ORIGINAL ARTICLE

Intrinsic viscosity of wormlike regular four-arm stars

Takuma Kaneshima, Daichi Ida and Takenao Yoshizaki

The ratio g_η between the values of the intrinsic viscosity $[\eta]$ of the Kratky–Porod wormlike regular four-arm star and linear touched-bead models, both having the same total contour length L and bead diameter d_b (both in units of the stiffness parameter λ^{-1}), was numerically evaluated using the Kirkwood–Riseman approximation. By examination of the behavior of g_η as a function of L and d_b , it was found that the ratio g_η/g_η^0 of g_η to its asymptotic value g_η^0 in the rod limit monotonically increases from 1 to 3.27 with increasing L and is almost independent of d_b for $d_b \lesssim 0.2$, although the behavior of g_η itself as a function of L has remarkable dependence on d_b . Furthermore, the behavior of the ratio $g_{\eta,4}/g_{\eta,3}$ between the values of g_η of four- ($g_{\eta,4}$) and three-arm ($g_{\eta,3}$) stars, both having the same L and d_b , was examined as a function of L and d_b . It was then found that $g_{\eta,4}/g_{\eta,3}$ first decreases from the asymptotic value 0.91 in the random-coil limit and then increases after passing through a minimum, with decreasing L in the range of d_b examined, and $g_{\eta,4}/g_{\eta,3}$ appreciably depends on d_b , as in the cases of $g_{\eta,4}$ and $g_{\eta,3}$ themselves.

Polymer Journal (2012) 44, 115–120; doi:10.1038/pj.2011.45; published online 1 June 2011

Keywords: intrinsic viscosity; Kirkwood–Riseman approximation; regular four-arm star polymer; semiflexible polymer; wormlike chain

INTRODUCTION

Ever since the establishment of polymer science, the intrinsic viscosity $[\eta]$, defined as an increase in the solution viscosity with the addition of a solute of unit mass at infinite dilution, has played an important role in the molecular characterization of polymers. In the beginning, the so-called Staudinger rule,¹ which erroneously assumed $[\eta]$ to be proportional to the polymer molecular weight M , functioned as a recipe for determining M ;² then, an improved version $[\eta] \propto M^\alpha$ called the Mark–Houwink–Sakurada relation^{3–5} was proposed and is still commonly used for practical purposes.⁶ As pointed out by Sakurada,⁵ the relation generally holds for flexible polymers over a limited range of M and the exponent α may decrease with increasing M because of chain flexibility (or stiffness), if the range of M under observation becomes wide. From an analysis of $[\eta]$ over such a range capturing the crossover from short (stiff) to long (flexible) chains, the molecular parameters, including the stiffness parameter λ^{-1} , of a given linear polymer may be evaluated on the basis of the Kratky–Porod (KP) wormlike chain model^{7,8} or the helical wormlike chain model.⁸

The effective volume V_η , defined by the Einstein formula for $[\eta]$ of rigid spheres,⁹

$$[\eta] = \frac{5 N_A V_\eta}{2 M} \quad (1)$$

with N_A the Avogadro constant, is a useful measure of the average chain dimension and is strongly influenced by the primary structures of polymers as well as by their chain stiffness. To quantitatively examine the effect of the chain stiffness on $[\eta]$ of branched polymers, we recently made a study of $[\eta]$ of semiflexible regular three-arm star polymers without excluded volume on the basis of the KP chain.¹⁰

It was then shown that the ratio g_η between the values of $[\eta]$ of the regular three-arm star and linear chains, both with the same total contour length and hydrodynamic thickness, decreases remarkably with increasing chain stiffness and is useful for characterizing the primary structure of a given star polymer.

As a continuation of the previous study,¹⁰ the present paper is aimed at elucidating the dependence of g_η on the number of arms constituting semiflexible regular star polymers. We calculated $[\eta]$ of the KP regular four-arm star without excluded volume using the touched-bead hydrodynamic model^{8,11} along with the Kirkwood–Riseman (KR) approximation.^{9,12}

MATERIALS AND METHODS

Basic equations

Consider a regular four-arm star touched-bead model composed of $4m+1$ identical spherical beads of (hydrodynamic) diameter d_b , whose centers are located on the KP regular four-arm star chain contour, as illustrated in Figure 1. For convenience, the four arms are designated the first through fourth arms and the m beads on the i th ($i=1, 2, 3, 4$) arm are numbered $(i-1)m+1, (i-1)m+2, \dots, im$ from the branch point (center) to the terminal end, with the center bead numbered 0. The angle between each pair of the unit vectors tangent to the KP contours at the branch point is fixed to be the tetrahedral angle θ_t , such that $\cos \theta_t = -1/3$. The linear touched-bead model, the counterpart of the star model mentioned above, is the KP touched-bead model composed of $n+1$ identical beads of diameter d_b , whose centers are located on the KP linear chain contour. We set $n+1$ equal to $4m+1$ such that $n=4m$. The $n+1$ beads are numbered 0, 1, 2, ..., n from one end to the other. For both the star and the linear touched-bead models, the contour distance between the two adjacent beads is set equal to d_b .

