

## 아미드 교환반응에 의한 아미드 중합체 및 공중합체의 합성과 반응속도에 관한 연구

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## Synthesis of Polyamide and Copolyamide by Amide-Interchange Reactions and Their Kinetics

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**요 약 :** 중축합 및 공중축합 반응의 단량체로서 N,N'-bis(aminoethyl) dodecanedioamide 와 N,N,N',N'-bis(diethyleneimino) dodecanedioamide를 합성하였다. 두 단량체의 아미드 교환 반응을 이용하여 아미노 말단기를 갖는 저분자량의 아미드 중합체 및 공중합체를 얻었다. 아미드 교환반응에 의한 아미드화 중합반응 및 공중합 반응속도는 반응 초기단계에서 아미노(혹은 이미노)기와 아미드기의 농도에 대하여 2차 임이 밝혀졌다. 공중축합 반응에 대하여 유도한 식을 이용하여 4가지의 속도상수와 반응성비를 결정하고 이 반응성비로부터 공중합체의 조성그림을 얻었다.

**Abstract :** The monomers, N,N'-bis(aminoethyl) dodecanedioamide and N,N,N',N'-bis(diethyleneimino) dodecanedioamide, were synthesized. The amino-terminated polyamide and copolyamide of low molecular weight were obtained via amide-interchange reactions of the two monomers. The kinetics of polyamidation and copolyamidation by amide interchange reactions were found to be the second-order with respect to the concentration of amino (or imino) and amide groups in the monomers at the initial stage of the reactions. The composition diagram was constructed by the reactivity ratios, which were calculated from the four rate constants determined by the derived equation for the copolycondensation.

### INTRODUCTION

Amino-terminated polyamide of low molecular weight can be synthesized by amide interchange reactions of diamine amide of dibasic acids as was reported in the previous paper.<sup>1</sup> The amino-terminated amide oligomers are expected to be potential prepolymers in the syn-

thesis of high polymer since they are difunctional and the amino groups have high reactivity. They can be used in the polyamide synthesis as partial substituents for the diamine components, and also incorporated easily not only into the polyurethane elastomer, but also into epoxy polymers, so that the physical properties of the polymer can be modified for the

purpose of some special uses.

The kinetics of the amide-interchange reactions during the polycondensation and copolycondensation were derived and verified; the four rate constants of the copolycondensation, such as those of homoreactions and cross reactions, were determined by the derived equation and the reactivity ratios were calculated on the basis of the four rate constants.<sup>1</sup>

In this paper we will report the synthesis of monomers, N,N,N',N'-bis (diethyleneimino) dodecanedioamide (DEID) and N,N'-bis (aminoethyl) dodecanedioamide (AED), and of their low molecular weight polymer as well as copolymer. The rate constants of the polycondensation and copolycondensation were determined by the derived equation. With the aid of the rate constants the reactivity ratios were calculated and the composition diagram was constructed.

## EXPERIMENTAL SECTION

### Synthesis of Monomers

#### N,N'-Bis(aminoethyl)Dodecanedioamide (AED)

Dimethyl dodecanedioate was synthesized by the conventional method<sup>2</sup> (bp 167-169°C) and 1,2-diaminoethane (DAE) was distilled before use (bp 117°C). In an autoclave (1L) a mixture of dimethyl dodecanedioate (75.1 g, 0.29 mol) and DAE (174.8 g, 2.9 mol) was heated at 175°C for 7 h under N<sub>2</sub> gas with stirring (autoclave pressure 7 atm). The reaction mixture was transferred to a flask and the excess DAE was removed by distillation under reduced pressure (40 mmHg) for 2 h. The residue was dissolved in methanol and the higher molecular weight compounds, being insoluble in boiling methanol, were removed by filtration. AED was crystallized several times from methanol; yield 24% : mp 132°C. AED was dissolved in methanol and the amino group concentration of AED was titrated with 0.1 N HCl, using bromophenol blue as indicator. The amino group

concentration was found to be 6.28 mol/kg, which is equivalent to a molecular weight of 318.5 (MW of AES=314.54). Anal. Calcd. : C, 61.09 : H, 10.92 : N, 17.82. Found C, 60.54 : H, 10.54 : N, 17.31.

