Kinetics of polysulphone synthesis: nuclear magnetic resonance spectroscopy and rheological investigation

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Time-dependent changes in monomers, dimers, end reactive groups and central links occurring in the synthesis of polysulphone derived from dichlorodiphenylsulphone and the sodium salt of diphenylolpropane in dilute solution in dimethylsulphoxide were investigated by nuclear magnetic resonance spectroscopy. On this basis, a kinetic model of the reaction was designed and elementary reaction constants, which appeared to be dependent on the chain length, were determined. Simultaneously, the time-dependent change in the viscosity of the reaction medium in concentrated solutions was measured and the results obtained were analysed by the rheokinetic method. A correlation was found to exist between the rheokinetic constants and the rate constants in sufficiently high-molecular-weight products determined by nuclear magnetic resonance spectroscopy.

(Keywords: polysulphone; nuclear magnetic resonance spectroscopy; kinetics; rheokinetics; polycondensation; viscosity)

INTRODUCTION

The kinetics of polycondensation reactions is one of the most fascinating problems in polymer chemistry. At the present time the crucial problem is to establish a correlation between the kinetics of the polymer synthesis process and the rate of the elementary reactions between the monomer and oligomer fractions. Although low-molecular-weight substances participate in the reaction when the degrees of polymerization are small, we cannot accept without question Flory's hypothesis concerning the independence of reactivity on the chain length during the major part of the reaction.

The present paper is devoted to the study of this problem as exemplified by the synthesis of polyarylenesulphoxide (PAS) derived from dichlorodiphenylsulphone and the sodium salt of diphenylolpropane.

The specific feature of this work is the parallel application of two principally different and independent methods for studying polycondensation kinetics. On the one hand, a quantitative analysis is made of the rate of formation of various products using n.m.r. spectroscopy of the reaction mixture during the initial stages of polymer synthesis in comparatively dilute solutions. This allows a study of the separate elementary reactions. On the other hand, the rheokinetic method allows estimation of the 'macrokinetics' of the synthetic process based on changes in the viscosity of the reaction medium. The first method is principally of chemical importance, whereas the second method is concerned with technological problems and relates to the quantitative characteristics of the process on the whole. The significance of the present work is the establishment of a relationship between the kinetic constants derived by different methods. Such an approach allows one to understand the physical meaning of the rheokinetic constants and to associate n.m.r. spectroscopy data with the macrokinetic parameters of polymerization.

EXPERIMENTAL

Polyarylenesulphoxide (PAS) was prepared by mixing equimolar solutions of dichlorodiphenylsulphone (D) and the sodium salt of diphenylolpropane (P) in dimethylsulphoxide (DMSO). The reaction was carried out in a 6% solution at 120°C for n.m.r. spectroscopy examination. The rheological investigations were carried out in a 50–80% solution in the temperature range 150–180°C; in view of considerations to be discussed later, 50 and 60% solutions will be regarded as moderate and 70 and 80% solutions as highly concentrated.

NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

Samples were taken every 1–2 min and later every 15–20 min to study the initial stages of the process, and were added to an HCl solution in DMSO in order to stop the reaction. As a result, phenols were formed from the sodium salts. The reaction mass was then extracted with chloroform to remove NaCl and precipitated from chloroform solution with Li–PrOH.

^{13}C n.m.r. Fourier spectra (22.63 MHz) of the reaction mixtures were recorded on a Bruker WH-80 spectrometer. Methylene chloride-d_2 was the solvent and hexamethyldisiloxane was used as internal reference. The signals were assigned from data[1].

After HCl treatment, the reaction mixture contained monomer compounds and condensation products.

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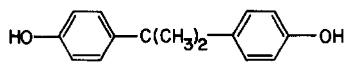
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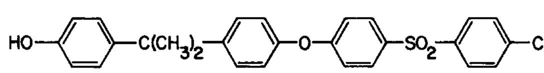
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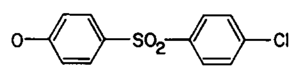
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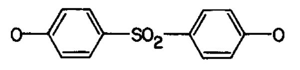
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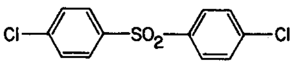
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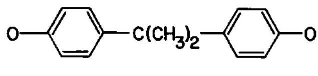
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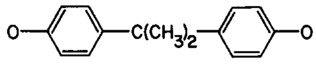

(P_{mid})

^{13}C n.m.r. spectra revealed the relative concentrations of the monomers D (y_1) and P (y_5), ends D_{end} (y_2) and P_{end} (y_6) and middle links D_{mid} (y_3) and P_{mid} (y_7) as well as 'dimer' (y_4).

The concentrations y_1 to y_7 were determined for various reaction states, i.e. n.m.r. spectroscopic data gave the kinetic dependences $y_1(t)$ to $y_7(t)$.

RHEOLOGICAL METHOD

The viscosity of the model solutions of PAS in DMSO and of the reaction medium was measured with a Rheotest-2 (GDR) rotational viscometer of the cylinder-to-cylinder type and with an original home-made viscometer[2] of the cone-to-plate type. To obtain rheokinetic data on PAS synthesis, the reaction was carried out directly in the Rheotest-2 viscometer. The process was controlled by the change in the viscosity $[\eta]$ of the reactive medium during continuous flow at a constant shear rate (9 s^{-1}). Viscosity errors when plotting the rheokinetic curves did not exceed 15%. Independent measurements in the region of moderately-concentrated solutions were also made under different shear rate conditions. This allowed us to prove the independence of the rheokinetic curves on the shear rate. However, situations may occur when the latter conclusion may appear to be imprecise. In order to correlate the rheokinetic data with the molecular characteristics of the polymer, a selection of samples were taken from the reaction system of separate experiments for molecular weight determination.

The intrinsic viscosity $[\eta]$ of the PAS solution in chloroform was determined with a Ubbelohde viscometer at 25°C. The average molecular weight was determined from the value $[\eta]$ according to[3]:

$$[\eta] = 2.4 \times 10^{-4} M^{0.72}$$

To simulate the polymer preparation conditions, the viscous properties of the PAS and DMSO solutions were studied when 20 wt% NaCl was added, since such an amount of sodium chloride precipitates as a result of polycondensation. The experimental solutions in the shear rate range under study (10^{-1} to 10^{+2} s^{-1}) display a weak non-Newtonian flow. Therefore a comparison of PAS samples of different molecular weights was made on the basis of the apparent viscosity at a constant shear stress τ (or a constant low shear rate corresponding to the Newtonian flow region, $\dot{\gamma}$ = constant). Such experimental dependences at a shear stress of 50 Pa for temperatures ranging from 150 to 180°C are given in *Figure 1*. The data obtained may be described in the conventional form for polymer solutions and melts[4]:

$$\eta(\bar{M}) = \begin{cases} K_1 \bar{M}^{a_1} & \bar{M} < \bar{M}_c \\ K_2 \bar{M}^{a_2} & \bar{M} \geq \bar{M}_c \end{cases}$$

where K_1, K_2 and a_1, a_2 are constants typical of each homologous polymer series, and M_c is the critical molecular weight value at which the character of the $\eta(\bar{M})$ dependence varies. This value equals 1.3×10^4 for the experimental polymer.

