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Nonstoichiometric Polycondensation I. Synthesis of Polythioether from Dibromomethane and 4,4'-Thiobisbenzenethiol

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Summary: High molecular weight poly(phenylene thioether) (**3**) was successfully obtained by the polycondensation of 4,4'-thiobisbenzenethiol (**1**) and dibromomethane (**2**) with a variety of feed ratios in the presence of 1,8-diazabicyclo[5,4,0]undec-7-ene (DBU) in 1-methyl-2-pyrrolidinone (NMP) at 75 °C. The resulting polymer showed the maximum inherent viscosity (η_{inh}) of 0.50 dL/g in 4 h when 1.5 equivalents excess of **2** was used. The model reaction using benzenethiol (**4**) and dichloromethane (**5**) in the presence of DBU in deuterated dimethylsulfoxide (DMSO-d_6) at 25 °C indicated that the rate of the second nucleophilic displacement reaction (k_2) is 61 times faster than that of the first one (k_1). The maximum of theoretical molecular weights calculated at various stoichiometric imbalance (S) under the condition of $k_2/k_1 = 61$ showed a good agreement with the experimental molecular weights at specific polymerization times.

Keywords: dibromomethane, kinetics, polycondensation, poly(phenylene thioether), stoichiometric imbalance

Introduction

In the synthesis of condensation polymers, the number-average degree of polymerization X_n is expressed in an extension of the Carothers equation[1-2] as

$$X_n = (1 + S) / (1 + S - 2p),$$

where S ($\geqq 1$) is the stoichiometric ratio of functional groups and, p is the extent of reaction. Thus, a stoichiometric balance of monomers is a critical factor to obtain a high molecular weight polymer. This classical theory is based on the concept of equal reactivity of functional

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groups. Thus, if the reactivity of a functional group is dependent on whether the other functional groups in the monomer have reacted, another theory should be applied for showing the relationship between X_n and S.

In the synthesis of poly(*p*-phenylene sulfide) by Edmons and Hill method,[3] significant deviations from classical theory was found, although the growth of the polymerization may be written as a series of conventional polycondensation; that is, polymer yields and molecular weights are adequate even at incomplete monomer conversion, and perfect stoichiometric monomer ratios are not required to achieve high molecular weight polymers. Odian et al. studied the kinetic of the polymerization with the change in reactivity of one functional group upon reaction of the other,[4] and showed the relationship between the degree of polymerization with time under various ratios (κ) of the reaction rate constants of the first and the second reacting functional groups. Kihara et al. investigated the polymerization of 2,2-dichloro-1,3-benzodioxole with 4,4'-isopropylidenediphenol and found that the highest molecular weight of polyorthocarbonate was obtained at 0.7 equivalent excess of 2,2-dichloro-1,3-benzodioxole.[5] Based on this finding, they concluded that the degree of polymerization is enhanced by stoichiometric imbalance if the first condensation of bifunctional monomer enhances the second condensation of the remaining functional group. Nomura et al. also reported the palladium catalyzed allylic substitution polymerization, where the unexpectedly high molecular weight polymer was obtained in non-stoichiometric conditions.[6] Quite recently, Hay et al. reported that high molecular weight aromatic polyformals were obtained by the polycondensation of potassium bisphenolate with excess amounts of **2** and pointed out the first intermediate, the bromomethyl ether, was much more reactive than **2**.[7] This polymerization would be another example to show the stoichiometric imbalance-enhanced polymerization. This system, however, is heterogeneous, and not suitable for conducting a kinetic study because too many kinetic parameters must be considered.

In the present study, we performed kinetic investigations on the polycondensation of **1** and **2** in the presence of DBU by changing the feed ratio of each monomer and found that this polycondensation is also the stoichiometric imbalance-enhanced polymerization.

Experimental Part

Materials. 4,4'-Thiobisbenzenthiol (**1**), dibromomethane (**2**), benzenethiol (**4**), dichloromethane (**5**), 1,8-diazabicyclo[5,4,0]undec-7-ene (DBU), and 1-methyl-2-pyrrolidinone (NMP) were distilled prior to use. Other reagents and solvents were used without further purification.

