INTRINSIC FLOW BIREFRINGENCE OF STIFF CHAINS

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Using the Svetlov theory, it is shown that the ratio of intrinsic flow birefringence to intrinsic viscosity is independent of the magnitude of the hydrodynamic interaction, in the case where the latter is consistently pre-averaged. The intrinsic birefringence has been calculated on Tagami's model for stiff chains, and the results are compared with earlier theories.

So far, intrinsic birefringence has been calculated for several models of stiff chains[1-4]. Some discrepancies are obvious in the results: different views have been expressed with respect to the influence of hydrodynamic interaction on the ratio of intrinsic birefringence and intrinsic viscosity[2-4], and relations describing the magnitude of the "optical segment"[1,2] have been found to depend on the chain model used.

All theories so far in existence contemplate only the "inherent" chain birefringence (the first term in Eq. (2) given below). With respect to the evaluation of experimental data, it seems desirable to extend the theory by calculating the interaction term (form effect – second term in Eq. (2) – discussed in more detail in ref.[5]). For this purpose, one needs a sufficiently realistic, though mathematically as simple as possible, model of the stiff polymer chain. In our view, such requirements are best met by the Tagami model[6,7]. Since not even the "inherent" birefringence itself has been calculated for this chain model, we calculate it in this work. The result is compared with the birefringence of a persistent chain, generally regarded as a satisfactory model of stiff chains.

In addition, we try to examine conditions under which the ratio of intrinsic birefringence $[n]$ to intrinsic viscosity $[\eta]$ is independent of hydrodynamic interaction, and contribute in this way to the elucidation of the differences mentioned above between the results obtained using existing theories.

Effect of Hydrodynamic Interaction on $[n]/[\eta]$

For the intrinsic birefringence $[n]$ of a polymer chain modelled by an assembly of frictional centres the following equation holds[5]:

$$[n] = \frac{\pi}{135kT} \cdot \frac{(n_s^2 + 2)^2}{\eta_s n_s} \cdot \frac{N_A}{M} \Delta \Gamma_f \,, \tag{1}$$

where k is the Boltzmann constant; T is absolute temperature; n_s and η_s are the refractive index of the solvent and the solvent viscosity, respectively; N_A is the Avogadro number; M is molecular weight of the polymer and $\Delta\Gamma_f$ for a polymer in the isotropic solvent is defined by

$$\Delta\Gamma_f = kT[\langle \mathcal{T}r\gamma\, \mathcal{T}r\mathbf{X} - 3\mathcal{T}r(\gamma\,.\,\mathbf{X})\rangle + \langle \mathcal{T}r\mathbf{A}\, \mathcal{T}r\mathbf{X} - 3\mathcal{T}r(\mathbf{A}\,.\,\mathbf{X})\rangle]\,, \quad (2)$$

where $\langle\ \rangle$ is the mean value; $\mathcal{T}r$ is the trace of the tensor; γ is the tensor of the optical polarizability of a polymer molecule; $\mathbf{A}$ is the tensor of the optical interaction defined in ref.[5]; and $\mathbf{X}$ is the hydrodynamic tensor obtained by Svetlov[8] by solving the Kirkwood–Risemann diffusion equation (it is defined in ref.[8]). ($\mathbf{X}'$ introduced in ref.[5] is defined by $\mathbf{X}' = -kT\mathbf{X}$ and not by $\mathbf{X}' = -\mathbf{X}$, as erroneously given in ref.[5]) In this work we try to calculate the 1st term in Eq. (2), in the same way as earlier authors[1–4,8].

