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Kinetics of Polycondensation and Copolycondensation by Ester-Interchange Reactions

Man Jung Han

Department of Chemical Engineering, Ajou Institute of Technology, Suweon, 170 South Korea. Received September 28, 1979

ABSTRACT: The kinetics of polycondensation and copolycondensation by ester-interchange reactions were investigated by using 2-hydroxyethyl terephthalate and 2-hydroxy-*n*-propyl terephthalate as monomers. It was found that the polycondensation of diol esters of dibasic acids followed second-order kinetics with respect to the concentrations of hydroxyl and ester groups in the monomers. New equations for calculation of the rate constants of cross reactions and of the composition ratios in the copolymer were derived. The reactivity ratios of the copolycondensations and the azeotropic composition were calculated on the basis of the rate constants. The composition diagram of the copolycondensation was obtained.

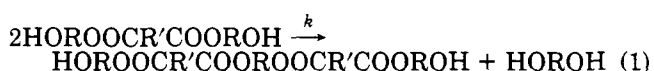
Hydroxyl-terminated aliphatic polyesters are important materials in the production of the polyurethane used in several fields as a thermoplastic elastomer. As is well-known, the polyester segments build the soft blocks in the polyurethane and the variation of the polyester composition changes the physical properties of the polyurethane. The variables in the polyester composition are the dibasic acids (succinic, glutaric, adipic, azelaic acids) and the diols (ethanediol, 1,2-propanediol, 1,4-butanediol, 1,6-hexanediol).

The urethane polymer formation is most easily controlled when the polyester contains only hydroxyl groups as reactive sites. Hence the preferred polyesters have been those with very low acid end groups and very low water content. In order to minimize the acid end groups and water content, laboratory and industrial syntheses have often involved ester-interchange reactions of the diol esters of dibasic acids.

Unlike polyesterification reactions of dibasic acids and diols, which have been studied in many laboratories,¹⁻⁵ studies on polycondensation of diol esters of dibasic acids by ester-interchange reactions are scarce. In this paper we report the kinetics of the polycondensation and copolycondensation of diol esters or dibasic acids by ester-interchange reactions.

Kinetics

Polycondensation. The polycondensation of the diol ester of a dibasic acid can be expressed generally as



If the concentration of the hydroxyl group is [OH] and the concentration of the ester group is [COO] and if the diols formed during the reaction are continuously removed and no catalyst is used, the kinetics of the polycondensation can be written as

$$-d[\text{OH}]/dt = k[\text{OH}][\text{COO}] \quad (2)$$

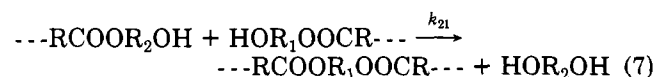
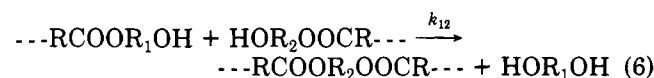
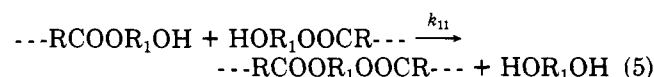
At the initial stage of the polycondensation the concentrations of hydroxyl and ester groups are equal; we obtain therefore second-order kinetics

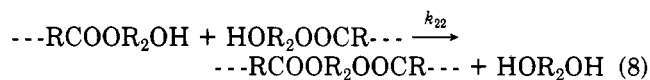
$$-d[\text{OH}]/dt = k[\text{OH}]^2 \quad (3)$$

Rearrangement and integration of the equation gives eq 4. A plot of $1/[\text{OH}]$ vs. time yields the rate constant of the polycondensation.

$$1/[\text{OH}] = kt + C \quad (4)$$

Copolycondensation. The copolycondensation of two different diol esters of dibasic acids for conditions where the hydroxyl group of the second chain end attacks the ester group of the first chain end can be written as the sequence of reactions in eq 5-8. Reactions 6 and 7 are





cross reactions, whereas reactions 5 and 8 are homoreactions in general terms. Expressing the concentrations of the hydroxyl and ester groups in chain end 1 as $[\text{OH}]_1$ and $[\text{COO}]_1$ and those of chain end 2 as $[\text{OH}]_2$ and $[\text{COO}]_2$, the formation rates of the diols (HOR_1OH and HOR_2OH) become

$$\frac{d[\text{HOR}_1\text{OH}]}{dt} = k_{11}[\text{COO}]_1[\text{OH}]_1 + k_{12}[\text{COO}]_1[\text{OH}]_2 \quad (9)$$

$$\frac{d[\text{HOR}_2\text{OH}]}{dt} = k_{21}[\text{COO}]_2[\text{OH}]_1 + k_{22}[\text{COO}]_2[\text{OH}]_2 \quad (10)$$

