

Electronic Supplementary Information

Conformational Change of a Amylose Derivative in Chiral Solvents: Amylose

Tris(*n*-butylcarbamate) in Ethyl Lactates

Shota Arakawa, Ken Terao,* Shinichi Kitamura, and Takahiro Sato

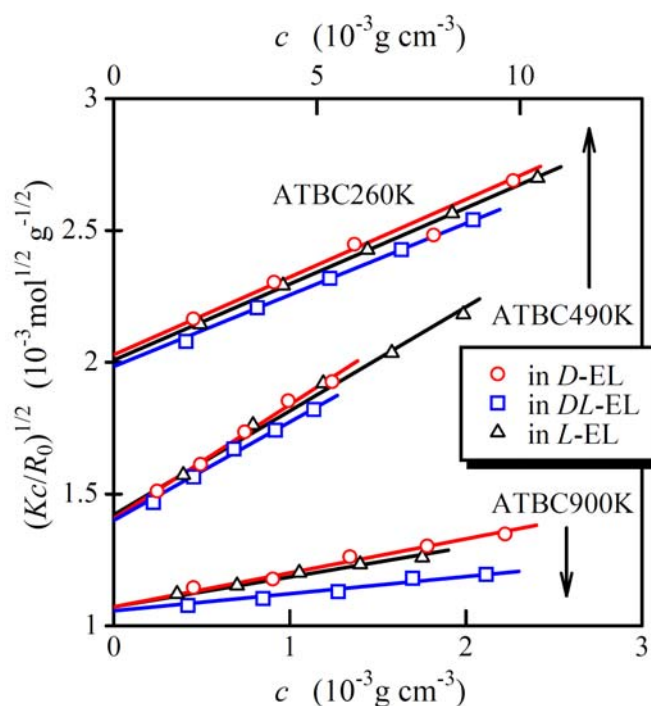


Fig. S1. Polymer mass concentration c dependence of $(Kc/R_0)^{1/2}$ for indicated ATBC samples in *D*-EL (red circles), *DL*-EL (black triangles), and *L*-EL (blue triangles) at 25 °C.

Cross Sectional Plot for a Core-Shell Cylinder Model. To demonstrate the negative d^2 for ATBC in ELs, we calculated $P(q)$ for a core-shell cylinder with the length L by¹

$$P(q) = \int_0^{2\pi} \left| \frac{d_i^2 \Delta\rho_i G(q, \theta, d_i) + d_o^2 \Delta\rho_o G(q, \theta, d_o) - d_i^2 \Delta\rho_o G(q, \theta, d_o)}{(\Delta\rho_i - \Delta\rho_o) d_i^2 + \Delta\rho_o d_o^2} \right| \sin \theta d\theta \quad (\text{S1})$$

with

$$G(q, \theta, d_x) = \frac{\sin[(qL/2)\cos\theta] J_1[(qd_x/2)\sin\theta]}{[(qL/2)\cos\theta][(qd_x/2)\sin\theta]} \quad (\text{S2})$$

where d_i and d_o are the diameter of the inner (or core) and outer (or shell) cylinders, $\Delta\rho_i$ and $\Delta\rho_o$ the corresponding excess electron densities. The obtained $\ln[q P(q)]$ from eq S1 with $L = 40$ nm, $d_i = 0.8$ nm, $d_o = 1.2$ nm, $\Delta\rho_i = 1.1$, and $\Delta\rho_o = 0.963$ are plotted against q^2 (the cross-sectional plot) in Fig. S2. They have a positive slope and are well fitted by the straight line calculated by the following approximate equation²

$$P(q) = \left\{ \frac{\text{Si}(qL)}{qL/2} - \left[\frac{\text{Sin}(qL/2)}{qL/2} \right]^2 \right\} \exp\left(-\frac{q^2 d^2}{16} \right) \quad (\text{S3})$$

when we choose with $L = 40$ nm and $d^2 = -0.5$ nm². This indicates that a core-shell model may explain the negative d^2 . It should be however noted that the obtained parameters might not be useful to know the detail electron density of ATBC since the scattering function at this q range is also affectable by the local helical structure and distribution of solvent molecules nearby the polymer chain.