Figure 1 Illustration of the Kratky–Porod (KP) regular four-arm star touched-bead model.

The intrinsic viscosity [η] of the touched-bead model composed of $4m+1$ (or $n+1$) identical spherical beads of diameter d_b may be written as the sum of the solution [η]_{KR} of the KR equation and the contribution [η]_E of the Einstein spheres.^{8,11} This is given by

$$[\eta] = [\eta]_{\text{KR}} + [\eta]_{\text{E}}, \quad (2)$$

where

$$[\eta]_{\text{KR}} = \frac{N_A}{M} \sum_{i=0}^{4m} \phi_{ii}, \quad (3)$$

$$[\eta]_{\text{E}} = \frac{5\pi N_A (n+1) d_b^3}{12M}. \quad (4)$$

In Equation (3), ϕ_{ij} is the solution of the following linear simultaneous equations,

$$\phi_{ij} + \frac{d_b}{2} \sum_{\substack{k=0 \\ k \neq i}}^{4m} \langle R_{ik}^{-1} \rangle \phi_{kj} = \frac{\pi d_b}{2} \langle \mathbf{S}_i \cdot \mathbf{S}_j \rangle, \quad (5)$$

where $\langle R_{ij}^{-1} \rangle$ is the equilibrium average of the reciprocal of the distance between the centers of the i th and j th beads and $\langle \mathbf{S}_i \cdot \mathbf{S}_j \rangle$ is the equilibrium average of the inner product of the vector distances $\mathbf{S}_i$ and $\mathbf{S}_j$ from the center of mass of the chain to the centers of the i th and j th beads, respectively. In what follows, all lengths are measured in units of the stiffness parameter λ^{-1} of the KP chain,⁸ unless otherwise specified.

Following the previous paper,¹⁰ we have adopted the values of $\langle R_{ij}^{-1} \rangle$ and $\langle \mathbf{S}_i \cdot \mathbf{S}_j \rangle$ of the (continuous) KP regular four-arm star chain of total contour length $L = (4m+1)d_b$ [or $(n+1)d_b$], as those of the regular four-arm star touched-bead model. Here, L has consistently been set equal to the total number $4m+1$ (or $n+1$) of beads multiplied by d_b for both the star and the linear chains. We note that the relation $L = (4m+1)d_b$ leads to the relation $L_a = (m+1/4)d_b$ between the contour length $L_a = L/4$ of each arm and d_b . Although the latter relation seems somewhat awkward because of the inclusion of the non-integer term $1/4$, it only reflects the fact that the center bead belongs to all four arms.

Average $\langle \mathbf{S}_i \cdot \mathbf{S}_j \rangle$

For the $[(i-1)m+k]$ th and $[(j-1)m+l]$ th beads ($i, j=1, 2, 3, 4$; $k, l=1, 2, \dots, m$) of the regular four-arm star chain, that is, the k th bead on the i th arm and the l th bead on the j th arm, respectively, $\langle \mathbf{S}_{(i-1)m+k} \cdot \mathbf{S}_{(j-1)m+l} \rangle$ may be given by

$$\langle \mathbf{S}_{(i-1)m+k} \cdot \mathbf{S}_{(j-1)m+l} \rangle = \langle \mathbf{S}(t_k^{(i)}) \cdot \mathbf{S}(t_l^{(j)}) \rangle, \quad (6)$$

where $\mathbf{S}(t_k^{(i)})$ is the vector distance from the center of mass of the KP regular four-arm star chain to the contour point on the i th arm with the contour distance $t_k^{(i)}$ from the branch point, such that

$$t_k^{(i)} = kd_b. \quad (7)$$

The average $\langle \mathbf{S}(t_k^{(i)}) \cdot \mathbf{S}(t_l^{(j)}) \rangle$ is given by Equations (A.1)–(A.4) of ref. 10 with $f=4$ and $\theta_{ij}=\theta_t$ and is explicitly given by

$$\begin{aligned} \langle \mathbf{S}(t_k^{(i)}) \cdot \mathbf{S}(t_l^{(j)}) \rangle = & \frac{L}{48} + \frac{(t_k^{(i)})^2 + (t_l^{(j)})^2}{2L} + \frac{t_k^{(i)} + t_l^{(j)}}{4} - \frac{u_{kl}^{(ij)}}{2} \\ & + \frac{1}{24} (1 - 4\delta_{ij}) [1 - \exp(-2t_k^{(i)}) - \exp(-2t_l^{(j)})] \\ & - \frac{1}{12} (1 + 2\delta_{ij}) \exp(-2u_{kl}^{(ij)}) \\ & + \frac{1}{4L} - \frac{1}{4L} e^{-L/2} [\cosh(2t_k^{(i)}) + \cosh(2t_l^{(j)})] \\ & + \frac{1}{4L^2} (1 - e^{-L}), \end{aligned} \quad (8)$$

where δ_{ij} is the Kronecker delta and $u_{kl}^{(ij)}$ is defined by

$$u_{kl}^{(ij)} = [(t_k^{(i)})^2 + (t_l^{(j)})^2 + 2(1 - 2\delta_{ij})t_k^{(i)}t_l^{(j)}]^{1/2}. \quad (9)$$

