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Ester-Ester Exchange Reactions of Aliphatic Polyesters

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ABSTRACT

The kinetics of ester-ester exchange reactions of poly(ethylene adipate) and poly(trimethylene adipate) at 312°C and in the absence of a solvent and catalysts has been reported previously. Independent investigations of the thermal degradation reactions of these polyesters under high vacuum have shown that pyrolysis already starts above 270°C. An ester-ester exchange mechanism via a reversible thermal degradation reaction is proposed.

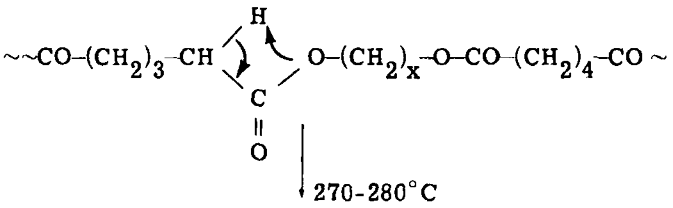
INTRODUCTION

The kinetics of ester-ester exchange reactions of poly(ethylene adipate) $(A)_n$ and poly(trimethylene adipate) $(B)_n$ was reported by Ramjit and Sedgwick [1]. These authors heated physical mixtures of these polyesters in the absence of catalysts and a solvent at 299-312°C and used mass spectrometry to follow the increase of AB units (m/e 359) and the decrease of AA (m/e 345) and BB units (m/e 373) in the polymers. They presumed the thermal stability of these polyesters in the range of 300-400°C and calculated the rate constants of the ester-ester exchange reaction and the corresponding Arrhenius parameters from the mass spectral data.

RESULTS AND DISCUSSION

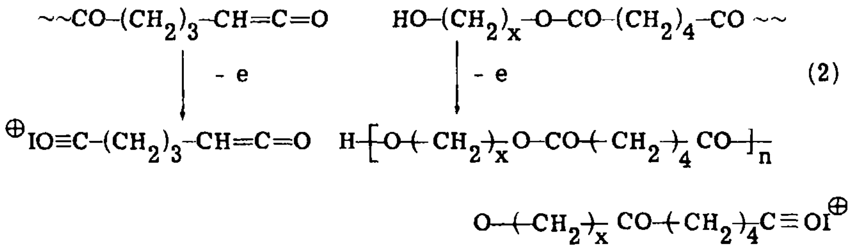
The thermal degradation reactions of poly(ethylene adipate), poly(trimethylene adipate) [2], and other aliphatic polyesters [3-5] by direct pyrolysis in a mass spectrometer have been previously described. In contrast to the assumption of Ramjit and Sedgwick [1], these polyesters decompose thermally at 280°C [$(A)_n$] and 270°C [$(B)_n$], and degradation rates of 0.5-1.0%/min (% loss of polymer/min) have been approximated about the total ion current. The pyrolysis mass spectra of poly(ethylene adipate) and poly(trimethylene adipate) are shown in Fig. 1, and the favored thermal degradation reaction at these conditions (high vacuum) is the cleavage of the ester bond [Eq. (1)].

The subsequent electron impact-induced fragmentation of the pyrolysis products yields mainly carboxonium ions with a thermally formed ketene and hydroxyl end group [Eq. (2)].



$$\sim\sim CO-(CH_2)_3-\underset{\underset{O}{\overset{\|}{C}}}{CH}\overset{H}{}O-(CH_2)_x-O-CO-(CH_2)_4-CO\sim \quad \xrightarrow{270-280^\circ C}$$

(1)



$$\sim\sim CO-(CH_2)_3-CH=C=O \qquad HO-(CH_2)_x-O-CO-(CH_2)_4-CO\sim\sim$$

$$\downarrow -e \qquad\qquad \downarrow -e$$

$$^{\oplus}IO\equiv C-(CH_2)_3-CH=C=O \qquad H-\!\!\left[O-(CH_2)_x-O-CO-(CH_2)_4-CO\right]_n$$

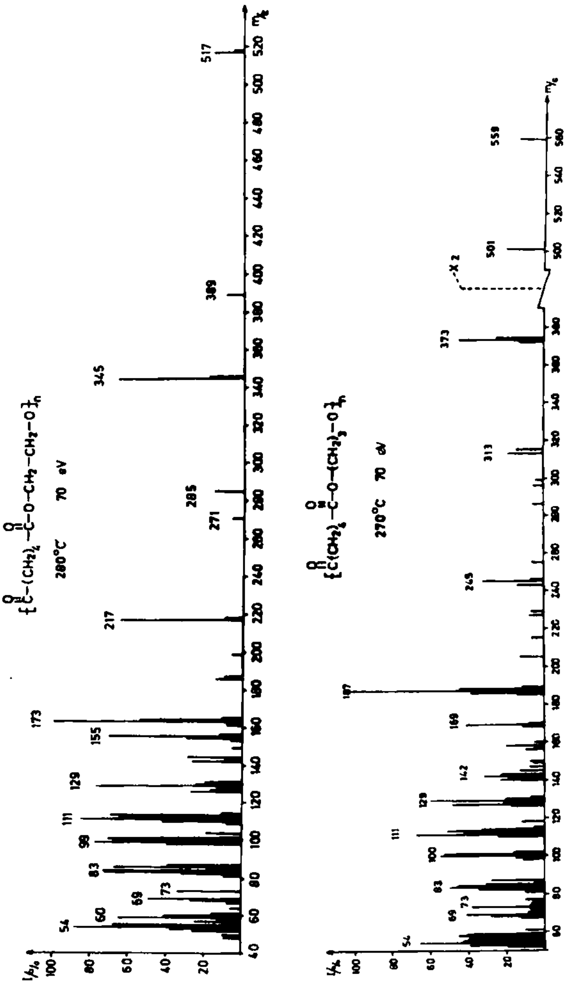
$$O-(CH_2)_x\,CO-(CH_2)_4C\equiv OI^{\oplus}$$