#### N,N,N',N'-Bis(diethyleneimino) dodecanedioamide (DEID)

Piperazine (PZ) was crystallized from benzene (mp 103°C). Dimethyl dodecanedioate (61.75 g, 0.24 mol) and PZ (206 g, 2.39 mol) were charged in an autoclave (1L), which was filled up with N<sub>2</sub> gas after evacuation of air, and heated at 200°C for 7 h with stirring (autoclave pressure 7 atm). The excess PZ was removed by distillation under reduced pressure (20 mmHg). Upon addition of equivalent conc. HCl, DEID hydrochloride salt was formed, which was crystallized several times from methanol. After neutralization of the salt with NaOH, DEID was extracted with chloroform. After evaporation of chloroform, DEID was crystallized from toluene : yield, 29.5% : mp 74°C. The imino group concentration was measured by titration as described above and found to be 5.38 mol/kg, which is equivalent to a molecular weight 371.75 (MW of DEID 366.62). Anal. Calcd. C, 65.52 : H, 10.47 : N, 15.29. Found C, 65.02 : H, 10.11 : N, 14.98.

### Polycondensation

The apparatus for the polycondensation was described elsewhere.<sup>3</sup> After the temperature of the apparatus was set at 200 or 300°C, about 20 g of AED or DEID was charged through a funnel, and vacuum was applied (20 mmHg) in the polycondensation apparatus with stirring. The diamines formed during the polycondensation were removed and polyamide samples were taken out from the reaction flask at required time intervals. The amino or imino concentrations of the samples were determined by titration as described above.

### Copolycondensation

The polycondensation apparatus was described elsewhere.<sup>1</sup> After the temperature of the apparatus was set at 200±1°C, a mixture of a

definite mole ratio of AED and DEID was charged and stirred. The mixture of diamines formed during the copolycondensation was condensed into the pot. The first few drops of condensed diamine mixture were rinsed out with methanol and the composition of the diamines in the methanol solution was analysed by G.C(column : 10% Carbowax 20M plus 5.0% KOH on chromosorb W A/W 2m : column temp. 80°C).

## RESULTS

### Synthesis of Monomers

The monomers, N,N,N',N'-bis(diethyleneimino)dodecanedioamide(DEID) and N,N-bis(aminoethyl)dodecanedioamide(AED), were synthesized by the aminolysis of piperazine and ethylene diamine on the dimethyl dodecanedioate, respectively, as shown in eq. (1) and (2).

Even though the reactions were carried out in excess of diamine components, considerable amounts of polymers were formed to be resulted in poor yields of the monomers.

### Polycondensation

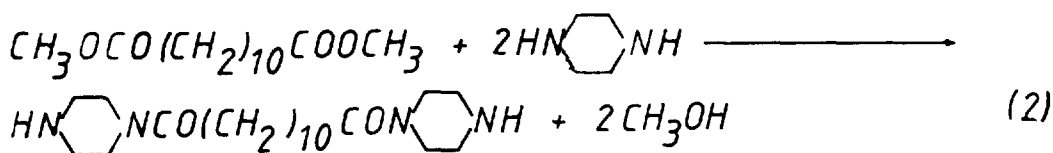
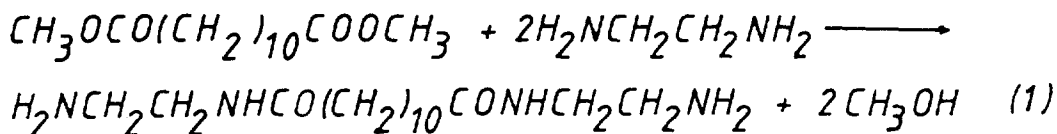
Polyesters were synthesized frequently by ester-interchange reactions of diol esters of dibasic acids, for example, poly(ethylene terephthalate). Similarly polyamides can be also synthesized by amide-interchange reactions of diamine amides of dibasic acids. The polyamidation of AED and DEID by amide-interchange reactions can be formulated as shown in eq. (3) and (4).

