Polycondensation kinetics of poly(phenylene ether sulphone)*

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The synthesis of poly(phenyl ether sulphone) (from the potassium salts of 4,4'-dihydroxydiphenyl sulphone and 4,4'-dichlorodiphenyl sulphone or 4-chloro-4'-hydroxydiphenyl sulphone) was found to have different reaction kinetics according to the route used. By discriminating between rate constants (between monomer/monomer, monomer/polymer, polymer/polymer) a set of multi-parameter kinetic equations is obtained. Experimental and simulated values of the individual rate constants were in good agreement (for both the reaction rate and molecular weight distribution). The polycondensation reaction can be analysed, in terms of the component reactions.

INTRODUCTION

It is well known that, in polycondensation kinetics, there are deviations from Flory's generalization of equal reactivity of functional groups[1], especially during the early stage of the reaction. Goel *et al.*[2] pointed out that the deviations are caused by the difference in reactivity between the monomer and the polymers. However, they only gave the theoretical derivation using two rate constants, and no experimental verification was presented.

In our study of the syntheses of poly(phenylene ether sulphone), we also noticed that the following two synthetic routes yield the same product but with different kinetics. Both of them achieve the same constant velocity
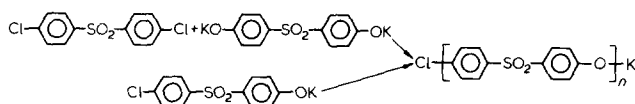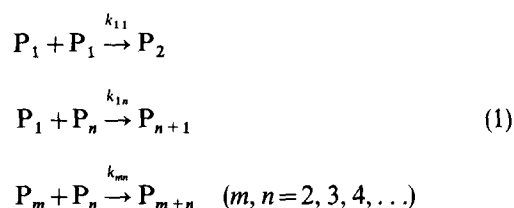

after a certain degree of polymerization is reached, while initially, route A reacts much faster than route B (a process which exhibits different reactivity between monomer and polymers).

THEORETICAL CONSIDERATIONS

For any polycondensation reaction with different reactivities between the monomer and polymers, the general scheme can be represented as follows[3], in which the rate constants between mers higher than dimers are assumed to be the same.

$$P_1 + P_1 \xrightarrow{k_{11}} P_2$$

$$P_1 + P_n \xrightarrow{k_{1n}} P_{n+1} \qquad (1)$$

$$P_m + P_n \xrightarrow{k_{mn}} P_{m+n} \quad (m, n = 2, 3, 4, \ldots)$$

that is, three parameters can be used to depict the whole course of the reactions. Thus,

$$\frac{d[P_1]}{dt} = -k_{11}[P]^2 - k_{1n}[P_1]\{[P] - [P_1]\}$$

$$\frac{d[P]}{dt} = -\tfrac{1}{2}k_{11}[P_1]^2 - k_{1n}[P_1]\{[P] - [P_1]\} \qquad (2)$$

$$\qquad -\tfrac{1}{2}k_{mn}\{[P] - [P_1]\}^2$$

with suitable substitutions, the following differential equations are obtained,

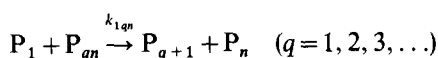$$\frac{dZ}{dX} = -R_1 Z^2 - R_2 Z(Y - Z) \qquad (3)$$

$$\frac{dY}{dX} = -\tfrac{1}{2}R_1 Z^2 - R_2 Z(Y - Z) - \tfrac{1}{2}(Y - Z)^2$$

where $[P] = \sum_{i=1}^{\infty} [P_i]$, $[P]_0$ is the initial concentration, and

$$X = [P]_0 k_{mn} t$$
$$Y = [P]/[P]_0$$
$$Z = [P_1]/[P]_0$$
$$R_1 = k_{11}/k_{mn}$$
$$R_2 = k_{1n}/k_{mn}$$

If the individual rate constant is known, this set of equations can be solved numerically (by the Runge–Kutta method using a computer). If the above mechanism is correct a plot of $1/Y$ versus X should correlate with the experimental values.