The constants a_1 and a_2 determined from the experimental data at τ = constant are $a_1 = 2.0$ and $a_2 = 3.7$, but if the viscosity dependence is considered at a constant shear rate ($\dot{\gamma} = 9\ s^{-1}$), then $a_1 = 1.7$, $a_2 = 3.4$.

The effect of temperature on the viscosity of a 50% PAS solution in DMSO is described by the Arrhenius equation with an activation energy of 32 kJ mol^{-1}. In the molecular weight range under study, the apparent activation energy for a viscous flow does not depend on the polymer molecular weight.

KINETIC MODEL FOR INITIAL STAGES OF THE REACTION

The construction of the kinetic model gives rise to a special discussion of two problems: the order of the reaction and the variation in the rate constant with time. According to the results given in ref. 5, the alkaline salts reaction of phenols and halogen phenols is second-order. The change in the reaction rate constant with time can be, in principle, due either to an increase in the reaction mass viscosity or to a change in the ionic strength or to a change in the mutual influence of the reaction centres as

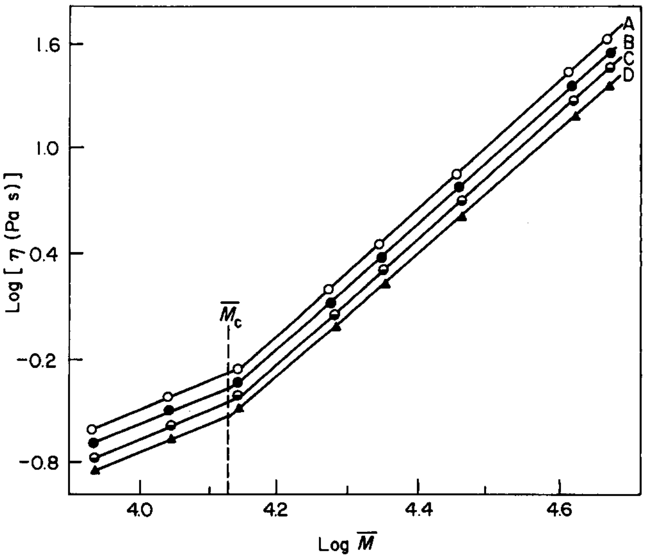


Figure 1 The molecular weight dependence of apparent viscosity at constant shear stress (50 Pa) of PAS solutions in DMSO at various temperatures: A, 150; B, 160; C, 170; and D, 180°C

the reaction proceeds. Since in this part of the work we are interested in polycondensation in a dilute solution, the change in the viscosity and its influence on the course of the process need not be taken into account as the reaction occurs in the kinetic (not in the diffusion) region. The ionic strength of the solution (0.45 g-equiv/l) does not change in the course of the reaction. As far as the mutual influence of the reaction centres is concerned, this is the problem discussed in this work. This factor within the framework of the approach developed below is taken into account by introducing different rate constants for free and end links.

Taking into account the fact that both comonomers have dependent reaction centres[5] and assuming that there are $m > 2$ monomer links (P–D) in the oligomer, no effects of long-range order are observed. The nucleophilic substitution process for the sodium salt P–D system can thus be described by the following set of differential equations[6]:

$$\begin{aligned}
\mathrm{d}y_1/\mathrm{d}t &= -K_{11}a_0y_1y_5 - K_{21}a_0y_1y_6 - K_{21}a_0y_1y_4 \\
\mathrm{d}y_2/\mathrm{d}t &= K_{21}a_0y_1y_6 + K_{21}a_0y_1y_4 + K_{22}a_0y_4^2 - K_{12}a_0y_2y_5 \\
&\quad - K_{22}a_0y_2y_6 \\
\mathrm{d}y_3/\mathrm{d}t &= K_{12}a_0y_2y_5 + K_{12}a_0y_4y_5 + K_{22}a_0y_2y_6 + K_{22}a_0y_4y_6 \\
&\quad + K_{22}a_0y_2y_4 + K_{22}a_0y_4^2 \\
\mathrm{d}y_4/\mathrm{d}t &= K_{11}a_0y_1y_5 - K_{12}a_0y_4y_5 - K_{21}a_0y_1y_4 - K_{22}a_0y_4^2 \\
&\quad - K_{22}a_0y_4y_6 - K_{22}a_0y_2y_4 \\
\mathrm{d}y_5/\mathrm{d}t &= -K_{11}a_0y_1y_5 - K_{12}a_0y_2y_5 - K_{12}a_0y_4y_5 \\
\mathrm{d}y_6/\mathrm{d}t &= K_{12}a_0y_2y_5 + K_{12}a_0y_4y_5 + K_{22}a_0y_4^2 - K_{21}a_0y_1y_6 \\
&\quad - K_{22}a_0y_2y_6 \\
\mathrm{d}y_7/\mathrm{d}t &= K_{21}a_0y_1y_4 + K_{21}a_0y_1y_6 + K_{22}a_0y_2y_6 \\
&\quad + K_{22}a_0y_4y_6 + K_{22}a_0y_4y_2 + K_{22}a_0y_4^2
\end{aligned} \tag{1}$$

Here, the independent kinetic constants are represented by four values of K_{ij}: K_{11}, the rate constant for P and D; K_{12}, the rate constant for P and D_{end} as well as for P and dimer; K_{21}, the rate constant for P_{end} and D as well as for dimer and D; K_{22}, the rate constant for P_{end} and D_{end}, for dimer and P_{end}, for dimer and D_{end} as well as for dimer and dimer. The value of a_0 is the initial concentration of the monomers (in our case a_0 is the same for P and D).

The differential equation set (1) coupled with the material balance equation

$$y_1 + y_2 + y_3 + 2y_4 + y_5 + y_6 + y_7 = 2 \tag{2}$$

makes up the four-parameter (according to the number of constants) mathematical model of the process, whose parameters are the desired K_{ij} values.

