pivalolactone (homopolymer), 24969-13-9; poly(pivalolactone) (SRU), 26497-98-3; β-propiolactone (homopolymer), 25037-58-5; poly(β-propiolactone) (SRU), 24938-43-0; lactic acid (homopolymer), 26100-51-6; poly(lactic acid) (SRU), 26023-30-3; glycolic acid (homopolymer), 26124-68-5; poly(glycolic acid) (SRU), 26009-03-0; ethylene succinate (copolymer), 25569-53-3; poly(ethylene succinate) (SRU), 25667-11-2; ethylene adipate (copolymer), 24938-37-2; poly(ethylene adipate) (SRU), 24937-05-1; glycolide, 502-97-6.

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Kinetics of the Copolycondensation by Aminolysis, Alcoholysis, and Interchange Reactions in the Synthesis of Poly(ester amide)

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ABSTRACT: Amino- and/or hydroxyl-terminated poly(ester amides) of low molecular weight were synthesized via aminolysis, alcoholysis, and interchange reactions of diamine amide and diol ester of dibasic acids. The kinetics of polycondensation with amide (or ester) interchange reaction and copolycondensation were investigated by using *N,N'*-bis(2-aminoethyl)sebacamide and bis(2-hydroxyethyl) sebacate as monomers. The rate constants of aminolysis and alcoholysis reactions in the copolycondensation and the ratios of diamine and diol components incorporated into the copolymer were determined from the equations derived previously. It was found that the rate constants of the four reactions had the following sequences under the same reaction conditions: aminolysis > ester interchange > amide interchange > alcoholysis reactions. The reactivity ratios of the copolycondensation ($r_1 = 10.03$, $r_2 = 0.19$) were calculated on the basis of the rate constants. The composition diagram of the copolycondensation was constructed, which was similar to the composition diagram of radical copolymerization in the case $r_1 > 1$ and $r_2 < 1$.

Introduction

Hydroxyl-terminated polyesters with low molecular weight were synthesized in many laboratories for use as the soft blocks in polyurethane.[1-4] The kinetics of the polyesterification between dibasic acids and diols and of the copolyesterification between different diol esters of dibasic acids by ester interchange reactions were also intensively investigated.[5-10]

By changing the soft blocks in the polyurethane molecules with hydroxyl- and/or amino-terminated poly(ester amide) instead of hydroxyl-terminated polyester, the physical properties of the polyurethane would be changed significantly. The amide groups in the poly(ester amide) had hence the capability of forming hydrogen bonds, contrary to the ester groups in the polyester. Recently several poly(ester amides) were synthesized.[11-17]

The synthesis of hydroxyl- and/or amino-terminated poly(ester amides) can be accomplished by the reaction of dibasic acid and diol together with diamine. Another way to obtain the poly(ester amide) is aminolysis, alcoholysis, and interchange reactions between diol ester and diamine amide of dibasic acids.

In the previous paper we reported the kinetics of copolyesterification of diol esters of dibasic acids[9] and of copolyamidation of diamine amides of dibasic acids.[10]

In this paper we report the synthesis of hydroxyl- and/or amino-terminated poly(ester amides) and the kinetics of copolycondensation of diol ester and diamine amide of dibasic acids by aminolysis, alcoholysis, and interchange reactions.

Kinetics

Polycondensation. It was found that the kinetics of polyesterification of diol ester of dibasic acid was second order with respect to the concentration of ester and hydroxyl groups as follows:[9]

$$\text{2 HOROOCR'COOROH} \xrightarrow{k_e} \text{HOROOCR'COOROOCR'COOROH} + \text{HOROH} \qquad (1)$$

$$-\mathrm{d}[\mathrm{OH}]/\mathrm{d}t = k_e[\mathrm{OH}][\mathrm{COO}] \qquad (2)$$

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

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$$-\mathrm{d}[\mathrm{OH}]/\mathrm{d}t = k[\mathrm{OH}]^2 \tag{3}$$

Rearrangement and integration of the above equation gives eq 4.