To calculate $\Delta\Gamma_f$ with an exact expression for $\mathbf{X}$ would be very difficult. We therefore use Svetlov's approximation[3], in which it is assumed that the tensor properties of $\mathbf{X}$ are the same as with the tensor of the moment of inertia, $\mathbf{I}$. In this case equation (3) holds for the tensor $\mathbf{X}$,

$$\mathbf{X} = 3\mathbf{I}(D_r\langle \mathcal{T}r\mathbf{I}\rangle)^{-1}\,, \quad (3)$$

where D_r is the rotational diffusion constant of the polymer molecule. By using only the first term in Eq. (2) and by substituting $\mathbf{X}$ with an expression from Eq. (3), we obtain

$$\Delta\Gamma_f = 3kT\langle \mathcal{T}r\gamma\, \mathcal{T}r\mathbf{I} - 3\mathcal{T}r(\gamma\,.\,\mathbf{I})\rangle\,(D_r\langle \mathcal{T}r\mathbf{I}\rangle)^{-1}\,. \quad (4)$$

Now we examine the effect of hydrodynamic interaction on $[n]/[\eta]$. According to the theory of Shimada and Yamakawa[4], and of Noda and Hearst[2], this ratio is in principle independent of hydrodynamic interaction. According to an estimate by Svetlov[3], who uses a model of an equivalent ellipsoid without preaveraging the hydrodynamic interaction in the calculation of $[\eta]$ and D_r, $[n]/[\eta]$ for a persistent chain depends on the hydrodynamic interaction.

If we start with Tsuda's theory, $[\eta]$ and D_r are described by the relations[9]:

$$[\eta] = \frac{N_A}{2M\eta_s}\left[\frac{1}{\zeta\sum_l\langle(\mathbf{r}^{(l)}\,.\,\mathbf{e}_x)^2\rangle} + \frac{1}{(\sum_l\langle(\mathbf{r}^{(l)}\,.\,\mathbf{e}_x)^2\rangle)^2}\sum_l\sum_s\{\langle(\mathbf{r}^{(l)}\,.\,\mathbf{e}_x) \quad (5)$$

$$(\mathbf{r}^{(s)}\,.\,\mathbf{e}_x)\,(\mathbf{e}_y\,.\,\mathbf{T}^{(ls)}\,.\,\mathbf{e}_y)\rangle + \langle(\mathbf{r}^{(l)}\,.\,\mathbf{e}_x)\,(\mathbf{r}^{(s)}\,.\,\mathbf{e}_y)\,(\mathbf{e}_x\,.\,\mathbf{T}^{(ls)}\,.\,\mathbf{e}_y)\rangle\}\right]^{-1},$$

$$D_r = \frac{kT}{2}\left[\frac{1}{\zeta\sum_l\langle(\mathbf{r}^{(l)}\cdot\mathbf{e}_x)^2\rangle} + \frac{1}{(\sum_l\langle(\mathbf{r}^{(l)}\cdot\mathbf{e}_x)^2\rangle)^2}\sum_l\sum_s\langle(\mathbf{r}^{(l)}\cdot\mathbf{e}_x)(\mathbf{r}^{(s)}\cdot\mathbf{e}_x)\right. \qquad (6)$$

$$\left.(\mathbf{e}_y\cdot\mathbf{T}^{(ls)}\cdot\mathbf{e}_y)\rangle - \langle(\mathbf{r}^{(l)}\cdot\mathbf{e}_x)(\mathbf{r}^{(s)}\cdot\mathbf{e}_y)(\mathbf{e}_x\cdot\mathbf{T}^{(ls)}\cdot\mathbf{e}_y)\rangle\}\right],$$

where ζ is the frictional resistance of the frictional centre, $\mathbf{r}^{(l)}$ and $\mathbf{r}^{(s)}$ are the position vectors of frictional centres l and s, $\mathbf{e}_x$, $\mathbf{e}_y$ are the unit vectors in the directions of the axes x and y of the laboratory system of coordinates, and $\mathbf{T}^{(ls)}$ is Oseen's tensor of hydrodynamic interaction defined in ref.[3,8,9].