We note that $\langle \mathbf{S}_{(i-1)m+k} \cdot \mathbf{S}_0 \rangle = \langle \mathbf{S}(t_k^{(i)}) \cdot \mathbf{S}(0) \rangle$ and $\langle \mathbf{S}_0 \cdot \mathbf{S}_0 \rangle = \langle \mathbf{S}(0) \cdot \mathbf{S}(0) \rangle$ are given by Equation (8) with $u_{kl}^{(ij)} = t_k^{(i)}$ and 0, respectively. In the rod limit of L (in units of λ^{-1}) $\rightarrow 0$, Equation (8) reduces to

$$\langle \mathbf{S}(t_k^{(i)}) \cdot \mathbf{S}(t_l^{(j)}) \rangle = \frac{1}{3} (4\delta_{ij} - 1) t_k^{(i)} t_l^{(j)} \text{ (rod limit)}. \quad (10)$$

Regarding the linear touched-bead model, $\langle \mathbf{S}_i \cdot \mathbf{S}_j \rangle$ may be given by

$$\langle \mathbf{S}_i \cdot \mathbf{S}_j \rangle = \langle \mathbf{S}(t_i) \cdot \mathbf{S}(t_j) \rangle, \quad (11)$$

where $\mathbf{S}(t_i)$ is the vector distance from the center of mass of the KP linear chain to its contour point with the contour distance t_i from one end, such that

$$t_i = \left(i + \frac{1}{2}\right) d_b. \quad (12)$$

The average $\langle \mathbf{S}(t) \cdot \mathbf{S}(t') \rangle$ is given by Equation (19) of ref. 13, and its asymptotic form in the rod limit is given by Equation (13) of ref. 10.

Mean reciprocal of R_{ij}

The mean reciprocal $\langle R_{[(i-1)m+k][(j-1)m+l]}^{-1} \rangle$ of the distance $R_{[(i-1)m+k][(j-1)m+l]}$ between the centers of the k th bead on the i th arm and l th bead on the j th arm ($j \neq i$) may be given by

$$\langle R_{[(i-1)m+k][(j-1)m+l]}^{-1} \rangle = \langle R^{-1}(t_k^{(i)}, t_l^{(j)}, \theta_t) \rangle, \quad (13)$$

where $\langle R^{-1}(t_1, t_2, \theta) \rangle$ is the mean reciprocal of the end-to-end distance of the once-broken KP chain of total contour length $t_1 + t_2$; that is, two KP subchains 1 and 2 of contour lengths t_1 and t_2 , respectively, are connected so that the angle between the unit vectors tangent to the contours of the subchains 1 and 2 at the broken point is θ (see Figure 2 of ref. 10). If a pair of beads are on the same (i th) arm, $\langle R_{[(i-1)m+k][(i-1)m+l]}^{-1} \rangle$ is given by $\langle R^{-1}(|t_k^{(i)} - t_l^{(i)}|, 0, \theta_t) \rangle$ and/or $\langle R^{-1}(0, |t_k^{(i)} - t_l^{(i)}|, \theta_t) \rangle$, where $\langle R^{-1}(t, 0, \theta) \rangle$ and/or $\langle R^{-1}(0, t, \theta) \rangle$ is equivalent to the mean reciprocal of the end-to-end distance of the KP linear chain of contour length t . We note that $\langle R_{0[(i-1)m+k]}^{-1} \rangle$ is given by $\langle R^{-1}(t_k^{(i)}, 0, \theta_t) \rangle$ and/or $\langle R^{-1}(0, t_k^{(i)}, \theta_t) \rangle$.

Following the same procedure as in the previous study,¹⁰ we constructed an interpolation formula for $\langle R^{-1}(t_1, t_2, \theta_t) \rangle$ on the basis of the asymptotic forms given by Equation (15) with Equations (16)–(18) of ref. 10 and of Monte Carlo (MC) results newly obtained for $\langle R^{-1}(t_1, t_2, \theta_t) \rangle$ in this study.

