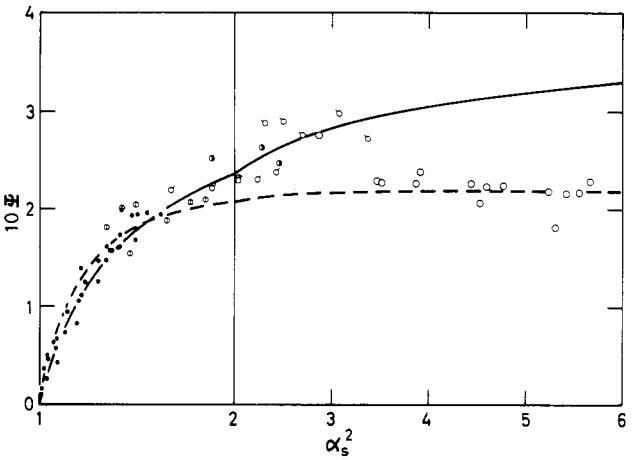

Figure 1. Comparison between theory (solid line, eq 3 and 5; broken line, eq 6 and 7) and experiment: polychloroprene (●) in *trans*-decalin, (Φ) in *n*-butyl acetate, and (◑) in carbon tetrachloride,[16] polyisobutylene (♂) in *n*-heptane and (♁) in cyclohexane,[17] and poly(D-β-hydroxybutyrate) (○) in trifluoroethanol.[18]

Experimentally, the usefulness of eq 2, or more correctly, the corresponding expression for $\langle S^2 \rangle$ (the mean-square radius of gyration)

$$\alpha_S^2 = 0.6089 + 0.3911(1 + 6.526z)^{1/2} \quad (3)$$

has repeatedly been demonstrated in plots of α_s^2 against z,[14,15] by using the experimental data which are considered as reliable. Here, another comparison with experiments will be presented in a different way by plotting Ψ against α_S^2. The penetration function, Ψ, is defined by

$$\Psi = A_2 M^2 / 4\pi^{3/2} N_A \langle S^2 \rangle^{3/2} \quad (4)$$

where A_2 is the second virial coefficient, M the molecular weight of a polymer molecule, and N_A the Avogadro number. So Ψ as well as α_S^2 may be determined with light scattering data alone. In Figure 1, experimental points calculated from data on polychloroprene,[16] polyisobutylene,[17] and poly(D-β-hydroxybutyrate)[18] are plotted and compared with the combined theoretical prediction of eq 3 for α_S^2 and the following expression for Ψ:[19,20]

$$\Psi = [1 - (1 + 3.573z/\alpha_S^3)^{-0.620}]/2.193 \quad (5)$$

Strictly speaking, these equations are not necessarily of the same theoretical nature. Since no higher than the third-order perturbation theory of A_2 is available to date, we are satisfied with eq 5, which is only valid up to the quadratic term of z. As a whole, one can see reasonable agreement between theory and experiment in a region of α_S^2 up to 3. For α_S^2 values higher than 3, the agreement becomes poor: Ψ in eq 5 diverges slowly, while the experiments on poly(D-β-hydroxybutyrate) yield an almost constant value of 0.22 ± 0.01. The disagreement could be a natural result due mainly to the limitation of eq 5.

It must be remarked here that the asymptotic behavior of Ψ has successfully been predicted by Oono with the renormalization theory.[21] His expressions for α_S^2 and Ψ are

$$\alpha_S^2 = (1 + Z)^{1/4}[1 - 13Z/96(1 + Z)] \quad (6)$$

and

$$\Psi = \frac{0.452}{\pi^{3/2}} \frac{Z}{1+Z} \exp\left[\left(\frac{13}{48} + \frac{4 \ln 2 - 1}{8}\right)\frac{Z}{1+Z} + \frac{1}{2}\right] \quad (7)$$

The new variable Z is the counterpart of z in the conventional two-parameter theory and is defined with the renormalized one instead of the cluster integral itself. At large α_S^2's, Ψ of eq 7 approximately takes the value 0.219, which coincides with the experimental values on highly expanded polymer molecules.[18] The prediction of eq 6 and 7 is also illustrated for comparison by the broken line in Figure 1. However, that Ψ has a crest around $\alpha_S^2 = 3$ can be explained neither by eq 5 nor by eq 7.[22] From this behavior of Ψ as well as the lack of higher order perturbation theory, one sees, when compared with those of α^2, that further developments in theory of A_2 are still desirable.

