Supplementary Information

Structure–Melt Viscosity Relationship of Discrete, Sequence-Specific Linear Oligo(Dimethylsiloxane-*co*-Diphenylsiloxane)s

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1. Table of Symbols

M, **D**, **P**: trimethylsiloxy, dimethylsiloxy, and diphenylsiloxy units

η: shear viscosity

$\dot{\gamma}$: shear rate

η_0: zero-shear viscosity

M: molecular weight

M_c: critical molecular weight of chain entanglement

N: number of the beads in a bead-spring model

$\zeta_{\mathrm{M}},\ \zeta_{\mathrm{D}},\ \zeta_{\mathrm{P}}$: friction coefficients of **M**, **D** and **P** units

k: spring constant

$\sigma_{\mathrm{M}} = {}^{k}/_{\zeta_{\mathrm{M}}},\ \sigma_{\mathrm{D}} = {}^{k}/_{\zeta_{\mathrm{D}}},\ \sigma_{\mathrm{P}} = {}^{k}/_{\zeta_{\mathrm{M}}}$

$\boldsymbol{A}$: symmetric matrix for a coupled oscillator with $N-1$ bonds

p: number of a normal mode ($p = 1, 2, 3, \ldots\ N-1$)

λ_p: the eigenvalue of the matrix $\boldsymbol{A}$ $(p = 1, 2, 3, \ldots\ N-1)$

$\boldsymbol{\Lambda}$: the eigenvalue matrix of the matrix $\boldsymbol{A}$

$\boldsymbol{Q} = [q_{ij}]$: the diagonalization matrix of the matrix $\boldsymbol{A}$. $\boldsymbol{\Lambda} = \boldsymbol{Q}^{\boldsymbol{T}}\boldsymbol{A}\mathbf{Q}$

τ_p: relaxation time of mode p

k_B: Boltzmann constant

T: absolute temperature

v: molecular volume of an oligomer

α: parameter for the enhancement of friction by consecutive **P** units

κ_{ij}: bond-bond correlation between the i-th and the j-th bonds in a chain ($0 \leq \kappa_{ij} \leq 1$)

$\boldsymbol{K} = [\kappa_{ij}]$

e: bond-bond correlation between the **P**-**P** bonds in **PPP** triad sequence

f: bond-bond correlation between the **P**-**P** bond and the **P**-**D** bond in **PPD** triad sequence

g: bond-bond correlation between the **P**-**D** bonds in **PDP** triad sequence

$$\boldsymbol{L} = \frac{1}{2}\boldsymbol{\Lambda}^{-\mathbf{1}}$$

$S_{\mathrm{M}},\ S_{\mathrm{D}},\ S_{\mathrm{P}}$: surface area values of **M**, **D** and **P** units

$\phi_{\mathrm{M}},\ \phi_{\mathrm{D}},\ \phi_{\mathrm{P}}$: surface area fractions of **M**, **D** and **P** units, calculated for each oligosiloxane

$\tilde{\zeta}_{\mathrm{M}},\ \tilde{\zeta}_{\mathrm{D}},\ \tilde{\zeta}_{\mathrm{P}}$: composition-dependent effective friction coefficients of **M**, **D** and **P** units, calculated for each oligosiloxane

2. Viscosity Measurement

The sear viscosity was measured on an Anton-Paar MCR302 rheometer using a sand-blasted parallel plate (25.0 mmϕ) to avoid the wall slip. The sample temperature was controlled with Peltier devices.

3. Model calculations

On Phyton 3.11.7, NumPy 1.26.4, SymPy 1.12, and SciPy 1.11.4, matrices representing the oligosiloxane sequences were diagonalized to estimate the relaxation times and viscosities of viscous liquids. For oligodimethylsiloxanes, the viscosity and density values were taken from the literatures (ref. 1, 2).

3.1. Discrete Rouse model of Block Structures

By taking 10-mer **5** as an example of block co-oligomers, discrete Rouse model calculation (ref. 3) is briefly described. In the bead-spring model with friction and relaxation, its simultaneous equations of motion were shown as