$$1/[\mathrm{OH}] = kt + C \tag{4}$$

The kinetics of polyamidation of diamine amide of dibasic acid (eq 5) was also found to be second order with respect to the concentration of amino and amide groups (eq 6) at the initial stage of the reaction as follows:[10]

$$2\mathrm{H_2NRNHOCR'CONHRNH_2} \xrightarrow{k_\mathrm{a}} \mathrm{H_2NRNHOCR'CONHRNHOCR'CONHRNH_2} + \mathrm{NH_2RNH_2} \tag{5}$$

$$-\mathrm{d}[\mathrm{NH_2}]/\mathrm{d}t = k_\mathrm{a}[\mathrm{CON}][\mathrm{NH_2}] \tag{6}$$

One can obtain eq 7 in a similar way to the derivation of

$$1/[\mathrm{NH_2}] = k_\mathrm{a}t + C \tag{7}$$

eq 4. Both eq 4 and 7 are valid at the initial stages of polycondensations, because the conditions for the derivations of the equations, [OH] = [COO] and $[\mathrm{NH_2}]$ = [CON], are satisfied only at the beginning of the polycondensation.

Copolycondensation. When a diamine amide of a dibasic acid ($\mathrm{H_2NRNHOCR'CONHRNH_2}$) and a diol ester of a dibasic acid (HOROOCR′COOROH) are copolycondensed under the condition that the amino or hydroxyl group of the second chain end attacks the amide or ester groups of the first chain end, the following sequence of reactions should be considered to take place:

$$-\mathrm{R'CONHRNH_2} + \mathrm{H_2NRNHOCR'}- \xrightarrow{k_{11}} -\mathrm{R'CONHRNHOCR'}- + \mathrm{H_2NRNH_2} \tag{8}$$

$$-\mathrm{R'CONHRNH_2} + \mathrm{HOROOCR'}- \xrightarrow{k_{12}} -\mathrm{R'COOROOCR'}- + \mathrm{H_2NRNH_2} \tag{9}$$

$$-\mathrm{R'COOROH} + \mathrm{H_2NRNHCOR'}- \xrightarrow{k_{21}} -\mathrm{R'CONHRNHOCR'}- + \mathrm{HOROH} \tag{10}$$

$$-\mathrm{R'COOROH} + \mathrm{HOROOCR'}- \xrightarrow{k_{22}} -\mathrm{R'COOROOCR'}- + \mathrm{HOROH} \tag{11}$$

The reactions 8–11 represent amide interchange, alcoholysis, aminolysis, and ester interchange reactions, respectively.

Expressing the concentrations of amide, amino, ester, and hydroxyl groups as [CON], $[\mathrm{NH_2}]$, [COO] and [OH], respectively, one can write the rates of diamine or diol formation as follows:

$$\mathrm{d}[\mathrm{NH_2RNH_2}]/\mathrm{d}t = k_{11}[\mathrm{CON}][\mathrm{NH_2}] + k_{12}[\mathrm{CON}][\mathrm{OH}] \tag{12}$$

$$\mathrm{d}[\mathrm{HOROH}]/\mathrm{d}t = k_{21}[\mathrm{COO}][\mathrm{NH_2}] + k_{22}[\mathrm{COO}][\mathrm{OH}] \tag{13}$$

The incorporation of diamine and diol components in the poly(ester amide) by aminolysis, alcoholysis, and interchange reactions is given by

$$\mathrm{d}[-\mathrm{NHRNH}-]/\mathrm{d}t = k_{11}[\mathrm{CON}][\mathrm{NH_2}] + k_{21}[\mathrm{COO}][\mathrm{NH_2}] \tag{14}$$

$$\mathrm{d}[-\mathrm{ORO}-]/\mathrm{d}t = k_{12}[\mathrm{CON}][\mathrm{OH}] + k_{22}[\mathrm{COO}][\mathrm{OH}] \tag{15}$$

In the previous papers we have derived the kinetics of copolyesterification by ester interchange reactions[9] and of copolyamidation by amide interchange reactions.[10] Since the sequences of the reactions 8–11 correspond to those of the copolyesterification, the kinetics of the latter can be applied for the former; then eq 16, which is derived for

