

Syntheses of Functional Condensation Polymers. II. A Polyamide Having Epoxy Groups and Its Ring-Opening Derivatives

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Synopsis

Polyamides having epoxy groups and their ring-opening derivatives were prepared and characterized, and some of their properties were investigated. Reaction conditions for the low-temperature polycondensation of *cis*-2,3-epoxysuccinyl chloride (ESC) with aromatic diamines and the interfacial copolycondensation of ESC and adipyl chloride (AC) with aromatic diamines were established to obtain a high molecular weight polyamide having epoxy groups. In addition, the ring-opening reactions of the epoxy groups in the polyamides were carried out with various amines in order to obtain polyamides having hydrophilic pendent groups such as amino and hydroxyl. It was found that the polyamides prepared by ring-opening reaction of the epoxy group with ethylenediamine (EDA) or ethanolamine (EA) had a higher affinity for moisture than those with hexamethylenediamine (HMD) or *n*-butylamine (*n*-BA), which might be ascribed to the distance of hydrophilic groups from the polyamide chain. Those polyamides having hydrophilic pendent groups decomposed upon heating at less than 200°C.

INTRODUCTION

In recent years a number of publications¹⁻³ have dealt with the preparation of functional condensation polymers. The conventional melt polycondensation of monomers having pendent functional groups causes crosslinking reactions of the reactive side groups or thermal degradations of functional groups at elevated temperature, so that the preparation of functional condensation polymers is usually carried out by polymer reactions.

It has been reported previously⁴ that polyesters having pendent functional groups such as hydroxyl, formyl, aldoxime, aminomethyl, and hydroxymethyl could be prepared by using the epoxidation and the hydroformylation of unsaturated polyesters, and so on. That is, the hydroformylation could be used to incorporate formyl side groups into the unsaturated polyesters; these groups in the modified polyesters could then be converted to alcohol or aldoxime groups and finally to the amino derivatives. Epoxidation of the unsaturated polyesters, followed by hydrolysis of the epoxy groups, has been also carried out to obtain hydrophilic polyesters having pendent diol groups.

Recently, there has been considerable interest in functional polyamides having hydroxyl or amino groups which have hydrophilic properties. However, the hydroformylation of unsaturated polyamides with $\text{RhH}(\text{CO})(\text{PPh}_3)_3$ did not take place under conditions as described in a previous paper⁴ because of coordination of the rhodium catalyst to the amide groups in the polymer.

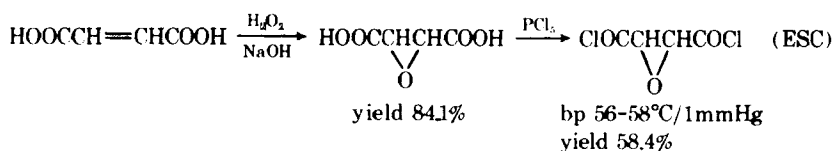
This paper describes the results of the use of dicarboxylic acid chloride having

an epoxy group as monomer for the preparation of polyamides having epoxy groups. Low-temperature and interfacial polycondensations of dicarboxylic acid chloride having an epoxy group with aromatic diamines have been carried out to obtain polyamides having epoxy groups. Furthermore, ring-opening reactions of the epoxy groups in the polyamides with various amines were carried out in order to convert the epoxy polyamide into hydrophilic polyamides.

EXPERIMENTAL

Materials

cis-2,3-Epoxy succinyl chloride (ESC) was prepared as described by Payne⁵ and Campbell⁶ from maleic acid via the following route:



The ESC obtained was purified by repeated distillation under reduced pressure.

Commercially available hexamethylenediamine (*HMD*) and *n*-butylamine (*n-BA*) were purified by vacuum distillation, and hydrazine hydrate (*HH*) and extrapure reagents of *m*- and *p*-phenylenediamine (*MPD* and *PPD*) were used as purchased. All solvents used were purified before use by conventional methods.

Model Reaction

A condensation reaction of 2 mmole ESC with 4 mmole aniline in 10 ml acetone was carried out in the presence of 4 mmole triethylamine. The structure of the resulting *cis*-2,3-epoxy succinyl dianilide (*ESDA*) was identified by elemental, infrared, and NMR analyses: mp 156°C, yield 80.7%.