$$\zeta_M \frac{dx_1}{dt} = k(x_2 - x_1),$$

$$\zeta_D \frac{dx_2}{dt} = -k(x_2 - x_1) + k(x_3 - x_2),$$

$$\zeta_P \frac{dx_3}{dt} = -k(x_3 - x_2) + k(x_4 - x_3),$$

$$\zeta_P \frac{dx_4}{dt} = -k(x_4 - x_3) + k(x_5 - x_4),$$

$$\zeta_P \frac{dx_5}{dt} = -k(x_5 - x_4) + k(x_6 - x_5),$$

$$\zeta_P \frac{dx_6}{dt} = -k(x_6 - x_5) + k(x_7 - x_6),$$

$$\zeta_P \frac{dx_7}{dt} = -k(x_7 - x_6) + k(x_8 - x_7),$$

$$\zeta_P \frac{dx_8}{dt} = -k(x_8 - x_7) + k(x_9 - x_8),$$

$$\zeta_D \frac{dx_9}{dt} = -k(x_9 - x_8) + k(x_{10} - x_9),$$

$$\zeta_M \frac{dx_{10}}{dt} = -k(x_{10} - x_9).$$

Here x_i and ζ_i is the x coordinate and friction coefficient of the *i*-th bead (*i*=1-10), and k is the spring constant. The subscript **M**, **D**, and **P** indicate the trimethysiloxy, dimethylsiloxy, and diphenylsiloxy units respectively. The equations were transformed into linear differential equations of nine bonds $x_{i+1} - x_i$ (*i*=1-9).

$$\frac{d}{dt}\begin{bmatrix} x_2 - x_1 \\ x_3 - x_2 \\ x_4 - x_3 \\ x_5 - x_4 \\ x_6 - x_5 \\ x_7 - x_6 \\ x_8 - x_7 \\ x_9 - x_8 \\ x_{10} - x_9 \end{bmatrix} = -A \cdot \begin{bmatrix} x_2 - x_1 \\ x_3 - x_2 \\ x_4 - x_3 \\ x_5 - x_4 \\ x_6 - x_5 \\ x_7 - x_6 \\ x_8 - x_7 \\ x_9 - x_8 \\ x_{10} - x_9 \end{bmatrix}.$$

Here A is a real symmetric matrix:

$$A = \begin{bmatrix} \sigma_M+\sigma_D & -\sigma_D & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ -\sigma_D & \sigma_D+\sigma_P & -\sigma_P & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & -\sigma_P & 2\sigma_P & -\sigma_P & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & -\sigma_P & 2\sigma_P & -\sigma_P & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -\sigma_P & 2\sigma_P & -\sigma_P & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & -\sigma_P & 2\sigma_P & -\sigma_P & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & -\sigma_P & 2\sigma_P & -\sigma_{\square\square} & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & -\sigma_P & \sigma_D + \sigma_P & -\sigma_D \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & -\sigma_D & \sigma_M + \sigma_M \end{bmatrix},$$

where $\boldsymbol{\sigma_i} = \frac{\boldsymbol{k}}{\boldsymbol{\zeta_i}}$.

It is noted that the matrix A is also obtained by the matrix multiplication,

$$A = G^T S G.$$

Here the 10 x 10 matrix S represents the oligomer units with $\boldsymbol{\sigma_i}$, the 10 x 9 matrix G is the incidence matrix for the sequence, and G^T is the transpose of G:

$$S = \begin{bmatrix} \sigma_M & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & \sigma_D & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & \sigma_P & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & \sigma_P & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & \sigma_P & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & \sigma_P & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & \sigma_P & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & \sigma_P & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \sigma_D & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \sigma_M \end{bmatrix},$$

and

$$G = \begin{bmatrix} -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 1 & -1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & -1 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & -1 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 1 & -1 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 1 & -1 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 1 & -1 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 1 & -1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 & -1 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \end{bmatrix}.$$

The matrix A was diagonalized as

$$Q^T A Q = \Lambda,$$

where Q is the diagonalizing matrix for A, and Q^T is the transpose of Q. The matrix Λ has diagonal components λ_p of the eigenvalues of A ($\lambda_p > 0$; the mode number p=1-9).

$$\Lambda = \begin{bmatrix} \lambda_1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & \lambda_2 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & \lambda_3 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & \lambda_4 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & \lambda_5 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & \lambda_6 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & \lambda_7 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & \lambda_8 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \lambda_9 \end{bmatrix}.$$

The sum of the relaxation times was calculated as

$$\sum \tau_p = \sum \frac{1}{2\lambda_p} = \frac{1}{2} trace(\Lambda^{-1}) = \frac{1}{2} trace(\mathrm{A}^{-1}).$$

The latter expression can omit matrix diagonalization computation, which we employed in the present work.

The zero-shear viscosity η_0 was estimated as

$$\eta_0 = \frac{k_B T}{v} \sum \tau_p,$$

where v is the molecular volume of the compound, k_B is Boltzmann constant, and T is absolute temperature.

