Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

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To cite this Article Ramjit, H. G.(1983) 'Trends in Kinetic Behavior during Ester-Ester Exchange Reactions in Polyesters by Mass Spectrometry. I', Journal of Macromolecular Science, Part A, 19: 1, 41 — 55
To link to this Article: DOI: 10.1080/00222338308069421
URL: http://dx.doi.org/10.1080/00222338308069421

J. MACROMOL. SCI.—CHEM., A19(1), pp. 41-55 (1983)

Trends in Kinetic Behavior during Ester-Ester Exchange Reactions in Polyesters by Mass Spectrometry. I

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ABSTRACT

The kinetics of the ester-ester exchange reaction between polyesters from adipic acid and various linear and branched glycols were investigated by mass spectometry using the dimer analysis method (DAM). Rate constants, activation energies, and frequency factors are given for reactions studied in the temperature range of 572-585 K. Correlation of glycol methylene ratios with activation energies and frequency factors shows an alternating trend in kinetic behavior. Reaction systems containing even numbers of methylene groups in the glycol moiety of the reactants exhibited slower reaction rates than systems with odd numbers of methylene groups, while branched reaction systems followed very similar trends when the influence of pendant groups is ignored.

INTRODUCTION

Addition polymers are superior to condensation polymers by virtue of the inherent stability of their structural units along the polymer chain backbone. They are not normally susceptible to intermolecular or intramolecular reactions, and are ideally suited to the production of block copolymers. Condensation polymers, on the other hand, are

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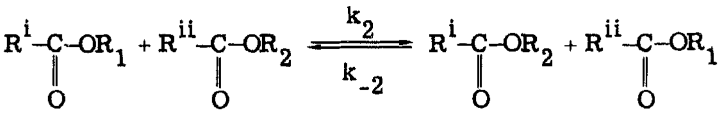
sensitive to the reactants and by-products of a reaction system and also to the resultant functional groups along a polymer chain. Accordingly, molecular weight distribution and randomization of structural units are unavoidable consequences of intermolecular and intramolecular reactions.

Due to low equilibrium constants, esterification reactions are not favorable to the formation of high molecular weight products, unless the by-products such as water and glycols are progressively removed from the reaction system. This is generally achieved at temperatures in excess of 200°C and under reduced pressures. Under these conditions the esterification reaction is accompanied by three types of competing reactions: alcoholysis, acidolysis, and ester-ester exchange [1-3].

Ester-ester exchange reactions involve the interchange between two ester groups to produce two different esters, wherein the bonds being broken and those formed are identical in the forward and reverse reactions:



$$R^{i}-\underset{\substack{\|\\ O}}{C}-OR_1 + R^{ii}-\underset{\substack{\|\\ O}}{C}-OR_2 \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} R^{i}-\underset{\substack{\|\\ O}}{C}-OR_2 + R^{ii}-\underset{\substack{\|\\ O}}{C}-OR_1$$

Reactions of this type were reported as early as 1865 by Friedel and Crafts. Isotope exchange methods [4] have been used to demonstrate the ester-ester exchange reaction between polyhexamethylene sebacate and deuterated diethyl succinate at temperatures of 250°C. Further classical evidence supportive of the occurrence of such reactions comes from the reaction of bis-2-acetoxy-ethyl-terephthalate and bis-2-benzoxy-ethyl-terephthalate at 305°C, as reported by Barton [5].