If in Eqs (5) and (6) tensor $\mathbf{T}^{(ls)}$ is replaced with tensor $\langle\mathbf{T}^{(ls)}\rangle\,\mathbf{E}$ ($\mathbf{E}$ is the unit tensor), as is usual in calculations of hydrodynamic quantities[10], we obtain, after averaging the right-hand sides of Eqs (5) and (6) over all orientations of the system of coordinates connected with the molecule with respect to the laboratory system, the known relation

$$\frac{kT}{D_r} = \frac{4M\eta_s}{N_A}[\eta]\,. \qquad (7)$$

It follows from the derivation that Eq. (7) is generally valid in the case of the preaveraging of hydrodynamic interaction, irrespective of the statistical model of the polymer chain under consideration. The same conclusion is reached if the Kirkwood–Riseman theory is used in the calculation of $[\eta]$ and D_r[10].

After substitution for D_r from Eq. (7) into Eq. (4), and for $\Delta\Gamma_f$ from Eq. (4) into Eq. (1), we obtain for $[n]/[\eta]$

$$\frac{[n]}{[\eta]} = \frac{4\pi}{45kT}\cdot\frac{(n_s^2+2)^2}{n_s}\cdot\frac{\langle\mathcal{T}\boldsymbol{\imath}\gamma\,\mathcal{T}\boldsymbol{\imath}\mathbf{l} - 3\mathcal{T}\boldsymbol{\imath}(\gamma\,.\,\mathbf{l})\rangle}{\langle\mathcal{T}\boldsymbol{\imath}\mathbf{l}\rangle} =$$

$$= \frac{4\pi}{45kT}\cdot\frac{(n_s^2+2)^2}{n_s}\Delta\alpha_{ef}\,. \qquad (8)$$

For a freely joined chain, $\Delta\alpha_{ef}$ defined by Eq. (8) is the anisotropy of a statistical segment. It follows from Eq. (8) that in the case of the preaveraging of hydrodynamic interaction in the calculation of $[\eta]$ and D_r, $[n]/[\eta]$ does not depend on hydrodynamic interaction, even if the Svetlov theory is used[3]. Such a conclusion is consistent with the results of the Shimada–Yamakawa[4] and Noda–Hearst theories[2]. The procedure employed in both theories corresponds to a consistent preaveraging of Oseen's tensor in all expressions.

If calculations of $[\eta]$ and D_r using Eqs (5) and (6) were carried out without the preaveraging of $\mathbf{T}^{(ls)}$, the relation between them would generally be dependent on the statistical chain model.

Such calculation for models of stiff chains (*e.g.* the Tagami or persistent model) would be rather labour-consuming. We believe that for a consistent investigation of the effect of the anisotropy of hydrodynamic interaction on $[n]/[\eta]$ one would have to compare the results obtained by means of the exact tensor $\mathbf{X}$ with those obtained for $\mathbf{X}$ given by Eq. (*3*) without the preaveraging of T in the equations for $[\eta]$ and D_r, on the one hand, and with the results obtained by a consistent preaveraging of T in all expressions, on the other. It should be pointed out, however, that calculations carried out by using the exact theory[8] can be performed only for the simplest chain models.

Let it be noted that by preaveraging the hydrodynamic interaction and by employing the procedure just outlined, one arrives at the conclusion that $[n]/[\eta]$ is independent of the magnitude of hydrodynamic interaction, even taking into account the second term in Eq. (*2*).

With respect to results of the above analysis of the effect of hydrodynamic interaction on $[n]/[\eta]$, the calculations presented in the subsequent part of this work are carried out only for a free-draining chain.

