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Significance of Stoichiometric *Imbalance* in Step Polymerization via Reactive Intermediate

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ABSTRACT: Basic aspects of step polymerization via reactive intermediate were elucidated for the first time by using a typical example. The polycondensations of 2,2-dichloro-1,3-benzodioxole (**1**) and 4,4′-isopropylidenediphenol (**2**) with a variety of feed ratios were carried out in refluxing chlorobenzene (2.5 mol/L) for 3 h with continuous removal of hydrogen chloride to give polyorthocarbonate **3**. The highest molecular weight of **3** was obtained when ca. 0.7 equivalent excess of **1** was used and was much higher than that calculated according to the conventional step polymerization theory. The excess **1** remained after the polymerization was completed. In the model reaction of **1** and phenol at −40 °C, the rate of the first nucleophilic displacement reaction (k_1') was 27 times lower than that of the second reaction (k_2') of monochloride formed by the first condensation. The attribution of the anomeric effect was assumed from the results of semiempirical molecular orbital calculation. Under the condition that the first condensation is 27 times faster than the second one, analyses of the kinetic equations of the polycondensation showed that the number-averaged molecular weight (M_n) of the polymer is higher with more stoichiometric imbalance (S) for a shorter polymerization time. As time elapses, a greater M_n is observed for smaller S value. Infinite M_n will be obtained for $S = 1$ at infinite time, which is impossible to reach. For step polymerization in which the first reaction gives rise to acceleration of rate of the second reaction, in general, stoichiometric imbalance practically enhances molecular weight of the polymer.

Introduction

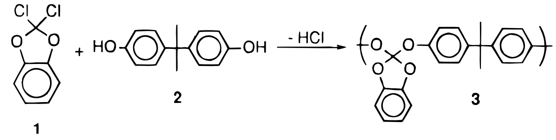
The basic principle in step polymerization is that stoichiometric imbalance in monomer feed ratio decreases degree of polymerization.[1,2] The highest molecular weight of linear polymer is obtained with the exactly stoichiometric amount of the monomers. Thus, the relationship between the stoichiometric balance of bifunctional monomers A−A and B−B, where B−B is fed in excess, and the number-averaged degree of polymerization P_n can be expressed by eq 1,

$$P_n = \frac{\frac{1}{2}(N_A + N_B)}{\frac{1}{2}\left[N_A(1-p) + N_B\left(1 - \frac{p}{S}\right)\right]} = \frac{1+S}{1+S-2p} \quad (1)$$

where N_A and N_B are the numbers of functional groups A and B, respectively, S is the stoichiometric imbalance ratio of the bifunctional monomers ($N_B/N_A > 1$), and p is the fraction of the functional group A that is reacted. Thus, p is referred to as the extent of the polymerization. According to eq 1, S should be unity to obtain the maximum P_n.

Equation 1, however, is derived without kinetic consideration. It has been reported that P_n is independent of p in some step polymerizations where the unit reaction contains an electron-transfer process.[3] In practice, P_n is larger than the value predicted from eq 1 after purification of the polymer since eq 1 counts unreacted monomer remaining in the system as the polymer. If a large amount of the monomer remains in the system for some reason, a high polymer can be obtained after removal of the monomer.

During our course of study on polymerizations of carbonate and orthocarbonate monomers,[4] we found that polycondensation of 2,2-dichloro-1,3-benzodioxole (**1**) and 4,4′-isopropylidenediphenol (bisphenol A, **2**) proceeded smoothly without any side reaction to give a high molecular weight polyorthocarbonate, **3** (eq 2).[4e]



(2)

The polymer **3** was thermally and chemically highly stable. Because of the good physical properties of **3**, we further examined the polymerization conditions to find that *the stoichiometric imbalance of **1** and **2** rather enhanced the degree of polymerization*.

To our knowledge, the polycondensation of dichlorobenzene and sodium sulfide to poly(phenylene sulfide) is the only example that has been reported so far, in which the degree of polymerization can be elevated by the stoichiometric imbalance as it is a polymerization via “reactive intermediate”.[5] This system, however, is heterogeneous, and it is very difficult to conduct kinetic analyses. Furthermore, one must consider too many kinetic parameters in this polycondensation.[6] In contrast, polycondensation of **1** and **2** proceeds under homogeneous conditions,[4e] and the reaction seems to be very simple to analyze. Thus, the polymerization of **1** and **2** should be a better system to exemplify the stoichiometric imbalance-enhanced polymerization.

Considering the importance of stoichiometry in step polymerization, we performed chemical and kinetic

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Table 1. Effect of Feed Ratio on the Polycondensation of 1 and 2[a]

1 (mmol)	**2** (mmol)	yield[b] (%)	M_n[c]	theoretical M_n[d]	M_w/M_n[c]
3	4	54	4600	1212	1.18
5[e]	5[e]	99	48000	∞	2.25
4	3	101	42000	1212	2.56
5	3	100	120000	693	2.52
6	3	102	30000	520	2.86
30	3	63	8600	212	2.31

[a] Conditions: in chlorobenzene 3 mL, reflux, 3 h. [b] Insoluble part in isopropyl ether. [c] Estimated by GPC (THF, based on PSt standards). [d] Calculated value based on eq 1. [e] In 2 mL of chlorobenzene.

investigations on this polymerization system. In this paper, we wish to report one significant conclusion: 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.*

Results and Discussion

Effect of Stoichiometric Imbalance in the Polycondensation of 1 and 2. We have already reported the polycondensation of **1** and **2**.[4e] After optimization of the conditions, polymerization in refluxing chlorobenzene (2.5 mol/L) for 3 h with continuous removal of hydrogen chloride gave both the highest yield and the highest molecular weight. Polymer **3** showed satisfactory ^{1}H and ^{13}C NMR spectra and elemental analyses, indicating no accompanied side reaction.