In addition to the inherent limitations of molecular weight distribution, randomization of structural units effectively restricts the production of block copolymers by well-known condensation methods. The extent of randomization is dictated by the structural characteristics of the component polyesters, reaction conditions, and the nature of the catalyst employed. In spite of these difficulties, block copolyesters have been synthesized with varying degrees of success by using molten state polycondensation methods [6, 7]. Even in the presence of ester exchange catalysts such as titanium alkoxides and arsenic pentoxide, the rates of ester-ester exchange reactions are influenced by the structural nature of the respective repeating units. Polyesters containing stearically hindered carbonyl groups randomize less readily than those which are less hindered. The former would undoubtedly react preferentially at their endgroups to yield block copolymers with a lower degree of randomization. Although the integrity of number-average molecular weight $\overline{M}_n$ is maintained, ester-ester exchange reactions lead to the randomization of structural units, with corresponding changes in the weight-average molecular weight $\overline{M}_w$. Consequently, the kinetics of such reactions can be readily followed by viscosity and melting point methods [8, 9]. Likewise, the heterolinkages so formed open the way for following these reactions by high resolution NMR [10] and mass spectrometry [11, 12]. The present work seeks to define trends in kinetic behavior during ester-ester exchange reaction between polyesters containing linear and branched glycol residues; polyesters with average molecular weight 2000 and thermal stability in the range 375-410°C were especially made from adipic acid and various glycols. Reactions were carried out in melt blends and followed by mass spectrometry. Rate constants, activation energies, and frequency factors were established for the following reaction systems:

a. Polyethylene adipate/polytrimethylene adipate
b. Polyethylene adipate/polytetramethylene adipate
c. Polyethylene adipate/polypentamethylene adipate
d. Polyethylene adipate/polyhexamethylene adipate
e. Polyethylene adipate/polypropylene adipate
f. Polyethylene adipate/polyneopentylene adipate
g. Polytetramethylene adipate/polyhexamethylene adipate
h. Polytrimethylene adipate/polypentamethylene adipate

THEORY

Carbonyl Equivalents "C"

Carbonyl equivalents, which defines the average number of ester linkages in a particular polyester, is directly related to the degree of polymerization $\overline{P}$. Thus, for the ester-ester exchange reaction between two polyesters A and B, any variation in carbonyl equivalent will be related to $\overline{P}$ in the following way:

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

where $\overline{M}_A$ and $\overline{M}_B$ are the molecular weights of reactants A and B, while m_a and m_b are the molecular weights of the repeat units a and b, respectively.

$-[CH_2CH_2OCO(CH_2)_4COO]_a-$ A

$-[(CH_2)_3OCO(CH_2)_4COO]_b-$ B

Maximum randomization can only be achieved when C = 1, i.e., when $\overline{P}_A/\overline{P}_B = C = 1$ in the homopolymers before reaction. Initially, if $\overline{P}_A$ is not equal to $\overline{P}_B$, then C would be less than 1 and would change during randomization.

Kinetic Expression

Since $\overline{P}_A/\overline{P}_B = 1$ at equilibrium, then the statistical distribution of structural units would be in the ratio of aa:bb:2ab as 1:1:2 for maximum randomization. Accordingly, the stoichiometric equation expressing the reaction to equilibrium is defined as

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

where

$$dx/dt = k_2(\alpha - x)^2 - k_{-2}(2x)^2 \tag{3}$$

at infinite time. x approaches an equilibrium x_e, and therefore

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

$$\int_0^t dt = 1/k_{-2} \int_0^x \frac{dx}{K(\alpha - x)^2 - (2x)^2} \tag{5}$$

Integration by partial fractions give the expression for an opposing bimolecular reaction:

$$t = \frac{1}{8k_{-2}} \left(\frac{1}{x_e} - \frac{1}{\alpha} \right) \ln \left[\frac{1 + x/x_e - 2x/\alpha}{1 - x/x_e} \right] \tag{6}$$

for statistical equilibrium $\alpha = 2x_e$. Substituting for x_e in Eq. (6) gives the final expression:

$$t = 1/k_{-2}\alpha \log \left[\frac{\alpha}{\alpha - 2x} \right] \tag{7}$$

The degree of randomization "q" can be expressed as

$$q = \left(\frac{x}{\alpha - x}\right) \tag{8}$$

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

For C = 1, initially, it is expected that q would be zero; and for complete randomization, $x = \alpha$ and q tends to infinity.

EXPERIMENTAL SECTION

Instrumentation

An AEI MS902 double focusing mass spectrometer, Dupont 950 Thermogravimetric Analyzer, and a Pye 104 Gas Chromatograph were used in this study. The gas chromatograph was modified by constructing a secondary oven within the main oven in order to accommodate the glass reaction vessel and to facilitate sampling of the reaction mixture without inducing temperature fluctuations.