The details of the procedure and MC calculations are omitted here for simplicity. The interpolation formula may be given by

$$\begin{aligned} \langle R^{-1}(t_1, t_2, \theta_t) \rangle = & \langle R^2 \rangle^{-1/2} [1 + A_1 \langle R^2 \rangle^{A_2}]^{-1} [f_{ee}(t_1, t_2, \theta_t) \\ & + A_3 \langle R^2 \rangle^{3/2} \\ & + A_4 t_1 t_2 (t_1 + t_2) e^{-A_5(t_1^2 + t_2^2)/(t_1 + t_2)} \\ & + A_1 \langle R^2 \rangle^{A_2} f_{DDe}(t_1, t_2, \theta_t)] \end{aligned} \quad (14)$$

with the coefficients A_i given by

$$A_1 = 5, A_2 = \frac{11}{2}, A_3 = 0.045, A_4 = 2.5, A_5 = 4.6. \quad (15)$$

In Equation (14), $\langle R^2 \rangle = \langle R^2(t_1, t_2, \theta_t) \rangle$ is the mean-square end-to-end distance of the above-mentioned once-broken KP chain with $\theta = \theta_t$ given by¹⁴

$$\begin{aligned} \langle R^2(t_1, t_2, \theta_t) \rangle = & t_1 + t_2 - \frac{1}{2} [1 - e^{-2(t_1 + t_2)}] \\ & - \frac{1}{2} (1 - e^{-2t_1})(1 - e^{-2t_2})(1 + \cos \theta_t). \end{aligned} \quad (16)$$

In Equation (14), $f_{ee}(t_1, t_2, \theta_t)$ is the asymptotic form of $\langle R^2(t_1, t_2, \theta_t) \rangle^{1/2} \times \langle R^{-1}(t_1, t_2, \theta_t) \rangle$ for $t_1 \ll 1$ and $t_2 \ll 1$ given by Equation (18) of ref. 10 with $\theta = \theta_t$, and $f_{DDe}(t_1, t_2, \theta_t)$ is given by

$$f_{DDe}(t_1, t_2, \theta_t) = \left(\frac{6}{\pi} \right)^{1/2} \left[1 - \frac{11}{40 \langle R^2 \rangle} + \frac{431}{4480 \langle R^2 \rangle^2} + \frac{C(t_1, t_2)}{\langle R^2 \rangle^2} \right], \quad (17)$$

where

$$C(t_1, t_2) = \frac{72\bar{t}^2 + 55\bar{t}^4}{360(1 + \bar{t}^4)} \quad (18)$$

with

$$\bar{t}^2 = (t_1^{-2} + t_2^{-2})^{-1}. \quad (19)$$

We note that $f_{DDe}(t_1, t_2, \theta_t)$ is a hybrid between the asymptotic forms of $\langle R^2(t_1, t_2, \theta_t) \rangle^{1/2} \langle R^{-1}(t_1, t_2, \theta_t) \rangle$ for $t_1 \gg 1$ and $t_2 \gg 1$ and for $t_1 \gg 1$ and $t_2 \ll 1$ given by Equations (16) and (17), respectively, of ref. 10 with $\theta = \theta_t$. In the rod limit of $t_1 \rightarrow 0$ and $t_2 \rightarrow 0$, Equation (14) reduces to

$$\langle R^{-1}(t_1, t_2, \theta_t) \rangle = [R_{\text{rod}}(t_1, t_2, \theta_t)]^{-1} \quad (\text{rod limit}), \quad (20)$$

where $R_{\text{rod}}(t_1, t_2, \theta_t)$ is the end-to-end distance of the once-broken rod composed of the two straight rods of lengths t_1 and t_2 with the angle θ_t and is given by

$$R_{\text{rod}}(t_1, t_2, \theta_t) = (t_1^2 + t_2^2 - 2t_1 t_2 \cos \theta_t)^{1/2}. \quad (21)$$

Figure 2 shows plots of $R_{\text{rod}}(t_1, t_2, \theta_t) \langle R^{-1}(t_1, t_2, \theta_t) \rangle$ against t_1 for the once-broken KP chain with $t_2 = 0.1, 1$ and 2 . The curves represent the values calculated from the interpolation formula (14) with Equations (15)–(19). It is seen that the interpolation formula may well reproduce the MC values represented by the open circles. We note that the approximate value of $\langle R^{-1}(t, 0, \theta_t) \rangle$ and/or $\langle R^{-1}(0, t, \theta_t) \rangle$ calculated from the interpolation formula with $t_1 = t$ and $t_2 = 0$ (and/or $t_1 = 0$ and $t_2 = t$) agrees with the value calculated from the Yamakawa–Fujii interpolation formula for the mean reciprocal end-to-end distance of the KP linear chain¹⁵ (with the cylinder diameter $d = 0$) within 0.1% over the whole range of t .

RESULTS AND DISCUSSION

We have calculated the KR contribution $[\eta]_{\text{KR}}$ to the intrinsic viscosity $[\eta]$ from Equation (3) with the numerical solutions ϕ_{ii} of the linear simultaneous equations (5) for both the KP regular four-arm star and the linear touched-bead models over the ranges of the total number $4m+1$ (or $n+1$) of beads from 5 to 2001 and bead diameter d_b from 0.001 to 0.4. Note that the total contour length L of the chain is equal to $(4m+1)d_b$ [or $(n+1)d_b$], as already mentioned. We then calculated

Figure 2 Plots of $R_{\text{rod}}(t_1, t_2, \theta_t) \langle R^{-1}(t_1, t_2, \theta_t) \rangle$ against t_1 for the once-broken Kratky–Porod chain with $t_2 = 0.1, 1$ and 2 . The curves represent the values calculated from the interpolation formula (14) with Equations (15)–(19), and the open circles represent the Monte Carlo values.

