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The Influence of Stereochemical Structure on the Kinetics and Mechanism of Ester-Ester Exchange Reactions by Mass Spectrometry. II

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ABSTRACT

Exter-ester exchange reactions in polyesters, formulated from adipic acid and various linear and branched glycols, were studied by mass spectrometry employing the Dimer Analysis Method (DAM). Activation energies (E) and frequency factors (A) were obtained for the reaction systems at temperatures of 572-585 K. The kinetic behavior of these reactions was influenced by the stereochemical structures of carbonyl oxygens along the polymer chain backbone. Syndiotactic/syndiotactic systems reacted slower than syndiotactic/heterotactic and heterotactic/heterotactic systems, respectively. Correlation of frequency factors (A) and stereochemical structures showed an alternating trend in kinetic behavior. An "associative reaction mechanism" was postulated since it satisfied the energetic and geometric requirements necessary for the simultaneous making and breaking of alkoxide bonds, and also gives a good fit to the kinetic expression derived for an opposing bimolecular reaction.

INTRODUCTION

Previously described trends in kinetic behavior during ester-ester exchange reactions between polyesters derived from adipic acid and various linear and branched glycols facilitated a correlation of frequency factors (A) and activation energies (E) with corresponding glycol methylene ratios [1, 2]. Reaction systems containing even and odd numbers of methylene groups along the polymer chain backbone exhibited alternating kinetic behavior. This trend was observed for linear reaction systems in which polyethylene adipate was maintained as the standard reactant and also for other reaction systems such as polytrimethylene adipate/polypentamethylene adipate and polytetramethylene adipate/polyhexamethylene adipate. Ignoring the influence of pendant groups and designating all carbon atoms within a glycol moiety along the polymer chain as methylene groups, it was demonstrated that branched reaction systems such as polypropylene adipate/polyethylene adipate and polyethylene adipate/polyneopentylene adipate also followed an alternating trend in kinetic behavior [2]. Such a trend seems to suggest that the overall reaction rate and the dominant ester-ester exchange reaction mechanism is dictated by the stereochemical structure of the carbonyl oxygens in the respective reactants and products. Indeed, the microtacticity of functional groups has been found to influence the rates of hydrolysis of methyl acrylate methacrylic acid copolymers, where isotactic polymers reacted faster than syndiotactic and atactic polymers, respectively [3-5].

Even in the presence of ester exchange catalysts such as arsenic pentoxide, the rates of ester-ester exchange reactions are influenced by steric factors [6]. Polyesters with sterically hindered carbonyl groups randomized less readily and reacted preferentially at the end-groups to give block copolymers. In the absence of catalysts and solvents and at elevated temperatures, ester-ester exchange reactions may be autocatalyzed by gamma hydrogens on the glycol moiety [7], or by thermal degradation products within the reaction system [8]. These autocatalytic reactions would undoubtedly exhibit complex reaction kinetics akin to the complex kinetics observed for polyesters containing free hydroxyl groups.

The present work provides an insight into the intramolecular participation of functional groups along a polyester chain and examines the influence of stereochemical structures on the rates and mechanism of ester-ester exchange reactions in multifunctional reactants. A distinction is therefore drawn between reactions taking place at monofunctional sites and those in which neighboring functional groups participate in maintaining the integrity of stereochemical structure of the reacting carbonyl groups.

Reactions taking place at monofunctional sites involve the formation of cyclic intermediates through hydrogen bonding of gamma hydrogens. These intermediates then break down to give acylium ions, carboxyl functionalities, and hydroxyl functionalities (autocatalytic mechanism)

which can readily propagate transesterification reactions. On the other hand, neighboring group participation enables the atactic, syndiotactic, and heterotactic conformations of the carbonyl groups to predominate, leading to the formation of association complexes [9, 10]. The simultaneous breaking and making of alkoxide bonds then lead to ester-ester exchange products. Correlation of kinetic parameters and stereochemical structure prompted the postulation of an "associative reaction mechanism."