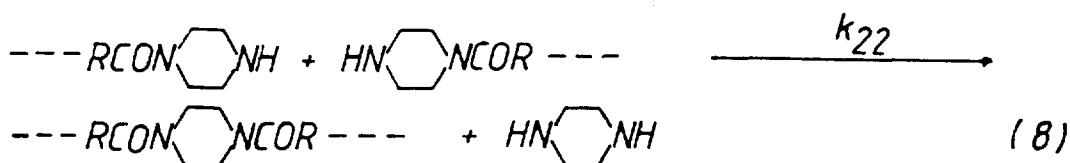
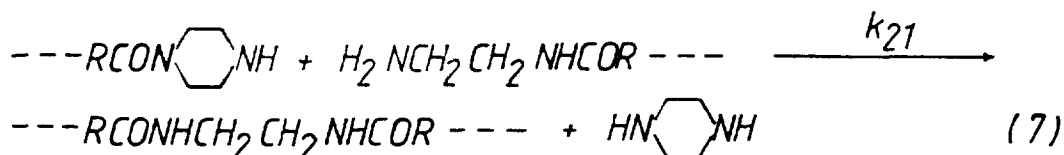
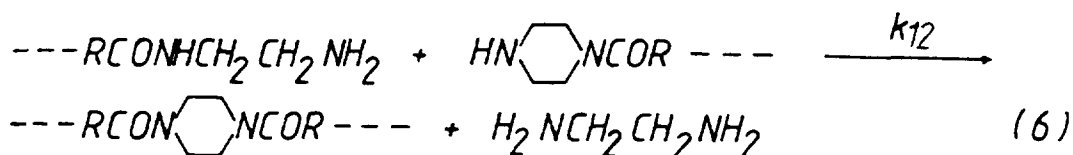
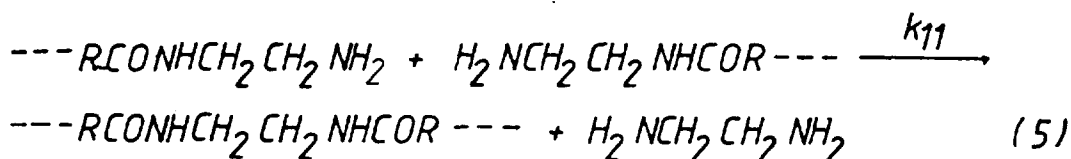
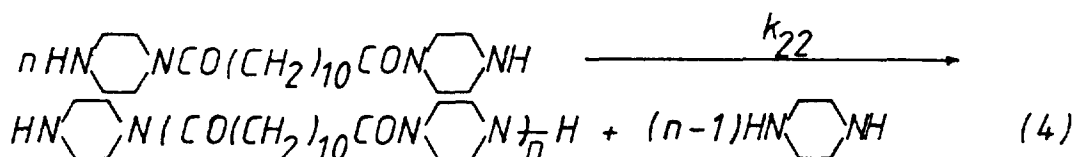
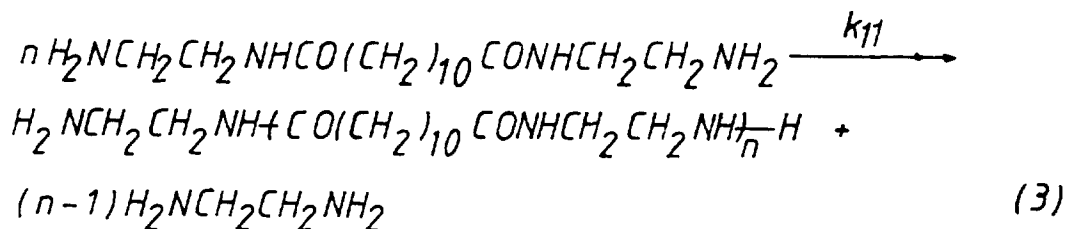
When the polycondensations were carried out at high temperature under vacuum, so that the diamines formed during polycondensations were removed, polyamides were expected to be formed. Since the rate constant of interchange reaction for polyamidation was found to be one order of magnitude lower than that for polyesterification,<sup>4</sup> more drastic conditions will be required to obtain polyamide, compared with those of polyesterifications. For the polyamidation of AED and DEID at 200°C, the increase in molecular weight of 60 was required ca. 6 h reaction time for AED and ca. 18 h for DEID. Poly(ethylene dodecanedioamide) of molecular weight of  $2.0 \times 10^3$  was obtained at 300°C for the reaction time of 6 hours. Amide-interchange reaction was the therefore suitable for the synthesis of amino-terminated oligoamides, which can be used in the synthesis of copolyamides, polyurethanes and epoxy polymers as diamine components.