Polyester Synthesis

Polyesters were synthesized by reacting an excess of glycol with adipic acid at 160°C in a nitrogen atmosphere. After 10 h, when the production of water ceased, the reaction temperature was increased to 220°C and the pressure reduced to 2 mmHg. Glycol produced at this stage of the reaction was progressively removed by distillation. The reaction was terminated after 20 h and the product cooled to room temperature under a nitrogen atmosphere. Molecular weights were determined by the method of endgroup analysis. Terminal hydroxyl groups were esterified by reacting two equivalents of acetic acid with the polyester at 120°C for 2 h. Excess acid and water were removed at 150°C under vacuum. Thermal stability was determined by TGA using the Dupont 950 Thermogravimetric Analyzer.

Procedure

The reaction vessel, continuously purged with dry nitrogen gas, was equilibriated to the desired reaction temperature. About 1.5 g of equivalent amounts of reactant polyesters, previously homogenized by melt blending at 80°C, was transferred to the reaction vessel and allowed to react. Changes in concentration of reactants and products during the reaction were followed by measuring the ion currents of the respective dimer units (Table 2) on an AEI MS902 mass spectrometer at a source temperature of 200°C and an ionization energy of 60 eV.

RESULTS AND DISCUSSION

The dimer analysis method (DAM), developed for studying ester-ester exchange reactions [11], is based on the readiness with which these molecules undergo the McLafferty rearrangement (Fig. 1) when subjected to electron impact (EI) ionizing conditions in the mass spectrometer. Accordingly, when homopolymers A and B and copolymer AB are analyzed by mass spectrometry, they yield ions with appreciable intensities which facilitate characterization of their repeat units, namely:

$$\text{A} \qquad -a\text{-}a\text{-}a\text{-}a- \longrightarrow Ha^+ + Haa^+ + Haaa^+ -$$

$$\text{B} \qquad -b\text{-}b\text{-}b\text{-}b- \longrightarrow Hb^+ + Hbb^+ + Hbb^+ -$$

$$\text{AB} \qquad -a\text{-}b\text{-}a\text{-}b- \longrightarrow Ha^+ + Hb^+ + Hab^+ + Hba^+ + Habab^+ -$$

Thus, when two polyesters A and B are allowed to undergo ester-ester exchange reactions to produce the copolyester AB, changes in concentration of reactants and products during the reaction could be followed by measuring the ion currents of the respective dimer units: Haa^+, Hbb^+, and Hab^+. It is assumed that the ion currents Iaa, Ibb, and Iab are proportional to the concentration of A, B, and AB, respectively. However, due to differences in activity coefficients and other parameters which influence their sensitivity to ionization, relative sensitivity coefficient(s) were introduced. For example, analyzing mixtures of polyethylene adipate (A) and polytrimethylene adipate (B), unreacted, and setting $S_A = 1$, the value of S_B was determined:

$$Ia_2S_A = Ib_2S_B; \qquad S_B = 1.5 \pm 0.1$$

Similarly, S_{AB} was determined by using the equilibrium product AB derived from the reaction between A and B:

$$(Ia_2 + Ib_2)(S_A + S_B) = 2S_{AB}Iab$$

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

TABLE 1. Values of k_2 and k_{-2} for the Reaction Systems (a-h)