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Kinetic Studies of Polyimine Formation

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Polyimine is the polymer produced by the condensation of a primary diamine and a dialdehyde. This polymer, having a CH=N backbone, is very attractive as an electrophysical material.[1] However, there have been many difficulties in obtaining high molecular weight polyimines

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Table I
Rate of Formation of Imino Bond at 293 K in *m*-Cresol

polymer	C_0, mol L^{-1}	k, L (g equiv)$^{-1}$ min^{-1}	k^*, L (g equiv)$^{-1}$ min^{-1}	K
O=(CHC_6H_4CH=NC_6H_4N)=H_2 (1)	0.133	8.0		
O=(CHC_6H_4CH=N(1,3-(6-$CH_3C_6H_3$))N)=H_2 (2)	0.200	2.1		
O=(CHC_6H_4CH=$NC_6H_4CH_2C_6H_4N$)=H_2 (3)	0.200	5.65	0.0292	194
O=(CHC_6H_4CH=$NC_6H_4OC_6H_4C(Me)_2C_6H_4OC_6H_4N$)=$H_2$ (4)	0.200	4.7 (0.14)[a]	0.0105	446
O=(CHC_6H_4CH=$NC_6H_4OC_6H_4SO_2C_6H_4C_6H_4N$)=$H_2$ (5)	0.200	2.18	0.0136	160
O=[CHC_6H_4CH=$N(CH_2)_6N$]=H_2 (6)	0.200	24.80	0.0340	730
C_6H_5N=CHC_6H_4CH=NC_6H_5 (7)	0.200	2.90 (1.03)[b]		

[a] In chlorobenzene. [b] In ethyl alcohol.

by means of solution polymerization because of their insolubility in common organic solvents.[2] Suematsu and co-workers reported earlier that *m*-cresol was one of the most adequate solvents to synthesize high molecular weight polyimines.[3] It dissolved most polyimines except for a group having an inflexible backbone. In this paper we will elucidate the specific feature of the *m*-cresol polymerization in comparison with other methods through kinetic studies.

Results and Discussion

The polymerization to form polyimine is represented by the following formula:

$$x\mathrm{OHCC_6H_4CHO} + x\mathrm{H_2NRNH_2} \rightleftarrows \mathrm{O{=}[CHC_6H_4CH{=}NRN]_x{=}H_2} + (2x-1)\mathrm{H_2O} \quad \text{(a)}$$

Under a given condition (293 K, 1 atm), when the consumption rate of the functional group (g equiv/L) was plotted against reaction time (min), the initial gradient of the curve was found to be in good agreement with a second-order equation. That is, if the concentration of CHO or NH_2 at t minutes is represented by C and the initial concentration is represented by C_0

$$v = -dC/dt = kC^2 \quad (1)$$

$$1/C = kt + 1/C_0 \quad (2)$$

In Table I, the k values of typical polyimines are shown. The coefficient k is 24.8 (g equiv/L)$^{-1}$ min^{-1} in aliphatic polyimine **6**, 2.1–8.0 (g equiv/L)$^{-1}$ min^{-1} in aromatic polyimines **1–5**, and 2.90 (g equiv/L)$^{-1}$ min^{-1} in a model compound, *p*-xylylidenedianiline. These are surprisingly large compared to those of the known polycondensations.[4] Under the same condition, for example, in the polymerization of sebacic acid and hexamethylenediamine, $k = 9 \times 10^{-10}$ (mol/L)$^{-1}$ min^{-1}. In the case of phthaloyl chloride and piperazine in H_2O–CCl_4, $k \leq 3.7 \times 10^{-2}$ (mol/L)$^{-1}$ min^{-1}. Thus we can admit the abnormal speed of the *m*-cresol polymerization. In the polymerization of **4** in chlorobenzene and **7** in ethyl alcohol, however, $k = 0.14$ and 1.03 (g equiv/L)$^{-1}$ min^{-1}, which are smaller than in *m*-cresol. Therefore, there must be some acceleration effect in *m*-cresol itself.