Measurements. FT-IR spectra were measured on a Horiba FT-720 spectrometer. Viscosity measurements were carried out by using an Ostwald viscometer in NMP at 30 °C. Thermal analyses were performed with a Seiko SSS5000 TG-DTA220 thermal analyzer at a heating rate of 10 °C min^{-1} for thermogravimetry (TGA) and a Seiko SSS5000 DSC220 at a heating rate of 10 °C min^{-1} for differential scanning calorimetry (DSC) under a nitrogen atmosphere, respectively. Solution state ^{1}H NMR spectra were recorded with a Bruker DPX300S spectrometer operating at 300.0MHz. Solid-state $^{13}C\{^{1}H\}$ cross-polarization magic angle spinning (CP/MAS) NMR spectra were recorded with a JEOL GSX-300 spectrometer operating at 75.45 MHz. The total suppression of spinning sideband (TOSS) pulse sequence was used to suppress spinning sidebands. The pulse sequence that combines TOSS and the dipolar dephasing (non-quaternary carbon suppression) (TOSS & DD) was also used for selective observation of non-protonated carbons. The contact time for CP was 2 ms, and the recycle was 5 s. The numbers of scans were 1500-1800. The chemical shifts were calibrated indirectly through the adamantane peak observed at lower frequency (29.5 ppm relative to tetramethylsilane (TMS)).

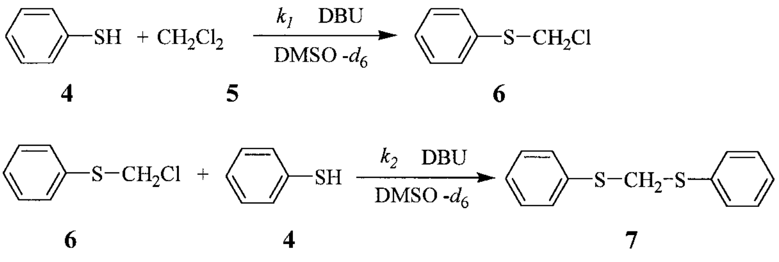
Model reaction using 4 and 5. Into a 1 mL of glass bottle were placed 0.917 g (8.32 mmol) of **4** and 1.270 g (7.30 mmol) of **5**. This was well mixed, and 40 μL of it was transferred to a new glass bottle. The mixture was diluted with 1 mL of dimethylsulfoxide-d_6 (DMSO-d_6) containing 1 μL of *tert*-butylanisole as an internal standard. From the bottle, 0.45 mL of the solution was transferred into a NMR test tube to determine the exact *S* value (2 $[\mathbf{5}]_0$ / $[\mathbf{4}]_0$) as 1.717 (function 2 arises from the mono functional group of **4**). The addition of 40 μL ($2.7\text{x}10^{-4}$ mmol) of DBU initiated the nucleophilic reaction that was monitored by the change of integration ratio between signals derived from **5** and bis(phenylsulfanyl)methane (7) in ^{1}H NMR spectra.

Polycondensation of 4,4'-thiobisbenzenethiol (1) and dibromomethane (2). Into a two-necked flask equipped with a reflux condenser were placed 0.5 g (2 mmol) of **1**, 2 mL of NMP, and 0.7 mL (4.7 mmol) of DBU under nitrogen stream. The solution was warmed to 75 °C, and then, the set amounts of **2** were added. After 2 h or 4 h, the viscous solution was diluted with NMP and poured into methanol to give white fibrous polymer. This was dried in vacuo at 70 °C for 24 h. Yield: 78–96 %. η_{inh} = 0.35–0.50 dL/g in NMP at 30 °C. IR (KBr): 744, 713 (CSC). ^{13}C NMR (solid): δ = 29.7(methylene) 126.4 (phenyl), 127.2 (phenyl), 132.6(phenyl), 135.3 (s phenyl). $(C_{13}H_{10}S_3)_n(264.2)_n$: Calcd. C 59.5, H 3.84, S 36.6; Found C 59.8, H 4.29, S 36.8.

Results and Discussion

Estimation of κ by model reaction. To conduct the polycondensation of **2** with a nucleophilie in homogeneous state, DBU was selected as an organic base in place of potassium hydroxide. Furthermore, bisphenol (pKa = 10) as the nucleophilie was replaced to **1** due to the higher acidity (pKa = 7), which means that complete formation of thiolate anion is possible by using DBU (pKa = 12.5).