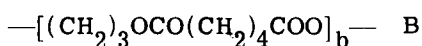
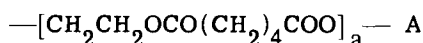
Reaction systems studied were polyethylene adipate/polytrimethylene adipate, polyethylene adipate/polytetramethylene adipate, polyethylene adipate/polypentamethylene adipate, polyethylene adipate/polyhexamethylene adipate, polyethylene adipate/polypropylene adipate, polyethylene adipate/polyneopentylene adipate, polytetramethylene adipate/polyhexamethylene adipate, and polytrimethylene adipate/polypentamethylene adipate.

Theory

The average number of ester linkages, defined as the carbonyl equivalent "C," is a function of the degree of polymerization \bar{P} . Thus, for binary reaction system (A + B) in which ester-ester exchange is the dominant reaction process, maximum randomization can only be attained when $C = 1$. Therefore, the precondition for experimental design must be such that $\bar{P}_A/\bar{P}_B = C = 1$ in the homopolymers before reaction. If \bar{P}_A is not equal to \bar{P}_B initially, then C would be less than 1 and would change during randomization. Indeed, variations in carbonyl equivalent are related to \bar{P} in the following way:

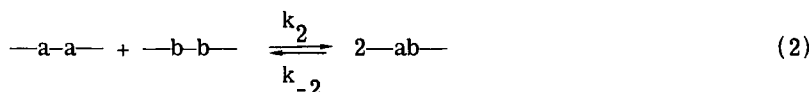
$$\frac{\bar{M}_A/m_a}{\bar{M}_B/m_b} = \frac{m_a \bar{P}_A}{m_b \bar{P}_B} \quad (1)$$

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



Kinetic Expression

In deriving the kinetic expression for an opposing bimolecular reaction, it was assumed that maximum randomization is attained when the statistical distribution of structural units are in the ratio of aa:bb:2ab as 1:1:2. Accordingly, the stoichiometric Eq. (1) was defined.



$$(\alpha - x) \quad (\alpha - x) \quad 2x \quad (3)$$

where

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

at infinite time, x approaches an equilibrium value x_e ,

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

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

Integration by partial fraction give the expression

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

At equilibrium, $\alpha = 2x_e$. Then substituting for x_e in Eq. (7) gives the final expression

$$t = \frac{1}{k_{-2}\alpha} \log \left[\frac{\alpha}{\alpha - 2x} \right] \quad (8)$$

Rate constants were obtained from graphs of $1/\alpha \log \left(\frac{\alpha}{\alpha - x} \right)$ as a function of time [1, 2], while activation energies (E) and frequency factors ($\log A$) were determined from graphs of $\log k_{-2}$ against $10^3 K/T$ as required by the Arrhenius equation:

$$k_{-2} = A e^{-E_a/RT} \quad (9)$$

EXPERIMENTAL SECTION

Instrumentation

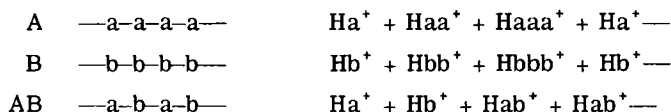
The AEI MS902 mass spectrometer, Dupont-950 Thermogravimetric Analyzer, and a Pye 104 gas chromatograph were employed in this study. A secondary oven was constructed within the main oven of the gas chromatograph to accommodate the glass reactor and to enable sampling of the reaction mixture without causing temperature variations.

Polyester Synthesis

Polyesters were made 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 temperature of the reaction system 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 was allowed to cool to room temperature under a nitrogen atmosphere. Molecular weights (2000-3000) were determined by endgroup analysis. Terminal hydroxyl groups were esterified by reacting two equivalents of acetic acid with the polyesters at 120°C for 2 h. Excess acid and water were removed at 150°C under vacuum. Thermal stability was measured by TGA using the Dupont 950 Thermogravimetric Analyzer.

