Polymerisation and Related Reactions involving Nucleophilic Aromatic Substitution. Part 3.[1] Mathematical Models of the Polycondensation Reactions of Halogenobenzophenones

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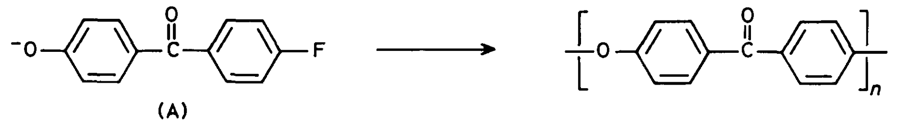
Linear free energy relations have been used to calculate rate coefficients for the stages in the polycondensation reaction of the potassium salt of 4-fluoro-4'-hydroxybenzophenone and for the polycondensation reactions of 4,4'-difluorobenzophenone with the dipotassium salt of 4,4'-dihydroxybenzophenone and the dipotassium salt of hydroquinone. These rate coefficients have been used in a kinetic model of the polycondensations to calculate how the concentrations of the individual molecular species formed vary with time. The kinetic model is used to show that the molecular composition of the solutions, when considered as a function of the percentage reaction, should be relatively insensitive to the initial monomer concentration and to medium effects provided that all of the species concerned are fully soluble.

The linear free energy relationships developed in Parts 1 and 2 are here applied to the three polycondensation reactions shown in equations (1)—(3); the first two of these reactions lead to the same polymer. In defining the reaction stages, the initial phenolic reactant is represented by (A), the initial halogeno compound by (B), and the initial product by (AB). Where only one reacting species is involved [equation (1)], it is represented by (A).

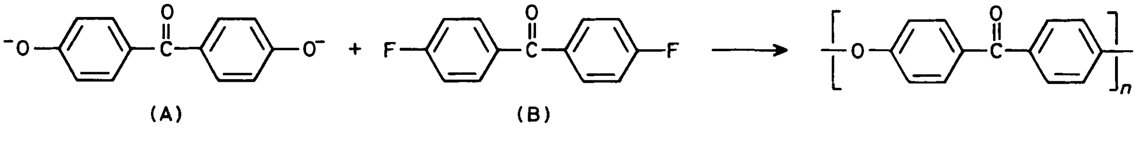
Calculation of Rate Coefficients.—The rate coefficients for the reaction stages in equations (1) and (2) were calculated from the linear free energy relationship given in equation (7) of Part 1 assuming a concentration of phenolate ions of 10^{-2} mol kg^{-1}. Thus, the calculation for the first stage of equation (1) has $X = O^-$ and $Y = F$. However, such calculations give the rate coefficient for a single pair of reacting centres and, in calculating the molecular rate coefficients during polymerisation, it is necessary also to consider the number of independent but equivalent ways in which a given reaction between two molecules can occur. Thus, a reaction between two dimers can occur at either of the C-F centres and, for a reaction involving a dimer with another dimer or higher polymer, such paths have been considered as equivalent. The resulting statistical factors are listed for each reaction stage in Table 1 and are included in the rate coefficients given in this Table.

This equivalence does not hold for the two reaction paths by which the monomer A [equation (1)] can react with the dimer, for the corresponding rate coefficients can be calculated to be 2×10^{-3} kg mol^{-1} s^{-1} for reaction at the C-F group of the monomer and 3.4×10^{-2} kg mol^{-1} s^{-1} for reaction at the C-F group of the dimer; the difference arises from the deactivating effect of the O^- group in the monomer on nucleophilic substitution in the adjacent ring. The quoted rate coefficient (Table 1) is the sum of these values. No information appears to be available on the σ values of substituted phenoxy groups[2] and so, in this and other calculations, these σ_p values have been put equal to those for the phenoxy group (−0.09).

The calculated rate coefficients for the reaction stages in equation (3) are based on the slopes of the linear free energy plots in Figures 1 and 2 of Part 2 and again refer to concentrations of phenolate ions of *ca.* 10^{-2} mol kg^{-1}. In these calculations, the σ_p value of C_6H_5CO (0.46)[2] has been taken as an approximation to that for p-FC_6H_4CO.