First, the model reaction of **4** with **2** was carried out in the presence of DBU in DMSO-d_6 for estimating the ratio (κ) of the rates of the first (k_1) and second nucleophilic reactions (k_2) between **1** and **2**. The reaction was monitored by successive measurements of NMR spectra of a drop of the reaction mixture at different times. The reaction, however, was too fast even at -20 °C. Thus, the model reaction using **5** in place of **2** was performed at 25°C (Scheme 1).



Scheme 1

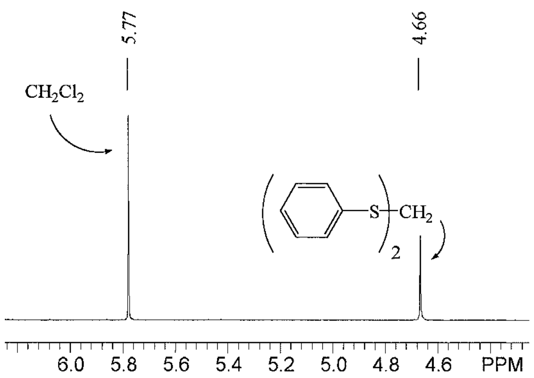


Fig. 1. Expanded ^{1}H NMR spectrum of the reaction mixture of **4** and **5** in DMSO-*d6* at 25 °C.

In the ^{1}H NMR spectra of the reaction mixture (Figure 1), product **7** was observed, but active intermediate **6** was not detected in any case. This suggests that k_2 is significantly larger than k_1. The ratio κ of the two rate constants (k_2/k_1) was determined from the time-dependent consumption of **5** according the theory in Appendix I.

Figure 2 shows the variations of the ratio (β)of the concentration of **5** at reaction time t ([**5**]) to the initial concentration of **5** ([**5**]$_0$).

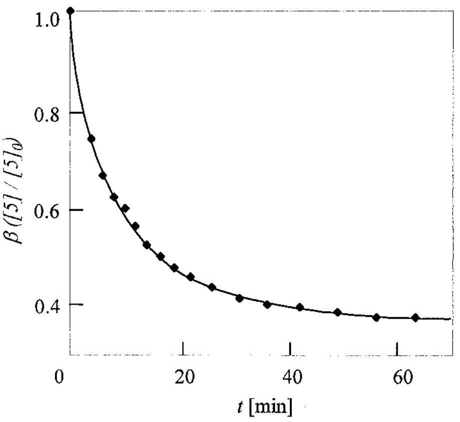


Fig. 2. Relationship between reaction time (t) and β ([**5**]/[**5**]$_0$) determined by ^{1}H NMR.

Using the array of β values obtained from the experiment, the corresponding τ values can be calculated for the array of t according to Eq.(14) (Appendix I) by assuming a certain κ value. As defined in Eq.(12), τ should be linearly proportional to t. Hence, the calculated τ values are plotted against t for a series of κ values, and the correlation coefficients (R^2) obtained from the fitting of linear equations using the least square method were evaluated as shown in Figure 3. Figure 4 shows the calculated R^2 values plotted against κ. Since the maximum R^2 was obtained at $\kappa = 61$, the second nucleophilic reaction was estimated to be 61 times faster than the first reaction.

Polymerization of 1 with 2. The polymerization of **1** with **2** was carried out with changing the molar ratio of each monomer. A solution of **1** and excess amounts of **2** in the presence of DBU in NMP was vigorously stirred at 75 °C for a specified time (Scheme 2).

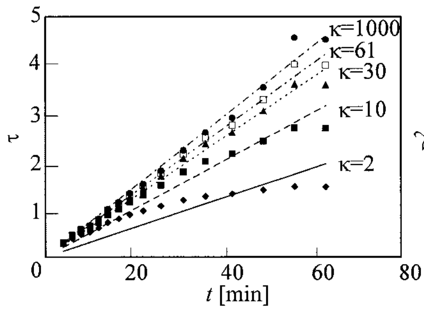


Fig. 3. Relationship between real time (t) and normalized time (τ) for various κ.

