of photolysis. On the basis of these data it must be concluded that practically no Barton reaction takes place in the polymeric matrix. The ketone formation results from hydrogen abstraction of the alkoxy radical by the NO radical (k_d) followed by disproportionation within the cage with simultaneous formation of hyponitrous acid.

The intramolecular H transfer (k_i), which requires a boat–chair conformation of the cyclooctane ring, necessitates a conformational ring mobility that is strongly reduced in the polymeric matrix. The two main reactions for the cage radicals are thus recombination (k_r) to cyclooctyl nitrite, which is responsible for the much lower quantum yield of photolysis in film than in solution, and disproportionation (k_d) to cyclooctanone and hyponitrous acid, which accounts for the high ketone formation efficiency E_K. In polymeric medium, formation of a nitroso monomer and/or oxime is therefore strongly reduced and is estimated at a maximum of 10%. Absence of a nitroso dimer results evidently from lack of diffusion in the solid medium. It is noteworthy that the physical state of the matrix (below and above T_g) does not affect the quantum yields Φ_N and Φ_K.

Conclusion

The photolysis of cyclooctyl nitrite in polymeric medium differs considerably from that in solution. Limited interconversion of ring conformations is responsible for a lower quantum yield of photolysis and for formation of cyclooctanone as the main reaction product in polymeric medium, instead of nitroso compound as expected from the Barton reaction.

Acknowledgment. We are indebted to the Ministry of Science and Scientific Programmation for supporting this research and to IWONL, Belgium, for a fellowship (C.J.).

References and Notes

(1) Barton, D. H. R.; Beaton, J. M.; Geller, L. E.; Pechet, M. M. *J. Am. Chem. Soc.* **1960**, *82*, 2640. *Ibid.* **1961**, *83*, 4076.
(2) Barton, D. H. R.; Beaton, J. M. *J. Am. Chem. Soc.* **1961**, *83*, 4083.
(3) Barton, D. H. R.; Hesse, R. H.; Pechet, M. M.; Smith, L. C. *J. Chem. Soc., Perkin Trans. 1* **1979**, 1159.
(4) Akhtar, M.; Barton, D. H. R.; Sammes, P. G. *J. Am. Chem. Soc.* **1965**, *87*, 4602.
(5) Kabasakalian, P.; Townley, E. R. *J. Org. Chem.* **1962**, *27*, 2918. *J. Am. Chem. Soc.* **1962**, *84*, 2711, 2723, 2724.
(6) James, B.; Hendrickson, J. *J. Am. Chem. Soc.* **1964**, *86*, 4854.
(7) Smets, G.; Nijst, G.; Schmitz-Smets, M.; Somers, A. *J. Polym. Sci., Polym. Symp.* **1980**, *No. 67*, 83.
(8) Smets, G.; Schmitz-Smets, M. "Structural Order in Polymers"; Ciardelli, Fr., Giusti, P., Eds.; IUPAC-Pergamon Press: Oxford, 1981; pp 221–230.
(9) Kornblum, N. *J. Am. Chem. Soc.* **1947**, *69*, 465.
(10) Baltazzi, E. S.; Dailey, E. E.; Datta, P.; Printy, H.; Wagner, W. *J. Photogr. Sci. Eng.* **1974**, *18*, 126.
(11) Akhtar, M.; Pechet, M. M. *J. Am. Chem. Soc.* **1964**, *86*, 265.
(12) Allen, J.; Boar, R. B. *J. Chem. Soc., Perkin Trans. 1* **1973**, 2402.

Kinetics of Polycondensation and Copolycondensation by Amide-Interchange Reactions

Man Jung Han

Department of Chemical Engineering, Ajou University, Suweon 170, South Korea.

Received August 12, 1980

ABSTRACT: Low molecular weight amino-terminated polyamides were synthesized via amide-interchange reactions of diamine amides of dibasic acids. The kinetics of polycondensation and copolycondensation by amide-interchange reactions were investigated by using *N,N′*-bis(2-aminoethyl)sebacamide and *N,N,N′,N′*-bis(diethylenimino)sebacamide as monomers. It was found that the polycondensation followed second-order kinetics with respect to the concentrations of amino and amide groups in the monomers at the initial stage of the reaction. The rate constants of cross reactions in the copolycondensation and the diamine component ratios incorporated into the copolymer were determined from the equations derived. The reactivity ratios of the copolycondensation were calculated on the basis of the rate constants.

