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The Kinetics of Ester-Ester Exchange Reactions by Mass Spectrometry

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ABSTRACT

The kinetics of ester-ester exchange reactions between poly(ethylene adipate) and poly(trimethylene adipate) have been studied by mass spectrometric techniques. Reactions were carried out in the absence of catalyst and solvent. Rate constants for the exchange reaction and corresponding Arrhenius parameters are given.

INTRODUCTION

In the synthesis of polyesters by direct esterification at elevated temperatures and in the presence of catalysts, esterification is accompanied by alcoholysis, acidolysis and ester-ester exchange reactions [1, 2]. The exchange reactions lead to randomization of the structural units when block copolyesters are synthesized by melt-blend or mixed-feed methods. Though the integrity of the

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number-average molecular weight is maintained during randomization [3], changes in physical properties are inevitable.

The kinetics of exchange reactions have been studied in the presence of various catalysts and by use of suitable instrumental techniques [4, 5]. Ester-ester exchange reactions, reported in 1865 by Friedel and Crafts, have received little attention, but catalytic ester-ester interchange reactions with the continuous removal of one of the esters by distillation have been patented [6].

Owing to the thermal instability of most esters, kinetics of the ester-ester exchange reaction in the absence of catalyst and solvent have not been studied. However, polyesters such as poly(ethylene adipate) (A) and poly(trimethylene adipate) (B), which

$$\left[(CH_2)_2OCO(CH_2)_4COO\right]_a \qquad \left[(CH_2)_3OCO(CH_2)_4COO\right]_b$$

(A) (B)

are thermally stable over the temperature range of 300-400° C, open a way for studying ester-ester exchange reactions.

THEORY

The degree of randomization between two polyesters resulting from ester-ester exchange reactions is influenced by their respective carbonyl equivalents. For the reaction between (A) and (B), any variation in the carbonyl equivalent will be related to the degree of polymerization $\overline{P}$:

$$\frac{\overline{M}_A/m_a}{\overline{M}_B/m_b} = \frac{m_a\overline{P}_A}{m_b\overline{P}_B} \tag{1}$$

Here $\overline{M}_A$ and $\overline{M}_B$ are the molecular weights of A and B, and m_a and m_b are the molecular weights of the respective repeat units. The ratio of carbonyl equivalents can be expressed as:

$$\overline{P}_A/\overline{P}_B = C \tag{2}$$

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Maximum randomization can only be achieved if C = 1, i.e., when $\overline{P}_A = \overline{P}_B$ in the homopolymers before reaction. If $\overline{P}_A \neq \overline{P}_B$ initially, then C < 1 and it changes during randomization. We define α, x by Eq. (3):

$$\underset{(\alpha - x)}{\text{—a-a—}} + \underset{(\alpha - x)}{\text{—b-b—}} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} 2\underset{2x}{\text{—a-b—}} \tag{3}$$

where

$$dx/dt = k_2(\alpha - x)^2 - k_{-2}(2x)^2 \tag{4}$$

At infinite time, x approaches an equilibrium value x_e.

$$K = k_2/k_{-2} = 4x_e^2/(\alpha - x_e)^2 \tag{5}$$

$$\int_0^t dt = \frac{1}{k_{-2}} \int_0^x \frac{dx}{K(\alpha - x)^2 - (2x)^2} \tag{6}$$

Integration by partial fractions gives the expression for opposing bimolecular reactions:

$$t = \frac{1}{8k_{-2}} \left(\frac{1}{x_e} - \frac{1}{\alpha} \right) \ln \left[\frac{1 + (x/x_e) - (2x/\alpha)}{1 - (x/x_e)} \right] \tag{7}$$

The degree of randomization q can be expressed as:

$$q = x/(\alpha - x)$$

where x is the number of ab units and α is the total number of a and b units.