(2)

m/e 111 m/e(n)

x = 2: 173(0) 345(1) 517(2)

x = 3: 187(0) 373(1) 559(2)



$\{\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}-O-CH_2-CH_2-O\}_n$

$\{\overset{O}{\overset{\|}{C}}(CH_2)_4-\overset{O}{\overset{\|}{C}}-O-(CH_2)_3-O\}_n$

FIG1. Pyrolysis-mass spectra of poly(ethylene adipate) and poly(trimethylene adipate).

Qualitative pyrolysis experiments of poly(ethylene adipate) and poly(trimethylene adipate) at reduced (~ 20 Torr) or normal pressure (under nitrogen) show a decomposition rate which is less than one tenth that in high vacuum (10^{-6} Torr). In addition, corresponding experiments with polycaprolactone at 220°C indicate that at a pressure of 80 Torr a decomposition rate of 0.05 %/min and the favored formation of monomeric caprolactone is found [6], whereas at the same temperature in high vacuum, pyrolysis proceeds at a rate of ~ 1 %/min via the cleavage of the ester bond into ketene and hydroxyl end groups [3]. To explain this difference in behavior, it might be supposed that the thermal cleavage of the ester bond is an equilibrium reaction, of which degradation products with the reactive ketene and hydroxyl end groups can only be separated in high vacuum [Eq. (3)].

$$\sim\sim CO-(CH_2)_4-CO-O-(CH_2)_x-O\sim \xrightleftharpoons{\Delta}$$

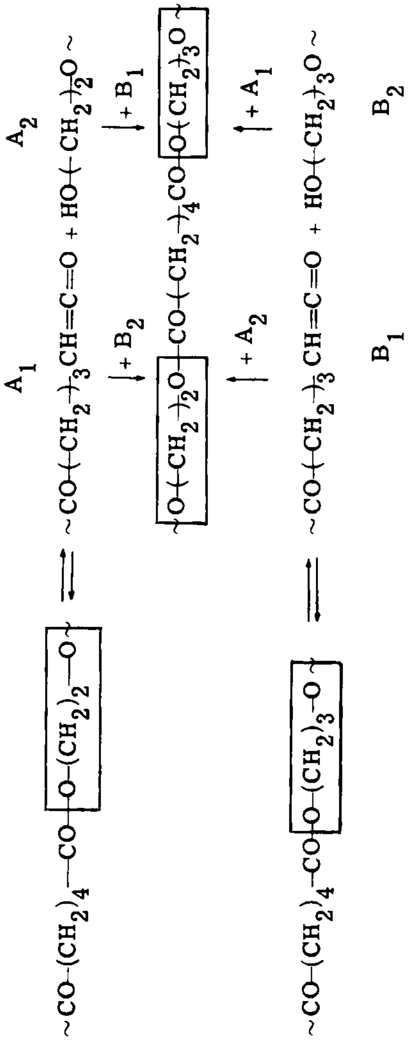
$$R-CO(-CH_2-)_3CH=C=O + HO(-CH_2-)_xO-R' \qquad (3)$$

$$\downarrow \text{high vacuum} \downarrow$$

Consequently, if the cleavage of the ester bond during thermal decomposition of poly(ethylene adipate) and poly(trimethylene adipate) in high vacuum is even observed at 270-280°C, an ester-ester exchange reaction at 312°C may be imaginable by the cleavage of the polyesters $(A)_n$ and $(B)_n$, corresponding to Eqs. (4) and (6) and an intramolecular back reaction [Eq. (5)].

EXPERIMENTAL

The experimental data of the pyrolysis-mass spectrometry of poly(ethylene adipate) and poly(trimethylene adipate) have been reported elsewhere [2]. The polyesters were prepared from the dimethyl ester of adipic acid and glycol and propanediol [7]. Molecular weights of approximately 12,000 were determined by the viscometric method.


~CO–(CH₂)₄–CO–O–(CH₂)₂–O~
~CO–(CH₂)₃CH=C=O + HO–(CH₂)₂–O~
A1
A2
+ B2
+ B1
~O–(CH₂)₂–O–CO–(CH₂)₄–CO–O–(CH₂)₃–O~
+ A2
+ A1
~CO–(CH₂)₄–CO–O–(CH₂)₃–O~
~CO–(CH₂)₃CH=C=O + HO–(CH₂)₃–O~
B1
B2

(4)

(5)

(6)

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