According to Cordes and Jenkes,[5] CH=N bond formation consists of two elementary reactions, an addition reaction of amine to aldehyde and a dehydration reaction of resultant carbinolamine.

$$\mathrm{RNH_2} + \mathrm{R'CHO} \overset{\mathrm{I}}{\rightleftarrows} \mathrm{RNHC(OH)HR'} \overset{\mathrm{II}}{\rightleftarrows} \mathrm{RN{=}CHR'} + \mathrm{H_2O} \quad \text{(b)}$$

In the first step, step I, two kinds of reaction, deactivation by the protonation to NH_2 and activation by the protonation to CHO, compete, thus forming a maximum point of velocity at the acid site. The dehydration of carbinolamine in the second step, step II, is catalyzed by acid. Consequently the rate of CH=N formation has a maximum point at pH $\simeq$4. At the acidic region from the point, the addition of NH_2 to CHO is rate determining and at the basic region, the dehydration of carbinolamine becomes rate determining.

Certainly, the moderate acidity of *m*-cresol can catalyze most effectively both of the elementary reactions in the meaning mentioned above, and this is the reason why k in *m*-cresol is distinguished from that in other solvents.

In Table I, it is seen that k varies considerably with the diamines used. It decreases in the order $H_2N(CH_2)_6NH_2$ > $H_2NC_6H_4NH_2$ > $H_2NC_6H_4OC_6H_4C(CH_3)_2C_6H_4OC_6H_4NH_2$ > $H_2NC_6H_4OC_6H_4SO_2C_6H_4OC_6H_4NH_2$, which corresponds to the order of the nucleophilicity of the diamines. Since the nucleophilicity of the diamines participates only in the first step, it is concluded that the addition reaction of the diamines is rate determining.

As mentioned already, except for the *m*-cresol method, polyimine syntheses by solution polymerization have not been successful.[3] Alcohol and benzene were the solvents tried generally. Here we will clarify the reason for the failure. According to polycondensation theory, in the case of AA–BB type polymerization, the number-average degree of polymerization $\langle x \rangle$ is given by

$$\langle x \rangle = (C_0/C)/2 \quad (3)$$

From eq 2

$$\langle x \rangle = (C_0kt + 1)/2 \quad (4)$$

which teaches $\langle x \rangle$ is the product of k and t. The above reason is easily explained in terms of two factors: (a) the low solubility of polyimines in common solvents precipitates the oligomers and terminates the propagation, thus shortening t in eq 4; (b) the small rate constants in ethyl alcohol and chlorobenzene as are shown in Table I. Both factors will produce smaller $\langle x \rangle$ according to eq 4. In Table II are compared $\langle x \rangle$ of polymer **1** prepared by the *m*-cresol method and others. Polymer **1** was insoluble in most solvents tried and precipitation started in various stages. It is seen, however, that the larger chain length from the *m*-cresol method draws a sharp line between others. This is undoubtedly based on the larger k and t values in *m*-cresol.

Although a $1/C$ vs. time plot has an approximately linear relationship in the initial stage of the polymerization, an immediate saturation of $1/C$ was observed, which means the existence of a fast depolymerization (Figure 1). Therefore, the kinetic equation should be written in the more precise form

$$v = k[\mathrm{NH_2}][\mathrm{CHO}] - k^*[\mathrm{CH{=}N}][\mathrm{H_2O}] \quad (5)$$

$$-dC/dt = kC^2 - k^*(C_0 - C)^2 \quad (6)$$

which gives

$$\frac{1}{C} = \frac{1}{C_0}\,\frac{(K^{1/2}+1) - (K^{1/2}-1)\exp(-2C_0kt/K^{1/2})}{1 + \exp(-2C_0kt/K^{1/2})} \quad (7)$$

Table II
Formation of Polyimine 1 in Various Solvents

no.	solvent	polymerization conditions	t,[a] min	$\langle x \rangle$	yield, %	ref
1	*m*-cresol	C_0 = 0.133 (g equiv)/L, T = 293 K	≃30	16	95	
2	ethyl alcohol	C_0 = 0.133 (g equiv)/L, T = 298 K	≃4	≤5	74	
3	chlorobenzene	C_0 = 0.133 (g equiv)/L, T = 333 K[b]	≃30	≤10	40	
4	benzene	reflux for 20 h		2		3
5	acetic acid	reflux for 5 h		4–5		3
6	dimethylformamide	10 h, T = 413 K		3–4		3

[a] t = time until precipitation of oligomer. [b] At 293 K the reaction could not be carried out because of insolubility of *p*-phenylenediamine.