For the oligodimethylsiloxanes $\mathbf{1_n}$, the viscosity and density values were taken from ref. 1, 2, and 4. In estimating the oligomer viscosities, the parameters σ_M and σ_D were optimized.

For the **P**-containing oligomers **2**-**10**, we assumed a molecular volume as the sum of the included unit volumes. From the specific volume of **MPM** trimer, denoted as **MD*M** in ref. 4, the **P** unit volume was estimated by interpolation at 70°C and by extrapolation at 110°C.

In the viscosity estimation for the **P**-repeat oligomers **2**-**6**, the parameter σ_P was optimized by least square fit between the measured and estimated viscosities in the logarithmic scale. The estimates of the oligomers **2**-**10** were compared with their measured values.

3.2. Model A (effects of consecutive **P**-repeats)

To model the effects of consecutive **P**-repeats on the oligomer viscosity, a parameter α was introduced in the estimation ($0 < \alpha < 1$). Here we multiply α with σ_P. As an example, oligomer **6** gives its matrix A as follows:

$$A = \begin{bmatrix} \sigma_M+\sigma_D & -\sigma_D & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ -\sigma_D & \sigma_D+\alpha\sigma_P & -\alpha\sigma_P & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & -\alpha\sigma_P & \alpha\sigma_P+\alpha^2\sigma_P & -\alpha^2\sigma_P & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & -\alpha^2\sigma_P & \alpha^2\sigma_P+\alpha^3\sigma_P & -\alpha^3\sigma_P & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & -\alpha^3\sigma_P & 2\alpha^3\sigma_P & -\alpha^3\sigma_P & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & -\alpha^3\sigma_P & \alpha^3\sigma_P+\alpha^2\sigma_P & -\alpha^2\sigma_P & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & -\alpha^2\sigma_P & \alpha^2\sigma_P+\alpha\sigma_P & -\alpha\sigma_P & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & -\alpha\sigma_P & \alpha\sigma_P+\sigma_D & -\sigma_D \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & -\sigma_D & \sigma_M+\sigma_M \end{bmatrix}.$$

The power factors α^n represent how accumulatively the consecutive **P** units pile up the friction toward the block center.

The matrix A with α can be also obtained by the matrix multiplication,

$$A = G^T S_\alpha G,$$

where $S_\alpha = \begin{bmatrix} \sigma_M & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & \sigma_D & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & \alpha\sigma_P & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & \alpha^2\sigma_P & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & \alpha^3\sigma_P & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & \alpha^3\sigma_P & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & \alpha^2\sigma_P & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & \alpha\sigma_P & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \sigma_D & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \sigma_M \end{bmatrix}$.

The parameters σ_P and α were optimized in the discrete matrix calculation, while the values of σ_M and σ_D were employed from the viscosity estimation of the oligodimethylsiloxanes.

The viscosity estimates of the oligomers **2**-**10** were compared with the measured values.

Note: although the oligomer **7** includes no consecutive **P** sequence, we also replaced the value σ_P with $\alpha\ \sigma_P$ in the estimation of **7**. Without this replacement, the estimate was 12 times lower than the measured one. Also for the **PDP** sequence, it was effective to assume the friction enhancement by the nearby **P** units in a chain.

3.3. Model B (semi-flexible chains)

The Rouse model variants for semi-flexible chains (ref. 5 - 9) take a bond-bond correlation parameter κ_{ij} between the i-th and the j-th bonds in a chain. Here $0 \leq \kappa_{ij} \leq 1$ and $\kappa_{ij} = \kappa_{ji}$. The value is zero for the bond pairs in independent directions. Value 1 is taken for the bonds in parallel or for the bond itself ($\kappa_{ii} = 1$). The intermediate values indicate semi-flexibility between two bonds. By introducing correlation parameters between adjacent bonds, the bond-bond correlation κ_{ij} through a chain can be evaluated as

In the present work, Model B introduced three adjacent-bond correlation parameters *e*, *f*, and *g* for the **PPP**, **PPD**, and **PDP** sequences.

(i) **PPP** sequence for the oligomers **2**-**6**, **9**, and **10**: the parameter *e* represents the correlation between the adjacent **P**-**P** bonds. Including two **PP** dyads, the **PPP** sequence can exhibit two pairs of intrachain π-π interaction at most, which is likely to give the local chain rigidity to the triad.

(ii) **PPD** sequence for the oligomers **2**-**6** and **8**, **9** and**10**: the parameter *f* represents the bond-bond correlation in the **PPD** sequence. The triad may attain its local rigidity by the CH-π interaction through the $SiPh_2$-O-Si-O-$SiMe_2$ linkage.