T (°K)	$\frac{1}{T\ (°K)}$	k_{-2} $dm^3\,mol^{-1}\,s^{-1}$	$\log k_{-2}$	k_2 $dm^3\,mol^{-1}\,s^{-1}$	$\log k_2$
		a. Polyethylene Adipate + Polytrimethylene Adipate			
572	1.748×10^{-3}	8.950×10^{-8}	-7.0482	3.58×10^{-7}	-6.4461
577	1.733×10^{-3}	11.710×10^{-8}	-6.9314	4.684×10^{-7}	-6.3294
580	1.724×10^{-3}	13.789×10^{-8}	-6.8607	5.516×10^{-7}	-6.2584
585	1.709×10^{-3}	17.100×10^{-8}	-6.7671	6.840×10^{-7}	-6.1650
		b. Polyethylene Adipate + Polytetramethylene Adipate			
572	1.748×10^{-3}	8.794×10^{-8}	-7.0558	3.5176×10^{-7}	-6.4538
577	1.733×10^{-3}	10.757×10^{-8}	-6.9686	4.3028×10^{-7}	-6.3662
581	1.721×10^{-3}	13.310×10^{-8}	-6.8758	5.3240×10^{-7}	-6.2738
585	1.709×10^{-3}	14.737×10^{-8}	-6.8307	5.8948×10^{-7}	-6.2295
		c. Polyethylene Adipate + Polypentamethylene Adipate			
574	1.742×10^{-3}	9.171×10^{-8}	-7.0376	3.6684×10^{-7}	-6.4355
578	1.730×10^{-3}	11.338×10^{-8}	-6.9455	4.5352×10^{-7}	-6.3434
582	1.718×10^{-3}	13.791×10^{-8}	-6.8604	5.5164×10^{-7}	-6.2584
587	1.703×10^{-3}	17.817×10^{-8}	-6.7492	7.1268×10^{-7}	-6.1471
		d. Polyethylene Adipate + Polyhexamethylene Adipate			
572	1.748×10^{-3}	8.155×10^{-8}	-7.0886	3.262×10^{-7}	-6.4875
577	1.733×10^{-3}	9.793×10^{-8}	-7.0091	3.916×10^{-7}	-6.4072
581	1.721×10^{-3}	12.381×10^{-8}	-6.9073	4.952×10^{-7}	-6.3052

(continued)

TABLE 1 (continued)

	1	k_{-2}		k_2	
T (°K)	T (°K)	$dm^3 mol^{-1} s^{-1}$	log k_{-2}	$dm^3 mol^{-1} s^{-1}$	log k_2
585	1.709×10^{3}	14.503×10^{-8}	-6.8386	5.801×10^{-7}	-6.2365
e. Polyethylene Adipate + Polyneopentylene Adipate					
573	1.745×10^{-3}	8.100×10^{-8}	-7.0915	3.240×10^{-7}	-6.4395
577	1.733×10^{-3}	9.730×10^{-8}	-7.0119	3.892×10^{-7}	-6.4099
581	1.721×10^{-3}	11.88×10^{-8}	-6.9251	4.752×10^{-7}	-6.3231
585	1.709×10^{-3}	14.07×10^{-8}	-6.8518	5.628×10^{-7}	-6.2497
f. Polyethylene Adipate + Polypropylene Adipate					
573	1.745×10^{-3}	7.999×10^{-8}	-7.0970	3.200×10^{-7}	-6.4949
577	1.733×10^{-3}	9.595×10^{-8}	-7.0178	3.838×10^{-7}	-6.4159
581	1.721×10^{-3}	11.195×10^{-8}	-6.9552	4.478×10^{-7}	-6.3489
585	1.709×10^{-3}	13.490×10^{-8}	-6.8700	5.396×10^{-7}	-6.2679
g. Polytetramethylene Adipate + Polyhexamethylene Adipate					
573	1.745×10^{-3}	7.709×10^{-8}	-7.1130	3.083×10^{-7}	-6.5110
577	1.733×10^{-3}	9.097×10^{-8}	-7.0411	3.638×10^{-7}	-6.4391
581	1.721×10^{-3}	10.707×10^{-8}	-6.9706	4.282×10^{-7}	-6.3684
585	1.709×10^{-3}	12.492×10^{-8}	-6.9034	4.996×10^{-7}	-6.3014
h. Polytrimethylene Adipate + Polypentamethylene Adipate					
573	1.745×10^{-3}	8.602×10^{-8}	-7.0653	3.4420×10^{-7}	-6.4633
577	1.733×10^{-3}	10.550×10^{-8}	-6.9767	4.220×10^{-7}	-6.3747
581	1.721×10^{-3}	12.790×10^{-8}	-6.8931	5.1170×10^{-7}	-6.2910
585	1.709×10^{-3}	16.190×10^{-8}	-6.7909	6.474×10^{-7}	-6.1888