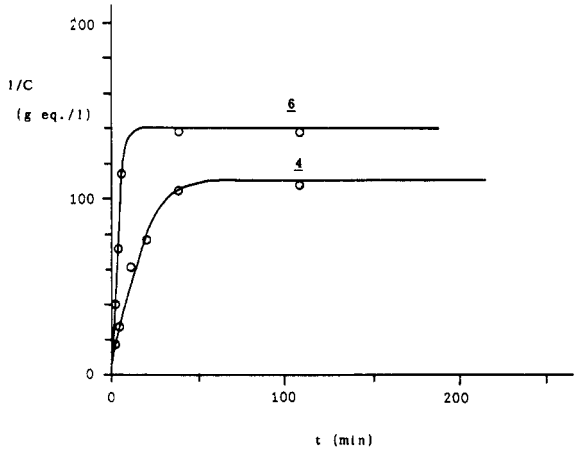

Figure 1. $1/C$ vs. t curves of polyimine **4** and **6** formation at 293 K in *m*-cresol: circles, observed; solid line, theoretical.

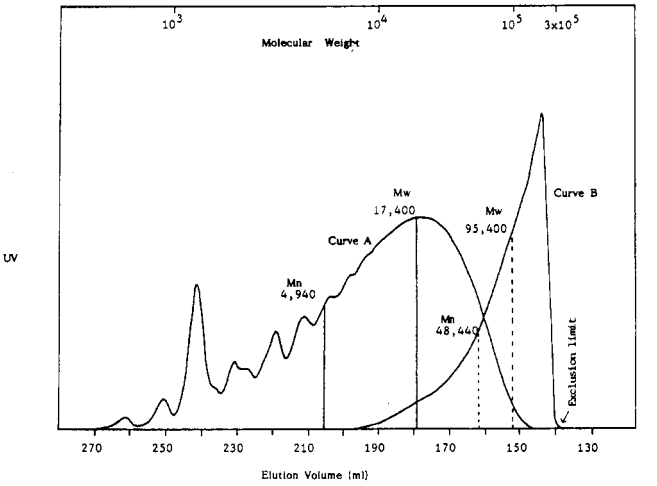

Figure 2. GPC chromatogram of polyimine **4**: curve A, a = 0; curve B, $a \simeq 0.95$. a is the mole fraction of excluded water.

where k^* is the rate constant of the depolymerization and $K = k/k^*$. Upon replacing t of eq 7 with $t = \infty$, we have

$$\langle x \rangle = (C_0/C)/2 = (K^{1/2} + 1)/2 \quad (8)$$

Typical k,k^*, and K values are shown in Table I. A most interesting feature is that the systems having large k have large k^* and those having small k have small k^*, suppressing K values and consequently leading to a maximum of $\langle x \rangle \approx 20$. According to eq 8, the shift of the equilibrium through the exclusion of the condensation water should produce larger $\langle x \rangle$.[6] If b moles of H_2O are excluded, $\langle x \rangle$ produced by the equilibrium shift should be given by

$$\langle x \rangle = \{([1/(1-a)] \times (2\langle x \rangle_0 - 1)^2 + \tfrac{1}{4}[a/(1-a)]^2)^{1/2} + \tfrac{1}{2}[a/(1-a)] + 1\}/2 \quad (9)$$

where $a = b/C_0$ and $\langle x \rangle_0$ is the equilibrium degree of polymerization in $b = 0$. In the range $0 \le b/C_0 \le 0.95$, eq 9 is approximately expressed as follows:

$$\langle x \rangle \simeq \{(1/(1-a))^{1/2}(2\langle x \rangle_0 - 1) + \tfrac{1}{2}[a/(1-a)] + 1\}/2 \quad (10)$$

Equation 10 was exemplarily applied to polymer **4**. $\langle x \rangle_0$ of polymer **4**, which was 11 at $b = 0$, increased to ≃22 ($a \simeq 0.75$) when the condensation water was taken off with a part of the solvent by distillation. Further, $\langle x \rangle$ increased to ≃36 ($a \simeq 0.90$) by heating the polymer solution at 333 K for 15 h and ≃48 ($a \simeq 0.95$) by further heating at 473 K for 4 h under reduced pressure. In Figure 2 are shown GPC curves of polymer **4**. Curve A corresponds to the case of $a = 0$ and curve B to $a \simeq 0.95$.

Experimental Section

Monomer. Terephthalaldehyde, supplied by Wako Co. (Japan), was recrystallized from chloroform and *n*-hexane. The diamines were purified by distillation under a vacuum (hexamethylenediamine and 2,4-diaminotoluene) or recrystallization from adequate solvents [hydrazine hydrate (diaminodiphenylmethane) and chlorobenzene (*p*-phenylenediamine)]. Synthesis and purification of the monomers having –O– bonds were carried out as follows.