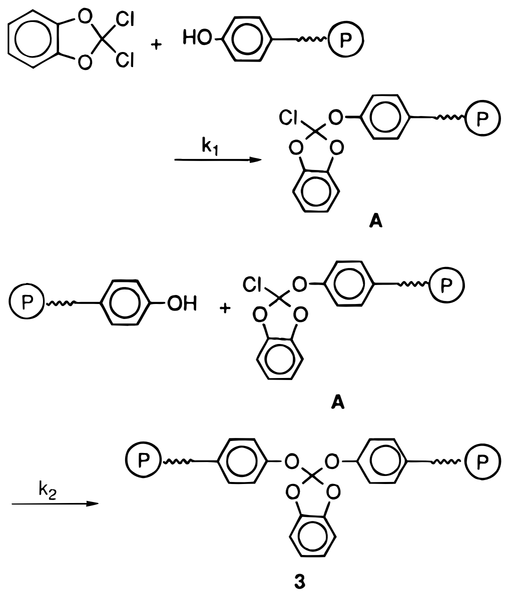
Further experiments were carried out with stoichiometric imbalance. The results are shown in Table 1. The highest molecular weight of **3** (M_n 120 000) was obtained when ca. 0.7 equiv excess of **1** was used, although M_n should be only 693 according to the conventional theory. All analytical data of the product were completely identical to those of **3**, except for the molecular weight. Purity of **1** was confirmed by all available spectroscopic and chromatographic methods. Furthermore, after the polymerization was finished, we found that a considerable amount of **1** remained in the system when an excess amount of **1** was used. From these results, neither side reaction, purity, nor decomposition of **1** could be the reason that excess **1** was necessary for the most effective polymerization.

In the standard theory for step polymerization, however, all monomers should be consumed in the early stage of the polymerization. This is independent of the stoichiometry of monomers.[2] Thus, we assumed that the first condensation of **1** with the phenolic hydroxy group enhanced the reactivity of monochloride intermediate **A**, and it would be the reason for the unusual enhancement of molecular weight by the stoichiometric imbalance of the monomers (Scheme 1).

To estimate the rate constants k_1 and k_2, we used a model system of this polycondensation. Phenol (**4**) was selected as a model compound of **2** to estimate the ratio of the corresponding rate constant k_1' and k_2' (Scheme 2). It is noteworthy that two phenolic hydroxy groups of **2** show almost the same reactivity in the polycondensation of **2** with bis(4-chlorophenyl) sulfone,[7] suggesting that **4** is a suitable model compound of **2**. Although *p*-alkyl substituents can have some effect on the reactivity of phenol, it is expected that the ratio k_1/k_2 is comparable to k_1'/k_2'. Since the reaction was too fast under the polymerization conditions (1.0−2.5 mol/L, 132 °C), the reaction of **1** and **4** was conducted in dichloromethane (0.1 mol/L) at −40 °C. The reaction mixture was poured into ethanol containing triethylamine by which all chlorides were converted to ethoxide quantitatively.[8] The mixture was analyzed by gas chromatography (GC). While symmetrical orthocarbonate **6** and **7** were detected in the reaction mixture, no detectable amount of asymmetrical orthocarbonate **8** was observed in any case. The sum of the yields of **6** and **7** was always ca. 100%. This observation indicates k_2' is larger than k_1'; that is, **5** is far more reactive than **1**. Time-yield curves clearly revealed that the reaction of **1** with **4** follows second-order kinetics (r = 0.999), and the net rate constant is 5.78×10^{-2} L·mol^{-1}·min^{-1}.

The ratio k_2'/k_1' was evaluated using a modified Frost's method[9] from the time-dependent consumption of **4** (Appendix I). The result, k_2'/k_1', was determined to be 27; k_1' and k_2' were 2.84×10^{-2} L·mol^{-1}·min^{-1} and 7.66×10^{-1} L·mol^{-1}·min^{-1}, respectively (Appendix II).

Scheme 1



Scheme 2

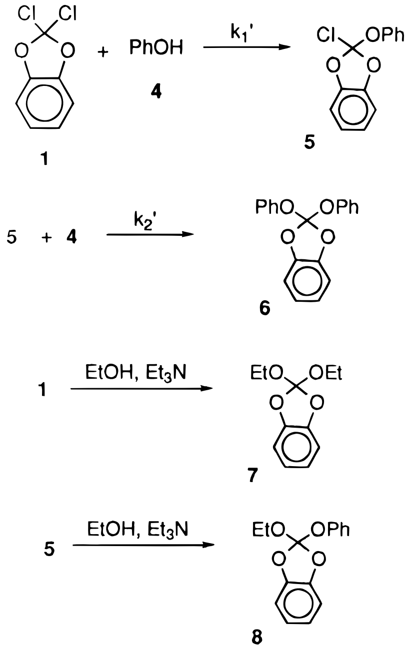


Table 2. Theoretical Yield of 6 and Conversion of 1 Calculated at $\kappa^a = 27$, and Corresponding Molecular Weight of 3

S^b	consumption time of **4**[c]	yield of **6** (%)	consumption of **1** (%)[d]	M_n[e]
1	4999.56[f]	99.99[f]	99.99[f]	3399874[f,g]
1.5	6.85	99.06	100.94	36836
2	4.57	98.11	101.89	18478
3	3.43	96.23	103.77	9299
4	3.05	94.34	105.66	6242

[a] $\kappa = k_2'/k_1'$. [b] $S = 2[\mathbf{1}]_0/[\mathbf{4}]_0$, which is a parameter of stoichiometric imbalance. [c] Normalized by dimensionless value τ $(=k_1'[\mathbf{1}]_0t)$. [d] Based on $[\mathbf{4}]_0$. [e] M_n of **3** after complete consumption of phenolic group. See Appendix III. [f] Normalized time for 99.99% consumption of **4**. Infinite time is necessary for complete consumption. [g] M_n = 5 209 at $\tau = 6.85$.