For C = 1, initially we would expect to observe q = 0; at statistical equilibrium, $x = \frac{1}{2}\alpha$ and q = 1, whereas for complete randomization $x = \alpha$ and q tends to infinity.

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EXPERIMENTAL

Polyesters A and B were prepared by reacting an excess of ethylene glycol and trimethylene glycol, respectively, with adipic acid in the presence of 0.1% (w/w) p-toluenesulfonic acid at 120° C. Molecular weights estimated by OH endgroup analysis were maintained at approximately 2000. The hydroxyl endgroups were esterified by adding two equivalents of acetic acid and heating for about 2 hr at 120° C. Excess acid, traces of water, and other impurities were removed under vacuum at 150° C. Thermal analysis was carried out by using the Dupont 950 thermogravimetric analyzer.

Equivalent amounts of A and B were thoroughly mixed in the melt at 80-90° C, then poured into the reaction vessel maintained at the required reaction temperature. Traces of moisture and oxygen from the atmosphere were removed by maintaining a constant flow of nitrogen gas through the system. The glass reaction vessel was assembled in a specially adapted Pye Unicam Series 104 oven, which enabled access for sampling without any appreciable drop in temperature. The Pye oven programmer facilitated control of the reaction temperature to ±0.5° C. Mass spectra of samples taken at different time intervals curing the reaction, were recorded at a source temperature of 200° C, by use of an A.E.I. MS 902 mass spectrometer.

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RESULTS AND DISCUSSION

When analyzed by mass spectrometry, the polyesters A and B and the equilibrium product AB, gave intense peaks for the a_2, b_2, and ab units, i.e., m/e 345, 359, and 373, respectively. To follow the reaction, it was assumed that the ion currents I_{a2} I_{b2} and I_{ab}, are proportional to the concentration of A, B, and AB, respectively. However, due to differences in activity coefficients and other properties which influence the sensitivity to ionization, relative sensitivity coefficients S_A, S_B, and S_{AB} were introduced. By using mixtures of A and B, unreacted, and setting $S_A = 1$, the value of S_B was determined:

$$I_{a2}S_A = I_{b2}S_B$$

with

$$S_B = 1.55 \pm 0.1$$

Similarly S_{AB} was determined by using the equilibrium product:

$$(I_{a2} + I_{b2})(S_A + S_B) = 2S_{AB}\,I_{ab}$$

$$S_{AB} = \tfrac{1}{2}(S_A + S_B) = 1.27 \pm 0.05$$

The general manner in which A, B, and AB behave with respect to time and temperature is shown for the reaction at 312° C, in Fig. 1. This confirms the stoichiometric equation (3) postulated for the opposing bimolecular reactions. In addition, the equilibrium concentrations imply that the degree of randomization q is at a maximum.