A nine-parameter (M9) model was constructed in addition to the four-parameter (M4) model, taking into account (with the help of constants K_{13}, K_{31}, K_{23}, K_{32} and K_{33} (*Table 1*)) the long-range effects up to $m = 3$. Also under consideration are two 'reduced' biparametric models (M2a and M2b). All the four models are displayed in *Table 1.*

The model parameters (K_{ij} constants) were determined by solving the inverse problem using the non-linear least squares method on the basis of the accumulated experimental data on $y_i(t)$ (*Figure 2*). The computations were made on an EC-1022 computer, the program being written in Fortran. The Kutta–Merson algorithm was used[7] to integrate the differential equation set (1).

The program provides the parameters and estimates of their confidence intervals (confidence level = 68%) and

Table 1 Reaction rate constants (120°C; $\phi = 0.49$ g-equiv/l)

Model	Rate constants (litre/g-equiv min)				
M9	K_{11}	K_{12}	K_{13}	K_{21}	K_{31}
	2.43±0.1	0.44±0.08	0.73±0.08	1.26±0.06	0.97±0.3
	K_{22}	K_{23}	K_{32}	K_{33}	
	–	0.14±0.2	0.43±0.2	0.09±0.004	0.028
M4	K_{11}	K_{12}	K_{21}	K_{22}	
	2.35±0.11	0.56±0.05	1.22±0.09	0.12±0.01	0.036
M2a	K_{1a}	K_{2a}			
	0.86±0.1	0.43±0.08	0.13		
M2b	K_{1b}	K_{2b}			
	1.16±0.05	0.087±0.01	0.068		

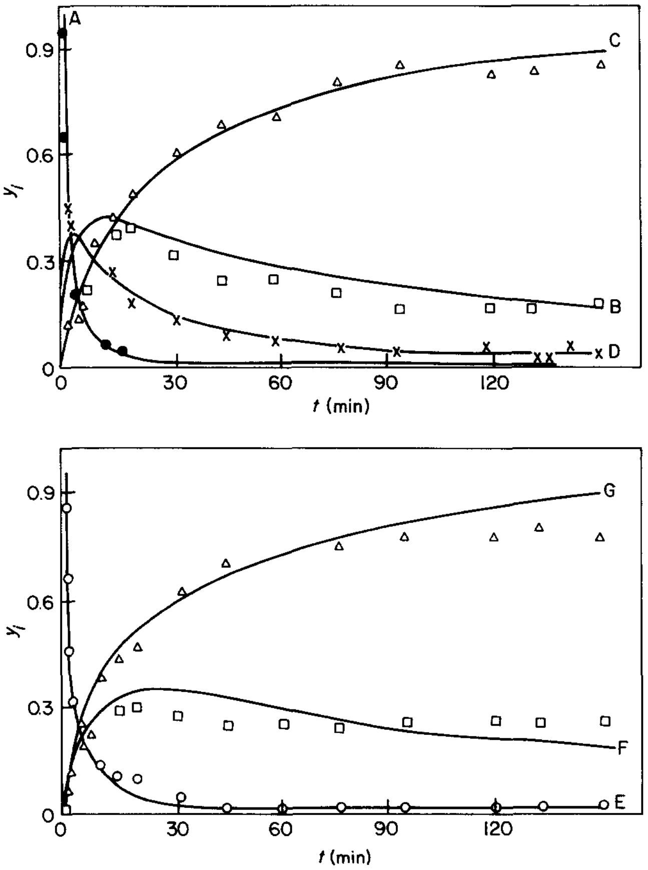


Figure 2 Variation with time of fraction y_i of the free (A, E), end (B, F) and bonded (C, G) dichlorodiphenylsulphone (A–C) and diphenylolpropane (D–G), as well as dimer (D) in the course of the condensation reaction in the sodium salt of diphenylolpropane–dichlorodiphenylsulphone at 120°C. The experimental points (y_i values) are determined from ^{13}C n.m.r. spectra: A–G are the calculations from equations (1) and (2)

residual mean-square deviation (σ) of the calculated y_i values from the experimental data.

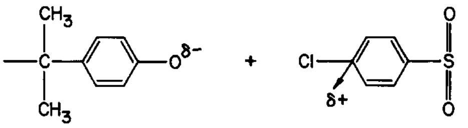
The analysis of the results given in *Table 1* enables us to arrive at the following conclusions.

(1) The calculations based on the experimental data appeared insufficient for a reliable determination of all the parameters in model M9 (in particular, we failed to determine constants K_{22} and K_{23}).

(2) The four-parameter model provides a good approximation both of the experimental data (*Figure 2*) and of model M9; the reaction rate constants between the monomers (K_{11}) in models M4 and M9 are the same, and the values of the rest of the constants of M4 (K_{12}, K_{21} and K_{22}) are located within the intervals of values corresponding to those of the M9 model constants. The volume and accuracy of the experimental data material are sufficient for a reliable determination of the parameters of this model.

(3) The two-parameter models offer a considerably rougher approximation than the four-parameter model. It is impossible to obtain within the framework of these models a true picture of the reactivity of the components. The best approximation to the experiment is provided by model M2b in which one rate constant (K_{1b}) represents all the reactions involving the participation of the monomers, whereas the other (K_{2b}) signifies reactions of all the oligomers (starting with a dimer).

Therefore, the results obtained in the present work are discussed within the framework of model M4. In synthesis of PAS, an interaction occurs between the nucleophilic (phenoxide ions) and electrophilic centres:



As is seen from the results obtained, the activity of the second electrophilic centre decreases two-fold when the first electrophilic centre has entered into the reaction ($K_{11}/2K_{12}=2.08$). Obviously, this is due to the electron donor properties of the residue P in the dimer and the D_{end}[5].

When the first nucleophilic centre has entered into the reaction, practically no change occurs in the activity of the second one ($K_{11}/2K_{21}=0.96$). This corresponds to a weak delocalization of the phenoxide charge in the dimer and in the P_{end}.

RHEOKINETIC MODEL AND ITS PARAMETERS

The rheokinetic method for investigation of polymer synthesis is based on correlation between the macrokinetic model and the results of the rheological properties of the reaction medium at all stages of synthesis[8]. This method, in particular, was successfully applied to analyses of radical[9], anionic[10] and polycondensation polymerizations[11]. In the case of polycondensation, the ratio of the concentration of reactive groups that have reacted to the initial value x_0 was taken for the degree of conversion β:

$$\beta=(x_0-x)/x_0 \qquad (3)$$

where x is the concentration of the reactive groups at any instant.