The following discussion is based on the assumption that k_2/k_1 is 27.

Calculation on the Effect of the Stoichiometric Imbalance. Oiwa has already shown that the net rate of the step polymerization increases as k_2/k_1 value increases.[10] In this case, the rate-determining step (k_1) governs the net rate of the polymerization. Since the rate of the first reaction increases as the concentration of **1** increases, the net rate of the polymerization increases, and a high molecular weight polymer would be obtained after a specific period. Although use of an equimolar amount of **1** and **2** would result in the highest molecular weight of the polymer, it can occur only after an infinite period. Within a finite period, molecular weight would be a function of both the efficiency of the polymerization and the stoichiometric balance of monomers.

To evaluate the effect of the excess amount of **1** from the viewpoint of the formation of orthocarbonate **6**, the time-dependent conversion and yield of each chemical species in the reaction system were calculated under the condition that k_2'/k_1' is 27. Table 2 shows the yield of **6** and the consumption of **1** at the time to be necessary for the complete consumption of **4**. The calculations were made for the series of the stoichiometric imbalance parameter S $(=2[\mathbf{1}]_0/[\mathbf{4}]_0)$. The times are shown in normalized value τ $(=k_1[\mathbf{1}]_0t)$.

If one uses stoichiometric amounts of **1** and **4** (S = 1), it takes an infinite period for the complete consumption of **4**. Conversion of **4** at $\tau = 4999.56$ is 99.99%, and that at $\tau = 49.51$ is 99.9%. If one uses **1** in 50% excess of the stoichiometric amount (S = 1.5), consumption of **4** is complete at $\tau = 6.85$. Here, the yield of **6** approaches to 99.06%, and the consumption of **1** is *only* 100.94% (based on **4**). Thus, the excess amount of **1** does not constrain the production of orthocarbonate **6** so much but evidently accelerates it. Analogous results can be seen in every calculation (S = 2, 3, and 4). It is noteworthy that the yield of **6** extremely decreases with an excess amount of **1** if k_2'/k_1' is equal to or less than unity. The divergence arises from higher reactivity of **5** that can react with **4** in preference to excess **1**. Figure 1 shows the time-dependent yield of **6**. Although the final yield of **6** is highest for S = 1, it takes too long to approach it. The yield of **6** reaches a high value more rapidly as excess **1** is used, although the maximum yield of **6** decreases as S increases.

Number-averaged molecular weight (M_n) and molecular weight distribution of **3** in the polymerization of **1** and **2** were calculated as the function of stoichiometric balance S $(=[\mathbf{1}]_0/[\mathbf{2}]_0)$ and polymerization time in τ. In this case, a conventional equation such as eq 1 is useless because one of the monomers, that is **1**, remains at the end of the polymerization. From the fraction of each functional group calculated for the reaction of **1** and **4** as described above, however, M_n and molecular weight distribution can be calculated by using a modified Case's method[11] (Appendix III).

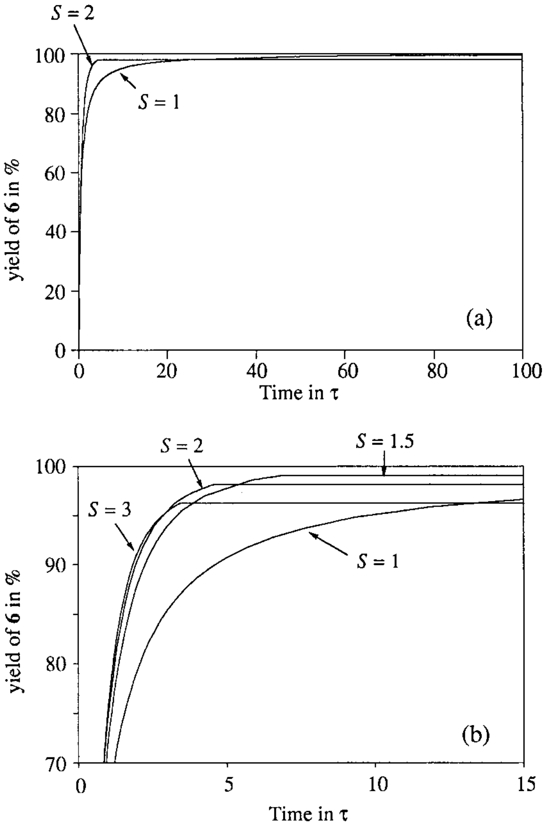


Figure 1. Time- (τ-) dependent yield of **6** calculated at various S values. Expansion of the important part is shown in part b.

First, we calculated the molecular weight of **3** at the point that phenolic hydroxy group is consumed completely. The results are summarized in Table 2. Even for S = 4, a high molecular weight value (M_n = 6242) is calculated in contrast to that calculated from eq 1 (M_n = 289), because only a nearly stoichiometric amount of **1** (105.64% based on **4**) is consumed. It is impossible to see such a behavior in a conventional step polymerization system where the first condensation would not increase the rate of the second condensation.[2]

Second, Figure 2 shows M_n of **3** as the function of time (τ) and stoichiometric imbalance (S). When S = 1, M_n increases linearly until infinite τ value as expected from the conventional theory. When S is larger than unity, however, the development of M_n becomes nonlinear. It is accelerated more as time elapses, and suddenly it ceases because all of the phenolic hydroxy group has been consumed. Although the acceleration becomes greater with the increase of the S value, the increase of M_n ceases in a shorter period while the maximum M_n is lower. Since the effect of stoichiometric imbalance on the acceleration of polymerization is so great, only a low M_n of the polymer is produced for S = 1 at the time that M_n with S >1 approaches its maximum value. As time elapses, however, the S value that gives the highest M_n shifts to a smaller value. Furthermore, the infinite M_n can be predicted for S = 1 at the infinite time, although it is impossible for practical reasons. As a result,