Introduction

Syntheses of polyamides can be categorized into three groups:[1] (1) heating the dibasic carboxylate salts of diamines, (2) reacting diamines with dibasic acid esters, and (3) reacting diamines with dibasic acid chlorides. In addition, amino-terminated polyamides can be obtained by polycondensation of diamine amides of dibasic acids by amide-interchange reactions in a manner analogous to the synthesis of hydroxy-terminated polyesters by polycondensation of diol esters of dibasic acids by ester-interchange reactions.[2]

Low molecular weight amino-terminated polyamides are expected to be potential prepolymers in the syntheses of high polymers since they are difunctional and the amino groups have high reactivity. The amino-terminated polyamides, in fact, can be easily incorporated into polyurethane elastomers. The succeeding polyamide blocks modify the physical properties of the polyurethane significantly.

In this paper we report syntheses of amino-terminated polyamides and the kinetics of polycondensation and copolycondensation of diamine amides of dibasic acids by amide-interchange reactions.

Kinetics

Polycondensation. The polycondensation of the diamine amides of dibasic acids by amide-interchange reactions can be expressed in general terms as

$$n\mathrm{H_2NRNHOCR'CONHRNH_2} \rightarrow \mathrm{H(HNRNHOCR'CO)}_n\mathrm{NHRNH_2} + (n-1)\mathrm{H_2NRNH_2} \tag{1}$$

When the diamines formed during the polycondensation are removed, polyamide is left behind.

The initial step of the polyamidation can be written as

$$2H_2NRNHOCR'CONHRNH_2 \xrightarrow{k} H_2NRNHOCR'CONHRNHOCR'CONHRNH_2 + H_2NRNH_2 \quad (2)$$

If the concentration of amino group is $[NH_2]$ and the concentration of amide group is [CON] and if the diamines formed during the reaction are continuously removed and no catalyst is used, the kinetics of the polyamidation can be expressed as

$$-d[NH_2]/dt = k[CON][NH_2] \quad (3)$$

At the initial stage of the polyamidation the concentrations of amino and amide groups should be equal, and eq 3 becomes

$$-d[NH_2]/dt = k[NH_2]^2 \quad (4)$$

Rearrangement and integration of eq 4 give

$$1/[NH_2] = kt + C \quad (5)$$

Plotting the reciprocals of amino concentration vs. time permits one to obtain the rate constant of the polyamidation from the slope.

When the concentration of amino end groups is expressed in molality, the molecular weight of the polyamide can be given as eq 6 since a polyamide molecule contains two amino end groups.

$$MW = (2/[NH_2]) \times 10^3 \quad (6)$$

Copolycondensation. When monomer 1 ($H_2NR_1NHOCRCONHR_1NH_2$) and monomer 2 ($H_2NR_2NHOCRCONHR_2NH_2$) are copolycondensed under the condition that the amino group of the second chain end attacks the amide group of the first chain end, the following sequence of reactions should be considered to take place:

$$\text{---}RCONHR_1NH_2 + H_2NR_1NHOCR\text{---} \xrightarrow{k_{11}} \text{---}RCONHR_1NHOCR\text{---} + H_2NR_1NH_2 \quad (7)$$

$$\text{---}RCONHR_1NH_2 + H_2NR_2NHOCR\text{---} \xrightarrow{k_{12}} \text{---}RCONHR_2NHOCR\text{---} + H_2NR_1NH_2 \quad (8)$$

$$\text{---}RCONHR_2NH_2 + H_2NR_1NHOCR\text{---} \xrightarrow{k_{21}} \text{---}RCONHR_1NHOCR\text{---} + H_2NR_2NH_2 \quad (9)$$

$$\text{---}RCONHR_2NH_2 + H_2NR_2NHOCR\text{---} \xrightarrow{k_{22}} \text{---}RCONHR_2NHOCR\text{---} + H_2NR_2NH_2 \quad (10)$$

Reactions 8 and 9 represent cross reactions, whereas reactions 7 and 10 are homoreactions in general terms.