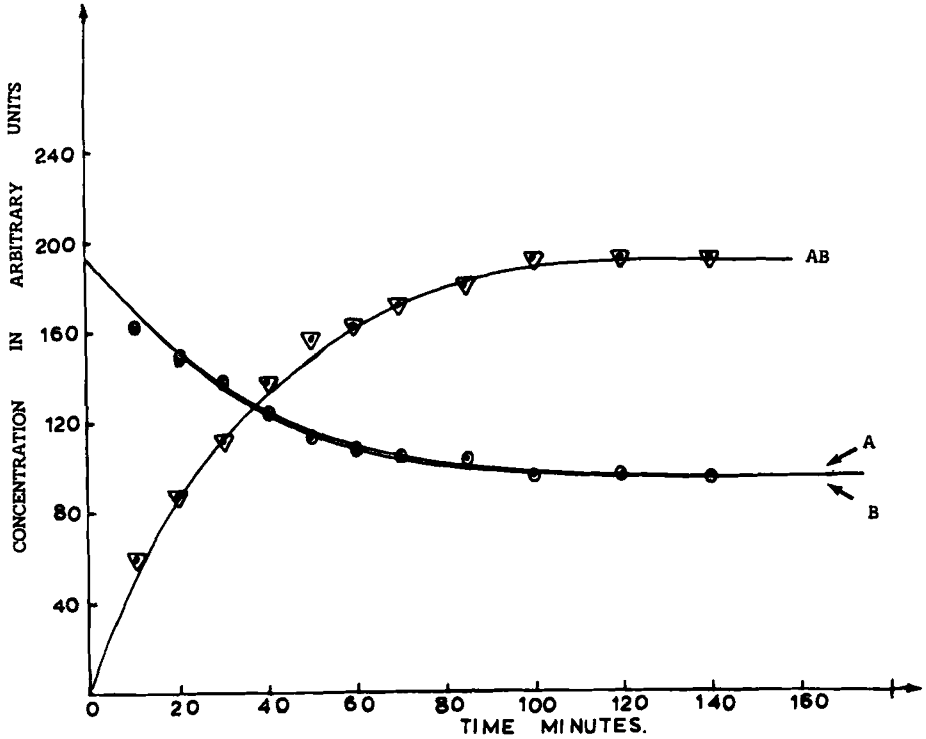

FIG. 1. Variation in the concentration of A and B and the randomized product AB for the exchange reaction at 312° C.

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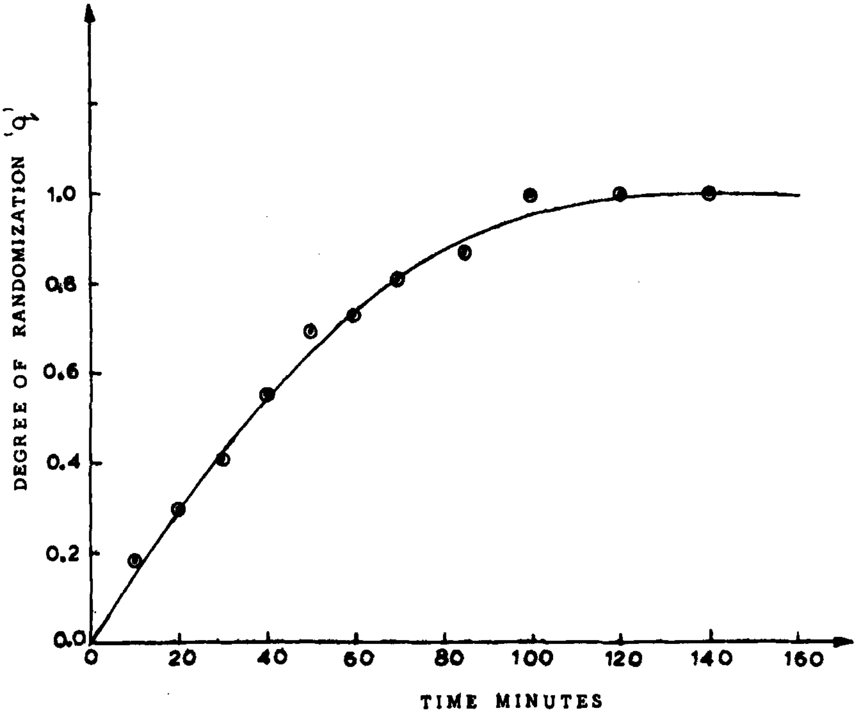

FIG. 2. Changes in the degree of randomization q during the ester-ester exchange reaction between A and B at 312° C.

The change in the degree of randomization during the reaction is shown in Fig. 2. The data suggest that as q approaches the limiting value of 1, the a and b units become randomly distributed, while for $q < 1$, the units tend to cluster in blocks [7].