(iii) **PDP** sequence for the oligomer **7**: the parameter *g* represents the correlation between the two **P**-**D** bonds in the sequence. Due to flexibility of the siloxane backbone, the triad can take conformations exhibiting intrachain π-π interaction through the SiPh-O-Si-O-SiPh linkage.

The conformations and intrachain interactions in the SiPh-O-SiPh or the SiPh-O-Si-O-SiPh linkage were discussed in fluorescence spectroscopy (ref. 10-13) and molecular dynamics calculation (ref. 14).

In contrast to these sequences, **MDD** and **DDD** sequences assumed zero bond-bond correlation, considering that oligodimethylsiloxanes were well modeled as flexible chains in the Rouse model. Note: for simplicity, we omitted the bond-bond correlation in **PDD** or **PDM** sequence; the correlation was not necessarily required for the estimations above coefficients of determination 0.9.

By multiplying the parameters *e*, *f*, and *g*, we calculated the κ_{ij} values through a chain

$$\kappa_{ij} = \kappa_{i\,i+1} \cdot \kappa_{i+1\,i+2} \cdot \cdots \kappa_{j-1\,j} \text{ for } i < j.$$

The κ_{ij} values are tabulated in a symmetric matrix $K = [\kappa_{ij}]$. For example, the matrix K for the oligomer **6** was represented as

$$K = \begin{bmatrix} 1 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 1 & f & ef & e^2f & e^3f & e^4f & e^4f^2 & 0 \\ 0 & f & 1 & e & e^2 & e^3 & e^4 & e^4f & 0 \\ 0 & ef & e & 1 & e & e^2 & e^3 & e^3f & 0 \\ 0 & e^2f & e^2 & e & 1 & e & e^2 & e^2f & 0 \\ 0 & e^3f & e^3 & e^2 & e & 1 & e & ef & 0 \\ 0 & e^4f & e^4 & e^3 & e^2 & e & 1 & f & 0 \\ 0 & e^4f^2 & e^4f & e^3f & e^2f & ef & f & 1 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \end{bmatrix}.$$

With the bond-bond correlation, the relaxation times τ_p were summed up as

$$\sum_p \tau_p = \sum_p \frac{1}{2\lambda_p} (\sum_{ij} \kappa_{ij} q_{pi} q_{pj}).$$

This sum includes the cross terms between different bonds in contrast to the flexible-chain models. In matrix operation, it was also calculated as

$$\sum_p \tau_p = \frac{1}{2} trace(\Lambda^{-1} Q^T K Q) = \frac{1}{2} trace(\mathrm{A}^{-1} K).$$

The latter expression can omit matrix diagonalization computation, which we employed in the present work.

Estimated from the viscosities of oligodimethylsiloxanes **1**$_n$, σ_M and σ_D were common among the Rouse model and Models A and B. In estimating the viscosities of the **P**-containing oligomers **2**-**6**, and **8**-**10**, the four parameters σ_P, α, e, f, and g were optimized by least square fit between the measured and the estimated viscosities in the logarithmic scale.

The viscosity estimates of the oligomers **2**-**10** were compared with the measured values.

3.4. Model C (composition-dependent friction coefficients)

Model C assumed the friction coefficients depending on the oligomer compositions. The oligomer conformations were calculated on MM2 in Chem3D 22.2.0 (Perkin Elmer Informatics, Inc.). Because of the largely fluctuating conformations, six conformational calculations were averaged in the calculation. The molecular surface areas were estimated as Connolly Accessible Area values. The surface areas S_M, S_D, and S_P of **M**, **D** and **P** units were evaluated as 230, 90 and 130 Å^2 respectively. After the surface area fractions ϕ_M, ϕ_D and ϕ_P were calculated for each compound, the effective friction coefficients $\tilde{\zeta}_M$, $\tilde{\zeta}_D$, and $\tilde{\zeta}_P$ of **M**, **D** and **P** units were estimated in the following equations:

$$\tilde{\zeta}_M = \phi_M \cdot \zeta_M + \phi_D \cdot \sqrt{\zeta_M \cdot \zeta_D} + \phi_P \cdot \sqrt{\zeta_M \cdot \zeta_P},$$
$$\tilde{\zeta}_D = \phi_D \cdot \zeta_D + \phi_M \cdot \sqrt{\zeta_M \cdot \zeta_D} + \phi_P \cdot \sqrt{\zeta_D \cdot \zeta_P},$$
$$\tilde{\zeta}_P = \phi_P \cdot \zeta_P + \phi_M \cdot \sqrt{\zeta_M \cdot \zeta_P} + \phi_D \cdot \sqrt{\zeta_D \cdot \zeta_P}.$$

The calculations employed the geometric means as the friction coefficients between **M** and **D**, **M** and **P**, and **D** and **P** units. The calculations employing the arithmetic and harmonic means gave similar values.