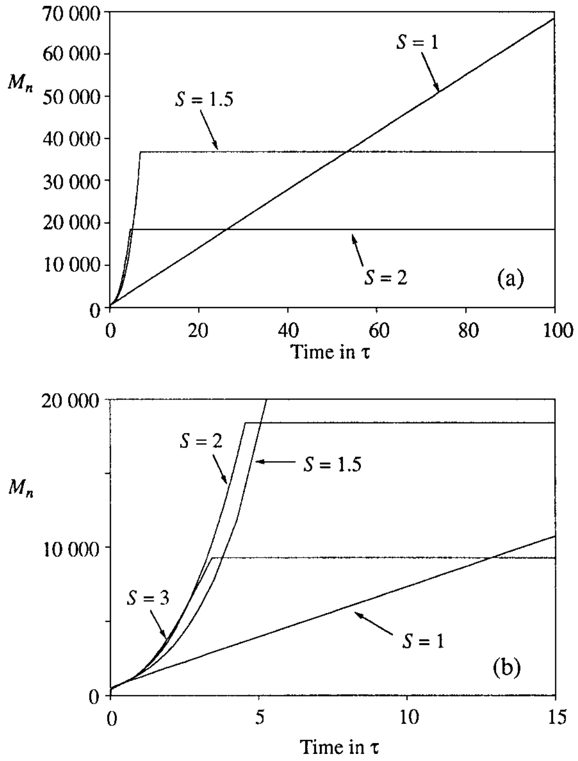


Figure 2. Time- (τ-) dependent $M_{\rm n}$ of **3** calculated at the S value. Expansion of the important part is shown in part b.

attainment of the efficient condensation predominates over the preservation of the stoichiometric balance to obtain a higher molecular weight of polymer within a limited period. In the case that the first condensation decreases the rate of the second condensation, the stoichiometric imbalance simply decreases $M_{\rm n}$.

Finally, the relation between the S value and $M_{\rm n}$ and its distribution was studied. Figure 3 shows molecular weight distribution curves as a function of S: (a) calculated curves for the system of $k_2/k_1 = 27$ at $\tau = 15$,[12] (b) calculated curves for the system of $k_2/k_1 = 1$ at $\tau = \infty$, and (c) experimental GPC traces of **3** obtained from **1** and **2**. The GPC curves (c) were closely related to the theoretical molecular weight distribution curves (a). The deviations might arise from the difference between k'_1 and k_1, and that between t and τ. Meanwhile, a small increase in the S value (from 1.01 to 1.1) considerably decreases $M_{\rm n}$ when $k_2/k_1 = 1$ (b). These results clearly indicate that all the calculations discussed above are consistent with the experimental results.

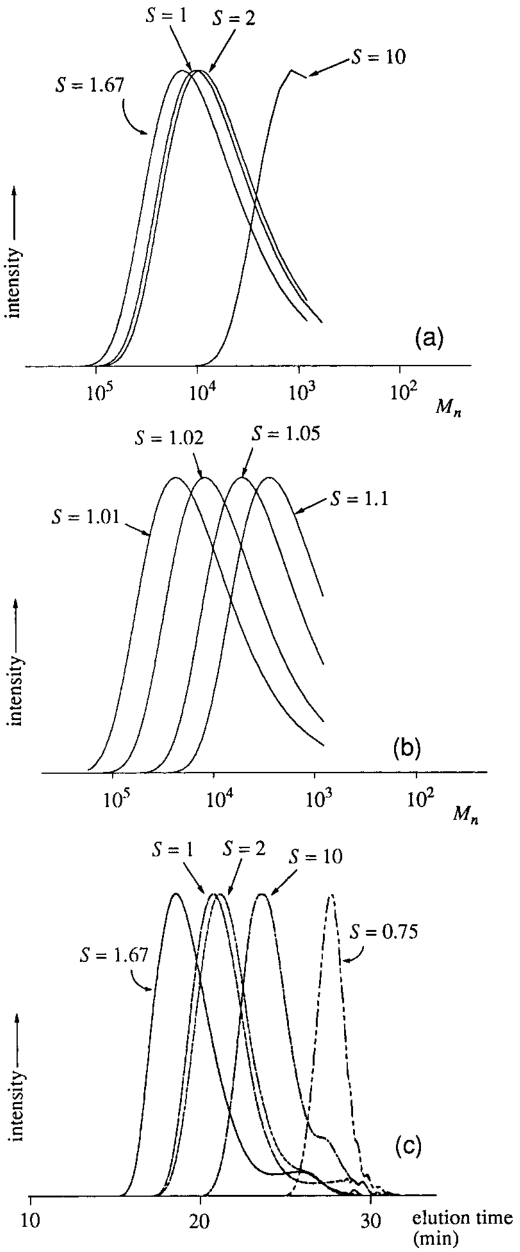


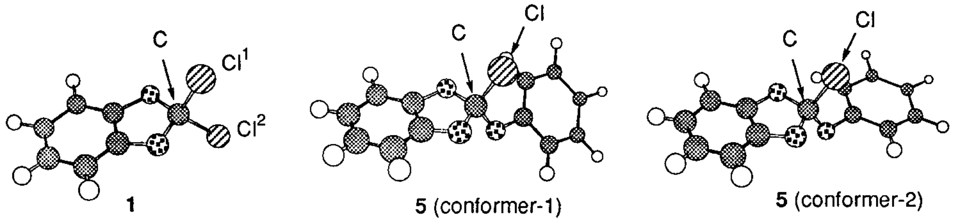
Figure 3. Molecular weight distributions of **3**: (a) calculated distribution for the system $k_2/k_1 = 27$ at $\tau = 15$; (b) calculated distribution for the system $k_2/k_1 = 1$ at $\tau = \infty$; (c) GPC trace of **3** obtained in chlorobenzene at 132 °C for 3 h.