$[\eta]$ from Equation (2) with the values of $[\eta]_{\text{KR}}$ so obtained along with $[\eta]_{\text{E}}$ calculated from Equation (4) for both the star and the linear chains. Finally, we evaluated g_η as a function of L and d_b from the defining equation,

$$g_\eta(L, d_b) = \frac{[\eta](\text{star})}{[\eta](\text{linear})} \quad (22)$$

with the values of $[\eta]$ so obtained for the star and linear chains having the same L and d_b .

Figure 3 shows plots of g_η against the logarithm of L . The open circles represent the theoretical values of g_η for $d_b = 0.001$ (pip up), 0.003 (pip right-up), 0.01 (pip right), 0.03 (pip right-down), 0.1 (pip down), 0.2 (pip left-down), 0.3 (pip left) and 0.4 (pip left-up), and the dashed curves smoothly connect the theoretical values at constant d_b . The solid curves represent the values calculated from an interpolation formula, which are obtained and discussed in a later subsection. The horizontal line segment indicates the value 0.82 obtained by Irurzun¹⁶ for the Gaussian regular four-arm star chain without excluded volume in the KR approximation. As in the case of the KP regular three-arm star touched-bead model,¹⁰ g_η first decreases and then increases after passing through a minimum, with decreasing L in the range of d_b investigated in this study, and the behavior of g_η shows remarkable dependence on d_b . The decrease in g_η with decreasing L (in units of λ^{-1}) over the range of rather large L indicates that the effective volume V_η of the regular star chain becomes much smaller than that of the corresponding linear chain as the chains become stiffer; such a tendency is enhanced by the decrease in d_b .

In the following subsections, we first examine the behavior of g_η in the random-coil and rod limits and then propose an interpolation formula for g_η . Finally, we compare the present results for the KP regular four-arm star touched-bead model with the previous results¹⁰ for the KP regular three-arm star.

Random-coil limit

The value of g_η becomes constant independent of d_b in the random-coil limit of L (in units of λ^{-1}) $\rightarrow \infty$. Figure 4 shows plots of $g_\eta(L, d_b)$ against $L^{-1/2}$ for $d_b = 0.1, 0.2, 0.3$ and 0.4 . All of the symbols have the same meaning as those in Figure 3. The dashed curves smoothly

Figure 3 Plots of $g_\eta(L, d_b)$ against $\log L$. The open circles represent the theoretical values, with various directions of pips indicating different values of d_b indicated. The dashed curves smoothly connect the theoretical values at constant d_b . The horizontal line segment indicates the value 0.82 obtained by Iruzun¹⁶ for the Gaussian regular four-arm star chain. The solid curves represent the values calculated from the interpolation formula (see the text).

Figure 4 Plots of $g_\eta(L, d_b)$ against $L^{-1/2}$. All of the symbols have the same meaning as those in Figure 3. The dashed curves smoothly connect the theoretical values at constant d_b and the solid straight lines indicate the respective initial tangents.

connect the theoretical values at constant d_b , and the solid straight lines indicate the respective initial tangents. It is seen that as $L^{-1/2}$ decreases to 0 ($L \rightarrow \infty$), g_η approaches the above-mentioned value¹⁶ 0.82, irrespective of the value of d_b . Based on these numerical results, it may be concluded that

$$\lim_{L \rightarrow \infty} g_\eta(L, d_b) = 0.817 \quad (\text{random-coil limit}). \quad (23)$$

We note that the values of g_η for smaller d_b have been omitted in Figure 4 because we cannot make $L^{-1/2} (= [(4m+1)d_b]^{-1/2})$ small enough to evaluate g_η at $L^{-1/2}=0$. We also note that the g_η value so obtained in the random-coil limit is almost identical with the value 0.82₃ obtained by Zimm and Kilb¹⁷ for the (dynamic) Gaussian spring-bead model^{9,18,19} without excluded volume and with the preaveraged Oseen tensor.

Figure 5 Plots of $g_\eta^0(L/d_b)$ against $[\ln(L/d_b)]^{-1}$. The open circles represent the theoretical values. The horizontal line segment indicates the asymptotic value $1/4$ in the limit of $[\ln(L/d_b)]^{-1} \rightarrow 0$ ($L/d_b \rightarrow \infty$). The curve represents the values of the interpolation formula (28), the solid part indicates the range of $L/d_b \gtrsim 10$ (see the text).

Figure 6 Plots of $g_\eta(L, d_b)/g_\eta^0(L/d_b)$ against $\log L$ for $L/d_b \geq 10$. All of the symbols have the same meaning as those in Figure 3. The solid curve represents the values calculated from the interpolation formula (29) (see the text).