In estimation of the viscosities of oligodimethylsiloxanes**,** the parameters σ_M and σ_D were optimized by employing the composition-dependent friction coefficients. The parameters σ_P, e, f and g were estimated similarly to Model B estimation. The viscosity estimates of the oligomers **2**-**10** were compared with the measured values.

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5. Figures and Tables

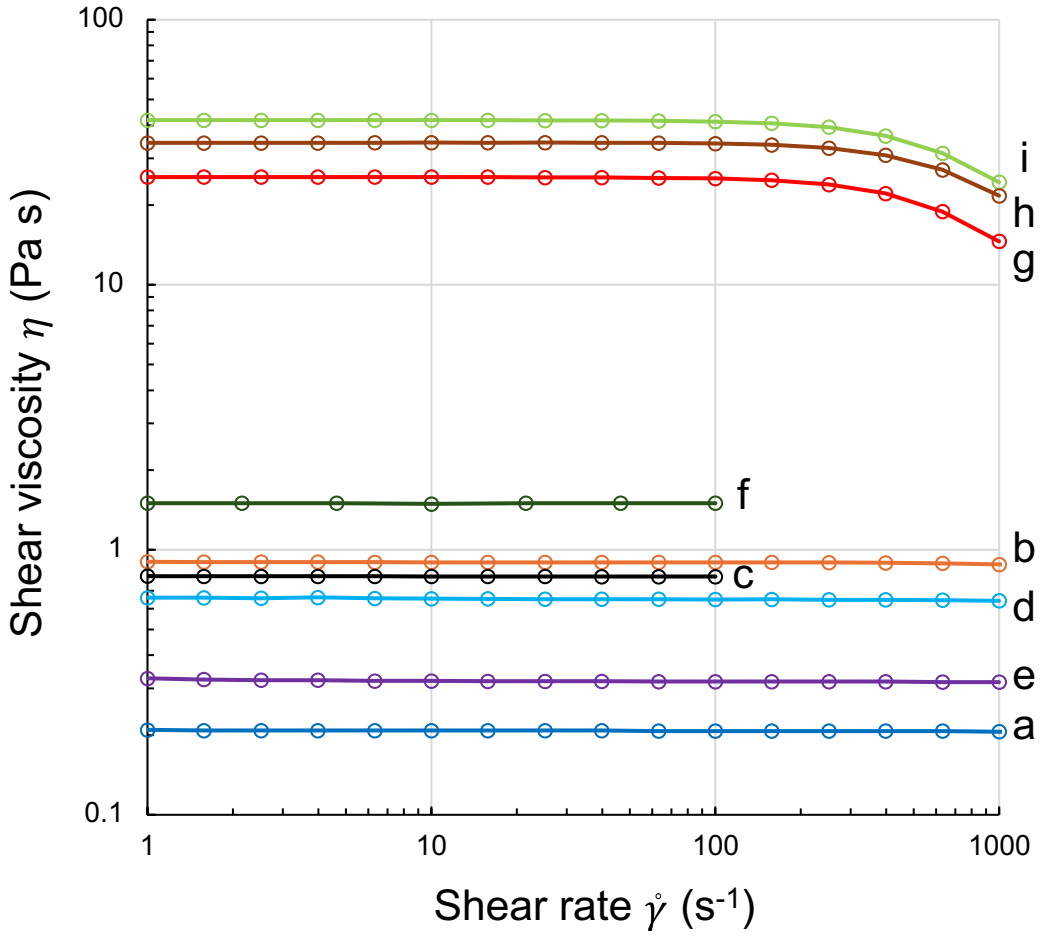

Figure S1. Flow curves of oligosiloxanes 2-10 in liquid above their melting temperatures. Each curve shows the result at the lowest temperature in measurement. a) 2 at 25 °C (blue), b) 3 at 25 °C (orange), c) 4 at 45 °C (black), d) 5 at 67 °C (light blue), e) 6 at 110 °C (purple), f) 7 at 50 °C (green), g) 8 at 15 °C (red), h) 9 at 15 °C (brown), and i) 10 at 15 °C (light green).