Molecular Orbital Aspects on Reactive Intermediate. The reason that **5** is chemically more reactive than **1** was evaluated by a semiempirical molecular orbital calculation with the PM3 Hamiltonian.[13] Table 3 shows structural and bond parameters for **1** and **5**. Two global minimum conformations were found for **5**. The C−Cl bond in each conformer of **5** is longer and lower in bond order than that of **1**. The Cl atom in **5** is more negative than that of **1**. Therefore, the C−Cl bond in **5** is more polarized than that in **1**. Furthermore, the net atomic charge on the center carbon increases from +0.159 for **1** to +0.307 or +0.309 for **5**. All these parameters rationalize that **5** and the analogous intermediates in the polymerization system have a higher reactivity toward nucleophilic attack of the phenolic hydroxy group than **1**. The polarization of the C−Cl bond and increase of electrophilicity of the center carbon in **5** can be reasonably explained by a typical anomeric effect.[14] Since the benzodioxole system is planar for every conformer, the lone pair on oxygen in this system cannot affect the C−Cl σ^* orbital. Furthermore, the lone pair on phenolic oxygen in **5** is positioned antiperiplanar to the C−Cl bond, which is suitable to show the maximum anomeric effect.

Conclusion

In this paper, we have described the first clear kinetic analysis on a step polymerization system in which the first reaction gives rise to enhancement of the rate of the second reaction, that is, so-called polycondensation through a reactive intermediate. Since $\kappa = 27$ was obtained for the exemplar polycondensation of **1** and **2**, all calculations were conducted using this condition. However, the results obtained are generally applicable.

Table 3. Structural and Electronic Parameters of 1 and 5[a]



unit	interatomic distance (Å)		net atomic charge			bond order	
			C	Cl^1	Cl^2		
1	C−Cl^1	1.788	+0.159	+0.012	+0.012	C−Cl^1	0.927
	C−Cl^2	1.788				C−Cl^2	0.927
5 (conformer 1)	C−Cl	1.802	+0.307	−0.001		C−Cl	0.909
5 (conformer 2)	C−Cl	1.800	+0.309	−0.002		C−Cl	0.911

[a] Calculated by MOPAC (ver. 7, PM3).

We conclude that the stoichiometric balance is *not* essential to obtain a high molecular weight of polymer in the step polymerization system through reactive intermediate. Efficiency of the polymerization is essential. If one uses excess amount of one of the monomers to accelerate the first reaction, higher molecular weight of polymer is obtained in a finite period. The suitable imbalance of monomers depends on not only the κ value but also the polymerization time. A longer reaction time reduces the effect of stoichiometric imbalance which increases the molecular weight of the polymer, and the effect finally disappeared. From a practical point of view, it is rather difficult to obtain a high molecular weight of polymer **3** from the equimolar mixture of **1** and **2** since polymerization is slow and the longer reaction time often results in an accompanying side reaction to stop the polymerization.

Although many step polymerizations of bifunctional monomers have been reported, the second reaction is normally slower than the first one. In a step polymerization of a monomer that has two similar functional groups with different reactivity, the more reactive functional group reacts first.[2,15] Furthermore, in many typical step polymerization systems, the first reaction is faster than the second one due to the electronic effect,[15,16] although the reactivity of the functional group is not significantly affected by the polymer chain length.[1] The rate enhancement of the second reaction by the first one is possible in the case that the two functional groups are present on the same atom or that the two functional groups are connected to each other through the conjugation. The polycondensation of **1** and **2** is one of the best examples of the former concept, while the polycondensation of sodium sulfide and dichlorobenzene is an example of the latter concept although it is not simple to analyze.[5] To our knowledge, polyformal synthesis using dichloromethane as a reactant and a solvent is one of the other good examples, while the best, stoichiometric imbalance, was not explored.[17] There are many other step polymerization systems where the second reaction is faster than the first one, although stoichiometric imbalance experiments have not been attempted.[18] We have a general prediction that stoichiometric imbalance should enhance the molecular weight of the polymer in these systems. The appropriate S value can be calculated as the function of τ. Figure 4 shows the prediction. Even with $\kappa = 2$, $S = 1.05$ is superior to $S = 1.00$ until τ approaches 36.

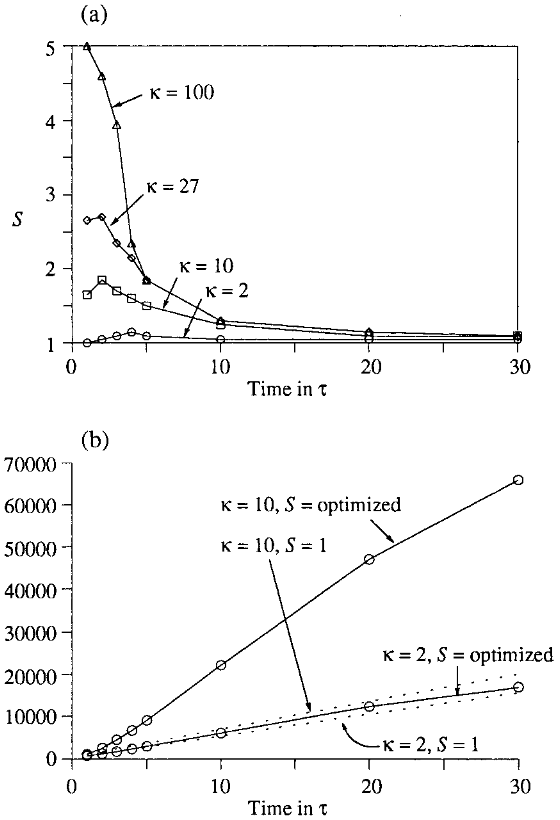


Figure 4. Effect of optimization of S: (a) S value that gives the maximum M_n at a given τ and (b) comparison of M_n between optimized S value and $S = 1$. Solid line is M_n at a given τ with optimized S value. Dotted line is the time-dependent change of M_n with a stoichiometrically balanced system ($S = 1$).