2,2-Bis[4-(4-aminophenoxy)phenyl]propane ($H_2NC_6H_4OC_6H_4C(CH_3)_2C_6H_4OC_6H_4NH_2$). To a separable flask equipped with a mechanical stirrer and a $CaCl_2$ tube were added 74 g (0.47 mol) of *p*-chloronitrobenzene, 45.6 g (0.2 mol) of bisphenol A, 76 g (0.55 mol) of anhydrous K_2CO_3, and 200 mL of dry dimethylformamide. The mixture was refluxed at 160 °C on an oil bath for 8 h and cooled, and 200 mL of 1:1 H_2O–C_2H_5OH was added to precipitate yellow crystals. Dinitro compound, 90 g (96%).

The dinitro compound (61 g), 0.2 g of 10% Pd–C, and 500 mL of C_2H_5OH were introduced into the separable flask and refluxed on the oil bath with stirring. To the suspension was added 90 mL of $NH_2NH_2{\cdot}H_2O$ dropwise for 1 h. An additional 0.2 g of Pd–C and 40 mL of $NH_2NH_2{\cdot}H_2O$ were added for 30 min. After 4 h, a colorless, clear solution with Pd–C powder was obtained. The whole was filtered to remove Pd–C and cooled to afford 40 g of colorless needles. Adding 200 mL of H_2O to the mother liquid yielded an additional 13 g. Diamino compound, 53 g (100%). A part of the product was purified by column chromatography on a silica gel, using chloroform as an eluent: mp 126 °C; IR (KBr) 3400 and 3340 (NH_2), 1220 cm^{-1} (–O–); ^1H NMR ($CDCl_3$) δ 1.64 (s, 6 H, CH_3), 3.3 (s, 4 H, NH_2).

2,2-Bis[4-(4-aminophenoxy)phenyl sulfone was prepared by a similar procedure; yield 68%. A part of the product was purified by column chromatography on a silica gel, using chloroform as an eluent: mp 193 °C; IR (KBr) 3460 and 3340 (NH_2), 1220 cm^{-1} (–O–); NMR ($CDCl_3$) δ 3.38 (s, 4 H, NH_2).

Solvent. *m*-Cresol, a mixture of 52% *m*-cresol, 31% *p*-cresol, 1% *o*-cresol, 15% xylenol, and 1% others, was purified by distillation under reduced pressure. Alcohols were dried with Mg metal and distilled before use.

Polymerization. The reaction was carried out in a dry atmosphere at 293 K using a conventional apparatus with a mechanical stirrer. A diamine was dissolved in freshly distilled *m*-cresol. To the solution an equimolar amount of a dialdehyde was added with vigorous stirring, instantaneously resulting in an orange to red polyimine solution. To the polymer solution was added anhydrous methanol to precipitate white to orange solid, which was washed throughly with anhydrous methanol and dried below 293 K under reduced pressure for spectroscopic measurements.

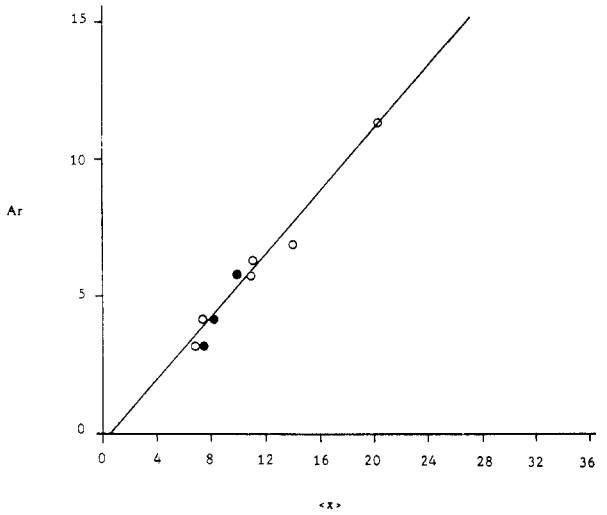

Figure 3. Relative absorbance plotted against $\langle x \rangle$: solid line, IR method, eq 12; unfilled circles, NMR method; filled circles, GPC method.

Measurements of the Rate of Polymerization. A portion of the solution methioned above was packed into a ^{1}H NMR (100 MHz) tube and the consumption of the functional group CHO proton at $\delta \simeq 10.0$ ppm was plotted against time (min). The equilibrium constant K was calculated according to eq 8

$$K = (C_0/\lim_{t\to\infty} C - 1)^2$$

and k^* from $K = k/k^*$.