Low-Temperature Solution Polycondensation

Equimolar amounts of ESC and diamines were dissolved in various solvents at a concentration of 0.1 mole/l. in the presence of triethylamine, and the solutions were kept at 30°C with stirring for a given period. The solutions were poured into excess acetone or methanol, and the polymers were filtered, followed by repeated washing with water and acetone and then drying.

Interfacial Copolycondensation

Copolycondensation of adipyl chloride (*AC*) and ESC with phenylenediamine was carried out as follows: 2 mmole *MPD* or *PPD* was dissolved in 10 ml water in the presence of 4 mmole sodium hydroxide, and a total amount of 2 mmole mixed *AC* and *ESC* at various feed ratios which was dissolved in 10 ml 1,2-dichloroethane was added to the aqueous solution of the diamines with vigorous stirring in a homoblender. After stirring was continued for 5 min, the solution

was poured into excess acetone, and the precipitated copolymer was filtered, followed by washing with water and drying.

Polymer Characterization

The structure of the polymers obtained was identified by infrared, elemental, and NMR analyses. Solution viscosities of the polyamides were measured in DMAc containing 2.5 wt-% LiCl or in DMSO at 30°C at a concentration of 0.1 g/10 ml. Thermal properties of the polyamides were determined by differential thermal or thermogravimetric analyses using the Rigakudenki Thermoflex 8075. Moisture adsorption of the polyamides was measured by weight increase after powder samples of dried polyamides were placed at 22°C for several days in a desiccator which contained air of a given relative humidity. BET surface area for the polyamides was determined from adsorption isotherm of nitrogen at liquid nitrogen temperature by using a standard gas-volumetric, high-vacuum glass system.

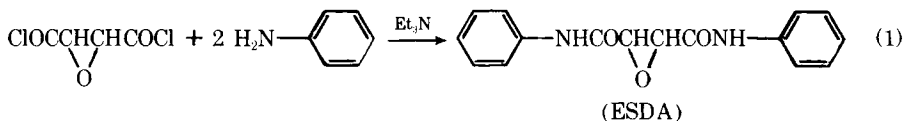
Ring-Opening Reaction of Epoxy Group

Polyamides having epoxy groups and excess amines such as HH, EDA, HMD, EA, and *n*-BA were dissolved in DMSO, and the solutions were kept at 60°C for 24 hr with stirring. The reaction mixtures were poured into excess methanol and the precipitates were filtered, washed with methanol, and then dried. It was confirmed from the results of the model reaction of ESDA with *n*-butylamine that the amide exchange reaction did not occur during the ring-opening reaction of the epoxy group in the polymers so as to reduce the molecular weight during the ring-opening reaction.

RESULTS AND DISCUSSION

Model Reaction

The condensation reaction of ESC with aniline in acetone was carried out using triethylamine as acid acceptor. The product was identified by elemental, infrared, and NMR analyses:



ANAL. Found: C, 68.78%; H, 4.64%; N, 10.02%, Calcd: C, 68.08%; H, 5.00%; N, 9.92%.

It was confirmed by NMR analysis that the epoxide content in the reaction product was 100 mole-%. The infrared spectrum of the reaction product exhibits two typical absorptions owing to amide I and II bands at 1650 and 1555 cm^{-1} . The NMR spectrum of the product showed chemical shifts of the epoxide methyl protons and the phenyl protons in the epoxy groups at 4.00 (singlet) and 7.0–7.7 (multiplet) ppm, respectively. Thus, the reaction product from ESC and aniline was confirmed to be ESDA, as shown in eq. (1), from elemental and these spectroscopic analyses.

Solution Polycondensation

Low-temperature solution polycondensation of ESC with MPD or PPD was carried out in various solvents. The results are summarized in Tables I and II, where it can be seen that the polyamides having relatively low solution viscosities were obtained from ESC and MPD or PPD. Solvents influenced neither polymer yield nor solution viscosity. MPD and PPD were also found to have almost the same reactivity toward ESC. Since succinyl chloride (SC) is known to give a low molecular weight polyamide, polyamides prepared from ESC and MPD or PPD as well as that from SC may not reach a higher molecular weight.