With the concentrations of amino and amide groups of chain end 1 expressed as $[NH_2]_1$ and $[CON]_1$ and those of chain end 2 expressed as $[NH_2]_2$ and $[CON]_2$, the rates of diamine ($H_2NR_1NH_2$ and $H_2NR_2NH_2$) formation become

$$d[H_2NR_1NH_2]/dt = k_{11}[CON]_1[NH_2]_1 + k_{12}[CON]_1[NH_2]_2 \quad (11)$$

$$d[H_2NR_2NH_2]/dt = k_{21}[CON]_2[NH_2]_1 + k_{22}[CON]_2[NH_2]_2 \quad (12)$$

The incorporation of diamine components in the copolyamide by homocondensation and by cross condensation are given by

$$d[\text{-}HNR_1NH\text{-}]/dt = k_{21}[CON]_2[NH_2]_1 + k_{11}[CON]_1[NH_2]_1 \quad (13)$$

$$d[\text{-}HNR_2NH\text{-}]/dt = k_{12}[CON]_1[NH_2]_2 + k_{22}[CON]_2[NH_2]_2 \quad (14)$$

In the previous paper[2] we derived the kinetics of copolyesterification by ester-interchange reactions. Since the sequences of copolyamidation reactions 7–10 correspond to those of the copolyesterification, the kinetics of the latter can be applied for the former; then eq 15, which is derived

$$ak_{11} - (b/a)k_{22} = bk_{21} - k_{12} \quad (15)$$

for the copolyesterification, is also applicable for the copolyamidation, 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; i.e.

$$a = [\text{monomer}]_1/[\text{monomer}]_2$$

$$b = d[H_2NR_1NH_2]/d[H_2NR_2NH_2] \quad (16)$$

The rate constants of homopolycondensations, k_{11} and k_{22}, are obtainable from eq 5. Plotting the left term of eq 15 as a function of b, one 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.

The diamine component ratio (c) incorporated into the copolyamide by reactions 7–10 can be calculated from[2]

$$c = \frac{d[\text{-}HNR_1NH\text{-}]}{d[\text{-}HNR_2NH\text{-}]} = a\frac{k_{21} + ak_{11}}{ak_{12} + k_{22}} \quad (17)$$

If an azeotrope exists, the azeotropic monomer ratio can be obtained from the rate constants according to eq 18, since a would be equal to c at the azeotropic composition.

$$a = c = (k_{21} - k_{22})/(k_{12} - k_{11}) \quad (18)$$

In this study *N,N'*-bis(2-aminoethyl)sebacamide (AES) and *N,N,N',N'*-bis(diethylenimino)sebacamide (DEIS) are chosen as monomer 1 and monomer 2, respectively.

Experimental Section

Synthesis of Monomers. *N,N'*-Bis(2-aminoethyl)sebacamide (AES). Dimethyl sebacate was synthesized by the conventional method[3] (bp_{20} 175 °C) and 1,2-diaminoethane (DAE) was distilled before use (bp 117 °C). In an autoclave (1 L) a mixture of dimethyl sebacate (73 g, 0.32 mol) and DAE (190 g, 3.16 mol) was heated at 150 °C for 6 h 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 5:1 (v/v) ethyl acetate–methanol and the higher molecular weight compounds, being insoluble at the boiling point of the solvent mixture, were removed by filtration. AES was crystallized several times from 2-propanol: yield 40%; mp 120 °C. AES was dissolved in methanol, and the amino concentration of AES was measured by titration with 0.1 N HCl, using bromophenol blue as indicator. The amino group concentration was found to be 6.92 mol/kg, which is equivalent to a molecular weight of 289 (MW of AES = 286.48). Anal. Calcd: C, 58.69; H, 10.58; N, 19.56. Found: C, 58.10; H, 10.21; N, 20.05.

***N,N,N',N'*-Bis(diethylenimino)sebacamide (DEIS).** Piperazine (PZ) was crystallized from benzene (mp 103 °C). In an autoclave (1 L) a mixture of PZ (201.6 g, 2.34 mol) and dimethyl sebacate (54 g, 0.23 mol) was heated at 200 °C for 7 h with stirring (autoclave pressure 7 atm). The reaction mixture was transferred to a flask and the excess PZ was removed under reduced pressure (40 mmHg) for 2 h. Upon addition of equivalent concentrated HCl, DEIS hydrochloride salt was formed, which was crystallized several times from methanol; mp 244 °C. After neutralization of the salt with NaOH, DEIS was extracted with chloroform. After

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

10^3(rate constant), h^{-1} (mol/kg)$^{-1}$	reactivity ratio
$k_{11} = 3.01$	$r_1 = 1.30$
$k_{22} = 1.70$	$r_2 = 0.59$
$k_{12} = 2.31$	
$k_{21} = 2.89$	

evaporation of the chloroform, DEIS was crystallized from toluene: yield 52%; mp 102 °C. The imino group concentration was measured by titration as aforedescribed and found to be 5.96 mol/kg, which is equivalent to a molecular weight of 335.6 (MW of DEIS = 338.56). Anal. Calcd: C, 63.85; H, 10.14; N, 16.55. Found: C, 63.10; H, 9.76; N, 16.21.