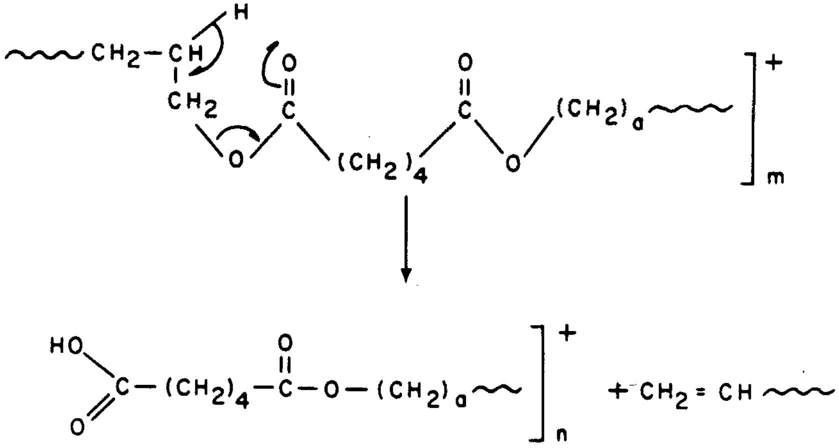


FIG. 1. McLafferty rearrangement.

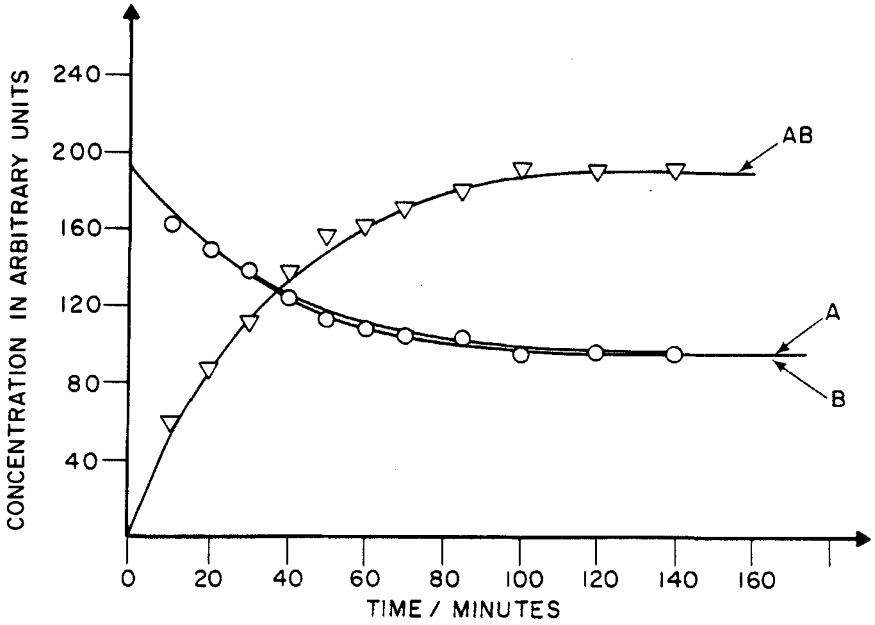


FIG. 2. Changes in concentrations of reactants and products during ester-ester exchange reaction between polyethylene adipate (A) and polytrimethylene adipate (B) at 312°C.