Calculation for the Tagami Chain Model

The distribution function of the position vectors $\mathbf{r}_0$ and $\mathbf{r}$ and tangential vectors $\mathbf{u}_0$, $\mathbf{u}$ of chain ends, $\rho(\mathbf{r}, \mathbf{u}, L \mid \mathbf{r}_0, \mathbf{u}_0)$, of the Tagami chain model has the form[7]

$$\rho(\mathbf{r}, \mathbf{u}, L \mid \mathbf{r}_0, \mathbf{u}_0) = \frac{e^{6\lambda L}}{8\pi^3 \Delta^{3/2}} \exp \left\{ -\frac{1}{2\Delta} \left[a(e^{2\lambda L}\mathbf{u} - \mathbf{u}_0)^2 + \right.\right.$$

$$\left.\left. + 2h(e^{2\lambda L}\mathbf{u} - \mathbf{u}_0)\left(\mathbf{r} + \frac{\mathbf{u}}{2\lambda} - \mathbf{r}_0 - \frac{\mathbf{u}_0}{2\lambda}\right) + b\left(\mathbf{r} + \frac{\mathbf{u}}{2\lambda} - \mathbf{r}_0 - \frac{\mathbf{u}_0}{2\lambda}\right)^2 \right] \right\}, \quad (9)$$

where

$$a = L/3\lambda \quad (10a)$$

$$b = (1/3)(e^{4\lambda L} - 1), \quad (10b)$$

$$h = (1/3\lambda)(e^{2\lambda L} - 1), \quad (10c)$$

$$\Delta = ab - h^2, \quad (10d)$$

$\lambda = 1/l$ is the reciprocal statistical segment, and L is the contour chain length.

The mean value of $F(\mathbf{r}, \mathbf{u}, \mathbf{r}_0, \mathbf{u}_0, L)$ is calculated using the expression

$$F(\mathbf{r}, \mathbf{u}, \mathbf{r}_0, \mathbf{u}_0, L) = \int_{-\infty}^{\infty} F(\mathbf{r}, \mathbf{u}, \mathbf{r}_0, \mathbf{u}_0, L)\, \rho(\mathbf{r}, \mathbf{u}, L \mid \mathbf{r}_0, \mathbf{u}_0)\, g(\mathbf{u}_0)$$

$$d\mathbf{r}\, d\mathbf{r}_0\, d\mathbf{u}\, d\mathbf{u}_0, \quad (11)$$

where $g(\mathbf{u}_0) = (1/4\pi)\, \delta(|\mathbf{u}_0| - 1)$, and δ is the Dirac delta function.

For a chain consisting of N rotationally symmetrical basic (not statistical) segments, the tensor of polarizability γ may be written in the form

$$\gamma = \sum_{i=1}^{N} \left(a_2 \mathbf{E} + \Delta a \mathbf{u}^{(i)} \mathbf{u}^{(i)} \right), \tag{12}$$

where a_1, a_2 are the polarizabilities of the segment in the direction of the chain and perpendicular to it, respectively, $\Delta a = a_1 - a_2$, and $\mathbf{u}^{(i)}\mathbf{u}^{(i)}$ is the dyadic product of tangential vectors to the chain in the centre of the i-th segment. For the tensor of the moment of inertia we have[3,8]

$$\mathbf{I} = \left(1/(N+1)\right) \sum_{k=0}^{N} \sum_{j=0}^{k-1} \left[\left(\mathbf{r}^{(kj)} \cdot \mathbf{r}^{(kj)} \right) \mathbf{E} - \mathbf{r}^{(kj)} \mathbf{r}^{(kj)} \right], \tag{13}$$

where $\mathbf{r}^{(kj)} = \mathbf{r}^{(k)} - \mathbf{r}^{(j)}$.