Polycondensation. The polycondensation apparatus was described elsewhere.[2] After the temperature of the apparatus was set at 200 °C, about 20 g of AES or DEIS was charged through a funnel, and vacuum (20 mmHg) was applied in the polycondensation apparatus, which was stirred. 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 measured by titrations as described above.

Copolycondensation. In order to collect distillate, a glass tube with a pot at one end was vertically connected to the inner wall of the neck of a flask (100 mL). The flask was immersed to its neck in an oil bath. After the temperature of the oil bath was set at 200 ± 1 °C, a mixture of the required amount of AES and DEIS was charged and stirred. As the reaction progressed 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 analyzed by GC (column: 10% Carbowax 20M plus 5.0% KOH on Chromosorb W A/W, 2 m; column temperature: 80 °C).

Results and Discussion

Polycondensation. The polycondensations of AES and DEIS were carried out under reduced pressure (20 mmHg) at 200 °C with stirring. Under these reaction conditions the diamines formed during the condensation, 1,2-diaminoethane (DAE) and piperazine (PZ), were removed so rapidly that the reverse reaction of eq 2 can be neglected. The concentrations of amino and imino groups of the polyamides sampled during the polycondensation were measured by titration. Since the polyamidation of DEIS proceeded very slowly, large sample quantities (ca. 0.2 g) were taken for the titration in order to minimize the titration errors.

Reciprocals of the amino and imino concentrations as a function of time are shown in Figure 1. As 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 concentration. Since the plots were shown to be straight lines, the kinetics of the polycondensations are second order with respect to the concentrations of amino (or imino) and amide groups at the initial stage of the reaction as predicted in eq 3. In the AES plot, the deviation from linearity after 6 h of polycondensation might be caused by midchain amide interchange. The molecular weight of the polyamide increased linearly with polycondensation time. High molecular weight polyamide can be obtained by a prolonged polycondensation time.

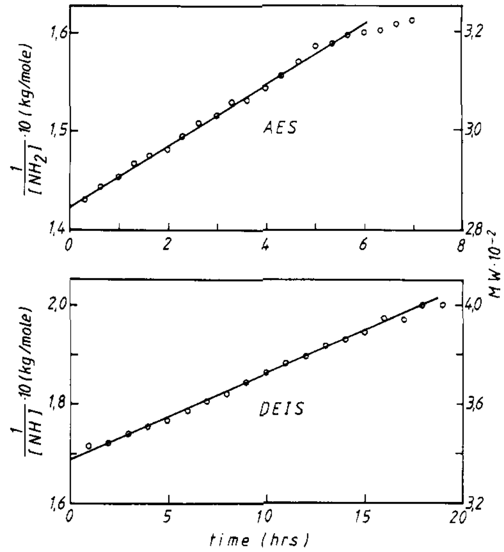

Figure 1. Reciprocals of amino and imino concentrations during polycondensation of AES and DEIS as a function of time at 200 °C and the molecular weight of the polymer against the time of polycondensation.

The rate constants obtained from the slopes in Figure 1 are given in Table I. The probable reason that the polycondensation of AES proceeded about 2 times faster than that of DEIS seemed to be the steric hindrance of the large piperazinyl groups in DEIS.

Copolycondensation. Piperazine (PZ) and 1,2-diaminoethane (DAE) formed during reactions 7–10 were distilled during the copolycondensation of AES and DEIS. GC analysis 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 of AES and DEIS.

Monomer mixtures with precise compositions of AES and DEIS were copolycondensed and the mixture of distilled diamines was recovered. Since 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

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

a ([AES]/[DEIS])	mol % of AES in monomer mixture	b ([DAE]/[PZ])	c^a ([-DAE-]/[-PZ-])	mol % of DAE in polymer^b	$(ak_{11} - (b/a)k_{22}) \times 10^3$
0.20	16.67		0.32	24.24	
0.40	28.57	0.52	0.63	38.65	−1.01
0.50	33.33	0.71	0.77	43.50	−0.91
0.82	45.05	0.97	1.23	55.15	0.46
1.18	54.13	1.29	1.72	63.24	1.69
1.51	60.15	1.70	2.16	68.35	2.63
2.01	66.78	2.28	2.84	73.96	4.12
2.39	70.50	2.42	3.34	76.96	5.47
10.00	90.91		13.32	93.02	

[a] Calculated by eq 17. [b] Calculated from c.