The number-averaged degree of polymerization $\bar{N}$ is expressed as

$$\bar{N}=(1-\beta)^{-1} \qquad (4)$$

In this case it is essential that the general concentration of all the products (oligomer and polymer) formed in the reaction system does not change in the course of the process and is always equal to unity. Then the viscosity of the reaction system depends only on the molecular weight of the polymer formed.

Let us now consider the form the rheokinetic equation assumed for the polycondensation processes of bifunctional compounds, which are not complicated because of diffusion limitations. The kinetics of such a reaction is described by an equation of second order, which in the case of equality of concentration of the reactive groups is expressed as:

$$\mathrm{d}x/\mathrm{d}t=kx^2 \qquad (5)$$

After integrating this equation within the usual assumptions for the polycondensation processes where $x_0kt \gg 1$, the change in the number-average degree of polycondensation $\bar{N}$ with time is described by the linear expression:

$$\bar{N}=x_0kt \qquad (6)$$

The dependence of viscosity of the reaction medium η on the molecular weight or degree of polycondensation may be presented in the following form[4]:

$$\eta=K\bar{N}^a \qquad (7)$$

From equations (6) and (7) it follows that in polycondensation, the time dependence of viscosity of the reaction medium is expressed as:

$$\eta=K(x_0kt)^a \qquad (8)$$

Consequently, the viscosity of the reaction medium is a power function of time, the exponent a being close to unity with $\bar{M}<\bar{M}_c$ ($t<t^*$) and $a=3.4$ with $\bar{M}\geqslant\bar{M}_c$ ($t>t^*$), where t^* is the time necessary for the molecular weight to reach the critical value $\bar{M}_c$ corresponding to the change in the mode of the intermolecular interaction of the flexible-chain macromolecule[4].

The constants K and k entering into formula (8) are exponential functions of temperature:

$$K=K_0\exp(E/RT) \qquad (9)$$

$$k=k_0\exp(-U/RT) \qquad (10)$$

where E and U represent the activation energies of viscous flow and chemical reaction, respectively. Generally speaking, E and U may depend on $\bar{N}$, which, as will be shown later, corresponds to the case under consideration.

Inserting (9) and (10) into (8) gives with $t=$ time of the dependence of the reaction medium viscosity on the temperature as expressed in the following relation:

$$\eta\sim\exp[(E-aU)/RT]$$

Accordingly, the 'apparent' value of the activation energy for increasing the viscosity in polycondensation (which is determined by plotting $\ln \eta$ vs. $1/T$ at t = time) equals:

$$E_t = E - aU \qquad (11)$$

If a definite reaction medium viscosity level $\eta = \eta^*$ is prescribed and if we consider the temperature dependence in time for achieving η, then the 'apparent' activation energy of such a process equals:

$$E_\eta = U - (E/a) \qquad (12)$$

The above relations make it possible to determine the polycondensation kinetics on the basis of the experimental data obtained from the increasing viscosity of the reaction medium.

Experimental

The experimental data characterizing the viscosity growth of the reaction medium in the process of PAS formation are given in *Figure 3*; a 50% solution at various temperatures was taken as an example. The dependence of viscosity on time should be represented by two linear sections having different slopes a, the numerical values of the coefficient having been determined in an independent rheological experiment on simulated systems (see *Figure 1*).

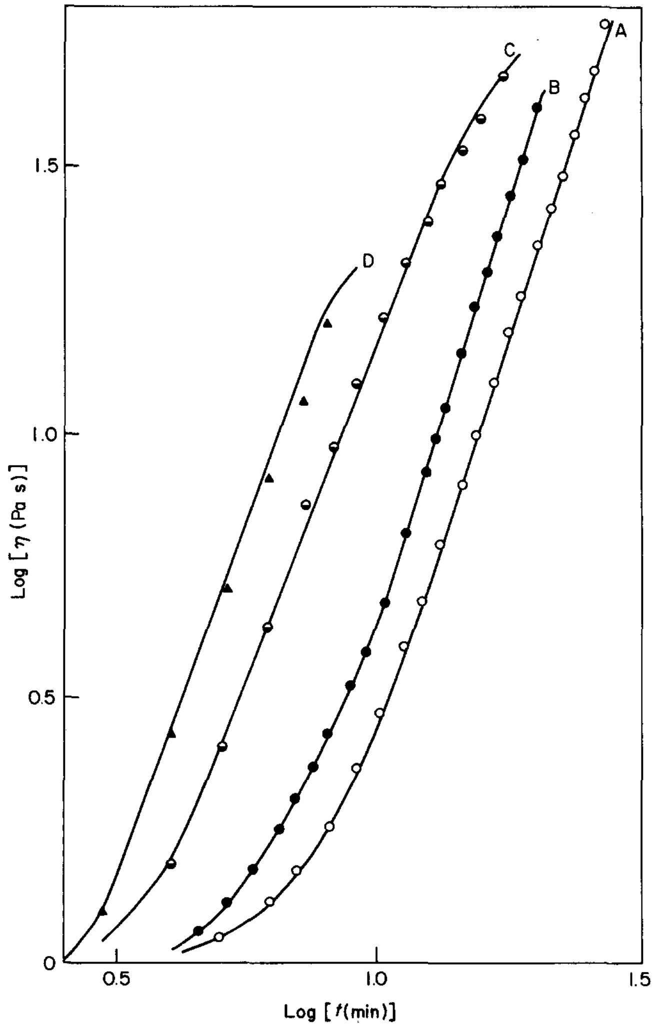


Figure 3 The dependence of viscosity of the reaction system for 50% polymer solution in dimethylsulphoxide on reaction time at various temperatures: A, 150; B, 160; C, 170; and D, 180°C

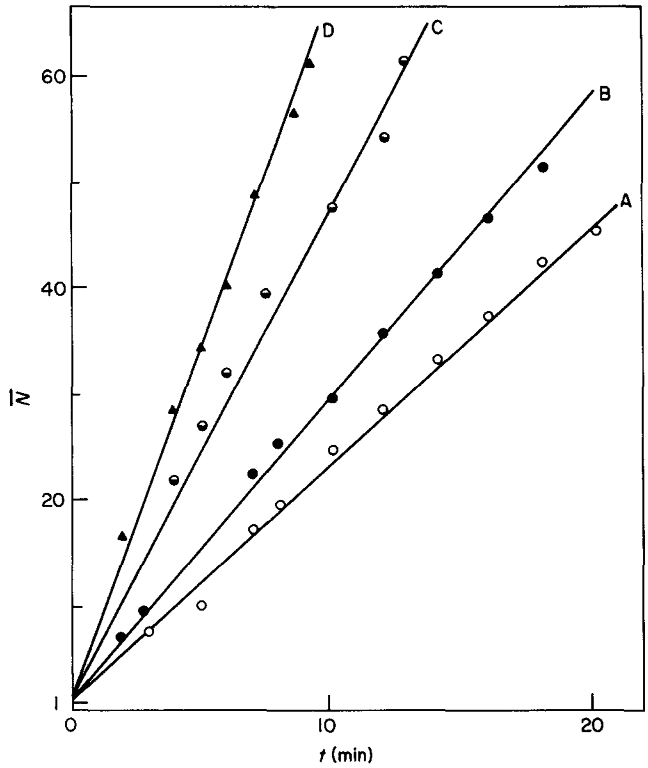


Figure 4 The time dependence of number-average degree of polycondensation at various temperatures: A, 150; B, 160; C, 167; and D, 180°C