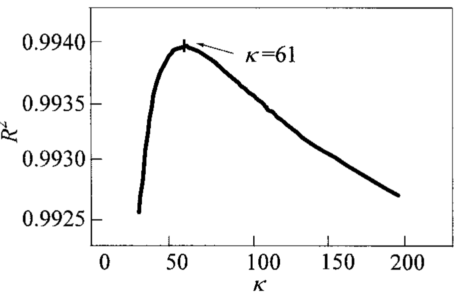
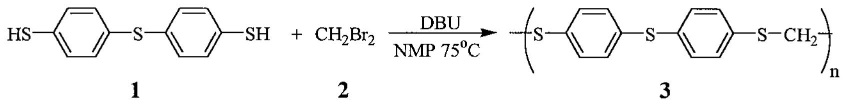


Fig. 4. Relationship between κ (k_2/k_1) and correlation coefficient R^2 (see text).



Scheme 2

Figures 5(a) and 5(b) illustrate the dependence of η_{inh} of the polymers on the stoichiometric imbalance S for polymerization times 2 h and 4 h, respectively.

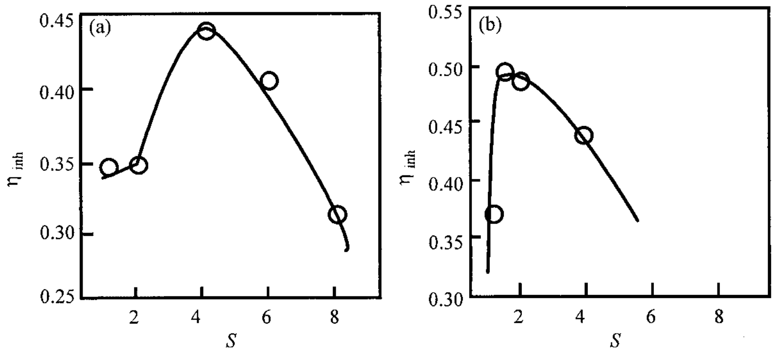


Fig. 5. Relationship between the monomer feed ratio S and the inherent viscosity η_{inh} of polymers obtained by the polycondensations for (a) 2 h and (b) 4 h.

The highest η_{inh} of the polymer was achieved for $S = 4$ at $t = 2$ h and for $S = 1.5$ at $t = 4$ h. These facts clearly indicate that the polymers having higher molecular weights an be obtained under non-stoichiometric conditions ($S > 1$), and the effect of non-stoichiometry is more significant at the shorter reaction time. In addition, the η_{inh} (0.44 dL/g) obtained for $S = 4$ at $t = 2$ h was not changed at $t = 4$ h, which indicates that the polymerization had already been terminated at 2 h under the highly non-stoichiometric condition. In contrast, the η_{inh}s (0.36 and 0.35 dL/g) obtained for $S = 1.5$ and 2 at 2 h are appreciably smaller than those at 4 h ($\eta_{inh} = 0.50$ and 0.48), indicating that the polymerization was still in progress at 2 h under the conditions with relatively smaller S values.

Time evolution of theoretical molecular weights. Theoretical number-averaged molecular weights (M_n) of polymers were calculated according to the theory in Appendix II by assuming that the second nucleophilic reaction is 61 times faster than that of the first reaction ($\kappa = 61$). Figures 6 shows the evolution of M_n with respect to the normalized polymerization time (τ) under different stoichiometric imbalance conditions. The highest M_n is realized in stoichiometric conditions ($S = 1$) at infinite time ($\tau > 110$), and it is obtained in larger stoichiometric imbalane at smaller τ. These phenomena support the experimental results; the η_{inh} values of the obtained polymers at $t = 4$ h decrease in the order of $S = 1.5 > 2.0 > 4.0 > 1.0$, and those at $t = 2$ h decrease as $S = 4.0 > 6.0 > 2.0 > 8.0$ (Figure 5). These orders can be seen from 6.0 to 20 and 1.75 to 2.25 in τ, respectively (Figures 6 (b) and (c)). These indicate that at shorter polymerization time polymers obtained under larger stoichiometric imbalance show higher molecular weights when the second nucleophilic reaction is faster than the first one.