Hence eq 11 can be derived by dividing eq 9 by eq 10

$$\frac{d[\text{HOR}_1\text{OH}]}{d[\text{HOR}_2\text{OH}]} = \frac{k_{11}[\text{COO}]_1[\text{OH}]_1 + k_{12}[\text{COO}]_1[\text{OH}]_2}{k_{21}[\text{COO}]_2[\text{OH}]_1 + k_{22}[\text{COO}]_2[\text{OH}]_2} \quad (11)$$

Rearranging and dividing the right term of eq 11 by $[\text{OH}]_2$, we obtain eq 12. Starting the copolycondensation with

$$\frac{d[\text{HOR}_1\text{OH}]}{d[\text{HOR}_2\text{OH}]} = \frac{[\text{COO}]_1}{[\text{COO}]_2} \frac{k_{11}[\text{OH}]_1/[\text{OH}]_2 + k_{12}}{k_{21}[\text{OH}]_1/[\text{OH}]_2 + k_{22}} \quad (12)$$

monomers, structurally $\text{HOR}_1\text{OOCR}\text{COOR}_1\text{OH}$ ([monomer]₁) and $\text{HOR}_2\text{OOCR}\text{COOR}_2\text{OH}$ ([monomer]₂), in general, the following conditions are satisfied at the initial stage:

$$\frac{[\text{monomer}]_1}{[\text{monomer}]_2} = \frac{[\text{OH}]_1}{[\text{OH}]_2} = \frac{[\text{COO}]_1}{[\text{COO}]_2} \quad (13)$$

Replacing the ratio of diols formed during the reaction with b and the ratio of monomers at the onset of the copolycondensation with a

$$\begin{aligned} b &= d[\text{HOR}_1\text{OH}]/d[\text{HOR}_2\text{OH}] \\ a &= [\text{monomer}]_1/[\text{monomer}]_2 \end{aligned} \quad (14)$$

and subsequently simplifying eq 12, eq 15 and eq 16 can be derived. Equation 16 is valid for the initial stage of

$$b = a \frac{ak_{11} + k_{12}}{ak_{21} + k_{22}} \quad (15)$$

$$ak_{11} - \frac{b}{a}k_{22} = bk_{21} - k_{12} \quad (16)$$

the copolycondensation because it was derived by replacing with eq 13. The rate constants of homopolycondensations, k_{11} and k_{22} , can be obtained from eq 4. If the left term of eq 16 is plotted as a function of b , the rate constants of the cross reactions, k_{21} and k_{12} , can be obtained from the slope and the intercept of the plot, respectively. Since the four rate constants of the copolycondensation are known, the reactivity ratios can be calculated.

The diol components incorporated in the copolyester by homocondensation and cross condensation are given by eq 17 and 18. Employing a method similar to the derivation

$$-\frac{d[-\text{OR}_1\text{O-}]}{dt} = k_{21}[\text{COO}]_2[\text{OH}]_1 + k_{11}[\text{COO}]_1[\text{OH}]_1 \quad (17)$$

$$-\frac{d[-\text{OR}_2\text{O-}]}{dt} = k_{12}[\text{COO}]_1[\text{OH}]_2 + k_{22}[\text{COO}]_2[\text{OH}]_2 \quad (18)$$

of eq 15 and setting diol ratios in the copolyester as c , where

$$c = d[-\text{OR}_1\text{O-}]/d[-\text{OR}_2\text{O-}] \quad (19)$$

we obtain

$$c = a \frac{k_{21} + ak_{11}}{ak_{12} + k_{22}} \quad (20)$$

Equation 20, contrary to the eq 15, is the mole ratio of diols which are incorporated in the copolyester by the condensation reaction. The copolymer composition diagram can be constructed by calculating the ratios of diols in the polymer, c , at given ratios of monomers, a .

The azeotropic monomer ratio can be calculated with the rate constants according to eq 21, since a is equal to c at the azeotrope.

$$a = c = (k_{21} - k_{22})/(k_{12} - k_{11}) \quad (21)$$

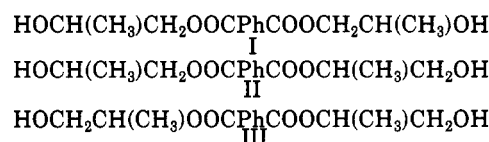
In this investigation, 2-hydroxyethyl terephthalate (HET) and 2-hydroxy-*n*-propyl terephthalate (HPT) are chosen as monomers 1 and 2, respectively.