From experimental observations at all temperatures studied, the observed distribution is identical with that predicted for a purely statistical distribution, i.e., $a_2 : b_2 : ab = 1:1:2$. Thus, at equilibrium, $\alpha = 2x_e$ and $K = 4.0$. Substituting for x_e in Eq. (7) gives:

$$t = \frac{1}{8k_{-2}\alpha} \ln \left[\frac{\alpha}{\alpha - 2x} \right] \tag{8}$$

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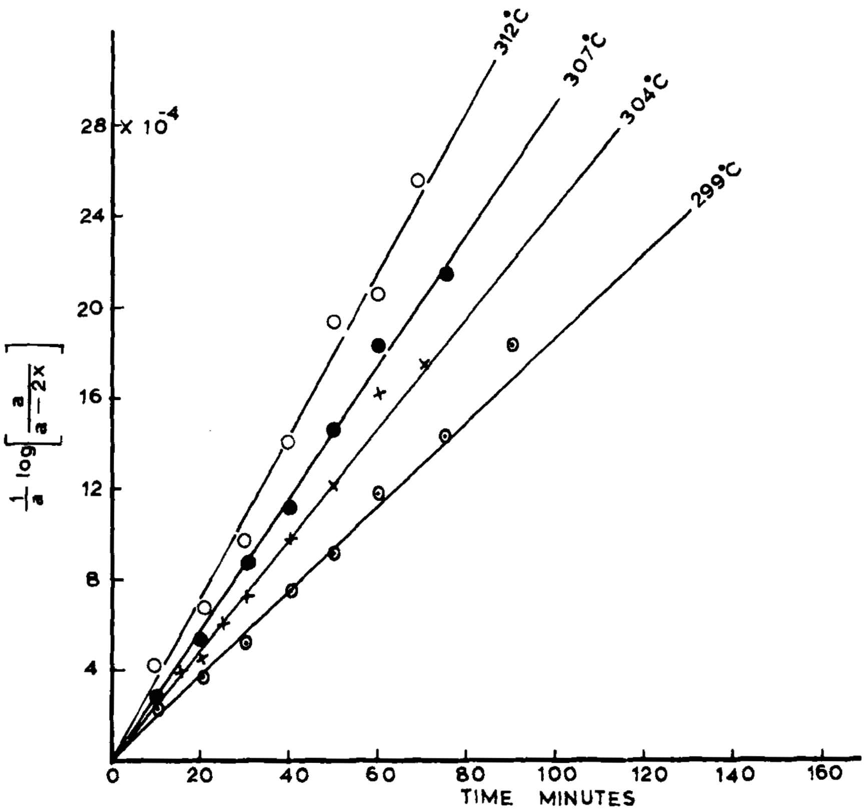

FIG. 3. Plot of $(1/\alpha)\log[\alpha/(\alpha - 2x)]$ against time for the ester-ester exchange reaction between A and B at different temperatures.

The plot of $(1/\alpha)\log[\alpha/(\alpha - 2x)]$ against time gives the rate constant k_{-2} (see Fig. 3.), while k_2 is derived by using Eq. (5). The results are summarized in Table 1.

The Arrhenius parameters ($k = Ae^{-E/RT}$) were obtained from the plot of log k against 1/T (see Fig. 4).

$$k_2 = 8.11 \times 10^6 \exp\{-146\ \text{kJmole}^{-1}/RT\}\ \text{dm}^3/\text{mole-sec}$$