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

copolyesterification, is also applicable for reactions 8–11, where a is the mole ratio of diamine amide of dibasic acid (monomer 1) and diol ester of dibasic acid (monomer 2) at the onset of copolycondensation

$$a = \frac{[\mathrm{H_2NRNHOCR'CONHRNH_2}]}{[\mathrm{HOROOCR'COOROH}]} = \frac{[\mathrm{CON}]}{[\mathrm{COO}]} = \frac{[\mathrm{NH_2}]}{[\mathrm{OH}]} \tag{17}$$

and b is the ratio of diamine and diol formed at the initial stage of copolycondensation

$$b = \mathrm{d}[\mathrm{H_2NRNH_2}]/\mathrm{d}[\mathrm{HOROH}] \tag{18}$$

The rate constants of polyamidation, k_{11}, and of polyesterification, k_{22}, are obtainable by plotting reciprocals of hydroxyl or amino group concentration against time. Plotting the left term of eq 16 as a function of b, one can obtain the rate constant of aminolysis, k_{21}, and that of alcoholysis, k_{12}, from the slope and from the intercept of the plot, respectively. The reactivity ratios can be calculated by the four rate constants measured for the copolycondensation.

The ratio of diamine and diol components incorporated in the poly(ester amide) by reactions 8–11 can be calculated from[9]

$$d = \frac{\mathrm{d}[-\mathrm{NHRNH}-]}{\mathrm{d}[-\mathrm{ORO}-]} = a\frac{k_{21} + ak_{11}}{ak_{12} + k_{22}} \tag{19}$$

In this study *N*,*N*′-bis(2-aminoethyl)sebacamide (AES) and bis(2-hydroxyethyl) sebacate (HES) are chosen as monomer 1 and monomer 2, respectively.

Experimental Section

Synthesis of Monomers. *N*,*N*′-Bis(2-aminoethyl)sebacamide (AES) was synthesized by the method described in our previous paper[10] (mp 120 °C). Bis(2-hydroxyethyl) sebacate (HES)-dimethyl sebacate was synthesized by the conventional method[8] (bp 175 °C (20 mmHg)) and ethanediol was distilled (bp 193 °C (13 mmHg)). In a round-bottom flask a mixture of dimethyl sebacate (69.1 g, 0.3 mol) and ethanediol (186.2 g, 3 mol) was heated at 198 °C and the methanol formed was continuously removed by distillation through a 30-cm fractionation column. A quantitative amount of methanol was recovered. The reaction mixture was poured into 500 mL of ice water and filtered. The filter cake was dissolved in 300 mL of benzene by heating and the water contained in the filter cake was removed by azeotropic distillation with benzene. After evaporation of the benzene, the solid residue was crystallized in methanol and HES was filtered from methanol at a temperature below −30 °C (yield: 52%, mp 39 °C). The hydroxyl concentration of HES was measured[18] and found to be 6.93 mol/kg, which was equivalent to a molecular weight of 288.6 (MW of HES: 290). Anal. Calcd C, 57.91; H, 9.03. Found C, 57.54; H, 8.92.

Polycondensation. The polycondensation apparatus was described elsewhere.[9] After the temperature of the apparatus was set at 200 °C, about 30 g of HES was charged through a funnel, vacuum (20 mmHg) was applied in the polycondensation apparatus, and the reactant was stirred. The diol formed during the polycondensation was removed and polyester samples were taken out of the reaction flask at required time intervals. In order to minimize the titration errors, large quantities (>1 g) of samples were taken for the titrations. The hydroxyl concentrations of the samples were measured by titration.[18] The reproducibility of this method was found to be 3%.

Copolycondensation. The copolycondensation apparatus was described elsewhere.[9] After the temperature of the oil bath was set at 200 °C, a mixture of the required amounts of AES and HES was charged and stirred. As the reaction progressed the mixture

Table I
Rate Constants and Reactivity Ratios of the Copolycondensation of AES and HES at 200 °C

rate constant × 10^3, h^{-1} $(mol/kg)^{-1}$	reactivity ratio
$k_{11} = 3.01$	$r_1 = 10.03$
$k_{22} = 34.70$	$r_2 = 0.19$
$k_{12} = 0.30$	
$k_{21} = 186.0$	

of diamine and diol formed during the copolycondensation was condensed into the pot. The first few drops of condensed diamine and diol mixture were removed into a weighing bottle. After the mixture was weighed, it was rinsed out with water, and the diamine content in the mixture was titrated with 0.1 N HCl with bromophenol as indicator. The reproducibility of this method was 4%.