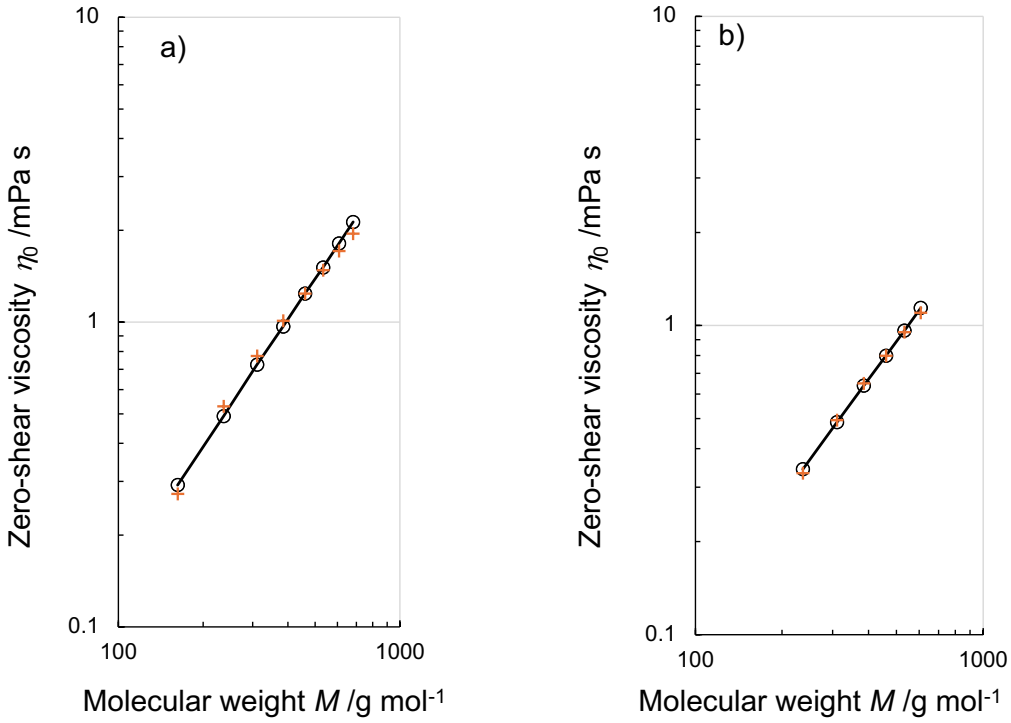

Figure S2. Zero-shear viscosities of dimethylsiloxane oligomers 1_n at 70 °C (a) and 110 °C (b). a) n=2-9, b) n=3-8. Open circles, the measured values in literature. Crosses, the estimated values in discrete Rouse model. The lines are eye-guides indicating $\eta_0 \sim M^{1.4}$ (a) and $\eta_0 \sim M^{1.3}$ (b).

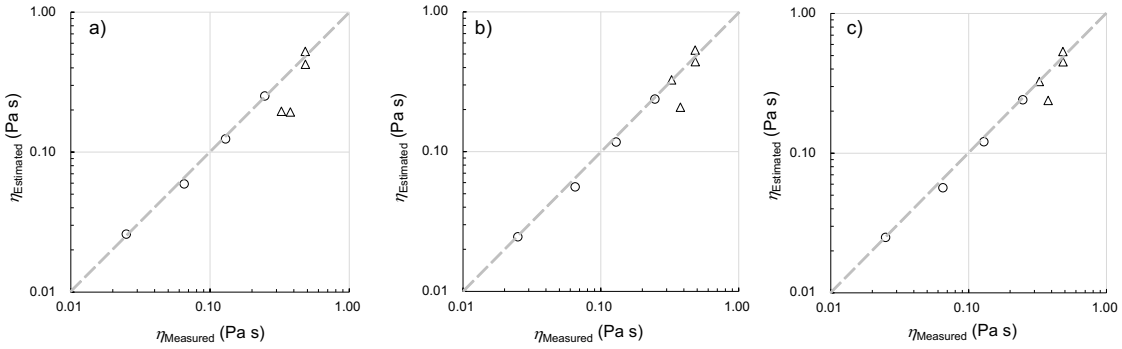

Figure S3. The measured and estimated viscosities at 85 °C of P-repeat siloxane oligomers **2**, **3**, **4**, and **5** (○) and 26-mers **7**, **8**, **9**, and **10** (△). a) Model A estimation. b) Model B estimation. c) Model C estimation. The dashed lines are eye-guides.

