder axis, respectively.

According to the theories of McLachlan[30,31] and Imura and Okano,[32] the local dispersion energy (or the van der Waals free energy) $G_{st}(s_a, s_b)$ between two unit-length portions of WSCs a and b of species s and t, respectively, on the contour points s_a and s_b is written as

$$G_{st}(s_a, s_b) = -(k_B T/x^6) \sum_{k,l=1}^{3} J_{st,kl} c_{kl}^2 \qquad (A1)$$

Here x is the distance between the contour points s_a and s_b, and

$$J_{st,kl} = \sum_{n=0}^{\infty}{}' \alpha_{s,k}(i\omega_n)\alpha_{t,l}(i\omega_n)/\varepsilon^2(i\omega_n) \qquad (A2)$$

where $i\omega_n \equiv 2\pi i n k_B T/\hbar$ is the imaginary frequency with the Planck constant $\hbar$, and the prime over the summation indicates that the $n = 0$ term is multiplied by $1/2$. The coupling constant c_{kl} is defined by

$$c_{kl} = a_k(s_a) \cdot a_l(s_b) - 3[a_k(s_a) \cdot e][a_l(s_b) \cdot e] \qquad (A3)$$

where $a_k(s_a)$ ($a_l(s_b)$) is a unit vector along the principal axis k (l) at the contour point s_a (s_b), and e is a unit vector directed from the contour point s_a to the point s_b. Assuming the pairwise additivity of the dispersion energy, we can calculate the total dispersion energy w_{st} between WSCs of species s and t by

$$w_{st} = \int_{-L_s/2}^{L_s/2} ds_a \int_{-L_t/2}^{L_t/2} ds_b G_{st}(s_a, s_b) \qquad (A4)$$

where L_s and L_t are the contour lengths of the WSC of species s and t, respectively. Since $G_{st}(s_a, s_b)$ is defined in solution, w_{st} should be regarded as the potential of mean

force.

Let us first consider two long WSCs of species s and t. We assume that the persistence lengths q_s and q_t of the WSCs are much longer than the interaction range of $G_{st}(s_a, s_b)$. [It is noted that $G_{st}(s_a, s_b)$ is a short range function of x from eq A1.] In such a case, two or more pairs of contour portions on the two interacting WSCs seldom come close within the interaction range simultaneously. Therefore, it is enough to consider only the case that the two WSCs interact with each other at one pair of contour portions (the single contact approximation). As a result, w_{st} calculated from eq A4 may be approximated by that for corresponding straight spherocylinders.

The binary cluster integral $\beta_{w,st}$ with respect to w_{st} for two long stiff WSCs may be written as[12]

$$\beta_{w,st} = \frac{\pi}{2} L_s L_t \delta_{st} \tag{A5}$$

with

$$\delta_{st} \equiv \frac{4}{\pi} \int_{(d_s + d_t)/2}^{\infty} \left\langle \frac{w_{st,\infty}}{k_B T} |\sin\gamma| \right\rangle dr \tag{A6}$$

where r is the shortest distance between the two spherocylinders, γ is the angle formed by the two tangent vectors of the spherocylinders at the closest contour points, $w_{st,\infty}$ is w_{st} for infinitely long spherocylinders of species s and t, and the angular brackets represent the orientational average of the two chains; one should not confuse δ_{st} with the Kronecker delta. (In eq A6, we used the high-temperature approximation for the Mayer function, and also assumed w to be zero at $r < d$.) We can calculate $w_{st,\infty}$ from eq A4, where x and e depend on s_a and s_b, but $a_k(s_a)$ and $a_l(s_b)$ do not depend on s_a and s_b. The final result is written as

$$w_{st,\infty} = -\frac{k_B T}{r^4 |\sin\gamma|} [J_{st,I} + J_{st,A} P_2(\cos\gamma)] \tag{A7}$$

where, P_2 is the second Legendre polynomial, and

$$J_{st,I} \equiv \frac{3\pi}{32} (19 J_{st,11} + 10 J_{st,13} + 3 J_{st,33}),$$

$$J_{st,A} \equiv \frac{\pi}{8} (J_{st,11} - 2 J_{st,13} + J_{st,33}) \tag{A8}$$

which depend on α and ε. Using eq A7, δ_{st} is calculated to be

$$\delta_{st} = \delta_{st,I} + \delta_{st,A} \eta_{st} \tag{A9}$$

with

$$\delta_{st,I} \equiv -32 J_{st,I} / 3\pi (d_s + d_t)^3,$$

$$\delta_{st,A} \equiv -32 J_{st,A} / 3\pi (d_s + d_t)^3 \tag{A10}$$

and

$$\eta_{st} \equiv \int\int d\mathbf{a} d\mathbf{a}' P_2(\mathbf{a} \cdot \mathbf{a}') \bar{f}_s(\mathbf{a}) \bar{f}_t(\mathbf{a}') \tag{A11}$$

where $\bar{f}_s(\mathbf{a})$ and $\bar{f}_t(\mathbf{a})$ are the orientational distribution functions of the unit tangent vector $\mathbf{a}$ to the wormlike chain contour for species s and t, respectively.