(1)



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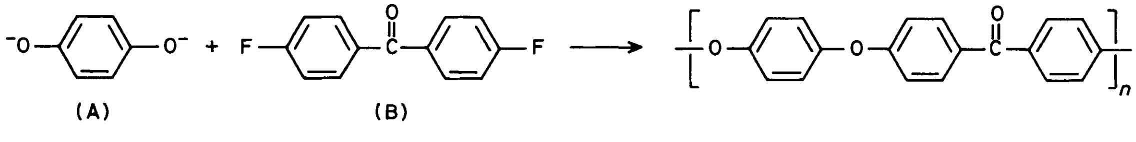

(3)

Table 1. Rate coefficients for the polycondensation reactions in equations (1)—(3)

Equation	Temp (°C)	Stage[a]	Statistical factor	$\frac{k_2}{\text{kg mol}^{-1}\,\text{s}^{-1}}$
(1)	200	$(A) + (A)$	2	3.3×10^{-3}
(1)	200	$(A) + (A)_n$	1[b]	3.6×10^{-2}
(1)	200	$(A)_n + (A)_m$	2	8.3×10^{-2}
(2)	200	$(A) + (B)$	4	0.97
(2)	200	$(A) + (AB)_n$	2	0.32
(2)	200	$(A) + B(AB)_n$	4	0.64
(2)	200	$(B) + (AB)_n$	2	0.13
(2)	200	$(B) + (AB)_nA$	4	0.25
(2)	200	$(AB)_n + (AB)_m$	2	8.3×10^{-2}
(2)	200	$(AB)_n + B(AB)_m$	2	8.3×10^{-2}
(2)	200	$(AB)_n + (AB)_mA$	2	8.3×10^{-2}
(2)	200	$(AB)_nA + B(AB)_m$	4	0.17
(3)	140	$(A) + (B)$	4	740
(3)	140	$(A) + (AB)_n$	2	260
(3)	140	$(A) + B(AB)_n$	4	520
(3)	140	$(B) + (AB)_n$	2	0.60
(3)	140	$(B) + (AB)_nA$	4	1.2
(3)	140	$(AB)_n + (AB)_m$	2	0.42
(3)	140	$(AB)_n + B(AB)_m$	2	0.42
(3)	140	$(AB)_n + (AB)_mA$	2	0.42
(3)	140	$B(AB)_n + (AB)_mA$	4	0.84

[a] For equation (1), $n, m \geqslant 2$; for equations (2) and (3), $n, m \geqslant 1$. [b] This reaction has two non-equivalent reaction paths: see text.

Table 2. Reaction classes (see text) involved in the formation and destruction of each type of polymer molecule

Molecular type	Class of reaction	
	Formation	Destruction
$(AB)_n$	0, 1	1, 2, 3
$(AB)_nA$	2	0, 2
$B(AB)_n$	3	0, 3

Model of Polycondensation.—The early treatments of polymerisation kinetics assumed that the rate coefficients of the individual stages were independent of the degree of polymerisation of the reacting species.[3] This approach has been recognised to be inadequate for the type of polycondensation reaction considered here and more complex models have been put forward which assign a different rate coefficient for the reaction of the monomer[4] or different rate coefficients for the monomer–monomer, monomer–polymer, and polymer–polymer reactions.[5] Another very recent model also takes account of changes in the viscosity of the medium.[6] These models do not, however, consider explicitly the concentrations and reactivities of the different molecular species which collectively make up the polymer.