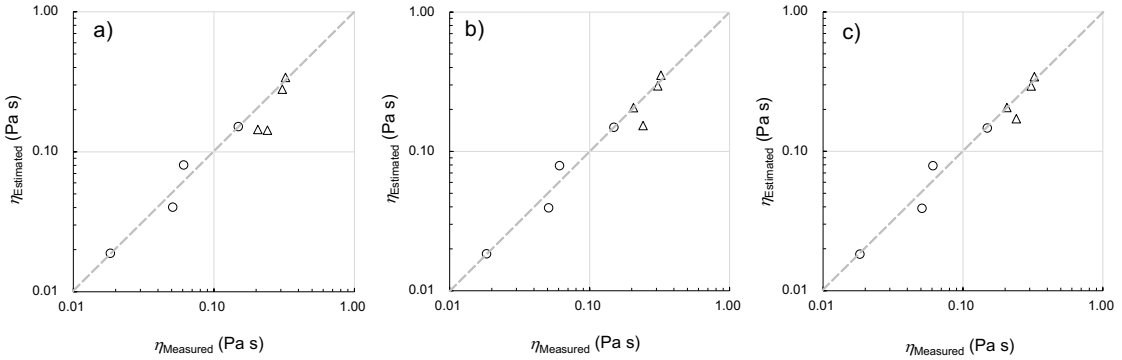

Figure S4. The measured and estimated viscosities at 100 °C of P-repeat siloxane oligomers **2**, **3**, **4**, and **5** (○) and 26-mers **7**, **8**, **9**, and **10** (△). a) Model A estimation. b) Model B estimation, c) Model C estimation. The dashed lines are eye-guides.

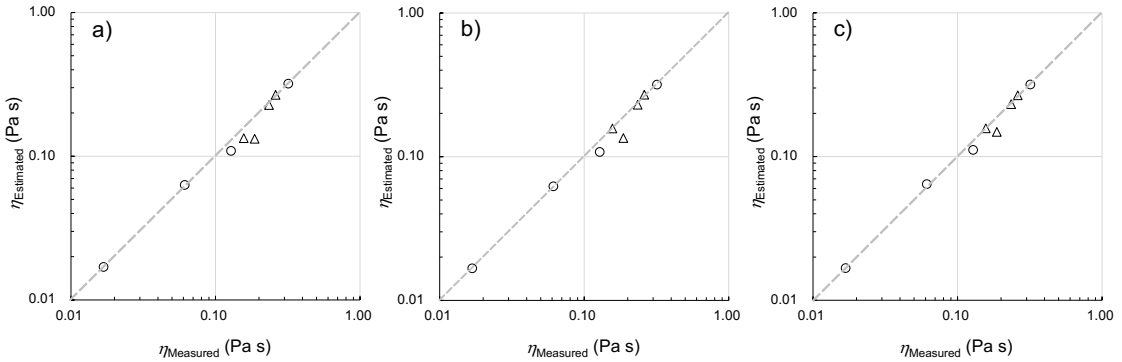

Figure S5. The measured and estimated viscosities at 110 °C of P-repeat siloxane oligomers **2**, **4**, **5**, and **6** (○) and 26-mers **7**, **8**, **9**, and **10** (△). a) Model A estimation. b) Model B estimation. c) Model C estimation. The dashed lines are eye-guides.

Table S1. The parameters in Models A, B and C at 70, 85, 100, and 110 °C.

	70 °C			85 °C			100 °C			110 °C		
	Model A	Model B	Model C	Model A	Model B	Model C	Model A	Model B	Model C	Model A	Model B	Model C
σ_M/ns^{-1}	10.6	10.6	13.4	13.3	13.3	13.0	17.6	17.6	17.5	19.0	19.0	19.1
σ_D/ns^{-1}	12.5	12.5	10.9	18.0	18.0	18.8	18.3	18.3	18.6	21.9	21.9	21.7
σ_P/ns^{-1}	0.172	0.415	0.170	0.569	0.609	0.267	0.685	0.715	0.323	0.609	0.623	0.278
α	0.280	0.183	0.217	0.208	0.207	0.240	0.244	0.243	0.281	0.302	0.301	0.346
e	-	0.000	0.000	-	0.000	0.000	-	0.000	0.000	-	0.000	0.000
f	-	0.202	0.136	-	0.172	0.167	-	0.131	0.121	-	0.462	0.0036
g	-	0. 954	0.650	-	0.776	0.550	-	0.475	0.316	-	0.194	0.053