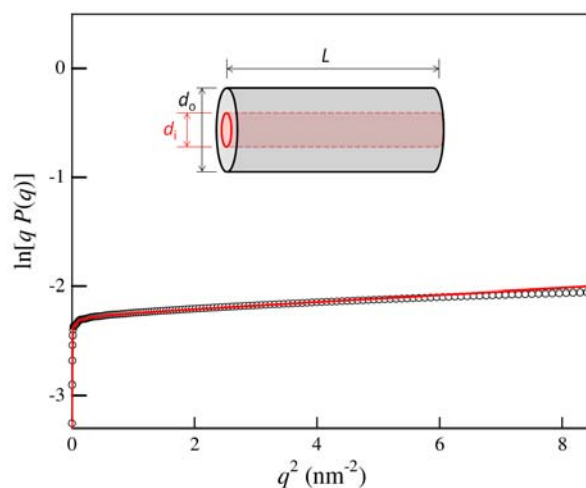


Fig. S2. Cross sectional plots for a core-shell cylinder model (circles) calculated from eq S1 with $L = 40$ nm, $d_i = 0.8$ nm, $d_o = 1.2$ nm, $\Delta\rho_i = 1.1$, and $\Delta\rho_o = 0.963$. Solid line, calculated from eq S3 with $L = 40$ nm and $d^2 = -0.5$ nm².

Two-States Wormlike Chain (TSWC) Model. The TSWC model is defined as the continuous limit of a freely rotating chain of N bonds in which each bond can take two states: the state 1 with the length b_1 , bond angle θ_1 , and probability f_1 , and the state 2 with the length b_2 , bond angle θ_2 , and probability f_2 . The continuous chain is obtained by taking the limit $N \rightarrow \infty$, $b_1 \rightarrow 0$, $b_2 \rightarrow 0$, $\theta_1 \rightarrow \pi$, and $\theta_2 \rightarrow \pi$ under the conditions that the following four parameters are constant:

$$Nb_1 = N_0h_1, \quad Nb_2 = N_0h_2, \quad \frac{1 - \cos \theta_1}{2b_1} = \lambda_1, \quad \frac{1 - \cos \theta_2}{2b_2} = \lambda_2 \quad (\text{S4})$$

where N_0 is the degree of polymerization, h_1 and h_2 are the contour lengths per monomer unit in the states 1 and 2, respectively [N_0h_1 (N_0h_2) is the contour length of the chain at $f_1 = 1$ ($f_2 = 1$)], and λ_1^{-1} and λ_2^{-1} are the Kuhn segment lengths in the states 1 and 2, respectively. If appearances of states 1 and 2 are completely independent along the chain, we can show that expressions for dimensional and hydrodynamic properties of the TSWC model are identical with those for the original wormlike chain model with the contour length per monomer unit h and the Kuhn segment length λ calculated by^{3,4}

$$h \equiv f_1h_1 + f_2h_2, \quad \lambda \equiv (f_1h_1\lambda_1 + f_2h_2\lambda_2)/(f_1h_1 + f_2h_2) \quad (\text{S5})$$

Heat of Dilution and Polymer-Solvent Interaction Parameter. Let us consider the dilution process of a polymer solution with a diluent. The diluent, the solvent (in the polymer solution), and polymer are denoted as components 0, 1, and 2, respectively. Using the lattice model,⁵ we may write enthalpies of the pure systems of components 0, 1, and 2 by

$$H_0 = \frac{1}{2} z n_0 \varepsilon_{00}, \quad H_1 = \frac{1}{2} z n_1 \varepsilon_{11}, \quad H_2 = \frac{1}{2} z n_2 \varepsilon_{22} \quad (\text{S6})$$

where n_0 , and n_1 are the numbers of diluent and solvent molecules, n_2 is the number of structural units of the polymer with the same volume as that of the diluent and solvent molecules, z is the coordination number, and ε_{ii} ($i = 0, 1$, and 2) are the intermolecular (or inter-segmental) attractive potential energies. It is noted that ε_{ii} 's are negative and their absolute values are larger for stronger interaction. According to van Laar and Scachard,³ the heat of dilution of the polymer solution with the diluent is written as

$$\Delta H_{0+12} = \frac{z n_0 \left\{ n_1^2 \left[\varepsilon_{01} - \frac{1}{2} (\varepsilon_{00} + \varepsilon_{11}) \right] + n_1 n_2 (\varepsilon_{01} + \varepsilon_{02} - \varepsilon_{00} - \varepsilon_{12}) + n_2^2 \left[\varepsilon_{02} - \frac{1}{2} (\varepsilon_{00} + \varepsilon_{22}) \right] \right\}}{(n_0 + n_1 + n_2)(n_1 + n_2)} \quad (\text{S7})$$