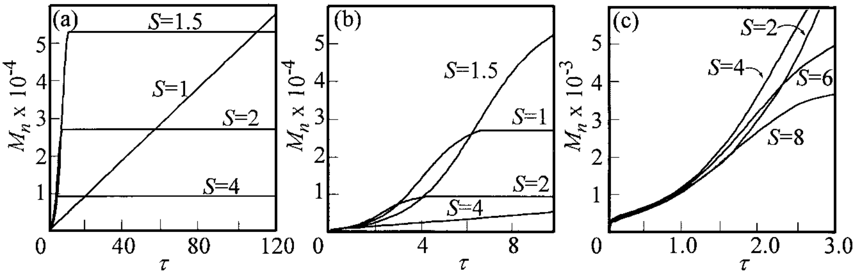
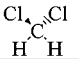
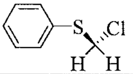
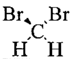
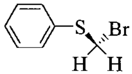


Fig. 6. Relationship between normalized polymerization time (τ) and theoretical M_n of **3** calculated for various S values using κ = 61. Expansion of the initial part is shown in (b) τ = 0 – 10, and (c) τ = 0 – 3.

Table 1. Optimized Geometries and Parameters Calculated from Density Functional Theory[a)]

		 CH_2Cl_2		 CH_2Br_2	
Interatomic distance of C-X [angstrom]		1.7906	1.8290	1.9520	2.0022
Bond order of C-X		0.2086	0.1805	0.2237	0.1875
Net atomic charge on	carbone	-0.5312	-0.6183	-0.6041	-0.6495
	halogen	-0.0340	-0.0946	+0.0078	-0.0652

[a)] B3LYP/6-311G*.

Molecular orbital consideration on reactive intermediate. The density functional theory (DFT) calculations using the B3LYP hybrid functional with the 6-311++G(d,p) basis set were performed to elucidate the reactivity of the monomers and the intermediates (Table 1). The C–Cl bond length of the optimized geometries of intermediate **6** is longer than that of **5**, and the C–Cl bond-order of the former is smaller than that of the latter. In addition, the chlorine atom in **6** is more negative than those in **5**. All these parameters indicates that the C–Cl bond in **6** is more weaker than those in **5**, and intermediate **6** is more reactive than **5**. Similar phenomena are also observed for the bromide compounds as shown in Table 1, supporting the experimental results observed in the polymerization reactions.

Polymer characterization. Polymer **3** is a white fibrous solid and soluble only in NMP. The TGA curve (Figure 7(a)) shows that the 5 % weight loss temperature is 325 °C, and a large endothermic peak due to the melting was observed at 144 °C in the DSC curve (Figure 7(b)). This indicates that the resulting product is a semi-crystalline polymer. The chemical structure was characterized as the desired poly(phenylene thioether) by IR, NMR, and elemental analyses as described in the experimental part. The IR spectrum shows characteristic absorptions at 744 and 713 cm^{-1} due to C-S-C stretching. Elemental analysis also supported the formation of expected polymer. The solid state ^{13}C CP/MAS spectrum (Figure 8(a)) shows well-resolved signals for the phenyl rings and a broad signal due to the

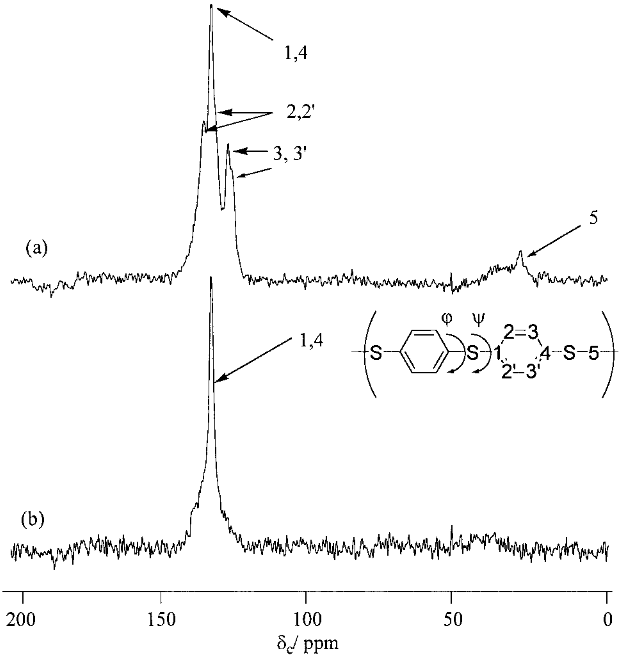


Fig. 7. Solid-state ^{13}C CP/MAS NMR spectra of **3** obtained using (a) TOSS and (b)TOSS & DD pulse sequences.