Experimental Section

General Data. Commercially available chlorobenzene was washed with concentrated sulfuric acid several times and with aqueous sodium carbonate, dried over calcium chloride, and distilled over phosphorus pentoxide after refluxing over phosphorus pentoxide for several hours. Commercial dichloromethane was distilled over phosphorus pentoxide and was further distilled over calcium hydride. Pentadecane was distilled over phosphorus pentoxide. Reagent grade 4,4′-isopropylidenediphenol (bisphenol A, **2**) was available from Tokyo Kasei Co. Ltd. and was used after recrystallization from methanol−chloroform (1/5 v/v). 2,2-Dichloro-1,3-benzodioxole (**1**) was synthesized by the reaction of 1,3-benzodioxole with phosphorus pentachloride according to the literature,[20] purified by distillation twice, and stored under an argon atmosphere in an ampule. 2,2-Diphenoxybenzo-1,3-dioxole (**6**)[21] and 2,2-diethoxybenzo-1,3-dioxole (**7**)[8] were synthesized according to the literature and were used as the authentic samples in GC experiments after recrystallization from methanol. Nitrogen was used after passing through calcium chloride.

Melting points were determined using a Yanaco micro melting point apparatus. Gas chromatographic (GC) analyses were performed with a Shimadzu GC-8A equipped with 1 m column packed with silicone SE−30. Gel permeation chromatographic (GPC) analyses were carried out using a Tosoh HLC-8020 equipped with TSKgel G5000HXL, G4000HXL, and G2500HXL columns and a UV-8011 detector operating at 270 nm, eluted by THF (1 mL/min, 35 °C). Calibration was carried out using polystyrene standards. ^{1}H and ^{13}C NMR spectra were obtained on a JEOL EX-90 spectrometer using tetramethylsilane as an internal standard. IR spectra were obtained on a JASCO FT/IR-3 spectrometer.

Calculations were made on Apple Power Macintosh 7600/200 using Visual Basic on Microsoft Excel ver. 5.0. Semiempirical molecular orbital calculations were made with MOPAC ver 7.0 using PRECISE keyword and PM3 Hamiltonian.

Polycondensation of 1 and 2. A General Method. To a solution of **1** dissolved in 4.0 mL of chlorobenzene under nitrogen atmosphere was added 1.14 g (5.00 mmol) of **2**, and the solution was refluxed for 3 h. Evolution of hydrogen chloride was observed, which was removed by the continuous flow of nitrogen. The resulting viscous mixture was diluted with 40 mL of tetrahydrofuran, and poured into 500 mL of methanol containing triethylamine. The white fibrous polymer precipitated was collected, washed with methanol, and dried in vacuo at 100 °C for 1 day.

IR (film): 1508, 1485, 1253, 1228, 1172, 1128, 1101, 1076, 1014, 1003, 914, 833, 814, 798, 736 cm^{-1}.

^{1}H NMR (90 MHz, $CDCl_3$): δ 6.97 (br, 8H), 6.70 (br, 4H), and 1.56 (s, 6H) ppm.

^{13}C NMR (22.5 MHz, $CDCl_3$, 60 °C): δ 149.53, 147.14, 145.38, 129.54, 127.55, 122.14, 120.67, 108.73, 42.30, and 30.90 ppm

Kinetics of the Reaction of 1 and 4. In a two-necked flask equipped with a septum rubber and nitrogen inlet and outlet tubes was placed a solution of 478 mg (2.50 mmol) of **1** and 69.1 μL of pentadecane in 25.0 mL of dichloromethane under nitrogen atmosphere. The solution was kept at −40 °C in an incubator. A solution of 471 mg (5.00 mmol) of **4** in 25.0 mL of dichloromethane was cooled at −40 °C, and was added to the solution of **1** at once to start the reaction. Periodically, 1.0 mL of the reaction mixture was withdrawn through the septum rubber by syringe, and was immediately poured into 2.0 mL of methanol-triethylamine mixture (50/1 v/v). After evaporation, 0.5 mL of ether added to the residue, and the ethereal solution was injected to GC to quantify **4** referring the intensity of the internal standard (pentadecane).

Appendix I[19]

For the following reactions

$$\mathbf{1} + \mathbf{4} \xrightarrow{k_1'} \mathbf{5} \tag{3}$$

$$\mathbf{5} + \mathbf{4} \xrightarrow{k_2'} \mathbf{6} \tag{4}$$

the reaction rates are given by

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

$$-\frac{d}{dt}[\mathbf{4}] = k_1'[\mathbf{1}][\mathbf{4}] + k_2'[\mathbf{4}][\mathbf{5}] \tag{6}$$

$$-\frac{d}{dt}[\mathbf{5}] = -k_1'[\mathbf{1}][\mathbf{4}] + k_2'[\mathbf{4}][\mathbf{5}] \tag{7}$$