When the diluent and solvent are *L*-EL and *D*-EL, respectively, $\varepsilon_{00} = \varepsilon_{LL} = \varepsilon_{DD} = \varepsilon_{11}$, $\varepsilon_{01} = \varepsilon_{LD}$, $\varepsilon_{12} = \varepsilon_{DP}$, $\varepsilon_{02} = \varepsilon_{LP}$, $\varepsilon_{22} = \varepsilon_{PP}$. On the other hand, in the opposite case, $\varepsilon_{00} = \varepsilon_{DD} = \varepsilon_{LL} = \varepsilon_{11}$, $\varepsilon_{01} = \varepsilon_{DL}$ ($= \varepsilon_{LD}$), $\varepsilon_{12} = \varepsilon_{LP}$, $\varepsilon_{02} = \varepsilon_{DP}$, $\varepsilon_{22} = \varepsilon_{PP}$. Inserting these relations into eq (S7), we obtain expressions for the heat of dilution $q_{D,\text{soln} \rightarrow L,\text{dil}}$ in the former case, and that $q_{L,\text{soln} \rightarrow D,\text{dil}}$ in the latter case as

$$q_{D,\text{soln} \rightarrow L,\text{dil}} = \frac{z n_0 \left\{ n_1^2 (\varepsilon_{LD} - \varepsilon_{DD}) + n_1 n_2 (\varepsilon_{LD} + \varepsilon_{LP} - \varepsilon_{DD} - \varepsilon_{DP}) + n_2^2 \left[\varepsilon_{LP} - \frac{1}{2} (\varepsilon_{DD} + \varepsilon_{PP}) \right] \right\}}{(n_0 + n_1 + n_2)(n_1 + n_2)} \quad (\text{S8})$$

and

$$q_{L,\text{soln} \rightarrow \text{D},\text{dil}} = \frac{zn_0 \left\{ n_1^2 (\varepsilon_{LD} - \varepsilon_{DD}) + n_1 n_2 (\varepsilon_{LD} + \varepsilon_{DP} - \varepsilon_{DD} - \varepsilon_{LP}) + n_2^2 \left[\varepsilon_{DP} - \frac{1}{2} (\varepsilon_{DD} + \varepsilon_{PP}) \right] \right\}}{(n_0 + n_1 + n_2)(n_1 + n_2)} \quad (\text{S9})$$

Likewise, heats at diluted by the solvents, $q_{D,\text{soln} \rightarrow \text{D},\text{dil}}$ and $q_{L,\text{soln} \rightarrow \text{L},\text{dil}}$, are expressed by

$$q_{D,\text{soln} \rightarrow \text{D},\text{dil}} = \frac{zn_0 n_2^2 \left[\varepsilon_{DP} - \frac{1}{2} (\varepsilon_{DD} + \varepsilon_{PP}) \right]}{(n_0 + n_1 + n_2)(n_1 + n_2)} \quad (\text{S10})$$

and

$$q_{L,\text{soln} \rightarrow \text{L},\text{dil}} = \frac{zn_0 n_2^2 \left[\varepsilon_{LP} - \frac{1}{2} (\varepsilon_{DD} + \varepsilon_{PP}) \right]}{(n_0 + n_1 + n_2)(n_1 + n_2)} \quad (\text{S11})$$

Using eqs (S8) – (S11), the difference among the above four heats of dilution is given by

$$\begin{aligned} (q_{D,\text{soln} \rightarrow \text{L},\text{dil}} - q_{D,\text{soln} \rightarrow \text{D},\text{dil}}) - (q_{L,\text{soln} \rightarrow \text{D},\text{dil}} - q_{L,\text{soln} \rightarrow \text{L},\text{dil}}) &= \frac{2n_0 n_2 z (\varepsilon_{LP} - \varepsilon_{DP})}{n_0 + n_1 + n_2} \\ &\approx 2n_2 z (\varepsilon_{LP} - \varepsilon_{DP}) \quad (n_0 \gg n_1 + n_2) \end{aligned} \quad (\text{S12})$$