The model now proposed does distinguish between the different components of the polymer. The calculation is carried out using a computer program written by two of us (D. B. H. and J. P. B. S.) and the method will be illustrated with reference to the reaction of a monomer (A) with a different monomer (B) as exemplified in equations (2) and (3). In this approach, the reacting species are divided into three types depending on the functional groups present:

$$\begin{array}{ll} \text{Type 1: } (AB)_n & n \geqslant 1 \\ \left.\begin{array}{l}\text{Type 2: } (AB)_nA \\ \text{Type 3: } B(AB)_n\end{array}\right\} & n \geqslant 0 \end{array}$$

The possible reactions between these species are divided into four classes:

Class 0: $(AB)_nA + B(AB)_m$
Class 1: $(AB)_n + (AB)_m$
Class 2: $(AB)_n + (AB)_mA$
Class 3: $(AB)_n + B(AB)_m$

The rate of each reaction is determined by a second-order rate coefficient k_{lmn} where the subscript l specifies the class of the reaction and the subscripts m and n specify the chain lengths of the reactants. The values of k_{lmn} for m 0, 1 and n 0, 1 are determined by linear free energy relationships as shown in Table 1, and the values for $m > 1$ and $n > 1$ are set equal to those for n 1 and m 1.

The calculation of the concentration of each molecular species is then carried out by dividing the time of reaction into a number (*N*cycle) of short intervals. Within each interval, the change in the concentration of each species is calculated by considering all the reactions that can lead to the formation of that species and all the reactions that can lead to the destruction of that species. The classes of reaction that can lead to the formation and destruction of each class of polymer molecule are summarised in Table 2 and an example of the terms leading to the formation and destruction of a particular molecular species $(AB)_p$ is given in equation (4).

$$\begin{aligned} d[(AB)_p]/dt = {} & \sum_{m,n} k_{0mn}[(AB)_mA][B(AB)_n] \\ & + \sum_{m,n} k_{1mn}[(AB)_m][(AB)_n] \\ & - \sum_{n} k_{1pn}[(AB)_p][(AB)_n] \\ & - \sum_{n} k_{2pn}[(AB)_p][(AB)_nA] \\ & - \sum_{n} k_{3pn}[(AB)_p][B(AB)_n] \end{aligned} \tag{4}$$

In equation (4), the first two terms correspond to the formation of the molecule $(AB)_p$ and so the values of m and n are restricted by $m + n + 1 = p$ (for the first term) and $m + n = p$ (for the second term). The maximum value of m is $p - 1$ for the first term but is taken as $\text{Int}(p/2)$ for the second

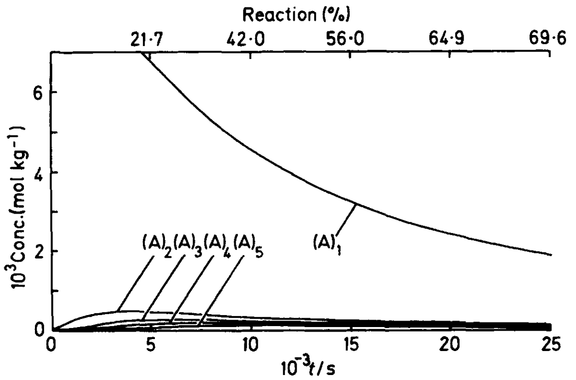

Figure 1. Calculated product composition during the polymerisation according to equation (1) at 200 °C. Initial concentration of monomer 0.01 mol kg^{-1}

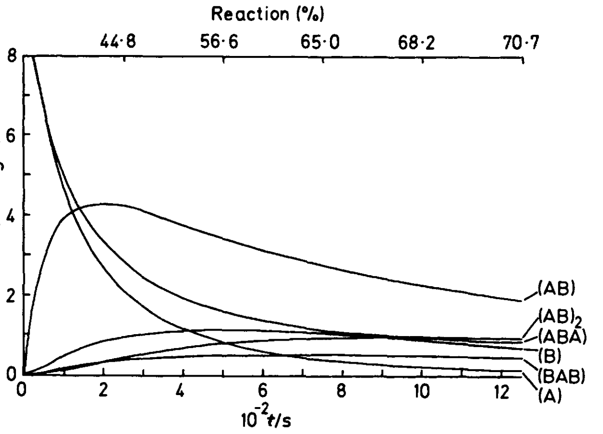

Figure 2. Calculated product composition during the polymerisation according to equation (2) at 200 °C. Initial concentration of both monomers 0.01 mol kg^{-1}