As mentioned in the previous study,¹⁰ the KR approximation may overestimate the g_η value because of the preaveraging of the Oseen tensor. Indeed, the g_η value of 0.75 obtained by Okumoto *et al.*²⁰ for regular four-arm star polystyrenes in cyclohexane at 34.5 °C (Θ) is $\sim 8\%$ smaller than the above asymptotic value in the random-coil limit.

Rod limit

In the rod limit of $L \rightarrow 0$, $[\eta]$ of the regular four-arm star touched-bead model in the thin rod limit of $L/d_b \rightarrow \infty$ may be evaluated analytically in the same manner as in the case of the regular three-arm star (see Appendix C of ref. 10), as follows,

$$\lim_{\substack{L \rightarrow 0 \\ L/d_b \rightarrow \infty}} [\eta] = \frac{\pi N_A L^3}{96 M \ln(L/d_b)} \quad (\text{thin rod limit, four-arm star}). \quad (24)$$

Figure 7 Plots of $g_{\eta,4}$ and $g_{\eta,3}$ against $\log L$. The solid and dashed curves represent the $g_{\eta,4}$ and $g_{\eta,3}$ values, respectively, with indicated values of d_b . The upper solid and dashed horizontal line segments indicate the asymptotic values 0.82 for the four-arm star and 0.90 for the three-arm star, respectively, in the random-coil limit obtained by Irurzun.¹⁶ The lower solid and dashed horizontal line segments indicate the asymptotic values 1/4 for the four-arm star and 4/9 for the three-arm star, respectively, in the thin rod limit.

Figure 8 Plots of $g_{\eta,4}/g_{\eta,3}$ against $\log L$. The solid curves represent the theoretical values calculated from the values of $g_{\eta,4}$ and $g_{\eta,3}$, shown in Figure 7. The upper and lower horizontal line segments represent the asymptotic values 0.91 in the random-coil limit and 9/16 in the thin rod limit, respectively.

The details of the evaluation are omitted here for simplicity. As for the linear chain, we have

$$\lim_{\substack{L \rightarrow 0 \\ L/d_b \rightarrow \infty}} [\eta] = \frac{\pi N_A L^3}{24M \ln(L/d_b)} \quad (\text{thin rod limit, linear}), \quad (25)$$

which has been obtained from the result¹³ for the cylinder model of diameter d along with the relation¹¹ $d=0.74d_b$.

In the rod limit, g_η should be a function only of L/d_b , that is,

$$\lim_{L \rightarrow 0} g_\eta(L, d_b) = g_\eta^0(L/d_b) \quad (\text{rod limit}). \quad (26)$$

From Equation (22) with Equations (24)–(26), we have

$$\lim_{L/d_b \rightarrow \infty} g_\eta^0(L/d_b) = \frac{1}{4} \quad (\text{thin rod limit}). \quad (27)$$

It is interesting to note that the ratio g_s between the values of the mean-square radius of gyration of the KP regular four-arm star and linear chains,¹⁴ both having the same L , also becomes 1/4 in the rod limit. We note that the asymptotic value 4/9 of g_η in the thin rod limit is equal to the asymptotic value of g_s in the rod limit also in the case of the regular three-arm star.¹⁰

We have also evaluated $g_\eta^0(L/d_b)$ at finite L/d_b numerically in the same manner as in the evaluation of $g_\eta(L/d_b)$ mentioned above using the expressions for $\langle R_{ij}^{-1} \rangle$ given by Equation (20) and $\langle S_i S_j \rangle$ given by Equations (10) and (13) of ref. 10 in place of those for the KP chain. Figure 5 shows plots of g_η^0 against $[\ln(L/d_b)]^{-1}$. The open circles represent the values so obtained, and the horizontal line segment indicates the asymptotic value of 1/4 in the limit of $[\ln(L/d_b)]^{-1} \rightarrow 0$ ($L/d_b \rightarrow \infty$). As $[\ln(L/d_b)]^{-1}$ decreases (L/d_b increases), g_η^0 monotonically decreases to 1/4. For later convenience, we have constructed an interpolation formula for $g_\eta^0(L/d_b)$ in the

range of $L/d_b \gtrsim 10$, which is given by

$$g_\eta^0(x) = \frac{1}{4} \frac{1 - 2.631(\ln x)^{-1} + 3.599(\ln x)^{-2}}{1 - 3.217(\ln x)^{-1} + 3.423(\ln x)^{-2}} \quad \text{for } x \gtrsim 10. \quad (28)$$

In Figure 5, the curve represents the values calculated from Equation (28) with $x=L/d_b$. The error in the value of $g_\eta^0(L/d_b)$ in the range of $L/d_b \gtrsim 10$ (solid part) does not exceed 0.2%.