When the structural unit of the polymer is changed from the segment (with same volume as the solvent) to the repeating unit, we should replace $n_2(\varepsilon_{LP} - \varepsilon_{DP})$ by the $n_p(\varepsilon'_{LP} - \varepsilon'_{DP})$ where n_p is the number of the repeating units in the diluted solution, and ε'_{LP} and ε'_{DP} are the attractive potential energies per repeating unit. Finally, we obtain the following equation

$$(q_{D,\text{soln} \rightarrow \text{L},\text{dil}} - q_{D,\text{soln} \rightarrow \text{D},\text{dil}}) - (q_{L,\text{soln} \rightarrow \text{D},\text{dil}} - q_{L,\text{soln} \rightarrow \text{L},\text{dil}}) = 2n_p z (\varepsilon'_{LP} - \varepsilon'_{DP}) \quad (\text{S13})$$

In the text, we discuss the relation between the heat of dilution and the intramolecular hydrogen binding between the neighboring glucose residues connected by the glucosidic linkage, of which internal rotation determines the local conformation of ATBC. However, the choice of the normal glucose residue as the repeating unit is inconvenient to discuss the above relation, because the glucosidic linkage, we are interested in, is not included in the repeating unit. We can escape this inconvenience by choosing the structural unit enclosed by the dotted ellipsoid in the following scheme as the repeating unit.

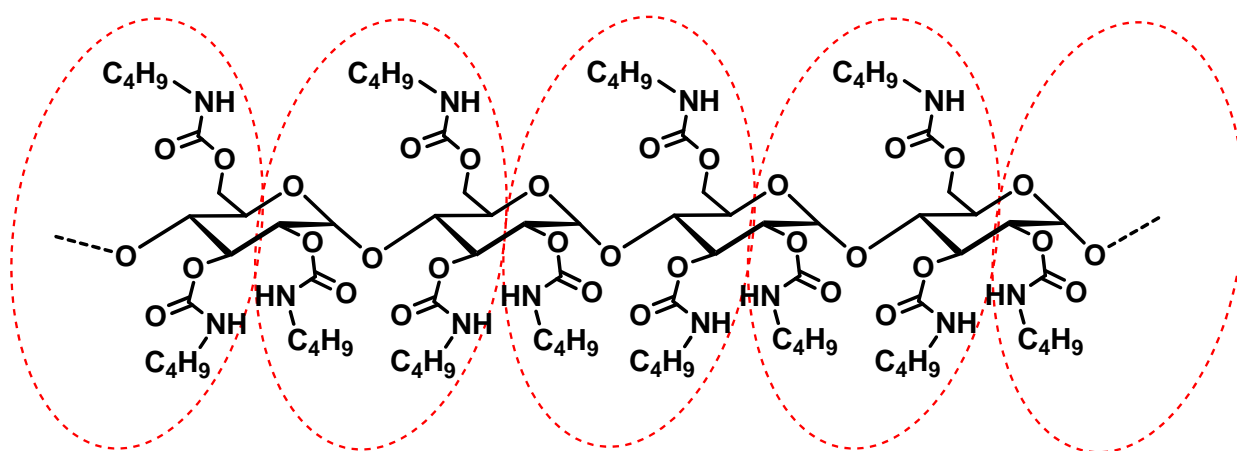


Fig. S3. Schematic representation of the repeating units in the lattice model.

References and Notes

1. I. Livsey, *J. Chem. Soc. Faraday. Trans. 2*, 1987, **83**, 1445-1452.
2. T. Konishi, T. Yoshizaki, T. Saito, Y. Einaga and H. Yamakawa, *Macromolecules*, 1990, **23**, 290-297.
3. O. Kratky and G. Porod, *Recl. Trau. Chim. Pays-Bas*, 1949, **68**, 1106.
4. M. L. Mansfield, *Macromolecules*, 1986, **19**, 854-859.
5. P. J. Flory, *Principles of Polymer Chemistry*, Cornell University Press, Ithaca, NY, USA, 1953.