Table 3. The calculated concentrations of each molecular species for the reaction shown in Figure 2 at *t* 1 250 s

	Class		
n	$(AB)_n$	$(AB)_nA$	$B(AB)_n$
0		1.15×10^{-4}	6.72×10^{-4}
1	1.88×10^{-3}	8.33×10^{-4}	4.64×10^{-4}
2	9.27×10^{-4}	2.94×10^{-4}	1.77×10^{-4}
3	2.75×10^{-4}	1.09×10^{-4}	6.27×10^{-5}
4	1.22×10^{-4}	3.92×10^{-5}	2.33×10^{-5}
5	3.68×10^{-5}	1.44×10^{-5}	8.35×10^{-6}
6	1.45×10^{-5}	5.17×10^{-6}	3.03×10^{-6}
7	4.80×10^{-6}	1.86×10^{-6}	1.09×10^{-6}
8	1.90×10^{-6}	6.73×10^{-7}	3.94×10^{-7}
9	6.24×10^{-7}	2.43×10^{-7}	1.41×10^{-7}
10	2.37×10^{-7}	8.74×10^{-8}	5.10×10^{-8}
11	8.09×10^{-8}	3.15×10^{-8}	1.85×10^{-8}
12	3.06×10^{-8}	1.13×10^{-8}	6.60×10^{-9}
13	1.05×10^{-8}	4.08×10^{-9}	2.37×10^{-9}
14	3.91×10^{-9}	1.47×10^{-9}	8.54×10^{-10}
15	1.36×10^{-9}	5.28×10^{-10}	3.07×10^{-10}

term to prevent the reaction between each pair of species being considered twice. The last three terms correspond to reactions that decrease the concentration of $(AB)_p$ and so here the maximum value of n is limited only by the maximum permitted in the calculation. A statistical factor of two has to be included in the middle term of the equation when $n = p$ since one unit of reaction then removes two molecules of $(AB)_p$ from the solution.

Expressions analogous to that in equation (4) are evaluated for each molecular species for each time interval and the corresponding change in the concentration of that species is calculated by the modified Euler method.[7] In this way, each molecular species created in one step is included among the reactants in the next step. To avoid excessive demand on computer time, it is of course necessary to set a limit on the maximum degree of polymerisation that can be considered and in the following calculations the maximum value of n (Nmax) was set at 25 or 40. For the calculation to be valid, the value of Nmax must be sufficiently high for the concentrations of the species with $n = N$max to be negligible in comparison with the concentrations of the other species considered. This condition is met in the calculations reported below.

The calculations also assume, of course, that all the species concerned are fully soluble. Unfortunately, the dipotassium salts of the dianions in equations (2) and (3) are very poorly soluble in diphenyl sulphone; some calculations refer therefore to ideal rather than actual conditions. The general conclusions from the calculations serve, however, as a guide to what may be expected when the solubility condition is satisfied.

Results

Reaction (1) is the simplest of the reactions to be considered since, in this, all of the terms for the formation of a molecule $(A)_p$ are of the class $[(A)_m + (A)_n]$ where $m + n = p$ and all of the terms for the destruction of a molecule $(A)_p$ are of the class $[(A)_p + (A)_n]$ where $(A)_n \leqslant N$max. The variation of the composition of the system at different times and different percentages of reaction is shown in Figure 1. The calculation of the percentage reaction is based on the amount of potassium fluoride that should be formed.

The characteristics of this reaction are determined by the fact that the first stage of the reaction is very much slower than all later stages. Hence, as soon as the dimer is formed, the other polymeric species are formed rapidly from it. For the extents of reaction shown in Figure 1, a polymer molecule $(A)_m$ is formed mainly by the reaction of the molecule $(A)_{m-1}$ with the monomer (A), and the destruction of the molecule $(A)_m$ also occurs mainly by reaction with the monomer: this explains why the concentrations of the different polymer species rapidly become very similar (Figure 1). For clarity, only the species up to $(A)_5$ are shown in Figure 1.