(i) After σ_M an σ_D were estimated for dimethylsiloxane oligomers, the other parameters were estimated in the calculations for **P**-repeat oligomers and 26mers.
(ii) *e*, correlation of the **P**-**P** bonds in **P**-**P**-**P** sequence. *f*, correlation of the **P**-**P** and **P**-**D** bonds in **P**-**P**-**D** sequence. *g*, correlation of the **P**-**D** bonds in **P**-**D**-**P** sequence. The parameters *e, f* and *g* are between 0 and 1. In the main text, the zero value of *e* is discussed in relation to the parameter α.
(iii) The molecular areas of the oligomers were estimated as Connolly accessible areas on Chem3D. The surface areas S_M, S_D, and S_P were estimated as 230 Å^2, 90 Å^2, and 130 Å^2 respectively.

Table S2. The viscosities (mPa s) of dimethylsiloxane oligomers $\mathbf{1}_n$ evaluated by the literature measurements and the estimations at 70, 85, 100, and 110 °C.

Oligomer	70 ℃			85 ℃			100 ℃			110 ℃		
	Measurement	Model A	Model C	Measurement	Model A	Model C	Measurement	Model A	Model C	Measurement	Model A	Model C
$\mathbf{1}_2$	0.292	0.273	0.292	0.255	0.239	0.244	-	-	-	-	-	-
$\mathbf{1}_3$	0.491	0.529	0.479	0.429	0.450	0.456	0.374	0.362	0.362	0.343	0.333	0.334
$\mathbf{1}_4$	0.725	0.774	0.760	0.696	0.653	0.679	0.534	0.544	0.563	0.487	0.494	0.514
$\mathbf{1}_5$	0.967	1.01	0.994	0.825	1.04	1.04	0.705	0.731	0.731	0.639	0.650	0.653
$\mathbf{1}_6$	1.24	1.24	1.25	1.04	1.03	1.03	0.885	0.896	0.890	0.799	0.799	0.803
$\mathbf{1}_7$	1.51	1.48	1.53	1.27	1.21	1.20	1.07	1.06	1.05	0.964	0.952	0.959
$\mathbf{1}_8$	1.81	1.71	1.79	1.51	1.42	1.38	1.27	1.25	1.24	1.14	1.10	1.14
$\mathbf{1}_9$	2.13	1.95	2.08	-	-	-	-	-	-	-	-	-

Table S3. The viscosities (Pa s) of P-repeat oligomers **2**, **3**, **4**, and **5** and 26-mers **7**, **8**, **9**, and **10** evaluated by the measurements and the model estimations at 70, 85, and 100 °C.

Oligomer	70 ℃				85 ℃				100 ℃			
	Measured	Model A	Model B	Model C	Measured	Model A	Model B	Model C	Measured	Model A	Model B	Model C
						P-repeat oligomers						
2	0.040	0.042	0.042	0.040	0.025	0.026	0.025	0.025	0.0183	0.0189	0.0184	0.0183
3	0.104	0.100	0.100	0.096	0.065	0.059	0.056	0.057	0.0509	0.0402	0.0394	0.0391
4	0.168	0.218	0.208	0.213	0.129	0.124	0.117	0.121	0.0609	0.0806	0.0790	0.0790
5	0.459	0.472	0.450	0.449	0.247	0.252	0.238	0.241	0.149	0.151	0.149	0.147
						26-mers						
7	0.573	0.310	0.573	0.573	0.326	0.195	0.326	0.326	0.206	0.144	0.206	0.206
8	0.652	0.307	0.339	0.385	0.378	0.193	0.208	0.238	0.241	0.143	0.153	0.171
9	0.846	0.734	0.781	0.785	0.485	0.423	0.440	0.450	0.307	0.280	0.295	0.294
10	0.860	0.921	0.954	0.947	0. 484	0.524	0.532	0.534	0.324	0.339	0.352	0.343

Table S4. The viscosity values (Pa s) of **P**-repeat oligomers **2**, **4**, **5**, and **6** and 26-mers **7**, **8**, **9**, and **10** by the measurements and the model estimations at 110 °C.

Oligomer	Measuement	Model A	Model B	Model C
		P-repeat oligomers		
2	0.017	0.017	0.017	0.017
4	0.061	0.063	0.062	0.064
5	0.128	0.109	0.108	0.111
6	0.319	0.320	0.317	0.318
		26-mers		
7	0.157	0.133	0.157	0.157
8	0.187	0.132	0.135	0.148
9	0.235	0.227	0.230	0.232
10	0.261	0.267	0.270	0.266