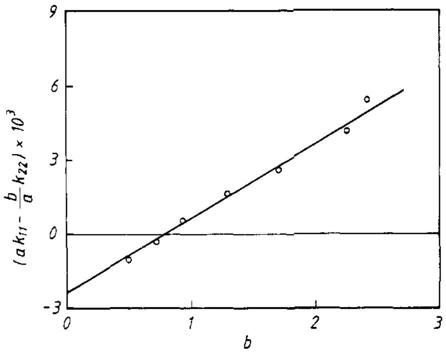

Figure 2. Plot of eq 15.

of the total amino and imino concentrations in the monomers, and the compositions of the mixture were analyzed by GC. The mole ratios of monomers ([AES]/[DEIS]), a, as well as those of diamines ([DAE]/[PZ]) distilled, b, are given in Table II.

The calculated values of the left terms in eq 15, $ak_{11} - (b/a)k_{22}$, are listed in Table II and these are plotted as a function of b in Figure 2. Since a straight line is obtained, we may conclude that eq 15 is also valid for the copolyamidation by amide-interchange reactions. The rate constant of cross reaction 9, k_{21}, and that of cross reaction 8, k_{12}, are obtained from the slope and from the intercept in Figure 2, respectively. The rate constants are given in Table I. The reactivity ratios given in Table I are calculated from the rate constants of the four reaction paths, i.e., reactions 7–10, of the copolycondensation.

The ratios of diamine components incorporated into the copolymer by reactions 7–10, c, calculated according to eq 17, are given in Table II. The mole ratios of the calculated values (c) as a function of monomer ratio are shown in Figure 3, which is quite similar to the radical copolymerization diagram[4] 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 1.30 and 0.59, respectively.

The azeotropic composition, calculated in accordance with eq 18, is found to be negative ($a = -1.7$) and it is practically meaningless since it has to be positive ($a > 0$). Consequently, it is not found in the diagram (Figure 3).

Cross reaction 9 of the amide groups in DEIS with the aminoethyl groups of AES proceeded faster than that (reaction 8) of the amide groups in AES with the piperazinyl groups of DEIS ($k_{21} > k_{12}$). The difference in reaction rates between reactions 8 and 9 can be explained in terms of steric hindrance since the piperazinyl group is larger than the aminoethyl group.

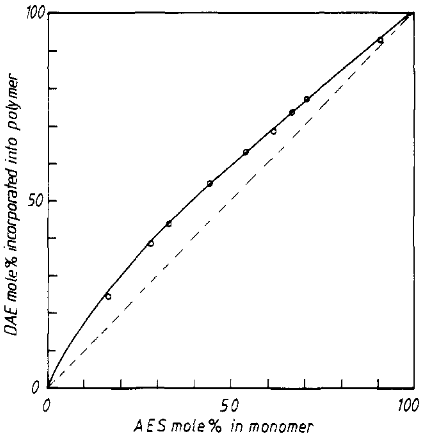

Figure 3. Calculated mole percent of diamines incorporated into the copolyamide by reactions 7–10 as a function of monomer mole percent.

Conclusions

(1) The polycondensation of diamine amides of dibasic acids obeys second-order kinetics with respect to the concentrations of amino and amide groups at the initial stage of the reaction.

(2) The rate constants of cross reactions of the copolycondensation are obtained from eq 15, and the reactivity ratios ($r_1 = 1.30$, $r_2 = 0.59$) are calculated from the four rate constants of the copolycondensation.

(3) The ratios of diamine components incorporated into the copolymer were calculated by eq 17, from which a diagram was constructed and found to be similar to the composition diagram of the radical copolymerization, which has reactivity ratios $r_1 > 1$ and $r_2 < 1$.

(4) The azeotropic composition was calculated by eq 18 and it was found to have a negative value. No azeotrope was found in the diagram.

Acknowledgment is made to the Ministry of Education for generous financial support of this work.

References and Notes

(1) Jones, D. C.; White, T. R. "Polyamide in Step-Growth Polymerization"; Solomon, D. H., Ed.; Marcel Dekker: New York, 1972; p 41.
(2) Han, M. J. *Macromolecules* **1980**, *13*, 1009.
(3) Becker, H., et al. "Organikum"; VEB Deutscher Verlag der Wissenschaften: Berlin, 1964; p 369.
(4) Vollmert, B. "Grundriss der Makromolekularen Chemie"; Springer-Verlag: Berlin, 1962; p 84.