Reaction (2) is more complex because, although the rate coefficient for reaction between monomers is considerably greater than that for reaction between dimers and higher polymers, the reaction does not proceed merely by an initial dimerisation to form (AB) followed by the polymerisation of this species. Instead, as shown in Figure 2, the concentrations of (A) and (B) in the solution become unequal when a significant amount of (AB) has been formed because of the relatively fast rate of reaction of (A) with (AB). In consequence, at *ca.* 70% reaction, the concentrations of the symmetrical species (B) and (ABA) (with two identical end-groups) are similar to that of the species $(AB)_2$ (Figure 2) and greater than those of the higher polymers.

The low concentrations of the higher polymers are not shown in Figure 2 but the set of concentrations up to n 15 at t 1 250 s is shown in Table 3. The calculated concentration of the species $(AB)_{25}$ is 4.9×10^{-14} mol kg^{-1}; this shows that the value of Nmax is sufficiently high to include all species present in significant concentration. A comparison of Figures 1 and 2 shows that,

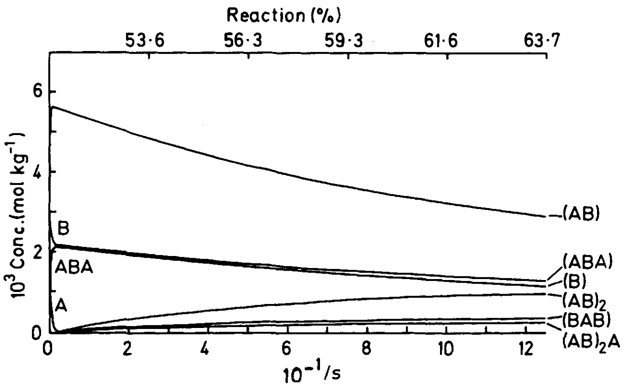

Figure 3. Calculated product composition during the polymerisation according to equation (3) at 140 °C. Initial concentration of both monomers 0.01 mol kg^{-1}

although these reactions form the same polymer, the distribution of the polymeric species during reaction is very different.

Reaction (3) is an example of a polymerisation involving two different monomers in which one of them (A) reacts very rapidly both with the other monomer and with many of the other molecular species formed. The results in Figure 3 show that the concentration of (A) drops effectively to zero over the first few seconds; the solution then contains mainly the dimer (AB) but also approximately equal concentrations of (B) and (ABA). The concentrations of these symmetrical species still exceed that of the species $(AB)_2$ at 63% reaction.

The plots of product composition against time are of limited value for the results depend very much on the reaction conditions but the relationship between the product composition and the percentage reaction (Figures 1—3) should be of more general significance. One reason for this is that the product composition at a given percentage reaction depends only on the ratios of the rate coefficients; it follows therefore that the results should be insensitive to the consequences of ion association and solvent effects provided that these effects modify the different rate coefficients by the same factor. Since all the reactions considered involve the same type of nucleophilic aromatic substitution, this is a reasonable first approximation. Another reason stems from the fact that all the reactions considered in the formation and destruction of a given species are of the same order (second); this implies that the calculated product composition at a given percentage reaction is independent of the initial concentration. It is likely therefore that the results above concerning, for example, the balance between the symmetrical species (A), (B), (ABA), (BAB), *etc.* and the unsymmetrical species (AB), $(AB)_2$, *etc.* at a given percentage reaction are applicable over a wide range of conditions provided, of course, that all the compounds considered are soluble.

The computer program used in this investigation can, in principle, be extended to include ether interchange reactions (where attack occurs at an ether link in a polymer chain) and co-polymerisation. One potential problem lies in the computer time involved; a typical calculation involving 12 500 reaction steps and the inclusion of species up to $(AB)_{25}$ took 200 s on a Cray-1S computer.

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