methylene units. The NMR signals of the quaternary carbons observed in the TOSS&DD spectrum (Figure 8(b)) can be fitted by overlap of a sharp Lorentian and a broad Gaussian signals having the same chemical shifts (133.6 ppm). The former was assigned to carbon 1, and the latter was assigned to carbon 4. The broad signals of carbons 4 and 5 suggest the large distribution of the conformations at the phenyl-S-CH_2-S-phenyl moiety. In contrast, the sharp signals for carbons 1, 2, 2', 3, and 3' indicates the restricted conformation at the diphenyl thioether moiety. Furthermore, the single peak of carbon 1 and the split peaks of 2,2' and 3,3' indicate that the diphenyl thioether structure take the C_2 symmetry (propeller-like conformation), and the dihedral angles (ϕ, ψ) are estimated as (45, 45°)–(60°, 60°) according to the DFT calculations of the nuclear shieldings for dipenyl thioether.[8]

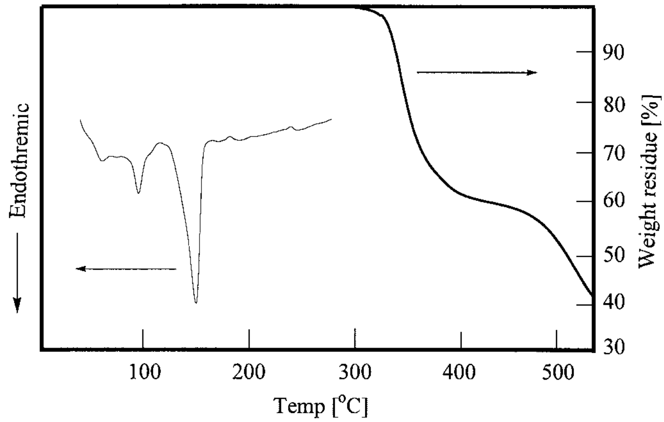


Fig. 8. TG and DSC traces of **3** measured under nitrogen.

Conclusions

The kinetics of polycondensation of **1** and **2** with a variety of monomer feed ratios in the presence of DBU in NMP at 75 °C was investigated. It was found that this polycondensation is a stoichiometric imbalance-enhanced polymerization, that is, the first condensation of **1** with the thiophenol group of **2** enhances the reactivity of the resulting bromomethyl thioether, and high molecular weight polymer **3** is obtained even in the presence of excess amount of **2**.

The ratio κ of two rate constants (k_2/k_1) was determined as 61 from the reaction of **4** and 5 in the presence of DBU in DMSO-d_6 at 25 °C. The time-evolution of the molecular weights of **3** calculated at various S values agrees well with inherent viscosities of polymers obtained by polycondensations for 2 h and 4 h. In addition, the higher reactivities of the intermediates compared with those of the monomers are rationalized by the density functional theory calculations.

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[Appendix 1]

Since the model reaction of **4** and **5** (Scheme 2) proceeds as a S_N2-type reaction, the kinetics can be expressed by the following equations.

$$-\frac{\mathrm{d}}{\mathrm{d}t}[\mathbf{5}] = k_1[\mathbf{4}][\mathbf{5}] \tag{1}$$

$$-\frac{\mathrm{d}}{\mathrm{d}t}[\mathbf{4}] = k_1[\mathbf{5}][\mathbf{4}] + k_2[\mathbf{6}][\mathbf{4}] \tag{2}$$

$$-\frac{\mathrm{d}}{\mathrm{d}t}[\mathbf{6}] = -k_1[\mathbf{4}][\mathbf{5}] + k_2[\mathbf{6}][\mathbf{4}] \tag{3}$$

The initial concentration of each compound is defined as $[\mathbf{4}]_0$, $[\mathbf{5}]_0$, $[\mathbf{6}]_0$, and $[7]_0$, respectively, where $[\mathbf{6}]_0=0$ and $[7]_0=0$. The variables α, β, γ and δ are introduced as

$$\alpha = \frac{[\mathbf{4}]}{[\mathbf{4}]_0},\ \beta = \frac{[\mathbf{5}]}{[\mathbf{5}]_0},\ \gamma = \frac{[\mathbf{6}]+[\mathbf{7}]}{[\mathbf{5}]_0},\ \text{and}\ \delta = \frac{[\mathbf{6}]}{[\mathbf{5}]_0}, \tag{4)–(7}$$