Mass Spectrometry

When polyesters such as polyethylene adipate (A), polytrimethylene adipate (B), and the exchanged product AB are subjected to electron ionization in the mass spectrometer, they readily undergo McLafferty's rearrangement to give ionic species which are characteristic of their repeat units, namely:



Thus, during ester-ester exchange reactions, changes in concentration of reactants and products was followed by measuring the ion currents of the respective dimer units: Haa^+ , Hbb^+ , Hab^+ (Table 1). It was

TABLE 1. Dimer Units Monitored by Mass Spectrometry during Ester-Ester Exchange Reactions in the Reaction Systems (a-h)

Reaction systems	Ions monitored (m/z)		
	aa	ab	bb
a. Polyethylene/polytrimethylene adipate	345	359	373
b. Polyethylene/polytetramethylene adipate	345	373	401
c. Polyethylene/polypentamethylene adipate	345	387	429
d. Polyethylene/polyhexamethylene adipate	345	401	457
e. Polyethylene/polypropylene adipate	345	359	373
f. Polyethylene/polyneopentylene adipate	345	387	429
g. Polytetramethylene/polyhexamethylene adipate	401	429	457
h. Polytrimethylene/polypentamethylene adipate	373	401	429

assumed that the ion currents of the different dimer units are proportional to the concentrations of A, B, and AB, respectively. Relative sensitivity coefficients were introduced to compensate for activity coefficients and other parameters which influence their sensitivity to ionization (dimer analysis method) [1, 2].

Procedure

The glass reaction vessel, which was continuously purged with dry nitrogen gas, was equilibrated to the required reaction temperature. About 1.5 g of equivalent amounts of reactant polyesters, previously homogenized by melt blending at 80°C, was transferred to the reactor and allowed to react. Samples were withdrawn at selected time intervals during the reaction and analyzed by mass spectrometry. Changes in the concentrations of reactants and products were measured from the ion currents of the respective dimer units (Table 1). The mass spectrometer source temperature was maintained at 200°C, ionization energy 60 eV, and resolution 2000. These conditions were maintained throughout the study.

RESULTS AND DISCUSSION

Stereochemical Structure of Carbonyl Oxygens

The influence of stereochemical structure on the reaction mechanism and rates of ester-ester exchange reactions necessitates the intramolecular participation of functional groups along the polymer chain, whereby the microtacticity of carbonyl oxygens could be defined. For the reactants polyethylene adipate (A), polytrimethylene adipate (B), and the equilibrium product (AB), containing even and odd numbers of methylene groups, the microtacticity of carbonyl oxygens will be syndiotactic (syn), heterotactic (h), and atactic (a), respectively (Fig. 1). When the reacting carbonyl group is flanked between two neighboring groups, as illustrated in the triads S and H, respectively (Fig. 1), its steric configuration will be maintained through the participation of neighboring functional groups. Consequently, when reactant molecules approach each other, the extent to which neighboring carbonyl groups participate in hindering or promoting the accessibility of an external reagent to the reaction site would be dictated by the methylene content of the glycol moiety and microtacticity of the carbonyl oxygens. Accordingly, these reaction systems being investigated can be ordered

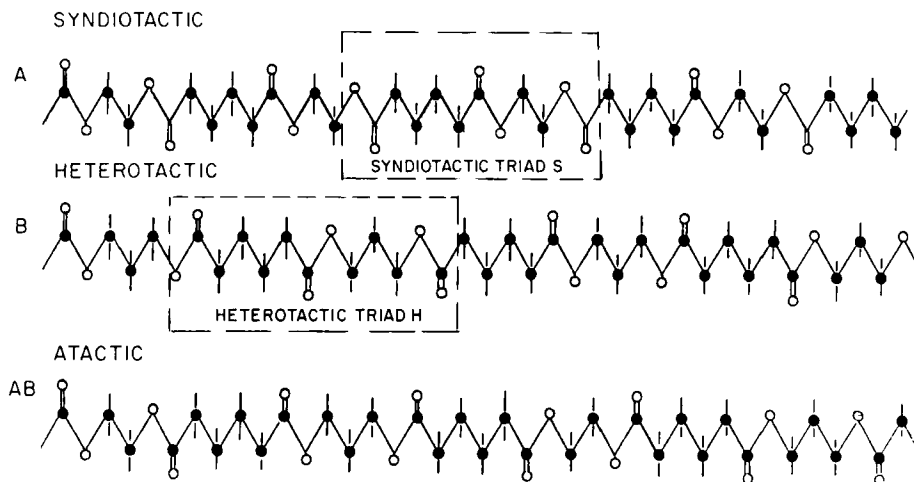
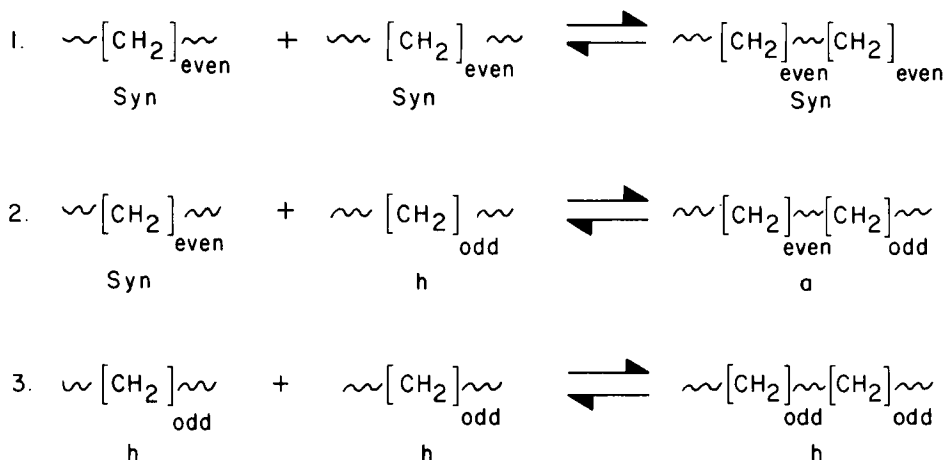