The initial concentration of each compound is defined to be $[\mathbf{1}]_0$, $[\mathbf{4}]_0$, $[\mathbf{5}]_0$, and $[\mathbf{6}]_0$, respectively, where $[\mathbf{5}]_0 = [\mathbf{6}]_0 = 0$. Thus

$$[\mathbf{1}]_0 = [\mathbf{1}] + [\mathbf{5}] + [\mathbf{6}] \tag{8}$$

$$[\mathbf{4}]_0 = [\mathbf{4}] + [\mathbf{5}] + 2[\mathbf{6}] \tag{9}$$

Furthermore, dimensionless variables α, β, and τ and the parameters κ and S are defined by

$$\alpha = \frac{[\mathbf{4}]}{[\mathbf{4}]_0} \tag{10}$$

$$\beta = \frac{[\mathbf{1}]}{[\mathbf{1}]_0} \tag{11}$$

$$\tau = k_1'[\mathbf{1}]_0 t \tag{12}$$

$$\kappa = \frac{k_2'}{k_1'} \tag{13}$$

$$S = 2\frac{[\mathbf{1}]_0}{[\mathbf{4}]_0} \tag{14}$$

where α and β are the fractions of **4** and **1**, respectively, τ is the normalized dimensionless time, κ is the ratio of the two rate constants, and S is the parameter of stoichiometric imbalance. If $\kappa \neq 1$, the coupled equations (5) and (7) can be solved to give

$$[\mathbf{5}] = \frac{k_1'}{k_2' - k_1'}[\mathbf{1}]\left(1 - \left(\frac{[\mathbf{1}]}{[\mathbf{1}]_0}\right)^{(k_2' - k_1')/k_1'}\right) \tag{15}$$

The combination of the equations (8), (9), and (15) gives

$$\alpha = 1 - S + \frac{S}{2(\kappa - 1)}\beta(2\kappa - 1 - \beta^{\kappa - 1}) \tag{16}$$

by which α value can be calculated at the specific β value. After eq 5 is rewritten by

$$-\frac{d}{dt}\beta = \frac{2[\mathbf{1}]_0 k_1'}{S}\alpha\beta \tag{17}$$

it can be solved to give

$$\tau = \int_\beta^1 \frac{dx}{x\left(\frac{2}{S} - 2 + \frac{1}{\kappa - 1}x(2\kappa - 1 - x^{\kappa - 1})\right)} \tag{18}$$

Equation 18 leads the connection between β and τ. Although we attempted to apply the Gauss method to solve eq 18, it gave significant errors. Thus, it was rewritten by using $w = 1/x$ to give

$$\tau = \int_{1/\beta}^1 \frac{dw}{\left(2 - \frac{2}{S}\right)w + \frac{1}{1 - \kappa}(2\kappa - 1 - w^{1 - \kappa})} \tag{19}$$

Equation 19 was compatible with Gauss' method, by which the τ value can be calculated at the specific β value.

If $\kappa = 1$, the following equations should be used instead of eqs 16 and 19.

$$\alpha = 1 - S + \frac{S}{2}\beta(2 - \ln \beta) \tag{16'}$$

$$\tau = \int_{1/\beta}^{1} \frac{\mathrm{d}w}{\left(2 - \frac{2}{S}\right)w - 2 - \ln w} \tag{19'}$$

The value of κ was determined experimentally as follows: To a solution of **1** and an internal standard was added 2.00 equiv of **4** ($S = 1$) all at once to start the reaction. The reaction condition was chosen so as to follow the reaction by chromatography. Periodically, a small portion of the reaction mixture was withdrawn and immediately poured into an alcohol containing triethylamine to quench the reaction. The consumption of **4** was monitored by gas chromatography referring to the internal standard. Thus, the array of α values (α_1, α_2, α_3, ..., α_n) was obtained at the corresponding time, t_1, t_2, t_3, ..., t_n. From eq 16, the array of β values (β_1, β_2, β_3, ..., β_n) that corresponds to the array of α values is calculated as a function of κ. The corresponding array of τ values (τ_1, τ_2, τ_3, ..., τ_n) was calculated from eq 19 in the same κ value using the Gauss method. Because $t_q/t_p = \tau_q/\tau_p$, the error function $f(\kappa)$ is defined by

$$f(\kappa) = \sum_{p=1}^{n}\sum_{q=1}^{n} \left|\frac{t_q}{t_p} - \frac{\tau_q}{\tau_p}\right| \tag{20}$$

Thus, $f(\kappa)$ was calculated and plotted against κ as shown in Figure 5. The minimum $f(\kappa)$ value was obtained at $\kappa = 27$.

At the specific β value, α and τ are calculated from eqs 16 and 19, respectively ($\kappa = 27$). [**5**]/[**4**]$_0$ and 2[**6**]/[**4**]$_0$ are calculated as a function of α and β from eqs 8 and 9.

Appendix II

From eqs 6 and 15

$$-\frac{\mathrm{d}}{\mathrm{d}t}[\mathbf{4}] = \left(k_1' + \frac{k_2'k_1'}{k_2' - k_1'}\left(1 - \left(\frac{[\mathbf{1}]}{[\mathbf{1}]_0}\right)^{(k_2'-k_1')/k_1'}\right)\right)[\mathbf{1}][\mathbf{4}] \tag{21}$$

Since

$$\frac{k_2' - k_1'}{k_1'} \gg 1 \rightarrow \left(\frac{[\mathbf{1}]}{[\mathbf{1}]_0}\right)^{(k_2'-k_1')/k_1'} \sim 0$$

then, the consumption of [**4**] follows second-order kinetics, and the net rate constant is $(2k_1'k_2' - k_1'^2)/(k_2' - k_1')$.

Appendix III

Case has derived averaged molecular weight and molecular distribution functions for various polycondensation systems.[11] However, some modifications were necessary for the system of the polycondensation between **1** and **2** because a significant amount of **1** remained without change when $S > 1$.