TLC Analysis. A Iatroscan TH-10 TLC analyser (Iatron Laboratories, Japan) was used for the analysis of the condensate. The distillate of the copolycondensation was spotted on the TLC bar and developed by ethanol. The chromatograms were taken by FID.

Results

Polycondensation. The rate constant for the polycondensation of AES was measured at 200 °C and found to be 3.01×10^{-3} h $(mol/kg)^{-1}$.[10] The polycondensation of HES was carried out under reduced pressure (20 mmHg) at 200 °C with stirring. Under this reaction condition the ethanediol (EDO), formed during the condensation, was removed so rapidly that the reverse reaction of eq 1 can be neglected. The concentration of hydroxyl groups of the polyester sampled during the polycondensation were measured by titration.[18] Reciprocals of the hydroxyl concentrations as a function of time are shown in Figure 1. The plot was shown to be a straight line within the first 1.5 h of the polycondensation, which is equivalent to ca. 10% conversion of hydroxyl concentration, and thereafter showed a deviation, which might be caused by mid-chain interchange, aminolysis, and alcoholysis. The kinetics of the polycondensation are, however, second order with respect to the concentration of ester and hydroxyl groups, as was found previously.[9] The rate constant, k_{22}, was obtained from the slope in Figure 1 and is given in Table I.

Copolycondensation. The monomer mixture with precise compositions of AES and HES was copolycondensed. The condensates distilled from the copolycondensation were analyzed by TLC analyser, as described in the Experimental Section. It was found that no other compounds existed in the distillate except ethanediol and 1,2-diaminoethane, and it can be asserted that no side reactions occurred at the initial stage of copolycondensation of AES and HES at 200 °C. The mixtures of 1,2-diaminoethane and ethanediol formed during reactions 8–11 were recovered to be analyzed for composition. Since the kinetics are valid for the initial stage of the copolycondensation, the distilled mixture of diamine and diol was collected before the extent of the copolycondensation reached 10% conversion of the total amino and hydroxyl concentration of the monomers. The composition of the distilled mixture was measured by titration of the diamine in the mixture with 0.1 N HCl solution. The mole ratios of the monomers ([AES]/[HES]) at the onset of copolycondensation, a, as well as those of diamine and diol ([DAE]/[EDO]) formed during the copolycondensation, b, are given in Table II. The calculated values of the left term of eq 16, $ak_{11} - (b/a)k_{22}$, are listed in Table II and these are plotted as a function of b in Figure 2. Since a straight line is obtained, eq 16 is also valid for the copolycondensation by aminolysis, alcoholysis, and interchange reactions. The rate constants of the alcoholysis (eq 9), k_{12}, and of the aminolysis (eq 10), k_{21}, are obtained from the intercept and from the slope in Figure 2, respectively. The rate constants are given in Table I. The rate constant of alcoholysis ($k_{12} = 0.30$) is negligible compared with that of aminolysis ($k_{21} = 186.0$). The reactivity ratios given in Table I are calculated from the rate constants of reactions 8–11. The ratios of diamine com-

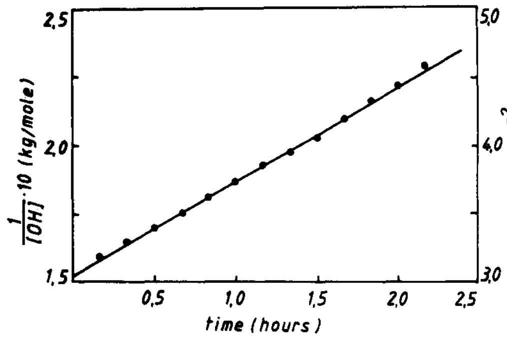

Figure 1. Reciprocals of the hydroxyl concentration during polycondensation of HES as a function of time at 200 °C and the molecular weight of the polymer against the time of polycondensation.