Experimental Section

Synthesis of Monomers. 2-Hydroxyethyl Terephthalate (HET). Dimethyl terephthalate was recrystallized from methanol (mp 140 °C) and ethanediol (ED) was distilled [bp 93 °C (13 mm)]. In a round-bottomed flask a mixture of dimethyl terephthalate (39 g, 0.2 mol) and ethanediol (124 g, 2 mol) was heated at 198 °C and methanol formed was continuously removed by distillation through a 50-cm fractionation column. A quantitative amount of methanol was recovered. After removal of the column the excess ED was removed by distillation [60 °C (1–2 torr)] for 6 h. The residue was dissolved in methanol and the higher molecular weight compounds precipitated at room temperature were removed by filtration. HET was crystallized from the filtrate by cooling and recrystallized several times in methanol (yield 60%, mp 102 °C). The hydroxyl concentration of HET was measured⁶ and found to be 7.89 mol/kg, which is equivalent to a molecular weight of 250. Anal. Calcd: C, 56.69; H, 5.55. Found: C, 56.98; H, 5.32.

2-Hydroxy-*n*-propyl Terephthalate (HPT). 1,2-Propanediol (PD) was distilled before use [bp 98 °C (20 mm)]. HPT was made according to a method similar to the synthesis of HET above. After removal of the excess PD, the viscous liquid was recrystallized several times from methanol (yield 7%, mp 136 °C). The hydroxyl concentration was measured⁶ and found to be 7.14 mol/kg, which is equivalent to a molecular weight of 280. Anal. Calcd: C, 59.57; H, 6.43. Found: C, 59.83; H, 6.22.

Separation of HPT Structural Isomers. The ester-interchange reaction between PD and dimethyl terephthalate results in three structural isomers



From the mixture of the three isomers, a viscous liquid, isomer I, i.e., HPT, is isolated by repeated fractional recrystallizations in methanol, and its NMR spectrum is shown in Figure 1. For comparison purposes, the chemical shifts of protons in PD and HPT are given in Table I. The structure of isomer I was assigned on the basis that the chemical shift of the CH_2 protons in HPT is, compared with that of the CH_2 protons in PD, shifted downfield by $\Delta\delta = 0.85$. A similar result was also observed in ED and HDT. The chemical shift of the CH_2 protons adjacent to the ester group in HET shows a downfield shift of $\Delta\delta = 0.85$, relative to the CH_2 protons in ED.

Polycondensation. A polycondensation apparatus was designed for the complete removal of the diols formed during the polycondensation. A round-bottomed flask (100 mL) equipped with a distillation head was placed in a glass oil bath, so that the whole apparatus was immersed in the temperature-controlled oil bath. The end of the distillation head was vertically connected

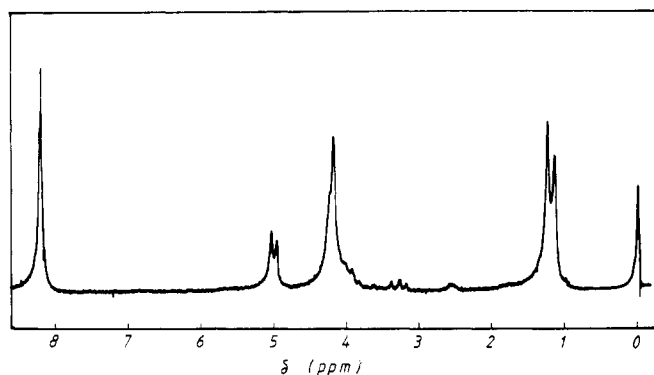
Figure 1. NMR spectrum of 2-hydroxy-*n*-propyl terephthalate.

Table I
Chemical Shifts of Protons in PD and HPT^a

	CH ₃	CH ₂	CH	OH	benzene ring
PD	1.08	3.30	3.65	4.67	
HPT	1.18	4.15	4.05	5.00	8.20

^a δ values measured in Me₂SO-*d*₆.

to a cylinder, which was cooled in a dry ice-methanol bath. The temperature of the oil bath was controlled within $\pm 1^\circ\text{C}$. After the temperature of the apparatus was set at 160°C , about 20 g of HDT or HPT was charged through a funnel and vacuum (20 mmHg) was applied in the polycondensation apparatus. The diols formed during the polycondensation were removed and polyester samples (ca. 1 g) were taken out from the reaction flask for a required time interval. The hydroxyl concentrations of the samples were measured by titration.⁶

Copolycondensation. After the temperature of the oil bath was set at 160°C , a mixture (ca. 15 g) of the required amount of HET and HPT was charged through a funnel and vacuum (20 mmHg) was applied in the polycondensation apparatus. The mixture of the diols formed during copolycondensation was condensed into the cylinder. The first few drops of the condensed diol mixture were removed and the composition of the diol mixture was analyzed by GC (column, Porapak Q; column temperature 200°C).