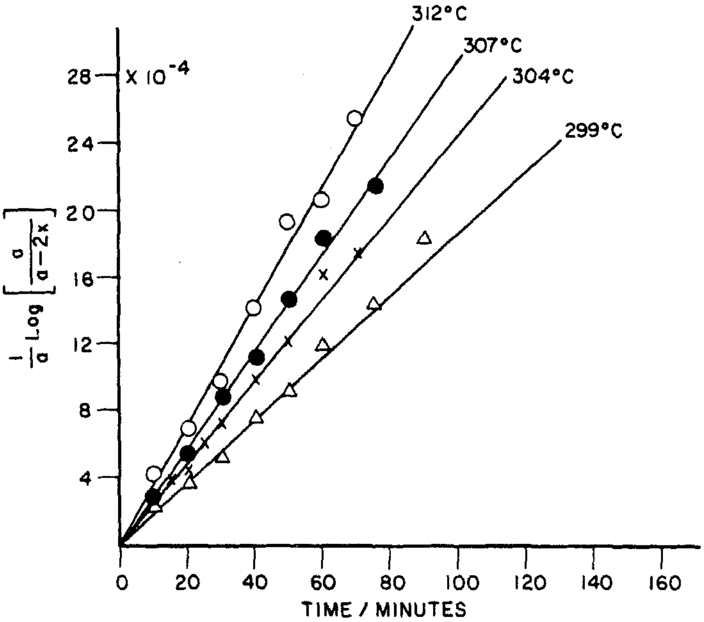


FIG. 3. Graph of $1/\alpha \log \alpha/(\alpha - x)$ as a function of time for the reaction between polyethylene adipate (A) and polytrimethylene adipate (B) at various temperatures.

Changes in concentration of reactants and products during ester-ester exchange reaction between polyethylene adipate A and polytrimethylene adipate B at 312°C (Fig. 2) confirms the stoichiometric Eq. (2) postulated for an opposing bimolecular reaction. Likewise, the equilibrium concentrations of A, B, and AB imply that the degree of randomization "q" is at a maximum.

Rate constants for the respective reaction systems (Table 1) were determined from graphs of $1/\alpha \log \alpha/(\alpha - x)$ as a function of time in accordance with the kinetic Expression (7), derived for an opposing bimolecular reaction. Typical curves are illustrated in Fig. 3 for the ester-ester exchange reaction between polyethylene adipate and polytrimethylene adipate at various temperatures. Slopes of these curves gave the rate constants k_{-2}, while k_2 was determined from Eq. (4). Activation energies and frequency factors (Table 2) were determined from graphs of $\log k_2$ against 10^3 K/T (Fig. 4) in accordance with the Arrhenius equation

$$k_r = A \exp(-E_a/RT) \tag{9}$$

TABLE 2. Dimer Units Monitored by Mass Spectrometry during Ester-Ester Exchange Reaction; Activation Energies, Frequency Factors, and Glycol Methylene Ratios for Reaction Systems (a-h)

Reaction systems	Ions monitored (m/z)			Activation energy (kJ/mol)	Frequency factor log A	Glycol methylene ratio
	aa	ab	bb			
a. Polyethylene/polytrimethylene adipate	345	359	373	139.15	6.22	0.66
b. Polyethylene/polytetramethylene adipate	345	373	401	114.55	3.36	0.50
c. Polyethylene/polypentamethylene adipate	345	387	429	141.46	6.38	0.40
d. Polyethylene/polyhexamethylene adipate	345	401	457	127.04	4.41	0.33
e. Polyethylene/polypropylene adipate	345	359	373	119.74	3.72	1.00[a]
f. Polyethylene/polyneopentylene adipate	345	387	429	129.16	4.60	0.66[a]
g. Polytetramethylene/polyhexamethylene adipate	401	429	457	112.24	3.68	0.66
h. Polytrimethylene/polypentamethylene adipate	373	401	429	145.11	6.70	0.60

[a] The influence of pendant groups is ignored. Carbon atoms along the polymer chain backbone are treated as methylene groups.