Interpolation formula

As in the case of the KP regular three-arm star touched-bead model,¹⁰ we constructed an interpolation formula for g_η of the KP regular four-arm star. Figure 6 shows plots of the ratio $g_\eta(L, d_b)/g_\eta^0(L/d_b)$ against the logarithm of L for $L/d_b \gtrsim 10$, where g_η/g_η^0 has been evaluated by dividing the g_η values shown in Figure 3 by the g_η^0 values calculated from Equation (28) with $x=L/d_b$. All of the symbols have the same meaning as those in Figure 3. It is seen that the circles form a single composite curve almost independent of d_b for $d_b \lesssim 0.2$, and the curve monotonically increases from 1 to 3.27 [=0.817/(1/4)] with increasing L . We have therefore assumed that g_η/g_η^0 may be represented by a function $f(L)$ only of L for $d_b \lesssim 0.2$ and have constructed an empirical interpolation formula for $f(L)$, which may be written in the form

$$f(L) = 1 + 0.2501L - 0.02260L^2 \quad \text{for } L \leq 3 \\ = 3.27 \frac{1 - 0.2183(\ln L)^{-1} + 3.186(\ln L)^{-2}}{1 + 0.03759(\ln L)^{-1} + 7.532(\ln L)^{-2}} \quad \text{for } L > 3 \quad (29)$$

The function $f(L)$ given by Equation (29) satisfies the asymptotic conditions $\lim_{L \rightarrow 0} f(L) = 1$ and $\lim_{L \rightarrow \infty} f(L) = 3.27$, which hold in the limit of $L/d_b \rightarrow \infty$. In Figure 6, the solid curve represents the values calculated from Equation (29). The factor $g_\eta(L, d_b)$ may then be approximately expressed as

$$g_\eta(L, d_b) = g_\eta^0(L/d_b) f(L), \quad (30)$$

where $g_\eta^0(L/d_b)$ and $f(L)$ are given by Equations (28) and (29), respectively.

In Figure 3, the solid curves represent the approximate values calculated from Equation (30) with Equations (28) and (29). It is

seen that the proposed interpolation formula for $g_\eta(L, d_b)$ may well reproduce the numerical theoretical values in the ranges of $d_b \lesssim 0.2$ and $L/d_b \gtrsim 10$. The error in the value of g_η in those ranges of d_b and L/d_b does not exceed 2%.

Comparison with the KP regular three-arm star

Here, we compare the behavior of g_η as a function of L for the four-arm star with that for the three-arm star. Hereafter, g_η 's for the four- and three-arm stars are designated $g_{\eta,4}$ and $g_{\eta,3}$, respectively. Figure 7 shows plots of $g_{\eta,4}$ and $g_{\eta,3}$ against the logarithm of L , both with $d_b = 0.001, 0.01$ and 0.1 . The solid and dashed curves represent the values of $g_{\eta,4}$ and $g_{\eta,3}$, respectively, with indicated values of d_b . The values of $g_{\eta,4}$ have been calculated from Equation (30) with Equations (28) and (29) and those of $g_{\eta,3}$ from Equation (40) with Equations (38) and (39) of ref. 10. The upper solid and dashed horizontal line segments indicate the asymptotic values 0.82 for the four-arm star and 0.90 for the three-arm star, respectively, in the random-coil limit obtained by Irurzun.¹⁶ The lower solid and dashed horizontal line segments indicate the above-mentioned asymptotic values 1/4 for the four-arm star and 4/9 for the three-arm star, respectively, in the thin rod limit. It is seen that $g_{\eta,4}$ is appreciably smaller than $g_{\eta,3}$ for given L and d_b , as a natural consequence of the fact that the average chain dimension of polymer chains becomes smaller with an increasing degree of branching.

Finally, we examine the behavior of the ratio $g_{\eta,4}/g_{\eta,3}$ for given L and d_b . We note that $g_{\eta,4}/g_{\eta,3}$ is identical with the ratio between the values of $[\eta]$ of the KP regular four- and three-arm star touched-bead models, both having the same L and d_b . Figure 8 shows plots of $g_{\eta,4}/g_{\eta,3}$ against the logarithm of L with $d_b = 0.001, 0.01$ and 0.1 . The solid curves represent the theoretical values calculated from the values of $g_{\eta,4}$ and $g_{\eta,3}$ shown in Figure 7 with indicated values of d_b . The upper and lower horizontal line segments represent the asymptotic values 0.91 ($=0.82/0.90$) in the random-coil limit and $9/16$ [$=(1/4)/(4/9)$] in the thin rod limit, respectively. As in the cases of $g_{\eta,4}$ and $g_{\eta,3}$ themselves, $g_{\eta,4}/g_{\eta,3}$ first decreases from the asymptotic value 0.91 in the random-coil limit and then increases after passing through a minimum, with decreasing L in the range of d_b examined, and $g_{\eta,4}/g_{\eta,3}$ appreciably decreases with decreasing d_b at constant L .