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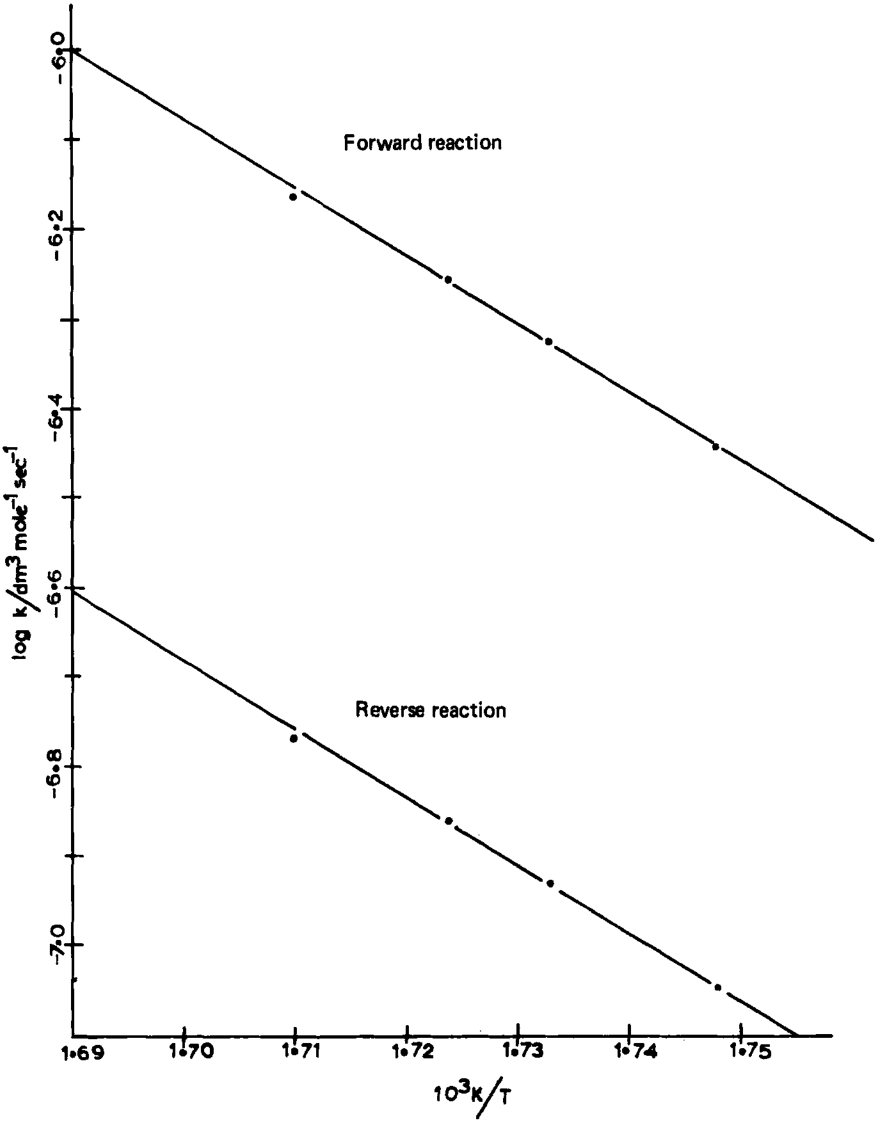

FIG. 4. Arrhenius plot based on the mass-spectrometric data for the ester-ester exchange reaction between A and B.

TABLE 1. Values of k_2, k_{-2}

K	T/K	K/T × 10^3	k_{-2} (dm^3/mole-sec)	k_2 (dm^3/mole-sec)
4.0	572	1.748	8.95×10^{-8}	3.58×10^{-7}
4.0	577	1.733	1.70×10^{-7}	4.68×10^{-7}
4.0	580	1.724	1.38×10^{-7}	5.52×10^{-7}
4.0	585	1.708	1.71×10^{-7}	6.82×10^{-7}

The observation that K is independent of temperature indicates that the enthalpy change for the exchange reaction ($\Delta H = E_2 - E_{-2}$) is effectively zero, within the experimental error of the measurements. This is consistent with an associative type of mechanism where the simultaneous making and breaking of bonds are operative.

Collision theory suggests that the pre-exponential factor A should be 4×10^{11} dm^3/mole-sec. The observed much lower values of 10^6 are characteristic of the operation of large steric factors influencing the rates of these reactions.

The method of analysis and kinetic parameters obtained for the ester-ester exchange reaction could be of importance in the synthesis of block copolyesters. However, further studies into the effect of steric factors built onto the glycol residues are being investigated.

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