Amide solvents such as DMF and DMAc could not be used as solvent in the solution polycondensation of ESC with diamines, because ESC reacts with amide solvents. The polyamide did not have a distinct melting point and started to decompose on heating at around 260°C. The degree of ring-opening reaction of epoxy groups was too small to be detected by NMR analysis although the epoxy group in diester monomers was expected to react with diamine under these polycondensation conditions. The resulting polyamide was soluble in DMAc containing 2.5 wt-% LiCl, indicating that the degree of crosslinking might be very small even though the ring-opening reaction occurred during the polycondensation reaction.

TABLE I
Solution Polycondensation of ESC with PPD in Various Solvents^a

Solvent	Yield, %	η_{sp}/C^b	Decomp. temp., °C
Chloroform	76.5	0.13	270
Nitrobenzene	59.4	0.09	255
Acetonitrile	70.9	0.16	272
Tetrahydrofuran	70.9	0.12	264
Cyclohexanone	63.8	0.09	268
1,2-Dichloroethane	74.8	0.14	279
1,2-Dichloroethane ^c	56.1	0.11	—

^a Monomer concentration, 0.10 mole/l.; acid acceptor, Et₃N.

^b 0.1 g/10 ml in DMSO at 30°C.

^c Monomer concentration, 0.05 mole/l.

TABLE II
Solution Polycondensation of ESC with MPD in Various Solvents^a

Solvent	Yield, %	η_{sp}/C^b	Decomp. temp., °C
Chloroform	59.5	0.11	266
Nitrobenzene	52.4	0.11	279
Acetonitrile	39.9	0.17	264
Tetrahydrofuran	58.4	0.15	263
Cyclohexanone	47.6	0.11	275
1,2-Dichloroethane	55.7	0.12	282
1,2-Dichloroethane ^c	62.5	0.15	—
1,2-Dichloroethane ^d	66.7	0.08	—

^a Monomer concentration, 0.10 mole/l.; acid acceptor, Et₃N.

^b 0.1 g/10 ml in DMSO at 30°C.

^c Monomer concentration, 0.20 mole/l.

^d Monomer concentration, 0.05 mole/l.

Interfacial Copolycondensation

Copolycondensation of AC and ESC with MPD or PPD was carried out by the interfacial polycondensation method in order to obtain a high molecular weight polyamide. Tables III and IV summarize results of the interfacial copolycondensation at various monomer feed ratios. It is clear from Table III that the yields, solution viscosities, and decomposition temperatures of copolyamides from AC and ESC with PPD decrease with increasing molar ratio of ESC in the feed. Unfortunately, compositions of the copolyamides from AC and ESC with PPD could not be determined by NMR analysis because of their poor solubilities in DMSO- d_6 .

On the other hand, the copolyamide from AC and ESC with MPD could be dissolved, and compositions in the copolyamides were determined by the NMR analyses. These results are indicated in Table IV. As shown in Table IV, the mole fraction of *cis*-2,3-epoxysuccinyl units in the copolyamides was somewhat smaller than that of ESC in the monomer feed, and the reason may be ascribed to the less reactivity of ESC.

It can be seen by comparing the results in Table III with those in Table IV that the yields and solution viscosities of copolyamides prepared from PPD were higher than those from MPD.

TABLE III
Interfacial Copolycondensation of AC and ESC with PPD^a

AC:ESC molar ratio in feed	Yield, %	η_{sp}/C^b	Decomp. temp., °C
8 : 2	90.2	0.52	323
6 : 4	80.9	0.43	306
5 : 5	73.7	0.36	255
4 : 6	69.0	0.28	263
2 : 8	55.8	0.21	266
0 : 10	54.7	0.15 ^c	240

^a Monomer concentration, [AC] + [ESC] = [PPD], 0.20 mole/l.

^b 0.1 g/10 ml in DMAc-LiCl (2.5 wt-%) at 30°C.

^c 0.1 g/10 ml in DMSO at 30°C.