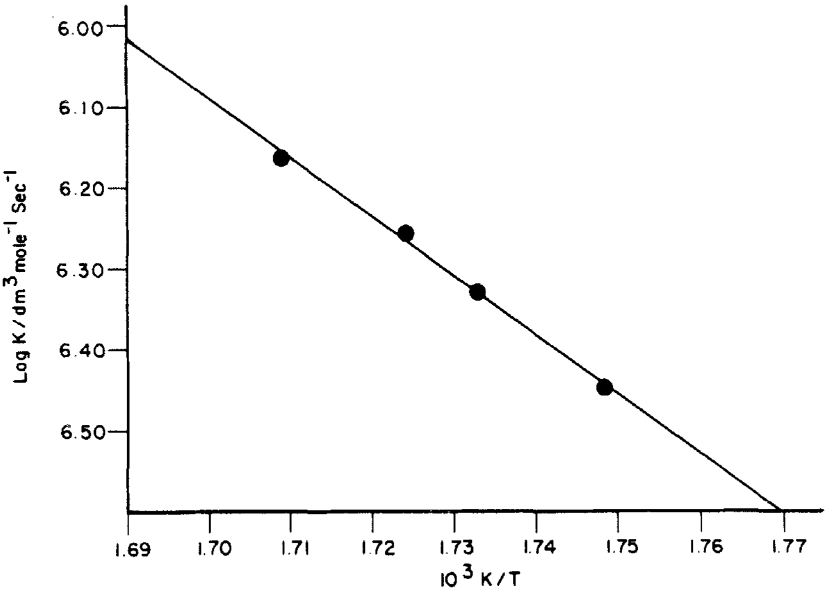


FIG. 4. Graph of log K against 10^3 K/T for the reaction between polyethylene adipate (A) and polytrimethylene adipate (B).

DISCUSSION

The linear reaction systems from polytrimethylene adipate to polyhexamethylene adipate, in which polyethylene adipate is maintained as the standard reactant, exhibit frequency factors and activation energies which bear a definite relationship to the ratio of methylene groups in the glycol residues. Reaction systems containing odd numbers of methylene groups exhibit higher frequency factors than those with even numbers (Fig. 5). This observation is consistent with other linear reaction systems, such as polytetramethylene adipate/polyhexamethylene adipate (log A = 3.68) and polytrimethylene adipate/polypentamethylene adipate (log A = 6.70).

Branching on the glycol residues would stearically hinder the accessibility of a substrate to the reaction site, causing a decrease in frequency factor. This is evident for the reactions between polyethylene adipate/polypropylene adipate (log A = 3.72) and polyethylene adipate/polyneopentylene adipate (log A = 4.60).

Branched reaction systems may also be classified on the basis of glycol methylene ratios. This would necessitate that the influence of pendant groups on the glycol moiety be ignored, while carbon atoms along the polymer chain be designated methylene groups. Accordingly,