After substitution for γ and $\mathbf{I}$ from Eqs (12), (13) we obtain

$$\langle \mathcal{T}r\gamma\, \mathcal{T}r\mathbf{I} - 3\mathcal{T}r(\gamma \cdot \mathbf{I}) \rangle = 3\, \frac{\Delta a}{N+1} \sum_{i=1}^{N} \sum_{k=0}^{N} \sum_{j=0}^{k-1} \langle (\mathbf{u}^{(i)} \cdot \mathbf{r}^{(kj)})^2 \rangle - \frac{\Delta a}{N+1} \sum_{i=1}^{N} \sum_{k=0}^{N} \sum_{j=0}^{k-1} \langle \mathbf{u}^{(i)2} \mathbf{r}^{(kj)2} \rangle . \tag{14}$$

Eq. (14) may be rewritten to become

$$\langle \mathcal{T}r\gamma\, \mathcal{T}r\mathbf{I} - 3\mathcal{T}r(\gamma \cdot \mathbf{I}) \rangle = \frac{\Delta a}{N+1} \sum_{k=0}^{N} \sum_{l=0}^{k-1} (N-k)\left(3A_1 + 3A_2 + 3A_3 - A_4 - A_5 - A_6\right), \tag{15}$$

where

$$A_1 = \langle (\mathbf{u}^{(0)} \cdot \mathbf{r}^{(kl)})^2 \rangle = \frac{1}{3\lambda} \left(s_k - s_l - \frac{1}{2\lambda} + \frac{1}{2\lambda} e^{-4\lambda s_k} + \frac{1}{2\lambda} e^{-4\lambda s_l} + \frac{1}{2\lambda} e^{-2\lambda(s_k - s_l)} - \frac{1}{\lambda} e^{-2\lambda(s_k + s_l)} \right), \tag{16}$$

$$A_2 = \langle (\mathbf{u}^{(l)} \cdot \mathbf{r}^{(k0)})^2 \rangle = \frac{1}{3\lambda} \left(s_k + \frac{7}{2\lambda} - \frac{4}{\lambda} e^{-2\lambda s_l} + \frac{1}{2\lambda} e^{-4\lambda s_l} + \frac{5}{2\lambda} e^{-2\lambda s_k} - \frac{4}{\lambda} e^{-2\lambda(s_k - s_l)} + \frac{1}{\lambda} e^{-4\lambda(s_k - s_l)} - \frac{1}{2\lambda} e^{-4\lambda(s_k + s_l)} + \frac{1}{\lambda} e^{-2\lambda(s_k + s_l)} \right), \tag{17}$$

$$A_3 = \langle (\boldsymbol{u}^{(k)} \, . \, \boldsymbol{r}^{(10)})^2 \rangle = \frac{1}{3\lambda} \left(s_1 - \frac{1}{2\lambda} + \frac{1}{2\lambda} e^{-2\lambda s_1} + \frac{1}{2\lambda} e^{-4\lambda s_k} + \right.$$

$$\left. + \frac{1}{\lambda} e^{-4\lambda(s_k - s_1)} - \frac{1}{2\lambda} e^{-4\lambda(s_k + s_1)} - \frac{2}{\lambda} e^{-2\lambda(2s_k - s_1)} + \frac{1}{\lambda} e^{-2\lambda(2s_k + s_1)} \right) \qquad (18)$$

$$A_4 = \langle \boldsymbol{u}^{(0)^2} \boldsymbol{r}^{(k1)^2} \rangle = \frac{s_k}{\lambda} - \frac{s_1}{\lambda} - \frac{1}{2\lambda^2} + \frac{1}{2\lambda^2} e^{-2\lambda(s_k - s_1)} \,, \qquad (19)$$

$$A_5 = \langle \boldsymbol{u}^{(1)^2} \boldsymbol{r}^{(k0)^2} \rangle = \frac{s_k}{\lambda} + \frac{1}{6\lambda^2} - \frac{2}{3\lambda^2} e^{-2\lambda s_1} + \frac{5}{6\lambda^2} e^{-2\lambda s_k} -$$

$$- \frac{2}{3\lambda^2} e^{-2\lambda(s_k - s_1)} + \frac{1}{6\lambda^2} e^{-4\lambda(s_k - s_1)} - \frac{1}{6\lambda^2} e^{-4\lambda(s_k + s_1)} + \frac{1}{3\lambda^2} e^{-2\lambda(s_k + 2s_1)} \qquad (20)$$