It is seen in *Figure 3* that with the exception of a relatively small initial reaction period ($\sim$10 min) the exponent $a = 3.4$. A slower viscosity growth compared with the predicted character of the $\eta(t)$ dependence on the initial reaction stage is associated with complicated processes occurring in the first steps of the reaction, which are, in general, not described by equation (4). Essentially, it was this fact that we emphasized in the previous part of this paper demonstrating the strong dependence of the rate constants on the degree of polymerization for initial oligomerization stages.

The experimental measurements of the viscosity growth in polycondensation, when the above ratios are used, enable us to record the increase in the number-average degree of polycondensation. The observed (*Figure 4*) linear $\bar{N}(t)$ shows that the formation of PAS proceeds in accordance with the second-order reaction scheme. The linear character of $\bar{N}(t)$ renders it possible to determine the chain growth reaction rate constants, k. The constant values at varied temperatures are presented in *Figure 5*.

The activation energy for polycondensation, U, derived from k values at various temperatures appeared to be equal to 59 kJ mol^{-1}. *Figure 5* also displays the time dependence for achieving a reaction system of viscosity $\eta = 1$ Pa s (10 P) from which the 'apparent' activation energy $E_\eta = 50$ kJ mol^{-1} was determined. The value obtained corresponds to formula (12) with the activation energy of viscous flow $E = 31.9$ kJ mol^{-1}. The same E value was derived independently.

Thus, the combination of the obtained numerical kinetic and rheometric constants corresponds to the rheokinetic relations (6) and (8) and serves as evidence of the validity of the chosen macrokinetic scheme with respect to the major part of the PAS synthesis (with the

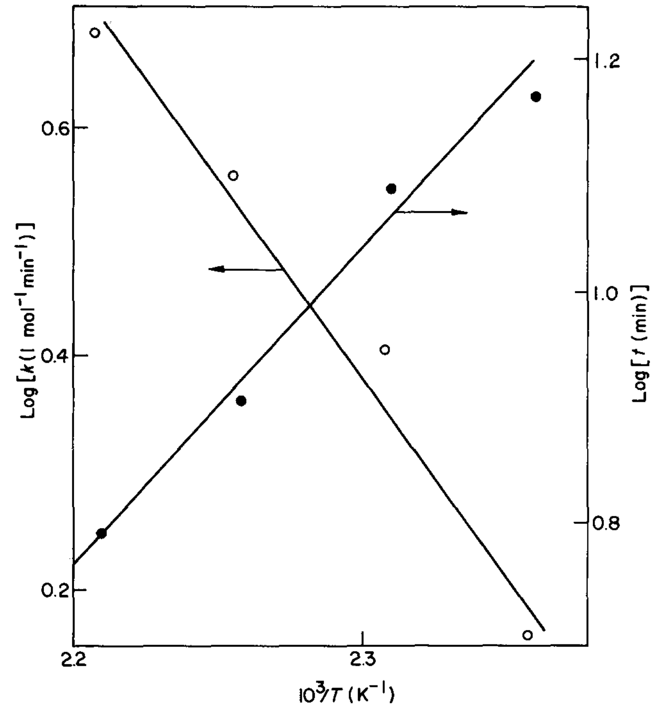


Figure 5 The temperature dependences of polycondensation rate constants and time for achieving viscosity equal to 1 Pa s

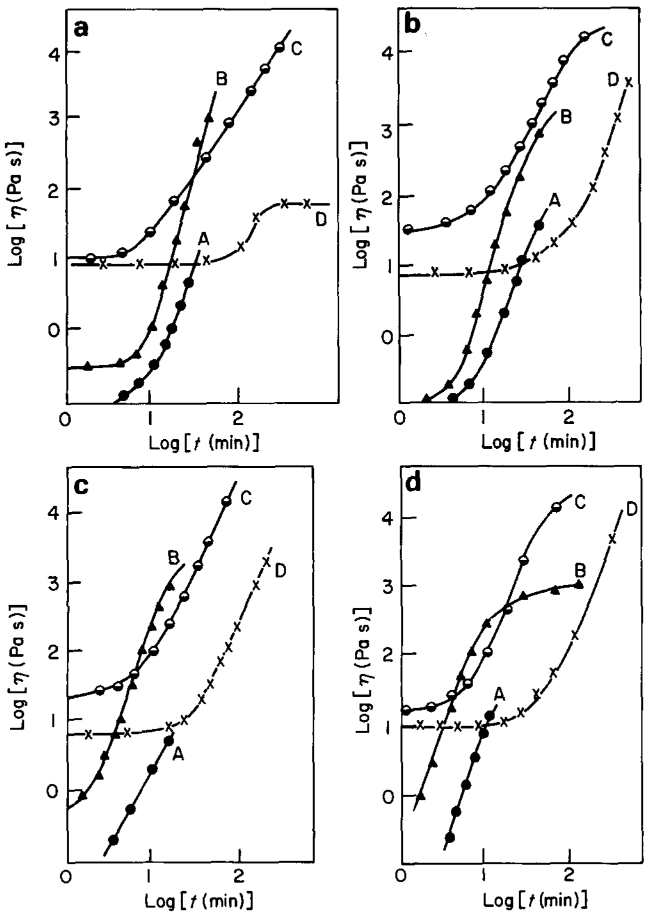


Figure 6 Viscosity change during PAS synthesis at temperatures of (a) 150, (b) 160, (c) 170 and (d) 180°C and various concentrations of the polymer in the reaction system: A, 50; B, 60; C, 70; and D, 80%

exception of the oligomerization stage) up to the end product.

Rheokinetic investigations of polycondensations at solution concentrations of 60, 70 and 80% were also carried out.