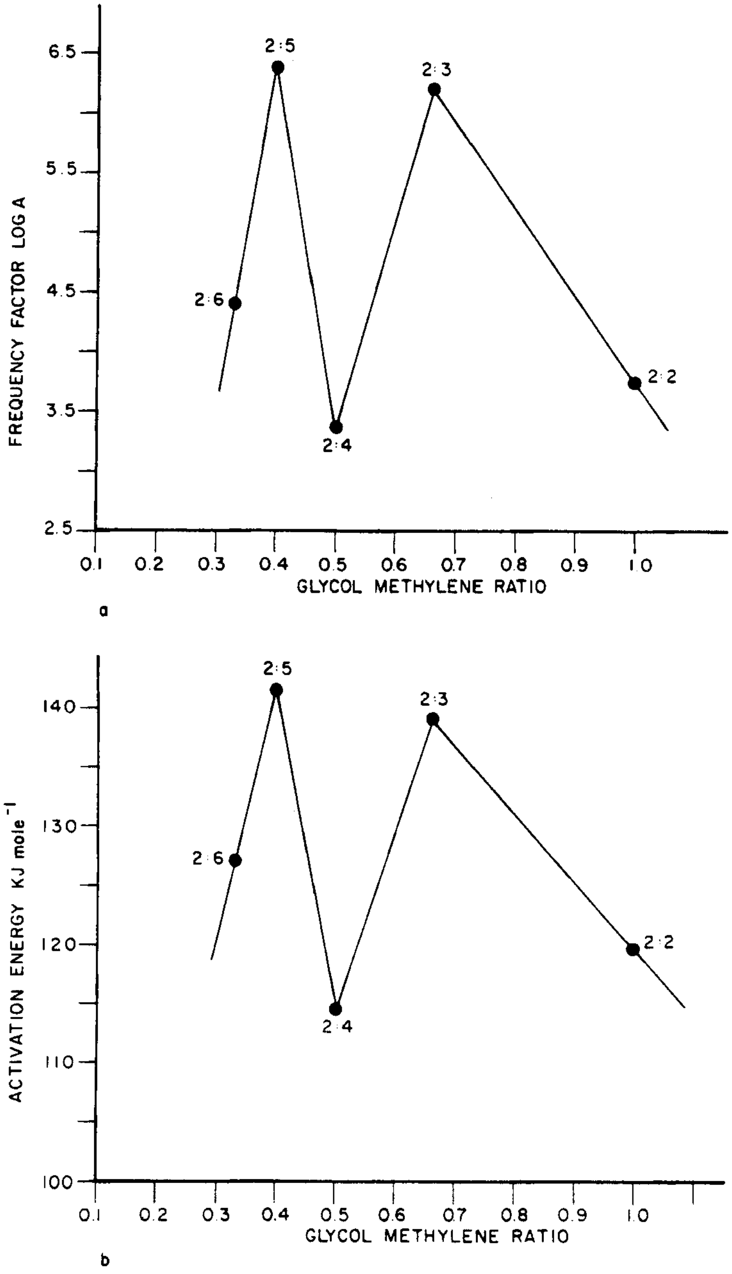


FIG. 5. Plots of (a) frequency factor (log A) and (b) activation energy (E) as a function of glycol methylene ratios.

the reaction systems polyethylene adipate/polypropylene adipate and polyethylene adipate/polyneopentylene adipate would have the equivalent of even and odd numbers of methylene groups, respectively, and would follow the general trend (Fig. 5a) established for the linear reaction systems. Based on glycol methylene ratios and frequency factors, the reaction systems are classified as follows:

$$-[CH_2]_{\overline{even}} + -[CH_2]_{\overline{even}} \rightleftharpoons -[CH_2]_{\overline{even}}[CH_2]_{\overline{even}} \qquad \text{Low A factor}$$

$$-[CH_2]_{\overline{odd}} + -[CH_2]_{\overline{even}} \rightleftharpoons -[CH_2]_{\overline{odd}}[CH_2]_{\overline{even}} \qquad \text{Higher A factor}$$

$$-[CH_2]_{\overline{odd}} + -[CH_2]_{\overline{odd}} \rightleftharpoons -[CH_2]_{\overline{odd}}[CH_2]_{\overline{odd}} \qquad \text{Higher A factor}$$

CONCLUSION

The simple kinetic treatment of these ester-ester exchange reactions to equilibrium assumes that reactant polymers are compatible, the integrity of homogeneity in a polymer blend is maintained during the reaction, reactivity of ester linkages along a polymer chain are equivalent and independent of chain length, exchange reactions are random, only one reaction along a polymer chain is permitted at any one time, and only those reactions leading to the formation of products are important.

Because of the complexity of these reaction systems, formation of the desired activated complex which leads to the formation of products is generally accompanied by a large decrease in entropy. It follows, therefore, that the frequency factor will increase or decrease accordingly, and would reflect the trends in kinetic behavior.

As these ester-ester exchange reactions involve the simultaneous making and breaking of alkoxide bonds, it was formally believed that by increasing the size of the glycol residues linearly, a corresponding decrease in reaction rate would be observed. However, the observed trend suggests that the overall reaction rate is related to the glycol methylene ratios of the reactants in the manner described, while linear displacement of carbonyl groups along the polymer chain imparts very little, if any, influence on the overall reaction rate. Of course, the even and odd numbers of methylene groups on the glycol moiety would dictate the microtacticity of the carbonyl oxygens, thereby facilitating the formation of a reaction intermediate which should satisfy the simultaneous making and breaking of alkoxide bonds in the absence of catalysts and solvents.

It is anticipated that the observed trends in kinetic behavior would foster a better understanding of transesterification reaction in multifunctional systems and aid in the formulation of better-defined products.

The influence of stereochemical structure on the rates of these reactions is to be published elsewhere.

ACKNOWLEDGMENT

Discussions with and comments by Dr R. D. Sedgwick (U.M.I.S.T., Manchester, England) are greatly appreciated.

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Accepted by editor April 5, 1982
Received for publication May 3, 1982