$$A_6 = \langle \boldsymbol{u}^{(k)^2} \boldsymbol{r}^{(10)^2} \rangle = \frac{s_1}{\lambda} - \frac{1}{2\lambda^2} + \frac{1}{2\lambda^2} e^{-2\lambda s_1} + \frac{1}{6\lambda^2} e^{-4\lambda(s_k - s_1)} -$$

$$- \frac{1}{6\lambda^2} e^{-4\lambda(s_k + s_1)} - \frac{1}{3\lambda^2} e^{-2\lambda(2s_k - s_1)} + \frac{1}{3\lambda^2} e^{-2\lambda(2s_k + s_1)} \,. \qquad (21)$$

Now we examine the behaviour of a chain represented by a continuous curve. In this case, Eq. (*15*) becomes

$$\langle \mathscr{T}\imath\gamma \, \mathscr{T}\imath\boldsymbol{I} - 3\mathscr{T}\imath(\gamma \, . \, \boldsymbol{I}) \rangle = \frac{\Delta a}{L} \int_0^L \int_0^{s_k} (L - s_k) \left(3A_1 + 3A_2 + 3A_3 - \right.$$

$$\left. - A_4 - A_5 - A_6 \right) ds_1 \, ds_k \,, \qquad (22)$$

where Δa is the optical anisotropy of the unit chain length. After substitution from Eqs (*16*)–(*21*) into Eq. (*22*) and integration, we obtain

$$\langle \mathscr{T}\imath\gamma \, \mathscr{T}\imath\boldsymbol{I} - 3\mathscr{T}\imath(\gamma \, . \, \boldsymbol{I}) \rangle =$$

$$= \Delta a \left(\frac{5}{9\lambda^2} L^2 - \frac{4}{3\lambda^3} L + \frac{41}{24\lambda^4} - \frac{1187}{1152\lambda^5 L} + \frac{5}{12\lambda^4} e^{-2\lambda L} + \frac{1}{16\lambda^4} e^{-4\lambda L} + \right.$$

$$\left. + \frac{23}{24\lambda^5 L} e^{-2\lambda L} + \frac{1}{12\lambda^5 L} e^{-4\lambda L} - \frac{1}{72\lambda^5 L} e^{-6\lambda L} + \frac{1}{384\lambda^5 L} e^{-8\lambda L} \right) . \qquad (23)$$

It follows from the definition of the tensor of the moment of inertia[3,8] and of the mean radius of gyration $\langle S^2 \rangle$ that

$$\langle \mathscr{T}r\,\mathbf{l} \rangle = 2L\langle S^2 \rangle\,. \tag{24}$$

Since the relation for the radius of gyration of the Tagami chain is the same as for that of the persistent chain[6,7], we obtain[11] for $\langle \mathscr{T}r(\mathbf{l}) \rangle$

$$\langle \mathscr{T}r\,\mathbf{l} \rangle = \frac{L^2}{3\lambda}\left(1 - \frac{3}{2\lambda L} + \frac{3}{2\lambda^2 L^2} - \frac{3}{4\lambda^3 L^3} + \frac{3}{4\lambda^3 L^3}\,\mathrm{e}^{-2\lambda L}\right). \tag{25}$$