When the solvent content in the reaction system is decreased, the reaction may pass into the diffusion-controlled stage. In this case a rise in the viscosity of the reaction mass may bring about a deceleration of the process. This situation is illustrated in *Figure 6*, showing the time dependence of the reaction system viscosity at various temperatures and solvent concentrations.

The experimental data have shown that with a 60% polymer concentration, and temperatures of 50 and 160°C, one may observe a change in the character of the $\eta(t)$ dependence and a reduction in the viscosity growth rate resulting from a decrease in the polymer formation rate constants. At temperatures of 170 and 180°C, practically no variations of the rate constants for 50 and 60% solutions are observed . This supports the fact that the process under such conditions occurs in the kinetic region.

A further increase in the polymer concentration leads to a deviation of $\bar{N}(t)$ from the linear form (*Figure 7*) and to a decrease in the reaction rate constants (*Figure 8*). The higher the constants, the lower the temperature for carrying out the process. For example, if the temperature is 150°C and the polymer concentration is 80%, the process is completed at the initial stage and the end number-average degree of condensation does not exceed 8–10. The set of rate constants, k, obtained as well as $\bar{N}_\infty$, and the activation energies U and E are tabulated in *Table 2*.

In order to discuss in more detail the reaction mechanism in concentrated solutions, let us consider the activation energy values, U, corresponding to the

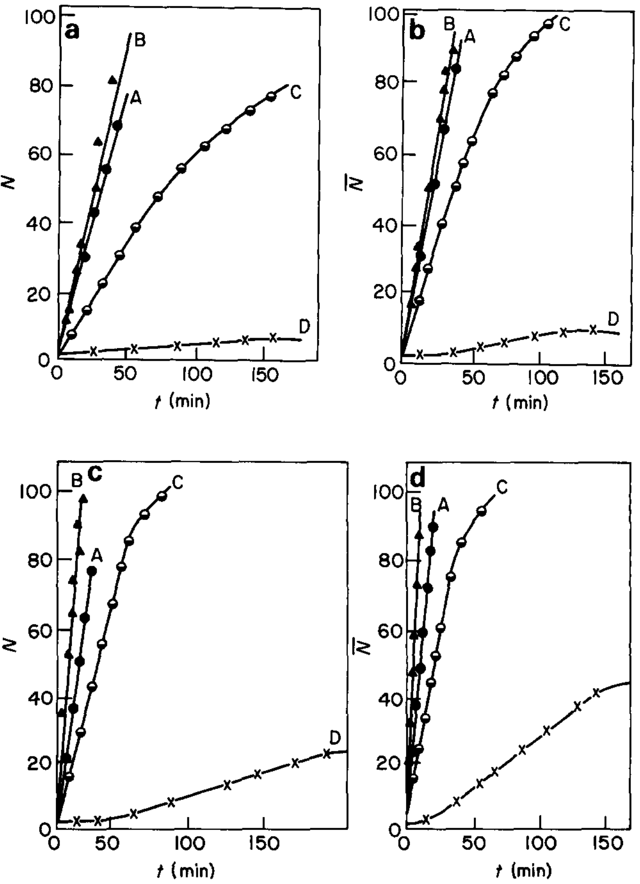


Figure 7 Change in the number-average degree of polycondensation in polysulphone synthesis at temperatures of (a) 150, (b) 160, (c) 170 and (d) 180°C and various concentrations of the polymer in the reaction system: A, 50; B, 60; C, 70; and D, 80%

particular section of the $\bar{N}(t)$ or $\eta(t)$ dependences where the reactions are described by an equation of second order, while its rate is characterized by the value k.

Figure 9 offers a comparison of U values for different concentrations and presents the values for the concentration dependence of E for solutions of corresponding concentrations in DMSO. For 50 and 60% solutions, U does not depend on the solution concentration, whereas, in the case of $U > E$, a decrease in the apparent activation energy of the chemical reaction up to a value of the activation energy of viscous flow indicates a passing of the process to the diffusion-controlled stage. Naturally, the viscous flow activation energy also varies, depending on the polymer concentration in the reaction system, which is clearly seen in *Figure 9*.

The influence of viscosity of the reaction system on the transition of the reaction to the diffusion-controlled stage and back again is shown by the following obvious experiment. An amount of solvent sufficient for decreasing ϕ to 60% was added to the sample inside the viscometer when the reaction at $\phi = 70\%$ was practically completed. The variations of the viscosity and degree of polycondensation prior to and after adding the solvent are given in *Figure 10* where the moment of introduction of the solvent is indicated by an arrow. The data presented indicate that the introduction of a solvent gives rise to a dramatic change in the rate of the polycondensation. A decrease in the concentration of the reaction groups does not lead to a proportional reduction but to a sharp rise in the reaction rate. This is apparently due to the reduction of the reaction medium viscosity and to the passage of the reaction from a diffusion-controlled to a kinetic region. In doing so, a total quantitative 'recovery' of the system takes place: the numerical constants after the transition point, i.e. after diluting the solution from 70 to 60%, coincide completely with the constants characteristic of the process occurring in the kinetic region.

Generall speaking, the viscosity of the system under investigation does not by itself determine the transition from the kinetic to the diffusion-controlled region. It is necessary also to take into account the mobility of the growing macromolecules, depending on their $\bar{N}$. An attempt at such an explanation may be made using the complex parameter $\eta\bar{N}$ as an argument in considering the isothermal rate constant. It is well known[12] that in different molecular theories the relaxation time is determined by $\eta\bar{N}$, so the diffusion transition rate may be determined. The results of the corresponding treatment of

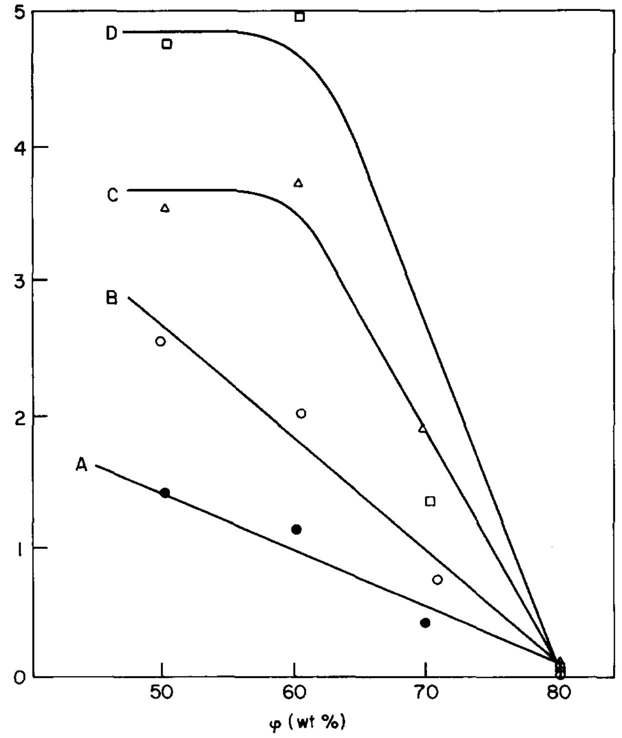


Figure 8 The dependences of the rate constants on the concentration of the polymer in solution at various temperatures: A, 150; B, 160; C, 170; and D, 180°C