### Copolycondensation

The copolycondensation of two different diamine amides of dibasic acids for conditions where the amino(or imino) group of the second chain and attacks the amide group of the first chain end can be written as the sequence of reactions in eq. 5~8. AED and DEID are designated as monomer 1 and monomer 2 for the copolycondensation, respectively.

In general terms reactions 5 and 8 are homocondensations between same chain ends, whereas reactions of 6 and 7 are cross-conden-





sations since different chain ends react each other. When diamines, formed during the copolycondensation, were evaporated continuously, we can obtain copolyamides containing different diamine components in the polymer chains. The copolyamide of molecular weight of  $1.5 \times 10^3$  was obtained at  $300^\circ\text{C}$  for 6 hours under vacuum (200 mmHg).

#### Kinetics

The condensation reactions were found to be

the second order with respect to the concentration of amide and amino (or imino) groups in the reactions of 3 and 4.<sup>1</sup> At the initial stage of the polyamidation, the concentrations of amino and amide groups should be equal, thus, the kinetics of polyamidation can be expressed as

$$-\frac{d[\text{NH}_2]}{dt} = k[\text{NH}_2]^2 \quad (9)$$

Where  $[\text{NH}_2]$  was the concentration of amino

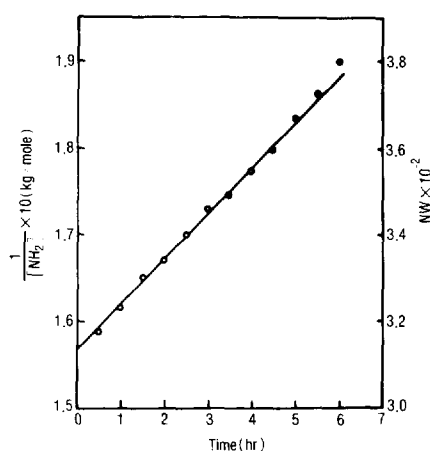


Fig. 1. Reciprocals of amino concentrations during polycondensation of AED as a function of time at 200°C and the molecular weight of the polymer against the time of polycondensation.

(or imino) group in the monomer. Rearrangement and integration of eq.<sup>9</sup> give

$$\frac{1}{[\text{NH}_2]} = kt + C \quad (10)$$

Plotting reciprocals of amino(or imino) concentration against time permits one to obtain the rate constant of polyamidation from the slope.

The polycondensations of AED and DEID were carried out under reduced pressure (20 mmHg) at 200°C with stirring. Under these reaction conditions the diamines formed during the condensations, 1,2-diaminoethane(DAE) and piperazine(PZ), were removed so rapidly that the reverse reactions of eq. 3 and 4 can be neglected. The concentrations of amino and imino groups of the polyamides sampled during the polycondensation were titrated by 0.1 N HCl after dissolving the sample in methanol.

Reciprocals of the amino and imino concentration vs. time are shown in Fig. 1 and 2, respectively. Since the kinetics of the polycondensations were applicable at the initial stage of the reaction, the data were plotted up to ca. 10% conversion of the total amino or imino concentrations. The rate constants obtained from

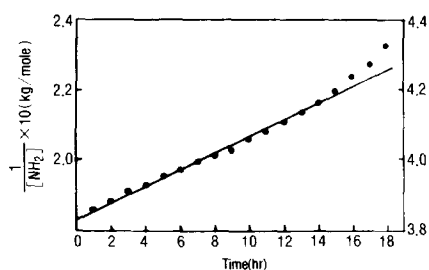


Fig. 2. Reciprocals of imino concentrations during polycondensation of DEID as a function of time at 200°C and the molecular weight of the polymer against the time of polycondensation.