CONCLUSION

We have evaluated the ratio g_η between the values of $[\eta]$ of the KP regular four-arm star and linear touched-bead models, where both have the same total contour length L and bead diameter d_b (both in units of λ^{-1}), in the KR approximation. We then examined its behavior as a function of L and d_b . It has been found that the ratio g_η/g_η^0 of g_η to its asymptotic value g_η^0 in the rod limit monotonically

increases from 1 to 3.27 with increasing L , almost independent of d_b for $d_b \lesssim 0.2$, although g_η itself as a function of L shows remarkable dependence on d_b . Such behavior of g_η of the four-arm star is qualitatively the same as that of the three-arm star examined previously.¹⁰ We have also examined the behavior of the ratio $g_{\eta,4}/g_{\eta,3}$ between the values of g_η of the four- ($g_{\eta,4}$) and three-arm ($g_{\eta,3}$) stars as a function of L and d_b , which is identical with the ratio between the values of $[\eta]$ of the four- and three-arm stars, both having the same L and d_b . As in the cases of $g_{\eta,4}$ and $g_{\eta,3}$, $g_{\eta,4}/g_{\eta,3}$ first decreases from the asymptotic value 0.91 in the random-coil limit and then increases after passing through a minimum, with decreasing L in the range of d_b examined, and $g_{\eta,4}/g_{\eta,3}$ appreciably decreases with decreasing d_b at constant L .

- 1 Staudinger, H. & Heuer, W. Über hochpolymere Verbindungen, 33. Mitteilung: Beziehungen zwischen Viskosität und Molekulargewicht bei Poly-styrolen. *Ber.* **63**, 222–234 (1930).
- 2 Flory, P. J. *Principles of Polymer Chemistry* (Cornell Univ. Press, Ithaca, New York, 1953).
- 3 Mark, H. in *Der feste Körper* (ed. Sänger, R.), 65–104 (Hirzel, Leipzig, 1938).
- 4 Houwink, R. Zusammenhang zwischen viscosimetrisch und osmotisch bestimmten Polymerisationsgraden bei Hochpolymeren. *J. Prakt. Chem.* **157**, 15–18 (1940).
- 5 Sakurada, I. *Kasen Koenshu* **5**, 33–44 (1940). Its English translation appears in this issue.
- 6 Kurata, M. & Tsunashima, Y. in *Polymer Handbook*, 4th ed. (ed. Brandrup, J., Immergut, E. H. & Grulke, E. A.) Ch. 7, VII/1–83 (John Wiley & Sons, New York, 1999).
- 7 Kratky, O. & Porod, G. Röntgenuntersuchung gelöster fadenmoleküle. *Recl. Trav. Chim. Pay-Bas.* **68**, 1106–1122 (1949).
- 8 Yamakawa, H. *Helical Wormlike Chains in Polymer Solutions* (Springer, Berlin, 1997).
- 9 Yamakawa, H. *Modern Theory of Polymer Solutions* (Harper & Row, New York, 1971). Available at: <http://www.molsci.polym.kyoto-u.ac.jp/archives/redbook.pdf>.
- 10 Ida, D., Nakamura, Y. & Yoshizaki, T. Intrinsic viscosity of wormlike regular three-arm stars. *Polym. J.* **40**, 256–267 (2008).
- 11 Yoshizaki, T., Nitta, I. & Yamakawa, H. Transport coefficients of helical wormlike chains. 4. Intrinsic viscosity of the touched-bead model. *Macromolecules* **21**, 165–171 (1988).
- 12 Kirkwood, J. G. & Riseman, J. The intrinsic viscosities and diffusion constants of flexible macromolecules in solution. *J. Chem. Phys.* **16**, 565–573 (1948).
- 13 Yamakawa, H. & Fujii, M. Intrinsic viscosity of wormlike chains. Determination of the shift factor. *Macromolecules* **7**, 128–135 (1974).
- 14 Mansfield, M. L. & Stockmayer, W. H. Unperturbed dimensions of wormlike stars. *Macromolecules* **13**, 1713–1715 (1980).
- 15 Yamakawa, H. & Fujii, M. Translational friction coefficient of wormlike chains. *Macromolecules* **6**, 407–415 (1973).
- 16 Irurzun, I. M. Hydrodynamic properties of regular star branched polymer in dilute solution. *J. Polym. Sci., Part B: Polym. Phys.* **35**, 563–567 (1997).
- 17 Zimm, B. H. & Kilb, R. W. Dynamics of branched polymer molecules in dilute solution. *J. Polym. Sci.* **37**, 19–42 (1959).
- 18 Rouse Jr, P. E. A theory of the linear viscoelastic properties of dilute solutions of coiling polymers. *J. Chem. Phys.* **21**, 1272–1280 (1953).
- 19 Zimm, B. H. Dynamics of polymer molecules in dilute solution: viscoelasticity, flow birefringence and dielectric loss. *J. Chem. Phys.* **24**, 269–278 (1956).
- 20 Okumoto, M., Terao, K., Nakamura, Y., Norisuye, T. & Teramoto, A. Excluded-volume effects in star polymer solutions: four-arm star polystyrene in cyclohexane near the Θ temperature. *Macromolecules* **30**, 7493–7499 (1997).