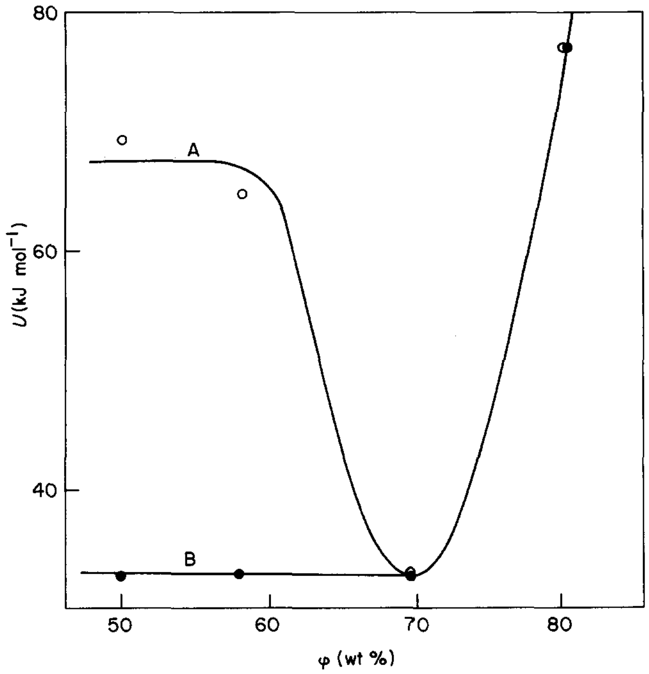


Figure 9 The concentration dependences of the activation energy for the polycondensation process (curve A) and for the viscous flow of the reaction solution (curve B)

Table 2 Kinetic parameters of polysulphone synthesis process

	150°C		160°C		170°C		180°C			
Concn. (%)	k_1 (l mol^{-1} min^{-1})	$\bar{N}_\infty$	k_1 (l mol^{-1} min^{-1})	$\bar{N}_\infty$	k_1 (l mol^{-1} min^{-1})	$\bar{N}_\infty$	k_1 (l mol^{-1} min^{-1})	$\bar{N}_\infty$	U (kJ mol^{-1})	E (kJ mol^{-1})
50	1.44	68[a]	2.56	96	3.6	68[a]	4.8	84[a]	69.6	31.9
60	1.125	90	2.0	96	3.75	108	5.0	102	65.1	31.9
70	0.39	77	0.79	100	0.92	108	1.32	110	33.6	31.9
80	0.018	8	0.03	14	0.05	28	0.073	44	77.7	77.7

[a] The values in this case are not $\bar{N}_\infty$, for the reaction was stopped for controlled determination of the molecular mass

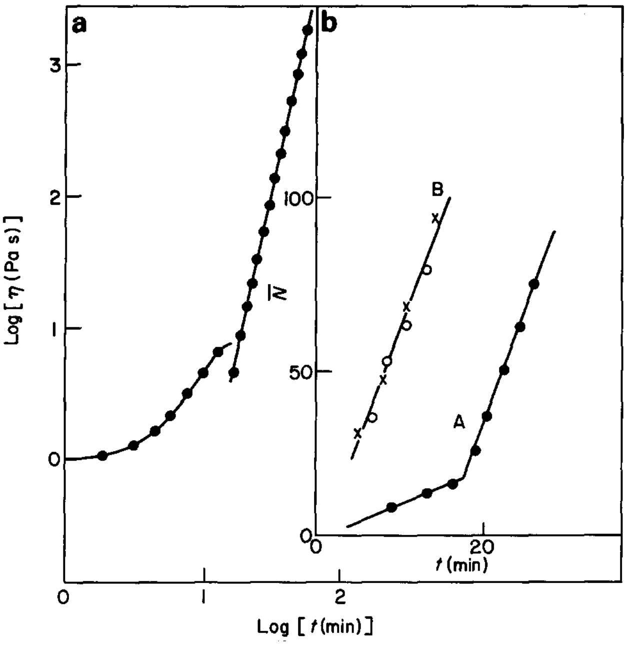


Figure 10 Change in the viscosity (a) and number-average degree of polycondensation (b) in polysulphone synthesis during a jump-like change in the concentration of the polymer in the reaction solution from 70 to 60%. Point A, the moment of solvent addition to the reaction solution. Line B, the dependence of $N(t)$ typical of the kinetic region (60% concentration)

the experimental data in the form of dependences of k on $\eta\bar{N}$ are presented in *Figure 11*. It reflects a very important fact: the K value does not depend on the parameter $\eta\bar{N}$ up to a certain critical $\eta\bar{N}$ value and then drops. The dependence of k on $\eta\bar{N}$ appears to be universal for solutions of any concentration, confirming the feasibility of using the complex parameter in the form $\eta\bar{N}$. This implies that the parameter $\eta\bar{N}$, i.e. the relaxation time, determines the condition for changing the controlling reaction mechanism.

Discussion

In ref. 5 for the same system ($\phi_0 = 0.15$ g-equiv/l; DMSO solvent, 120°C) the rate constants were determined for two regions of β values—conditionally called the monomeric ($\beta < 0.5$) and polymeric ($\beta > 0.5$) regions, using the chemical method of analysis. In doing so, the following results were obtained: $K_m = 1.06$ l/g-equiv min; $K_p = 0.45$ l/g-equiv min.

It should be noted, first of all, that both ref. 5 and the above-cited n.m.r. results are concerned with dilute solutions. Therefore the kinetic stage of the process without diffusion limitations is discussed. This is unambiguously confirmed by rheological data. So the difference in the values ϕ_0 should not in any way affect the kinetic constants, which justifies the comparison of the values to be discussed below.

The analysis of curves B, C, F and G in *Figure 2* (time gap 0–5 min) shows that not only a dimer (as was assumed in calculation of K_m in ref. 5) but also D_{end}, D_{mid}, P_{end} and P_{mid} are formed in the reaction mixture at $\beta < 0.5$. Hence, k_m is the brutto-constant, which includes not only K_{11}, but also the smaller rate constants K_{12}, K_{21} and K_{22} (see *Table 1* for model M4 data). This can explain why constant $K_m = 1.06$ l/g-equiv min is practically equal to constant K_{1b}, but considerably less than the interaction rate constant of the most active centres $K_{11} = 2.35$ l/g-equiv min (*Table 1*).