FIG. 1. Microtacticity of carbonyl oxygens in polyesters containing even and odd numbers of methylene groups in their respective glycol residues: (○) oxygen; (●) carbon.



SCHEME 1. Ordering of reaction systems according to the micro-tacticity of carbonyl oxygens. Pendant groups are ignored and all carbon atoms along the polymer chain are designated methylene groups: syn = syndiotactic; h = heterotactic, a = atactic.

into three groups (Scheme 1). Such a classification requires that the influence of pendant groups in branched reaction systems be ignored and carbon atoms along the polymer chain which constitute the glycol moiety be designated methylene groups [2]. The results, tabulated in Table 2, shows that Group 1 reaction systems exhibit frequency factors which are lower than those observed for Groups 2 and 3, respectively, indicating that microtacticity dictates the observed alternating trend in kinetic behavior (Fig. 2). In addition to stereochemical structures, linear displacement of carbonyl groups and branching of the glycol moiety would also influence the overall kinetic behavior of these reactions while maintaining the integrity of stereochemical structures. Correlation of linear displacement of ester linkages and frequency factors ($\log A$) for the reaction systems a-d (Table 2) affords the alternating trend illustrated in Fig. 2. The anticipated linear reduction in reaction rate is not apparent and it is inferred that the dominant parameter influencing the ester-ester exchange processes is the stereochemical structure of the carbonyl oxygen.

Steric crowding of the reaction site, attributed to branching of the glycol moiety, has the effect of lowering the reaction rate to an appreciable extent. For instance, the polyethylene adipate/polyneopentylene adipate reaction system gives a frequency factor ($\log A$) of 4.60 which is much lower than the value observed (6.22) for the analogous polyethylene adipate/polytrimethylene adipate reaction system. In spite of a reduction in steric crowding, polyethylene adipate/polypropylene adipate gives a frequency factor ($\log A$) of 3.72 which is lower than

TABLE 2. Molar Activation Energies, Frequency Factors, and Microtacticity of Carbonyl Oxygens for Ester-Ester Exchange Reactions between Reactants A and B

Reactant A	Mt _A ^a	Reactant B	Mt _B ^a	Frequency factor log A	Molar activation energy kJ/mol
a. Polyethylene adipate	syn	Polytrimethylene adipate	h	6.22	139.15
b. Polyethylene adipate	syn	Polytetramethylene adipate	syn	3.36	114.55
c. Polyethylene adipate	syn	Polypentamethylene adipate	h	6.38	141.46
d. Polyethylene adipate	syn	Polyhexamethylene adipate	syn	4.41	127.04
e. Polyethylene adipate	syn	Polypropylene adipate	syn	3.72	119.74
f. Polyethylene adipate	syn	Polyneopentylene adipate	h	4.60	129.16
g. Polytetramethylene	syn	Polyhexamethylene adipate	syn	3.68	112.24
h. Polytrimethylene adipate	h	Polypentamethylene adipate	h	6.70	145.11

^aMt_A, Mt_B are the microtacticities of carbonyl oxygens. syn = syndiotactic. h = heterotactic.