For the effective anisotropy of polarizability $\Delta\alpha_{ef}$, defined by Eq. (*8*), we may write

$$\Delta\alpha_{ef} = \frac{\Delta a}{\lambda}\left(\frac{5}{3} - \frac{4}{\lambda L} + \frac{41}{8\lambda^2 L^2} - \frac{1\,187}{384\lambda^3 L^3} + \frac{5}{4\lambda^2 L^2}\,\mathrm{e}^{-2\lambda L} + \right.$$
$$+ \frac{3}{16\lambda^2 L^2}\,\mathrm{e}^{-4\lambda L} + \frac{23}{8\lambda^3 L^3}\,\mathrm{e}^{-2\lambda L} + \frac{1}{4\lambda^3 L^3}\,\mathrm{e}^{-4\lambda L} - \frac{1}{24\lambda^3 L^3}\,\mathrm{e}^{-6\lambda L} +$$
$$\left. + \frac{1}{128\lambda^3 L^3}\,\mathrm{e}^{-8\lambda L}\right)\left(1 - \frac{3}{2\lambda L} + \frac{3}{2\lambda^2 L^2} - \frac{3}{4\lambda^3 L^3} + \frac{3}{4\lambda^3 L^3}\,\mathrm{e}^{-2\lambda L}\right)^{-1} \tag{26}$$

For the region of rod-like behaviour of the chain we obtain, by neglecting terms proportional to $(\lambda L)^k$ for $k > 1$ in Eq. (*26*),

$$(\Delta\alpha_{ef})_r = \Delta a\,.\,L\,. \tag{27}$$

It can be seen from Eq. (*27*) that Tagami's chain gives the correct expression for birefringence in the limit for a rod, as it does for the moments[6,12].

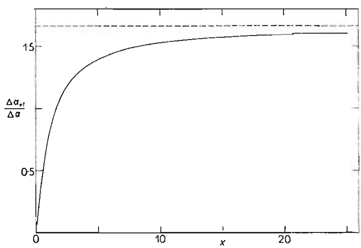

FIG. 1
Plot of $\Delta\alpha_{ef}/\Delta a$ against $x = \lambda L$

For the Gaussian region we obtain, by the limiting transition $L \to \infty$

$$\lim_{L \to \infty} \Delta\alpha_{cf} = \frac{5\,\Delta a}{3\lambda} = \frac{5}{3}\,\Delta a l_{st}\,, \tag{28}$$

where l_{st} is the length of a statistical segment. If we assume that

$$\lim_{L \to \infty} \Delta\alpha_{cf} = \Delta a \,.\, l_{op}\,, \tag{29}$$

we obtain in this case a relation between the length of the statistical and the optical segments, l_{op}

$$l_{op} = \tfrac{5}{3} l_{st}\,. \tag{30}$$

Such a result is in agreement with the theory of Noda and Hearst[2], while for a persistent chain both the Gotlib–Svetlov[1] and the Shimada–Yamakawa[4] theories give:

$$l_{op} = \tfrac{5}{6} l_{st} \tag{31}$$

We believe that the difference is due to the fact that both in the Tagami and in the modified Harris–Hearst model (employed by Noda and Hearst[2]) the condition $|\boldsymbol{u}| = 1$ has been removed, unlike the persistent chain. Essentially, the mode of calculation of $\Delta\alpha_{cf}$ used in our work is identical with that employed in the paper of Gotlib and Svetlov[1].

The difference between our result and that provided by the theory of Noda and Hearst[2], who obtained $(\Delta\alpha_{cf})_r = \frac{5}{3}\,\Delta a L$, in the limit $L \to 0$, is obviously due to the fact that unlike the Harris–Hearst model[12], in the case of Tagami model the tangential vector at the beginning of the chain $\boldsymbol{u}_0$ has been selected as a unit vector (Eq. (*11*)).

The persistent chain is evidently a more realistic model of polymer chain than the Harris–Hearst or Tagami model. A comparison of the dependence of $\Delta\alpha_{cf}/\Delta a$ on the reduced chain length for the Tagami model (Fig. 1) and for the persistent chain (Fig. 1 in ref.[1]) shows, however, that their shapes are very similar. We believe, therefore, that the Tagami model may serve (owing to its greater mathematical simplicity) as a useful model of the polymer chain, also with respect to the investigation of the dependence of the second term in Eq. (*2*) (or of similar physical quantities) on the chain length.

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