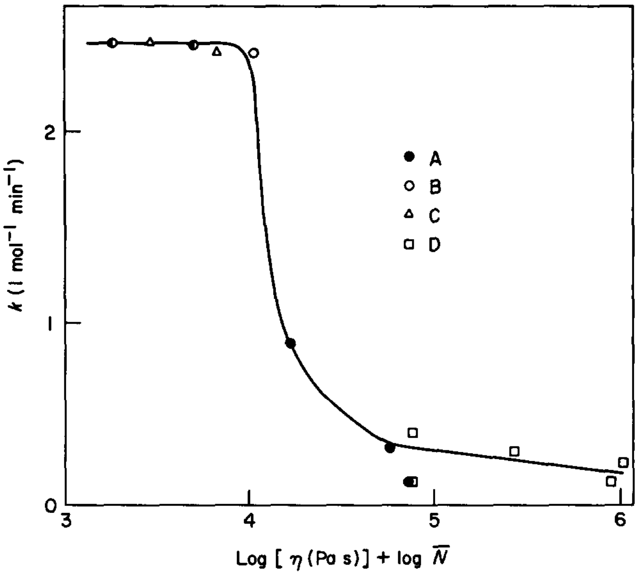


Figure 11 The dependence of the rate constant at different solution concentrations on the complex parameter $\eta\bar{N}$. The designation of the points is the same as in *Figure 8*

The analysis of curves A and E in *Figure 2* (time gap 5–20 min) shows that the reaction mixture with $\beta > 0.5$ still contains the initial compounds, D and P. Hence, K_p is also the brutto-constant, which except for K_{22} includes larger (*Table 1*, model M4) constants K_{11}, K_{12} and K_{21}. This is due to the fact that $K_p = 0.45$ l/g-equiv min) is practically equato to $K_{2a} = 0.43$ l/g-equiv min, but considerably larger than the rate constant of the less active centres, $K_{22} = 0.12$ l/g-equiv min (*Table 1*). At the same time the above comparison and the determination of K_m, K_{1b} and K_p, K_{2a} confirm the reality of the constant values obtained by us as well as the adequacy of the method applied for treatment of the experimental data.

Of special interest is the comparison of the constants obtained by the n.m.r. and the rheokinetic methods. Apparently, the rheokinetic method affords constant k_1 corresponding to the slowest interactions, and this value should be compared with constant K_{22} of model M4. The kinetic constant k_r was measured in the temperature range 150–180°C and showed an activation energy of 69.9 kJ mol^{-1}, thus the recalculation of k_r for 120°C affords 0.37 ± 0.33 l mol^{-1} min^{-1} (i.e. 0.18 ± 0.2 l/g-equiv min). Apparently, k_r is close enough to $K_{22} = 0.12$ l/g-equiv min.

Thus, the investigations produced a complete and, at the same time, a self-consistent picture of the relationship of the elementary interaction reaction rates for the synthesis of PAS. Besides a detailed kinetic analysis of the elementary reactions using the ^{13}C n.m.r. method, polycondensation in broad temperature and concentration ranges involving the transition to the diffusionally controlled region may be successfully studied with the aid of the rheokinetic method.

In the light of the results obtained it is informative to discuss the recently published results[13] on the kinetic parameters of polyesterosulphonic synthesis on simulated compounds, using chemical and g.p.c. methods of analysis. The comparative analysis of the results of ref. 13 and of ours has shown the following. First, the values of K of the nucleophilic substitution of the D–P system considerably exceed those of K_{ij} for the D–dioxydiphenylsulphone system[12]. This is likely to be due to the distinguishing nature of the nucleophilic centres, those of diphenylpropane (P) and dioxydiphenylsulphone. Secondly, in contrast to the above results, it was found in ref. 13 that the activity of the second electrophilic centre increases two-fold when the first enters into the reaction; it is still unclear why such a distinction exists.

REFERENCES

1 Bulai, A. Kh., Urman, Ya. G., Slonim, I. Ya., Bolotina, L. M., Reitburg, L. E., Gol'der, M. M., Shapovalova, A. I. and Sivakova, R. N. *Vysokomol. Soed. A* 1982, **24**, 1047 (in Russian)
2 Malkin, A. Ya., Askadsky, A. A., Chalykh, A. E. and Kovriga, V. V., 'Experimental Methods of Polymer Physics', Mir, Moscow, and Prentice-Hall, Englewood Cliffs, NJ, 1983
3 Vyrskii, Yu. P., Kuzyaeva, V. F., Akhmetova, E. I. and Akutin, M. S. *Plastmassy* 1968, **9**, 28 (in Russian)
4 Vinogradov, G. V. and Malkin, A. Ya., 'Rheology of Polymers', Mir, Moscow, and Springer Verlag, Berlin, 1980
5 Storozhuk, I. P., Mikataev, A. K. and Korshak, V. V., 'Polycondensational Processes and Polymers', Nal'chik, Kabardino-Balkarian University, 1976, p. 79
6 Klyuchnikov, V. N., Bulai, A. Kh., Urman, Ya. B., Slonim, I. Ya., Bolotina, L. M., Reitburg, L. E. and Gol'der, M. M. *Vysokomol. Soed. A* 1984, **26**, 1718
7 Calderbank, V. J. 'A Course on Programming in FORTRAN IV', Chapman and Hall, London, 1972
8 Malkin, A. Ya. *Polym. Eng. Sci.* 1980, **20** (15), 1035
9 Malkin, A. Ya., Kulichikhin, S. G., Emel'yanov, D. N., Smetanina, I. E. and Ryabokon' *Polymer* 1984, **25** (6), 778
10 Malkin, A. Ya., Kulichikhin, S. G., Ivanova, S. L. and Korchagina, M. A. *Vysokomol. Soed. A* 1980, **22**, 165
11 Kulichikhin, S. G., Kozhina, V. A., Bolotina, L. M. and Malkin, A. Ya. *Vysokomol. Soed. B* 1982, **24**, 309
12 Ferry, J. D. 'Viscoelastic Properties of Polymers', 3rd edn., Wiley, New York, 1981
13 Tong-Yin Yu, Shou-Kuan Fu, Shon-Jun Li, Cai-gui Ji and Weiz-huang Cheng *Polymer* 1984, **25** (9), 1369