In case there are other factors which affect the reaction kinetics, this method of approach can accommodate more parameters. For example, in route B, we found that there is an interchange reaction between the monomer and the polymers, thus introducing a new parameter k_{1qn}.

$$P_1 + P_{qn} \xrightarrow{k_{1qn}} P_{q+1} + P_n \quad (q = 1, 2, 3, \ldots)$$

$$\frac{d[P_1]}{dt} = -k_{11}[P_1]^2 - k_{1n}[P_1]\{[P] - [P_1]\}$$
$$- k_{1qn}[P_1]\{[P]_0 - 2[P] + [P_1]\} \quad (4a)$$

$$\frac{d[P]}{dt} = -\tfrac{1}{2}k_{11}[P_1]^2 - k_{1n}[P_1]\{[P] - [P_1]\}$$
$$- \tfrac{1}{2}k_{mn}\{[P] - [P^1]\}^2 \quad (4b)$$

If $R_3 = k_{1qn}/k_{mn}$, we obtain

$$\frac{dZ}{dX} = -R_1 Z^2 - R_2 Z(Y - Z) - R_3 Z(1 - 2Y + Z)$$

$$\frac{dY}{dX} = -\tfrac{1}{2}R_1 Z^2 - R_2 Z(Y - Z) - \tfrac{1}{2}(Y - Z)^2$$

All these rate constants can either be evaluated in separate reactions, or through simulation of the rate curve in case they are unavailable experimentally.

In order to compare the kinetic results with the molecular weight distribution data, let $N = [P]/[P]_0$, $N_1 = [P_1]/[P]_0$, from equations (4a and 4b) we get

$$\frac{dN_1}{dN} = \frac{k_{11}N_1^2 + k_{1n}N_1(N - N_1) + k_{1qn}N_1(1 - 2N + N_1)}{\tfrac{1}{2}k_{11}N_1^2 + k_{1n}N(N - N_1) + \tfrac{1}{2}k_{mn}(N - N_1)^2} \quad (5)$$

the boundary condition is when $N = 1$, $N_1 = 1$. Thus we are able to calculate the N_1/N values at different degrees of polymerization.

EXPERIMENTAL

Syntheses of monomers, dimers and model compounds

The compounds related to the present investigation are shown in *Table 1*.

4,4'-Dihydroxydiphenyl sulphone (I) was supplied by the Suzhou Resin Works and after recrystallization from aqueous alcohol (1:4) its m.p. was 247°–248°C (cf. literature[4], values of 249°C).

4,4'-Dichlorodiphenyl sulphone (II) was supplied by the Shanghai No 9 Dye-Chemical works and after recrystallizing twice for aqueous alcohol (1:9) its m.p. was 148°–149°C (cf. literature[5], 147.8°–149.2°C).

4-Chloro-4'-hydroxydiphenyl sulphone (III) was made by hydrolysing (II) with alkali, and recrystallizing from methanol and toluene. The m.p. of (III) was 148.5°–149°C (cf. literature[6], 150°C).

Table 1 Monomers, dimers and model compounds.

(I) HO—⟨O⟩—SO₂—⟨O⟩—OH

(II) Cl—⟨O⟩—SO₂—⟨O⟩—Cl

(III) Cl—⟨O⟩—SO₂—⟨O⟩—OH

(IV) Cl—⟨O⟩—SO₂—⟨O⟩—O—⟨O⟩

(V) Cl—⟨O⟩—SO₂—⟨O⟩—O—⟨O⟩—SO₂—⟨O⟩—OH

(VI) Cl—⟨O⟩—SO₂—⟨O⟩—O—⟨O⟩—SO₂—⟨O⟩

(VII) HO—⟨O⟩—SO₂—⟨O⟩—O—⟨O⟩—SO₂—⟨O⟩

4-(p-Chlorobenzenesulphonyl)diphenyl ether (IV) was prepared by heating a mixture of diphenyl ether (340 g), *p*-chlorobenzenesulphonyl chloride (422 g) and anhydrous ferric chloride (5 g) at 110°–120°C for 2 h. The reaction was fractionated and the distillate collected at 256°–280°C (0.5 mm Hg). Colourless crystals (200 g) with m.p. 95°–98°C were produced after recrystallizing twice from alcohol. The crude product was dissolved in benzene (550 ml), add petroleum ether (b.p. 60°–90°C) and needle-like crystals (m.p. 105°–107°C) recrystallized. The empirical formula of the crystals was $C_{18}H_{13}O_3ClS$: Calculated; C, 62.70%; H, 3.80%; Cl, 10.28%: Found; C, 62.75%; H, 3.82%; Cl, 10.29%.