Molecular Weight Determination. Number-average degree of polymerization $\langle x \rangle$ was calculated from the absorbance ratio of ν(CH=N) ($\sim$1620 cm^{-1}) and ν(CHO) ($\sim$1700 cm^{-1}) in the solid-state infrared spectrum. The polymer having the repeating unit O=(CHR'CH=NRN)$_x$=H$_2$ has one CHO and $(2n - 1)$ CH=N in a molecule. Thus relative absorbance A_r is given by

$$A_r = \frac{A(\text{CH=N})}{A(\text{CHO})} = (2\langle x \rangle - 1)\frac{\epsilon(\text{CH=N})}{\epsilon(\text{CHO})} \qquad (11)$$

where A(CH=N) and A(CHO) are the absorbances of ν(CH=N) and ν(CHO), respectively, and ϵ(CH=N) and ϵ(CHO) are the molar absorption coefficients of ν(CH=N) and ν(CHO), respectively. The mean value of ϵ(CHO)/ϵ(CH=N) was determined to be $\simeq$3.6, in the range $0 \le A_r \le 15$ from the study of the relative absorbance of ν(CHO) in terepthalaldehyde and ν(CH=N) in *p*-xylylidenedianiline. Hence, rearranging eq 11, we have

$$\langle x \rangle = \tfrac{1}{2}(3.6A_r + 1) \qquad (12)$$

Through spectral analysis A_r is easily calculated by using the equation $A = \log (T_0/T)$.

$\langle x \rangle$ was measured also by means of GPC (chloroform as an eluent, 293 K) and ^{1}H NMR and compared with that of the IR method. In the GPC method two kinds of molecular weight (M_n and M_w) were calculated according to the conventional technique. In the NMR method $\langle x \rangle$ in equilibrium was calculated according to eq 8. In Figure 3 and Table III are shown the results of three different measurements. They are in good agreement in the range of $\langle x \rangle \le 20$, although eq 12 gave smaller $\langle x \rangle$ compared to the GPC method in the region of higher molecular weight.

Appendix

According to Bradbury,[4c] the pseudo-first-order rate constant k_1 is 2.83×10^{-2} s$^{-1} \equiv 1.7$ min^{-1} in the interfacial polycondensation of terephthaloyl chloride–excess piperazine–hexane/water at 298 K.

If an equimolar amount of the monomers is used, the second-order rate constant k_2 will be necessarily $\ll$1.7 (mol/L)$^{-1}$ min^{-1}.

Here, we will consider a representative reaction.

$$A + B \rightarrow C$$

Table III
Molecular Weight of Polyimines

polymer	mol wt (M_n) IR	NMR	GPC
		$a = 0$	
1	2400	2294	
2	4500	4500	
3	2370	2208	2493 (M_w/M_n = 2.33)
4	5400	5620	4940 (M_w/M_n = 3.52)
5	3000	3617	3914 (M_w/M_n = 2.64)
6	2620	2998	
		$a \simeq 0.95$	
4	24400		48000
		$a \simeq 0.98$	
5	32200		58000

where A_0 and B_0 are the concentrations of A and B at $t = 0$ and A, B, and C are the concentrations of A, B, and C at t minutes. Then we obtain a general second-order equation

$$-dA/dt = k_2AB \qquad (A\text{-}1)$$

(1) If excess B_0 is used, $B_0 >> A_0$. From eq A-1

$$-dA/dt = k_2B_0A \simeq k_1A, \qquad k_1 = k_2B_0, \qquad k_1 \gg k_2$$

We have

$$1/A = (1/A_0)e^{k_1t} = (1/A_0)e^{k_2B_0t} \qquad (A\text{-}2)$$

(2) If an equimolar amount of monomers is used, $A_0 = B_0$. From eq A-1

$$-dA^*/dt = k_2A^{*2}$$

We have

$$1/A^* = (1/A_0)(A_0k_2t + 1) \qquad (A\text{-}3)$$

From eq A-2 and A-3

$$1/A - 1/A^* = (1/A_0)(e^{k_2B_0t} - A_0k_2t - 1) = (1/A_0) \times (1 + k_2B_0t/1! + (k_2B_0t)^2/2! + \ldots - A_0k_2t - 1) > 0$$

Accordingly, the following relationship is realized at any time t (min):

$$A^* > A$$

This means that the velocity of the second order equation can by no means exceed that of the first order equation.

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