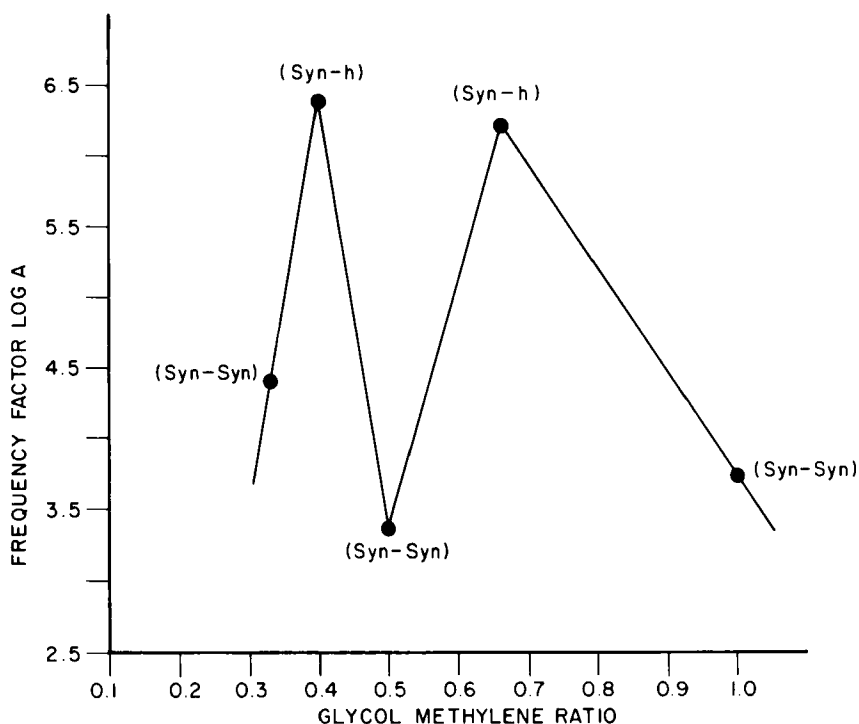


FIG. 2. Graph of frequency factor ($\log A$) as a function of glycol methylene ratio for syn-syn, and syn-h reaction systems: syn = syndiotactic; h = heterotactic.

that observed for polyethylene adipate/polyneopentylene adipate. This is supportive of the stereochemical influence on these reaction systems. It is noteworthy that the propylene glycol residue is further complicated by the inherent primary and secondary functionalities which would also contribute to the overall reaction processes.

Reaction systems a-f (Table 2), which constitute polyethylene adipate as the standard reactant, serve to demonstrate the influence of stereochemical structure on the ester-ester exchange reaction (Fig. 2). Similar trends are also observed when the reactants are modified (Table 2: g, h). Indeed, the syn-syn reaction system (g) exhibits lower frequency factor while the h-h system (h) gives a frequency factor which is similar to that observed for syn-h reaction systems.

Reaction Mechanism

The inherently low equilibrium constants apparent in esterification reactions would limit the formation of high molecular weight products unless by-products such as water and alcohol are progressively removed during the reaction. Experimental conditions commonly employed invariably involve the use of various acids, bases, and metal salts as catalysts. Under these conditions, the esterification reaction process is accompanied by competing reactions such as alcoholysis, acidolysis, and ester-ester exchange; consequently, the kinetics and mechanism of such reactions would be complex.

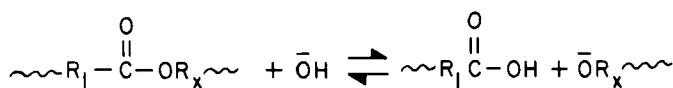
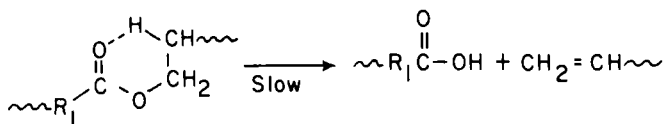
In the absence of catalysts and solvents and at elevated temperatures, blends of different polyesters would undergo ester-ester exchange reactions to give random copolymers, whereby the fundamental exchange process would involve the making and breaking of alkoxide bonds in a manner different from the usual esterification reactions.