4-(p-chlorobenzenesulphonyl)-4'-(p-hydroxybenzene sulphonyl)diphenyl ether (V) was prepared by heating a mixture of (IV) (34.5 g), phenyl carbonate-4,4'-disulphonyl chloride (20.6 g), nitrobenzene (50 ml) and anhydrous ferric chloride (0.2 g) at 110°C for 11–12 h. (87% of the theoretical volume of hydrogen chloride gas was evolved). Then cold methanol (200 ml) was added, and the resulting suspension was stirred, and then decanted. A further 200 ml of methanol were added, stirred and filtered. The filter cake was stirred in methanol (400 ml) and 50% potassium hydroxide (56 g) was added to hydrolyse the carbonate. The temperature was kept below 20°C, so that a clear solution resulted. Ice was added, and the gelatinous iron hydroxide was removed by filtration. The filtrate was diluted with ice (1:1), neutralized with 7 N hydrochloric acid to pH = 4. The suspension was stirred for a further half an hour, and filtered. The product was recrystallized in glacial acetic acid (yield 19 g), m.p. 243°–245°C. The empirical formula of the product was $C_{24}H_{17}O_6S_2Cl$: Calculated; C, 57.54%; H, 3.42%; Cl, 7.08%. Found: C, 57.28%; H, 3.65%; Cl, 7.19%.

The product was insoluble in glacial acetic acid. Further recrystallization was carried out by dissolving the product in dimethyl sulphoxide (DMSO), precipitation with ice water, and then recrystallization in glacial acetic acid.

4-(p-Chlorobenzenesulphonyl)-4'-(benzenesulphonyl)-diphenyl ether (VI) was prepared by heating a mixture of

nitrobenzene (40 ml), benzenesulphonyl chloride (38.8 g) and **(IV)** (69 g) at 110°C, followed by the addition of anhydrous ferric chloride (0.1 g). The reaction mixture was kept at 120°C for 9 h. (The hydrogen chloride gas evolved was close to 100%). Methanol (400 ml) and acetyl acetone (2 ml) were then added. The slurry was stirred and cooled to 10°C; and then filtered. The filter cake was washed 3 times with methanol, and dried. (Yield, 70 g, m.p. 152°–170°C).

70 g of the crude product were refluxed with ethanol (260 ml) and filtered. The filter cake was recrystallized twice in n-butyl alcohol, 31.3 g of the pure product were obtained, m.p. 187°–188°C. The empirical formula of the product was $C_{24}H_{17}O_5S_2Cl$: Calculated; C, 59.44%; H, 3.53%; Cl, 7.31%. Found: C, 59.30; H, 3.48; Cl, 7.51%.

4-(p-Hydroxybenzenesulphonyl)-4'-benzenesulphonyl)-diphenyl ether **(VII)**. A mixture of nitrobenzene (120 ml), 4,4'-di(chlorosulphonylphenyl) carbonate (61.8 g) and 4-(benzene sulphonyl)diphenyl ether (93 g) was heated under nitrogen atmosphere. Anhydrous ferric chloride (0.6 g) was added. The hydrogen chloride gas evolved after 2 h was 91.5% of the theoretical value. Then cold, methanol (500 ml) was added with stirring. The mixture was filtered, and the filter cake washed with methanol, and dried at 40°C. (Yield, 100 g).

The crude product was recrystallized with 400 ml glacial acetic acid, m.p. 174°–175°C (cf. literature[7], 165–167°C). The empirical formula was $C_{24}H_{18}O_6S_2$: Calculated: C, 61.79%; H, 3.89%; S, 13.75%. Found: C, 61.56%; H, 3.88%; S, 13.58%.

Potassium salt formation

The phenols used in these experiments were in the form of potassium salts. They were made by dissolving the corresponding phenols in methanol, and titrating potentiometrically with 4 N potassium hydroxide. The salts obtained on evaporation were dried under vacuum.

Kinetic study

A 250 ml flask was fitted with stirrer, condenser, thermometer and nitrogen inlet tube. The temperature was kept to within ±1°C using an oil bath. The monomers, dimers and DMSO (weighed accurately), were introduced into the flask. The temperature was raised quickly to the desired value. Samples for analysis (about 1.5 g) were taken out at intervals, and put into titration flasks containing 20 ml water. With methyl orange as indicator, the solution was titrated with 0.1 N hydrochloric acid. By plotting $1/(1-p)$ against t, the rate constant k was evaluated from the initial slope of the curve.

Gel permeation chromatography

The apparatus used was a Shimadzo LC-3A, with zorbax-PSM$_{60s}$ as the packing material; column dimension, 6.3 mm × 25 cm; detector, UVD-2, $\lambda = 254$ nm.

Since the solubility of the K-salts is limited in $CHCl_3$, the reaction products were treated with HCl to liberate the free phenols, and then the precipitate was dissolved in $CHCl_3$ and worked as usual.