Table 1. Rate Constants and Reactivity Ratios of the Copolycondensation of AED and DEID at 200°C

$10^3(\text{rate constant}),$ $\text{h}^{-1}(\text{mol/kg})^{-1}$	Reactivity ratio
$k_{11}=5.25$	$r_1=1.54$
$k_{22}=2.44$	$r_2=0.37$
$k_{12}=3.40$	
$k_{21}=6.60$	

the slopes in Fig.1 and 2 are given in Table 1. The probable reason that the polycondensation of AED proceeded about 2 times faster than that of DEID seemed to be the steric hindrance of the large piperazinyl groups in DEID.

Since the concentration of amino(or imino) end groups is expressed in molality and polyamide molecule contains two amino(or imino) end groups, the molecular weight of the polyamide can be given as eq. 11.

$$\text{MW} = (2/[\text{NH}_2]) \times 10^3 \quad (11)$$

The increases in molecular weight of polyamides as a function of polycondensation time are shown in Fig.1 and 2.

In the previous paper we have derived the kinetics of copolycondensation by amideinterchange reaction.<sup>1</sup>;

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

Where  $a$  and  $b$  are the mole ratios of monomers at the onset of copolycondensation and of diamines formed at the initial stage of the copolycondensation, respectively : i.e.

$$a = \frac{[\text{monomer}_1]}{[\text{monomer}_2]} = \frac{[\text{AED}]}{[\text{DEID}]}, \quad b = \frac{d[\text{DAE}]}{d[\text{PZ}]} \quad (13)$$

The rate constants of homopolycondensations,  $k_{11}$  and  $k_{22}$ , can be obtained from eq.10. Plotting the left term of the eq.12,  $ak_{11} - (\frac{b}{a})k_{22}$ , as a function of  $b$ , we can obtain the rate constants of the cross reactions,  $k_{21}$  and  $k_{12}$ , from the slope and the intercept of the plot, respectively. Knowing the four rate constants of the copolycondensation permits calculation of the reactivity ratios, since  $r_1 = k_{11}/k_{12}$ , and  $r_2 = k_{22}/k_{21}$ .

DAE and PZ formed during reactions 5~8 were distilled while the copolycondensations of AED and DEID were proceeded. Analysis by G.C. indicated that no other compounds existed in the distillate except DAE and PZ, and it can be asserted that no side reactions occurred during the copolycondensation even though the copolycondensation were carried out at high temperature(200°C).

The mixture of the distilled diamines was recovered during the copolycondensation of monomer mixture with precise composition of AED and DEID. As the derived kinetics are valid for the initial stage of the copolycondensation, the distilled mixture of diamines was collected before the extent of the copolycondensation reached 10 % conversion of the total amino and imino concentrations in the monomers. The composition of the distilled mixture was analysed by G.C. The mole ratios of monomers at the onset of copolycondensation ( $[\text{DEA}]/[\text{DEID}]$ ),  $a$ , as well as those of diamines distilled ( $[\text{DEA}]/[\text{PZ}]$ ),  $b$ , are given in Table 2.

The calculated values of the left terms in eq. 12,  $ak_{11} - (\frac{b}{a})k_{22}$ , are listed in Table 2 and these are plotted as a function of  $b$  in Fig.3, which shows a straight line. The rate constants of cross

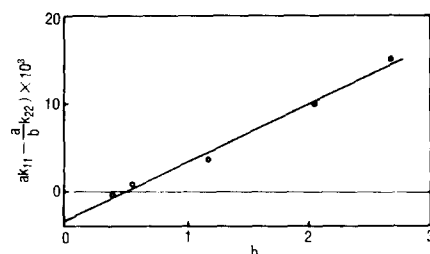


Fig. 3. Plot of equation 12.

reaction 7,  $k_{21}$ , and that of eq.6,  $k_{12}$ , are obtained from the slope and from the intercept in Fig.3, respectively. The rate constants are given in Table 1. The rate constant of eq.7 was found to be about 2 times faster than that of eq.6. This can be ascribed to the steric hindrance of the voluminous piperazinyl group in eq.6, compared with the small aminoethyl group in eq.7. The reactivity ratios given in Table 1 were calculated from the rate constants of the four reactions.