Ester-ester exchange reactions may follow either an "autocatalytic" or an "associative reaction mechanism" when carried out in the absence of catalysts and solvents and at elevated temperatures. Autocatalyzed reactions may be promoted by hydrogen bonding [7] or by thermal degradation products within the reaction system [8]. The presence of gamma hydrogens on the glycol moiety would involve the formation of a cyclic intermediate which then dissociates to give reactive carbonyl endgroups, hydroxyl ions, and acylium ions (Scheme 2). Ester-ester exchange reactions are then propagated by nucleophilic substitution at the ester linkages along the polymer chain. The autocatalytic reaction mechanism, however, does not fit the simple kinetic scheme described [1, 2]; it is akin to the complex kinetics observed for polyesters containing free hydroxyl groups.

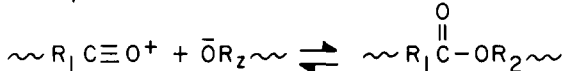
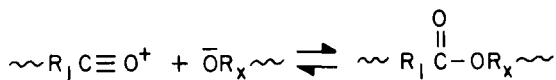
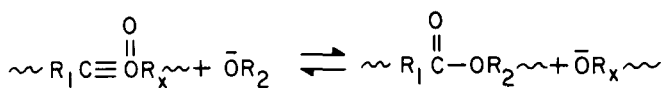
Since the observed trend in kinetic behavior is a fundamental consequence of the stereochemical structure of carbonyl oxygens along the polymer chain and the assumed equilibrium constant is independent of temperature [1, 2], the postulation of an "associative reaction mechanism" (Scheme 3) would seem plausible. Such a mechanism necessitates the formation of an association complex which would not only satisfy the energetic and geometric requirements necessary for the simultaneous breaking and making of alkoxide bonds, but also give a good fit to the kinetic expression derived for an opposing bimolecular reaction.

The principle of association complex formation [9, 10] requires that carbonyl oxygens must be of different steric configurations in order to promote complex formation. Thus, when two different polyester chains are brought together in the molten state (Fig. 3), although the number of coincidences between ester linkages may be large, asso-

INITIATION :



PROPAGATION :

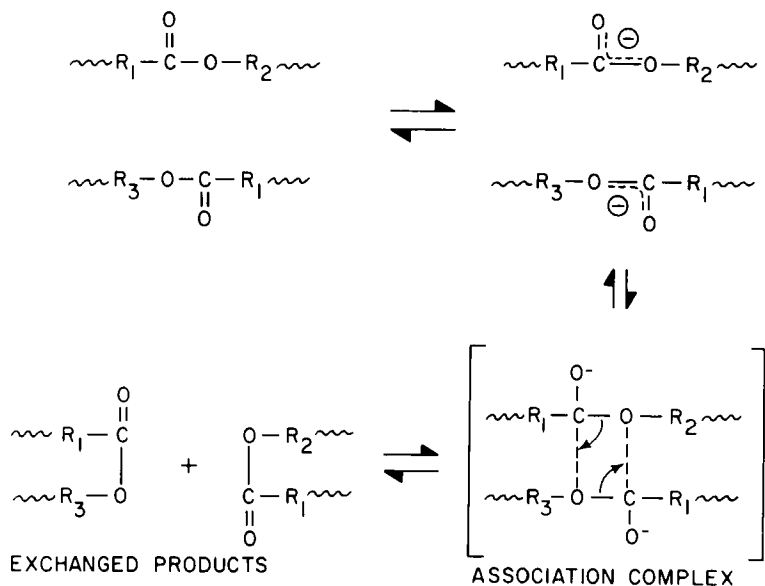


SCHEME 2. Autocatalytic reaction mechanism for ester-ester exchange between two polyesters in the absence of catalysts and solvents: R_1 = acid residue; R_2 and R_x = glycol residues.

ciation complex formation will only be possible when the geometric requirements are satisfied. It is conceivable, therefore, that structural arrangements b and d (Fig. 3), which are derived from syn-h and h-h reaction systems, will readily form association complexes. On the other hand, structural arrangements such as a, c, e, and f (Fig. 3) will have to overcome the conformational internal energies in order to form complexes. This is consistent with the observed alternating trend in kinetic behavior (Fig. 2).