RESULTS AND DISCUSSION

The values of rate constants for route A and route B obtained experimentally are listed in *Table 2*, all the

constants are in the units 10^{-5} l mol^{-1} s^{-1}. It is known that the polycondensation reaction is a second order nucleophilic substitution reaction, in which the nucleophilic phenolate ion displaces the chlorine atom. Because the sulphonyl group can transfer the electronic effect, the two substituents on the monomer are able to affect each other. In the case of dimers and higher mers, the presence of ether linkages will block the passage of the electronic effect so that the two functional groups on each end are essentially separated[8]. Thus, the functional group reactivity in dimers (and higher mers) can be considered as constant; as confirmed by Flory's polycondensation kinetics. It is quite clear that k_{22}, which is the reaction constant between two model dimers, is close to that of overall reaction constant, k_{mn}. As a result, both the phenolate ion and the chlorine atom in monomer **(I)** and **(II)** are strengthened by each other. For route A the rate constant k_{11} is 16.4 (at 120°C), while in route B, the phenolate ion and chlorine atom in monomer **(III)** weaken each other, the rate constant k_{11} is only 0.011 (1500 times smaller than for route A). Hence the reaction rate of route A is too fast at the beginning, while in route B, the reaction starts from a lower rate and gradually rises to a constant reaction rate, $k_{mn} = 1.36$.

Route A (at 120°C), consists of two reactions running simultaneously, namely, reactions between **(I)** and **(VI)**, **(VII)** and **(II)** (rate constants are $k_{12} = 17.6$ and $k_{21} = 0.90$ respectively). This enables k_{1n} to be calculated, since the two reactions are consecutive reactions, k_{1n} should be close to 0.90. Thus, we get $R_1 = 16.4/1.36 = 12$, $R_2 = 0.90/1.36 = 0.66$. By substituting these values into equation (2) and evaluating the numerical solution, we obtain the curve shown in *Figure 1* in which the theoretical curve is quite close to the experimental results.

In order to evaluate the rate constant k_{1n} for route B at 165°C, we have to consider the coupled reactions, **(III)** + **(VI)** and **(VII)** + **(III)**. In the actual polycondensation process, the two reactions run simultaneously, so the k_{1n} should be the sum of k_{12} and k_{21}, which is 36.6.

In substituting these values into equation (3) and calculating the numerical solution, the result obtained is different from the experimental value. This disparity must be due to unknown factors, which had not been included in the calculations.

First, in deriving equations (2) and (4), no discrimination is made between route A and route B; in the former, two different monomers react with each other, while in the latter, only one monomer is present. Hence

Table 2 Rate constant k in DMSO

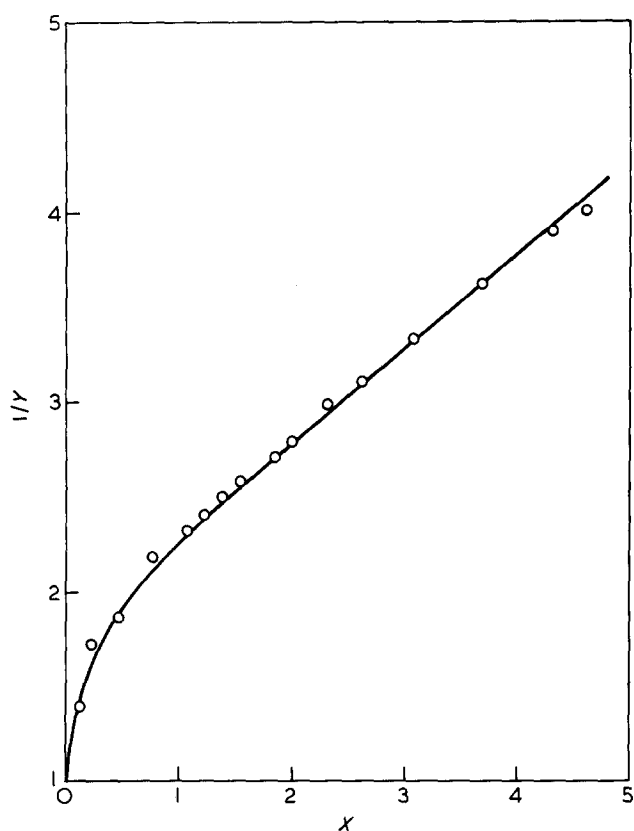|	Reaction	k	Temperature (°C)			
			120	145	165	178
Route A	(I) + (II)	k_{11}	16.4	—	—	—
	(I) + (VI)	k_{12}	17.6	—	—	—
	(VII) + (II)	k_{21}	0.90	—	—	—
	(VI) + (VII)	k_{22}	1.32	—	—	—
		k_{mn}	1.36	8.2	38	88
Route B	(III) + (III)	k_{11}	0.011	0.10	0.51	1.20
	(III) + (VI)	k_{12}	—	—	36.1	—
	(VII) + (III)	k_{21}	—	—	0.51	—
	(VI) + (VII)	k_{22}	1.32	—	—	—
		k_{mn}	1.36	8.2	38	88