The integral in eq A4 for w_{st} cannot be expressed in an analytical form when $L_{c,s}$ and $L_{c,t}$ are finite, and thus it is not easy to incorporate the end effect of spherocylinders on $\beta_{w,st}$. Here we treat the end effect, according to Sato and Teramoto[33] who previously considered the same problem for stiff polyelectrolytes. They approximated the electrostatic interaction potential of a stiff polyelectrolyte by a square-well potential to calculate the electrostatic binary cluster integral. Similarly, we approximate w_{st} of spherocylinders with a soft dispersion potential by the following square-well potential:

$$w_{st} = \begin{cases} w_{st}^\circ, & (d_s + d_t)/2 \leq r \leq (d_s + d_t)/2 + \Delta_{st} \\ 0, & \text{otherwise} \end{cases} \tag{A12}$$

where w_{st}° and Δ_{st} are two constants. When the solution is isotropic, this potential yields

$$\beta_{w,st} = \frac{\pi}{2} [L_{c,s} L_{c,t} + 2(L_{c,s} + L_{c,t})(d_s + d_t) + 2(d_s + d_t)^2] \delta_{1,st} \tag{A13}$$

where $\delta_{1,st} \equiv w_{st}^\circ \Delta_{st} / k_B T$, and terms of order of $\delta_{1,st} / (d_s + d_t)$ were omitted.[*3] This equation reduces to eq A5 in the isotropic state, when both $L_{c,s}$ and $L_{c,t}$ are much larger than $d_s + d_t$. Although Sato and Teramoto calculated the electrostatic cluster integral also in an anisotropic state, we do not discuss the end effect on the anisotropic part of $\beta_{w,st}$ in this paper.

REFERENCES

1. M. B. Huglin, Ed., "Light Scattering from Polymer Solutions," Academic Press, London & New York, 1972.
2. H. Yamakawa, "Modern Theory of Polymer Solutions," Harper & Row, New York, N.Y., 1971.
3. J. G. Kirkwood and R. J. Goldberg, J. Chem. Phys., 18, 54 (1950).
4. W. H. Stockmayer, J. Chem. Phys., 18, 58 (1950).
5. E. F. Casassa and H. Eisenberg, J. Phys. Chem., 64, 753 (1960).
6. E. F. Casassa and H. Eisenberg, J. Phys. Chem., 65, 427 (1961).
7. H. Eisenberg, J. Chem. Phys., 36, 1837 (1962).
8. H. Yamakawa, J. Chem. Phys., 46, 973 (1967).
9. T. Sato, Y. Jinbo, and A. Teramoto, Polym. J., 27, 384 (1995).
10. T. Sato, Y. Jinbo, and A. Teramoto, Macromolecules, 30, 590 (1997).
11. M. Kurata, "Thermodynamics of Polymer Solutions," Harwood Academic Publishers, Chur, 1982.
12. Y. Jinbo, T. Sato, and A. Teramoto, Macromolecules, 27, 6080 (1994).
13. T. Sato, T. Shoda, and A. Teramoto, Macromolecules, 27, 164 (1994).
14. P. Sharp and V. A. Bloomfield, Biopolymers, 6, 1201 (1968).
15. J. des Cloizeaux, Macromolecules, 6, 403 (1973).
16. R. Koyama, J. Phys. Soc. Jpn., 34, 1029 (1973).
17. T. Norisuye, M. Motowoka, and H. Fujita, Macromolecules, 11, 966 (1978).
18. T. Yoshizaki and H. Yamakawa, Macromolecules, 13, 1518 (1980).
19. K. S. Schweizer and J. G. Curro, Phys. Rev. Lett., 58, 246 (1987).
20. J. G. Curro and K. S. Schweizer, Macromolecules, 20, 1928 (1987).

[*3] Previously, we proposed a different expression of β_w for polymer chains whose end portions possess different interaction properties from those of the middle portion. Equation A13 does not consider such a difference.

21. J. G. Curro and K. S. Schweizer, *J. Chem. Phys.*, **87**, 1842 (1987).
22. K. G. Honnell, J. G. Curro, and K. S. Schweizer, *Macromolecules*, **23**, 3496 (1990).
23. K. S. Schweizer and J. G. Curro, *Phys. Rev. Lett.*, **60**, 809 (1988).
24. K. S. Schweizer and J. G. Curro, *J. Chem. Phys.*, **91**, 5059 (1989).
25. T. Norisuye and H. Fujita, *Polym. J.*, **14**, 143 (1982).
26. C. G. Gray and K. E. Gubbins, "Theory of Molecular Fluids," Vol. 1, Fundamentals, Clarendon Press, Oxford, 1984.
27. H. Benoit and M. Benmouna, *Macromolecules*, **17**, 535 (1984).
28. T. Itou, H. Chikiri, A. Teramoto, and S. M. Aharoni, *Polym. J.*, **20**, 143 (1988).
29. H. Yamakawa, "Helical Wormlike Chains in Polymer Solutions," Springer-Verlag, Berlin & Heidelberg, 1997.
30. A. D. McLachlan, *Proc. R. Soc. London*, **A271**, 387 (1963).
31. A. D. McLachlan, *Proc. R. Soc. London*, **A274**, 80 (1963).
32. H. Imura and K. Okano, *J. Chem. Phys.*, **58**, 2763 (1973).
33. T. Sato and A. Teramoto, *Physica*, **A176**, 72 (1991).