Conclusion

To attain complete randomization of structural units during ester-ester exchange reactions, the preconditions for experimental design



SCHEME 3. Associative reaction mechanism for ester-ester exchange reactions between two polyesters in the absence of catalysts and solvents. R_1 = acid residue; R_2 and R_3 = glycol residues.

are that reactant polyesters must be compatible, and the ratio of carbonyl groups should be unity in the homopolymers before reaction ($\bar{P}_A/\bar{P}_B = C = 1$). In addition, the simple kinetic treatment of ester-ester exchange reactions in the absence of catalysts and solvents assumes that the stereochemical structure of carbonyl oxygens along a polymer chain are dictated by the methylene content of the glycol residue, stereochemical structures of reactant polymer chains must be different in order to form association complexes, the integrity of homogeneity in polymer blends is maintained during the reaction, reactivity of ester linkages along a polymer chain are equivalent and independent of chain length; ester-ester exchange reactions are random, only one reaction along a polymer chain is permitted at any time, and only reactions leading to the formation of products are important.

Stereochemical structure of carbonyl oxygens in multifunctional reaction systems exerts the major influence on the dominant mechanism and overall rates of ester-ester exchange reactions. It is therefore inferred that stereochemical structures of carbonyl oxygens

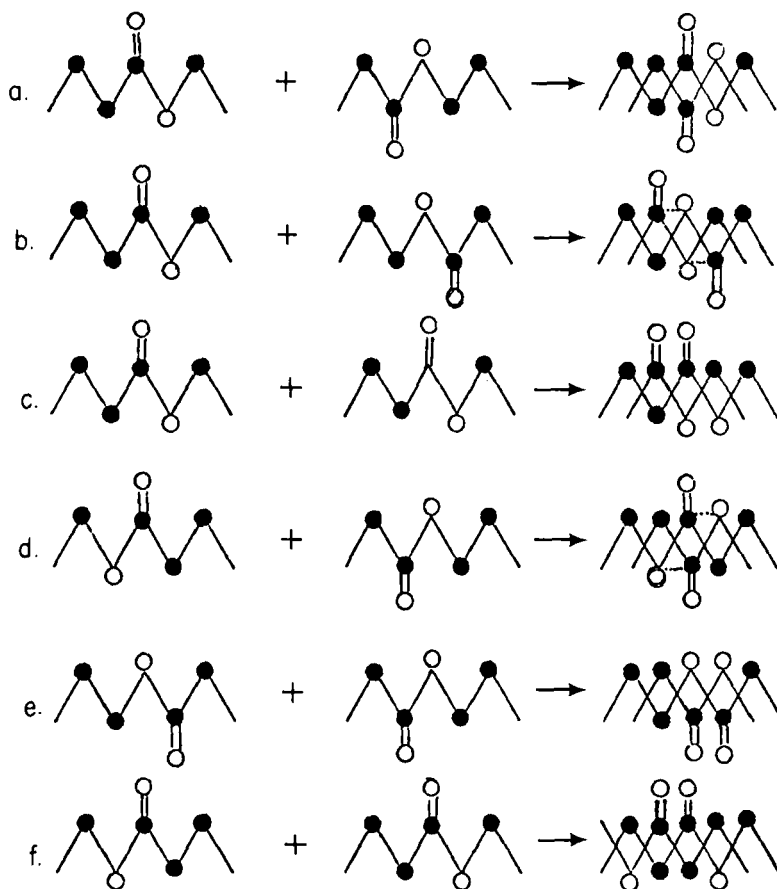


FIG. 3. Illustration of structural arrangements of reactant carbonyl groups in the formation of association complexes: (o) oxygen; (•) carbon.

along a polymer chain are good indicators of polymer compatibility and may be used as an arbitrary guide to product design in systems where solvents and catalysts are not employed.

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