Results and Discussion

Polycondensation. The polycondensations of HET and HPT were carried under vacuum (20 mmHg) at 160°C . Under these reaction conditions the diols formed during the condensation were removed so rapidly that the reverse reaction of eq 1 could be neglected. The hydroxyl concentrations of the polyesters sampled during the polycondensation were measured by titration.⁶ The concentrations, in molality, of the hydroxyl groups in the polycondensation of HET and HPT are plotted as a function of time in Figure 2.

In order to prevent side reactions the polycondensations were carried out, compared with the reaction conditions of conventional polycondensations, at a relatively low temperature, though they proceeded slowly. Since the kinetics of the condensation are applicable at the initial stage of the reaction, it was plotted to 20% conversion of the total hydroxyl concentration in the monomer.

Reciprocals of the hydroxyl concentrations as a function of time are shown in Figure 3. The plots were shown to be straight lines within the first 20 h of the polycondensation and thereafter showed a deviation, which might be caused by mid-chain ester interchange. The kinetics of the polycondensations are, however, second order with respect to the concentrations of ester and hydroxyl groups, as predicted in eq 2.

The rate constants obtained from the slopes in Figure 3 are given in Table II. The fact that the polyconden-

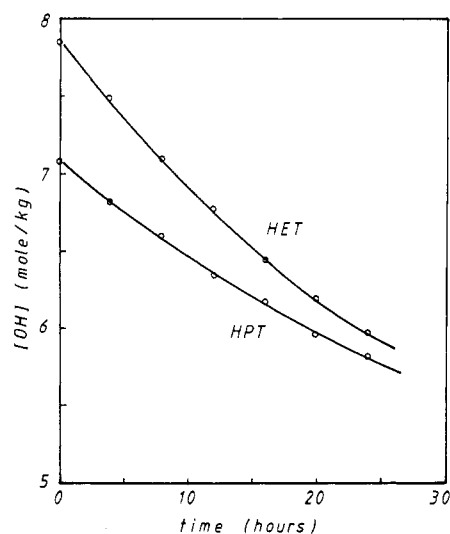
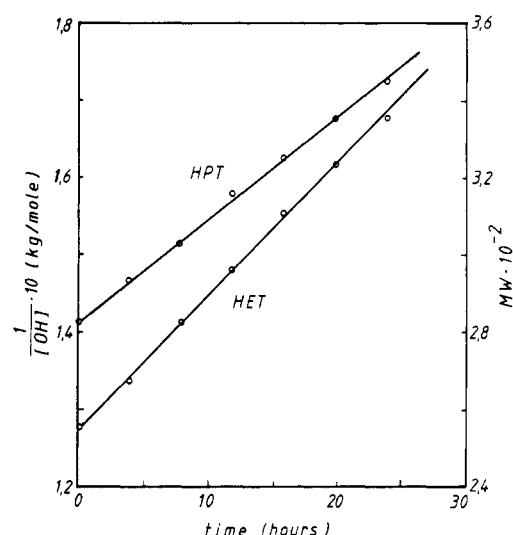
Figure 2. Hydroxyl concentration during the polycondensation of HET and HPT as a function of time at 160°C .Figure 3. Reciprocals of hydroxyl concentration during polycondensation of HET and HPT as a function of time at 160°C and the molecular weight of the polymer against time of polycondensation.

Table II
Rate Constants and Reactivity Ratios of Copolycondensation of HET and HPT at 160°C

$10^3[\text{rate const}]$, $\text{h}^{-1} (\text{mol/kg})^{-1}$	reactivity ratio
$k_{11} = 1.69$	$r_1 = 4.23$
$k_{22} = 1.31$	$r_2 = 1.70$
$k_{21} = 0.77$	
$k_{12} = 0.40$	

sation of HET proceeded faster than that of HPT seemed to be a result of the steric hindrance of the methyl groups in HPT. Since the hydroxyl concentrations are expressed in molality, the molecular weight of the polyester can be given as eq 22. As shown in Figure 3, the molecular weight of the polyester increased linearly with the time of polycondensation.