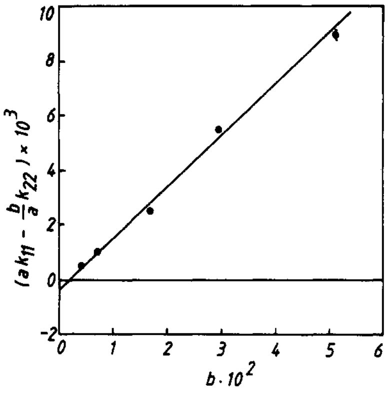

Figure 2. Plot of eq 16.

Table II
Kinetics Parameters of the Copolycondensation of AES and HES at 200 °C

a, [AES]/[HES]	AES in monomer mixture, mol %	b, [DAE]/[EDO]	c,[a] [-DAE-]/[-EDO-]	DAE in polymer,[b] mol %	$(ak_{11} - (b/a)k_{22}) \times 10^3$
0.10	9.09		0.54	35.06	
0.20	16.67		1.07	51.69	
0.33	25.00	4.38	1.77	63.90	0.53
0.50	33.33	7.01	2.69	72.90	1.02
1.00	50.00	17.20	5.40	84.38	2.41
2.00	66.67	29.30	10.88	91.58	5.51
3.00	75.00	51.24	16.44	94.27	8.44
10.00	90.91		57.32	98.29	

[a] Calculated by eq 19. [b] Calculated from "c".

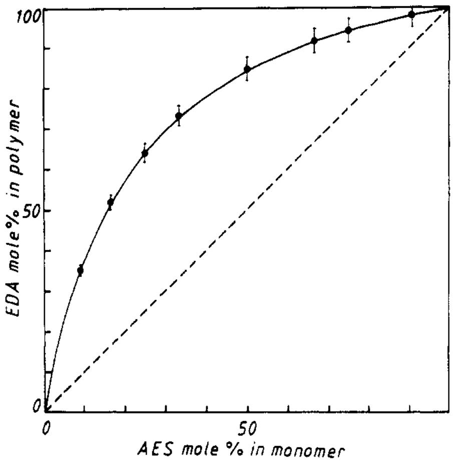

Figure 3. Calculated mole % incorporated into the copolymer by reactions 8–11 as a function of monomer mole %.

ponents incorporated according to eq 19 are given in Table II.

Figure 3 shows the composition diagram in which the mole ratios of the calculated values (*c*) are plotted as a function of monomer ratio. This composition diagram is quite similar to that of the radical copolymerization in the case of $r_1 > 1$ and $r_2 < 1$. This result was expected because r_1 and r_2 are found to be 10.03 and 0.19, respectively.

Conclusion

(1) Amino- and/or hydroxyl-terminated poly(ester amide) can be synthesized by the copolycondensation of diamine amide and the diol ester of dibasic acids.

(2) In this copolycondensation there are four different reactions, such as ester interchange, amide interchange, aminolysis, and alcoholysis, and all of these reactions are found to be second order with respect to terminal amino (or hydroxyl) and amide (or ester) groups in the chain.

(3) The rate constants of aminolysis and alcoholysis of the copolycondensation are obtained from eq 16 and the rate constants of the four different reactions are found to be in the following sequence under the same reaction conditions: aminolysis > ester interchange > amide interchange > alcoholysis.

(4) The reactivity ratios ($r_1 = 10.03$, $r_2 = 0.19$) are calculated from the four rate constants of the copolycondensation. The ratios of diamine to diol incorporated into the copolymer were calculated from eq 19, from which a composition diagram was constructed and found to be similar to that of the radical copolymerization which had reactivity ratios $r_1 > 1$ and $r_2 < 1$.

Registry No. AES, 80621-15-4; HES, 17200-46-3; (AES)·(HES) (copolymer), 101835-16-9; $HOCH_2CH_2OH$, 107-21-1; dimethyl sebacate, 106-79-6.

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