Figure 1 $1/Y$ *versus* X for route A at 120°C in DMSO: curve: theoretical; ○: experimental
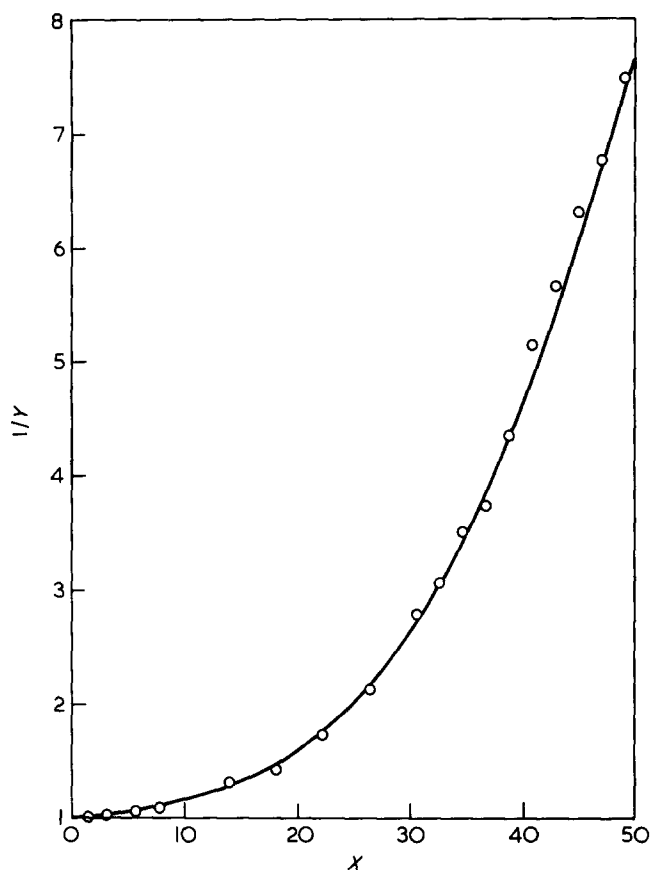
Figure 2 $1/Y$ *versus* X for route B at 165°C in DMSO: curve: theoretical; ○: experimental

Table 3 Comparison of N_1/N values

$\bar{x}_n$	N_1/N (%)	
	Theoretical	Experimental
1.14	96.9	97.6
1.76	79.8	79.5
1.92	76.3	75.3
2.19	73.3	71.4

the concentration of monomer in rate equations in route B, and also polymers, is twice that in route A, thus a factor of 4 should be taken into consideration.

Second, in route B, the monomer might possibly attack the polymers formed, leading to ether exchange. In route B, the initial reaction is very slow, with a lot of monomers present; while in route A, the initial reaction is very quick and not many monomers are left soon after the reaction is started. (It is unnecessary to bother with this side reaction).

The absence of a polycondensation equilibrium is proved by starting with dimer (V) as the raw material; so that no monomer could be detected in the reaction mixture by g.p.c.

From these considerations, we have $R_1 = 0.51 \times 4/38 \times 4 = 0.013$, $R_2 = 36.6/38 \times 4 = 0.24$, for R_3, which is the exchange constant and is unable to be worked out by experiment, we get the value $R_3 = 0.11$ by simulating from the polycondensation curve (*Figure 2*), from which k_{1qn} will be 16.8. This clearly shows that the rate constant of either exchange is much larger than k_{11} at the beginning of polycondensation reaction and hence it cannot be ignored. In order to confirm this kind of reaction kinetics, a molecular weight distribution experiment was carried out. The results are listed in *Table 3*, in which the experimental values of N_1/N, the mole ratio of monomer to total mers, are compared with the theoretical values calculated from equation (5), using the same sets of rate constant and the values coincide rather well. The $\bar{x}_n$ values were determined by end-group titration.

CONCLUSIONS

The following results are obtained in this investigation:

(1) A set of four-parameter differential equations for the polycondensation reaction are derived and proved experimentally. These equations can be expanded further to accommodate more parameters if necessary.

(2) Hence, the mechanism of the polycondensation reaction can be studied (including the component reactions), and their rate constants can be evaluated through curve simulation (in case they cannot be obtained experimentally).

(3) The different behaviour of routes A and B in the manufacture of poly(phenylene ether sulphone) is explained. This could result in better control of the production process.

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