The diamine component ratio( $c$ ) incorporated into the copolyamide by reactions 5~8 can be calculated from eq.14.<sup>1</sup>

$$c = a \frac{k_{21} - ak_{11}}{ak_{12} + k_2} \quad (14)$$

They are calculated according to the above eq. 14 and are given in Table 2. The mole ratios of the calculated values( $c$ ) as a function of fe-

Table 2. Kinetics Parameters from Copolycondensation of AED and DEID at 200°C

$a$ ( $\frac{[\text{AED}]}{[\text{DEID}]}$ )	mol% of AED in monomer mixture	$b$ ( $\frac{[\text{DAE}]}{[\text{PZ}]}$ )	$c$ ( $\frac{[\text{DAE}]}{[\text{PZ}]}$ )	mol% of DAE in polymer	( $ak_{11} - (\frac{b}{a})k_{22}$ ) $\times 10^3$
0.10	9.09	—	0.26	20.63	—
0.20	16.67	—	0.49	32.89	—
0.39	28.06	0.40	0.90	47.37	-0.46
0.59	37.11	0.56	1.29	56.33	0.78
1.16	53.70	1.18	2.31	69.79	3.61
2.31	69.79	2.06	4.20	80.77	9.95
3.25	76.47	2.68	5.70	85.07	15.05
10.00	90.91	—	16.22	94.19	—

a) : calculated from eq. 14

b) : calculated from " $c$ "

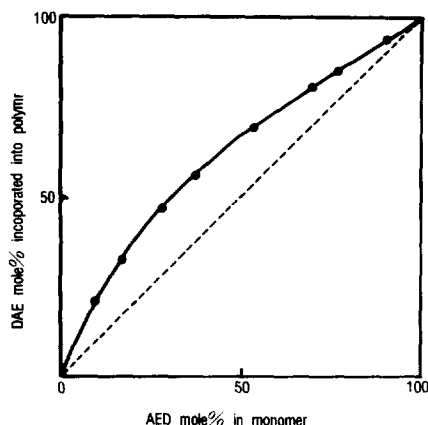


Fig. 4. Calculated mole percent of diamines incorporated into the copolyamide by reaction (5)-(8) as a function of monomer mole percent.

eding monomer ratios are shown in Fig.4, which is quite similar to the radical copolymerization diagrams in the case of  $r_1 > 1$  and  $r_2 < 1$ , as expected, since the reactivity ratios  $r_1$  and  $r_2$  in the copolycondensation are found to be 1.54 and 0.37, respectively.

If an azeotrope exists, the azeotropic monomer ratio can be obtained from the rate constants according to eq.15<sup>1</sup>

$$a=c=\frac{k_{21}-k_{22}}{k_{12}-k_{11}} \quad (15)$$

The azeotropic composition, calculated according to the above eq.15, is found to be negative ( $a=-2.25$ ) and it is practically meaningless because it has to be positive ( $a>0$ ). Consequently the azeotrope was not found in the diagram (Fig.4).

## CONCLUSION

The rate constants of polyamidation and co-

polyamidation by amide-interchange reactions are one order of magnitude lower than those of polyesterification and copolyesterification by ester-interchange reactions. Oligoamides can be, therefore, obtained by the amide-interchange reactions of similar reaction conditions to those of the polyesterifications. The aminoterminated polyamide and copolyamide of low molecular weight can be incorporated in the polymers, such as polyurethane, polyamide and epoxy resin, so that the physical properties of the polymers can be modified to be suitable for special uses.

The copolycondensation equation derived previously can be applied for amide-interchange as well as ester-interchange reactions. Although the copolymerization parameters, such as the rate constants of cross-reactions ( $k_{12}$  and  $k_{21}$ ) and the reactivity ratios ( $r_1$  and  $r_2$ ), were determined by different methods from the measurements of the radical copolymerizations, the applicability and definition of the parameters are the same as those in the radical copolymerization. The composition diagram of the copolycondensation, constructed by calculations with the aid of rate constants, was found to show the same trend to that of radical copolymerization with the values of similar reactivity ratios.

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