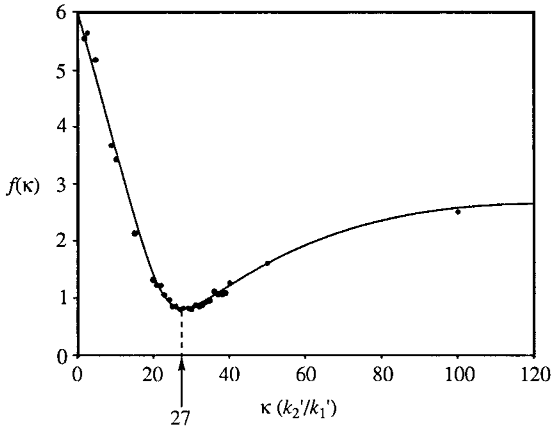


Figure 5. Relationship between κ and error function $f(\kappa)$.

For the polycondensation where monomer A−A is reacting with monomer B−C (B reacts before C), the probabilities of reacting the functional groups A, B, and C are denoted by a, b, and c, the numbers of monomer molecules are denoted by N_{AA} and N_{BC}, and the weights of reacted A−A and B−C units are denoted by W_{AA} and W_{BC}. The total number of ends in polymer N_E is the subtraction of the total numbers of ends in the monomers from that in the system.

$$N_E = 2N_{AA}(1 - a) + N_{BC}(2 - b - c) - 2N_{AA}(1 - a)^2 - 2N_{BC}(1 - b) \tag{22}$$

Since the total weight of the polymer is $N_{AA}W_{AA}(1 - (1 - a)^2) + N_{BC}W_{BC}b$, the number-averaged molecular weight of the polymer M_n is given by

$$M_n = \frac{N_{AA}W_{AA}(1 - (1 - a)^2) + N_{BC}W_{BC}b}{\frac{1}{2}N_E} \tag{23}$$

For the polycondensation of **1** (B−C type monomer) and **2** (A−A type monomer)

$$N_{BC} = SN_{AA} \tag{24}$$

$$a = 1 - \frac{[\mathbf{4}]}{[\mathbf{4}]_0} \tag{25}$$

$$b = \frac{[\mathbf{5}] + [\mathbf{6}]}{[\mathbf{1}]_0} \tag{26}$$

$$c = \frac{[\mathbf{6}]}{[\mathbf{1}]_0} \tag{27}$$

$$W_{AA} = 226.27 \tag{28}$$

$$W_{BC} = 120.11 \tag{29}$$

Thus

$$M_n = \frac{\left(1 - \frac{[\mathbf{4}]^2}{[\mathbf{4}]_0{}^2}\right)W_{AA} + S\left(1 - \frac{[\mathbf{1}]}{[\mathbf{1}]_0}\right)W_{BC}}{\frac{[\mathbf{4}]}{[\mathbf{4}]_0} - \frac{[\mathbf{4}]^2}{[\mathbf{4}]_0{}^2} + \frac{[\mathbf{5}]}{[\mathbf{4}]_0}} \tag{30}$$

Each parameter in eq 30 for specific β value is obtained as the function of κ and S as described in Appendix I.

The molecular weight distribution function can be evaluated by considering the probability of choosing a given stating group in the polymer chain, the probability of finding a given end group, and the product of the probabilities that each bond in the chain is formed (from the start to the end). Only one arrangement of each unit in the chain is possible in this case. There are four types of polymer chains, I, II, III, and IV, in the system. The distribution of each chain, D_{I}, D_{II}, D_{III}, and D_{IV}, and the weight of each chain, W_{I}, W_{II}, W_{III}, and W_{IV}, can be expressed as follows:

type I (starting group = A, end group = A, nA−A units and (n − 1)B−C units)

$$D_{\mathrm{I}} = N_{\mathrm{AA}}(1 - (1 - a)^2)(1 - a)(1 - a)a^{n-1}d^{n-1} \tag{31}$$

$$W_{\mathrm{I}} = nW_{\mathrm{AA}} + (n - 1)W_{\mathrm{BC}} \tag{32}$$

type II (starting group = A, end group = C, nA−A units and nB−C units)

$$D_{\mathrm{II}} = N_{\mathrm{AA}}(1 - (1 - a)^2)(1 - a)(1 - d)a^{n}d^{n-1} \tag{33}$$

$$W_{\mathrm{II}} = nW_{\mathrm{AA}} + nW_{\mathrm{BC}} \tag{34}$$

type III (starting group = C, end group = A, nA−A units and nB−C units)

$$D_{\mathrm{III}} = N_{\mathrm{BC}}b(1 - d)(1 - a)a^{n-1}d^{n-1} \tag{35}$$

$$W_{\mathrm{III}} = nW_{\mathrm{AA}} + nW_{\mathrm{BC}} \tag{36}$$

type IV (starting group = C, end group = C, nA−A units and (n + 1)B−C units)

$$D_{\mathrm{IV}} = N_{\mathrm{BC}}b(1 - d)(1 - d)a^{n}d^{n-1} \tag{37}$$

$$W_{\mathrm{IV}} = nW_{\mathrm{AA}} + (n + 1)W_{\mathrm{BC}} \tag{38}$$

where d is the probability of group C connecting to group A, that is

$$d = \frac{[\mathbf{6}]}{[\mathbf{5}] + [\mathbf{6}]} \tag{39}$$

The nonnormalized number distribution function Fn and weight distribution function Fw are given by

$$\mathrm{Fn} = D_{\mathrm{I}} + D_{\mathrm{II}} + D_{\mathrm{III}} + D_{\mathrm{IV}} \tag{40}$$

$$\mathrm{Fw} = D_{\mathrm{I}}W_{\mathrm{I}} + D_{\mathrm{II}}W_{\mathrm{II}} + D_{\mathrm{III}}W_{\mathrm{III}} + D_{\mathrm{IV}}W_{\mathrm{IV}} \tag{41}$$

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