and the parameters κ is defined as

$$\kappa = \frac{k_2}{k_1} \tag{8}$$

According to the definition of S, represented as follows in the model reaction

$$S = 2\frac{[\mathbf{5}]_0}{[\mathbf{4}]_0}. \tag{9}$$

Using the relationships, $[\mathbf{5}]_0 = [\mathbf{5}] + [\mathbf{6}] + [\mathbf{7}]$ and $[\mathbf{4}]_0 = [\mathbf{4}] + [\mathbf{6}] + 2[\mathbf{7}]$, γ and δ can be expressed as

$$\gamma = 1 - \beta \text{ and } \delta = \alpha - 1 + S(1 - \beta). \qquad (10),(11)$$

In addition, the normalized dimensionless time τ is defined as

$$\tau = k_1[\mathbf{5}]_0 t. \qquad (12)$$

By solving the coupled equations (1) and (3), α value at a specific β can be expressed as

$$\alpha = 1 - S + \frac{S\beta}{2(\kappa - 1)}(2\kappa - 1 - \beta^{\kappa-1}). \qquad (13)$$

Furthermore, Eq.(1) can be solved as

$$\tau = \int_1^{1/\beta} \frac{\mathrm{d}w}{(\frac{2}{S} - 2)w + \frac{1}{\kappa - 1}(2\kappa - 1 - w^{1-\kappa})} \qquad (14)$$

The right side of Eq. (14) can be numerically calculated using Romberg's method. The computation program was written in Microsoft Basic language, and all non-integer variables were defined as double precisions in the program. The criteria for the convergence of iterative integrations was $1.0\text{x}10^{-12}$.

[Appendix 2]

In the polycondensation in Scheme 1, monomer a-a (**1**) reacts with monomer b-c (**2**), where only the reactivity of b-c changes after the first nucleophilic reaction. For convenience of using the equations deduced in Appendix I, we consider Scheme 3 as polycondensation reactions, where compounds **4** and **5** are treated as a-a and b-c type monomers, respectively. When the number of monomer molecules are denoted by N_{aa} and N_{bc}, the total number of ends in polymer ($N_{\text{E}}^{\text{Poly}}$) and monomer ($N_{\text{E}}^{\text{Mono}}$) can be expressed as

$$N_{\text{E}}^{\text{Poly}} = 2N_{aa}\alpha + 2N_{bc}(2 - \gamma - \delta) \qquad (15)$$

$$N_{\text{E}}^{\text{Mono}} = 2N_{aa}\alpha^2 + 2N_{bc}(1 - \gamma). \qquad (16)$$

Since the total weight of polymer is $N_{\text{aa}}W_{\text{aa}}(1-\alpha^2)+N_{\text{bc}}W_{\text{bc}}\gamma$, the number-averaged molecular weight of polymer M_{n} is given by

$$M_{\text{n}} = \frac{N_{\text{aa}}W_{\text{aa}}(1 - \alpha^2) + N_{\text{bc}}W_{\text{bc}}\gamma}{(N_{\text{E}}^{\text{Poly}} - N_{\text{E}}^{\text{Mono}})/2}, \qquad (17)$$

where the weights of reacted a-a and b-c are W_{aa} and W_{bc}, respectively.
According to the definition of S, $N_{\text{bc}}=SN_{\text{aa}}$ in polymerizarion
and Using Eqs.(4)-(7), (8), (9), (15) and (16), M_{n} is rewritten as

$$M_{\mathrm{n}} = \frac{W_{\mathrm{aa}}(1-\alpha^2) + W_{\mathrm{bc}}S(1-\beta)}{2\alpha - \alpha^2 + S - 1 - S\beta} \quad . \tag{18}$$

The procedure for estimating the τ dependence of M_{n} under specific values of S and κ is as follows.

Calculate W_{aa} and W_{bc} for the polymerization considered.
A certain value of β is taken between 1.0 and $(1-1/S)$.
The corresponding τ is calculated according to Eq.(14).
The value of α is calculated according to Eq.(13).
The M_n is calculated according to Eq.(18).
The M_n is plotted against the corresponding τ.
The value of β is gradually brought close to the limit of $(1-1/S)$, and repeat (2)-(6) for each β.