$$\text{MW} = (2/[\text{OH}]) \times 10^3 \quad (22)$$

Copolycondensation. The monomer mixtures with precise compositions of HET and HPT were copolymerized and the diol mixtures were recovered before the extent of the copolycondensation reached 10% con-

Table III
Kinetics Parameters from Copolycondensation of HET and HPT at 160 °C

a ([HET]/[HPT])	HET mol % in monomer mixt	b ([ED]/[PD])	c ([−ED−]/[−PD−])	ED mol % in polym	$10^3(ak_{11} - (b/a)k_{22})$
0.20	16.67		0.17	14.53	
0.48	32.43	0.34	0.52	34.21	−0.11
1.14	52.61	1.25	1.78	64.03	0.51
1.71	63.10	2.22	3.20	76.19	1.22
2.21	68.85	3.06	4.61	82.17	1.96
10.00	90.91		33.58	97.11	

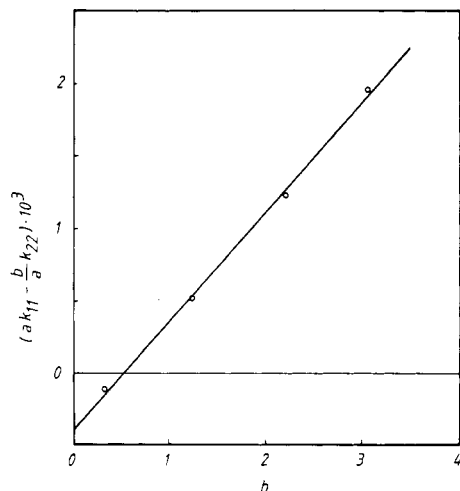


Figure 4. Plot of eq 16.

version of the total hydroxyl concentration in the monomers. The compositions of the evaporated mixtures of ethanediol (ED) and 1,2-propanediol (PD) were analyzed by GC. The mole ratios of monomers ([HET]/[HPT]), a , as well as those of diols ([ED]/[PD]) evaporated, b , are given in Table III.

In order to obtain the rate constants of the cross reactions, the left terms of eq 16, given in Table III, are plotted as a function of b in Figure 4. Since a straight line is obtained, we may conclude that eq 16 is valid for the copolycondensation. The rate constant of the cross reaction 7, k_{21} , and that of reaction 6, k_{12} , are obtained from the slope and from the intercept of Figure 4, respectively, and are given in Table II. The reactivity ratios, given in Table II, are calculated from the rate constants of the four reactions (5)–(8) in the copolycondensation.

The ratios of diol compositions in the copolymer, c , calculated according to eq 20, are given in Table III. Figure 5 shows the copolymer composition as a function of monomer ratio, which is quite similar to the radical copolymerization diagram in the case of $r_1 > 1$ and $r_2 > 1$, as expected, since the reactivity ratios in the copolycondensation r_1 and r_2 are found to be 4.23 and 1.70, respectively. The azeotropic composition of the copolycondensation is calculated by eq 21 and found to be 29.5 mol % of HET in the monomer mixture.

In both polycondensation and copolycondensation, the ester groups having ED terminal groups show a higher reactivity than those having PD terminal groups. The

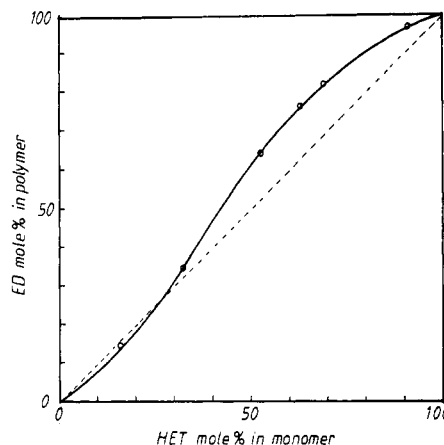


Figure 5. Copolymer composition as a function of monomer ratio.

rates of homoreactions are higher than those of the cross reactions.

Conclusions

We summarize here the main points of the kinetics of the polycondensation and copolycondensation by ester-interchange reactions.

(1) The polycondensation of diol esters of dibasic acids obeys second-order kinetics with respect to the concentrations of ester and hydroxyl groups.

(2) The rates of cross reactions of the copolycondensation are obtained from eq 16, and hence the reactivity ratios of the copolycondensation are calculated.

(3) A copolycondensation composition diagram can be constructed by calculating the ratios of diols incorporated and the azeotropic compositions in the copolymer by eq 20 and 21, respectively.

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