TABLE IV
Interfacial Copolycondensation of AC and ESC with MPD^a

AC:ESC molar ratio in feed	Yield, %	η_{sp}/C^b	Decomp. temp., °C	ESC in copolymer, ^c mole-%
8 : 2	43.0	0.30	244	10
6 : 4	47.4	0.33	256	27
5 : 5	49.8	0.30	256	39
4 : 6	46.8	0.29	267	45
2 : 8	41.8	0.17	283	77
0 : 10	39.8	0.14	280	100

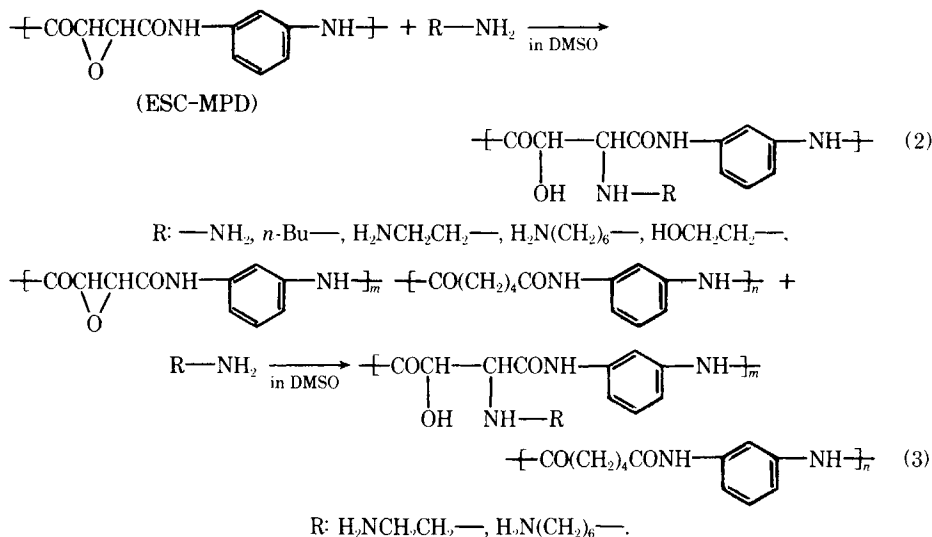
^a Monomer concentration, [AC] + [ESC] = [MPD], 0.20 mole/l.; acid acceptor, 0.40 mole/l. NaOH.

^b 0.1 g/10 ml in DMAc-LiCl (2.5 wt-%) at 30°C.

^c Estimated from NMR analysis.

Ring-Opening Reaction of Epoxy Group

Ring-opening reactions of epoxy groups in the polyamides were carried out with excess amines such as HH, EDA, HMD, EA, and *n*-BA as shown in eqs. (2) and (3):



Results are summarized in Tables V and VI. The products prepared by ring-opening reactions of the epoxy group in the polyamides have a poor thermal stability. That is, their decomposition temperatures were lower than those of the original polyamides having epoxy groups. It was found that the ring-opening reaction of the epoxy group in the polyamide with HH caused a great decrease

TABLE V
Polyamides Prepared by Ring-Opening Reaction of Epoxy Group with R-NH₂

Polyamide R	η_{sp}/C^a	Decomp. temp., °C
ESC-MPD	0.14	264
<i>n</i> -Bu-	0.21	180
H ₂ N-	0.06	141
H ₂ NCH ₂ CH ₂ -	0.11	164
HOCH ₂ CH ₂ -	0.19	208
N ₂ N(CH ₂) ₆ -	0.32	170

^a 0.1 g/10 ml in DMSO at 30°C.

TABLE VI
Copolyamides Prepared by Ring-Opening Reaction of Epoxy Group with R-NH₂

Copolyamide R	η_{sp}/C^a	Decomp. temp., °C	ESC units in copolymer, mole-%
ESC/AC-MPD	0.28	256	39
H ₂ NCH ₂ CH ₂ -	0.34	—	—
H ₂ N(CH ₂) ₆ -	0.21	—	—

^a 0.1 g/10 ml in DMSO at 30°C.

in the solution viscosity. This decrease in solution viscosity may be due to chain degradation by HH.

Properties

The moisture adsorptions for powder samples of the modified polyamides in the ESC-MPD series at various relative humidities at 22°C are shown in Figure 1, where those of the original polyamide and the polyamide from SC and MPD are compared. (Details of the measurements are indicated in the experimental section.) The polyamides modified by ring-opening reaction of the epoxy group with EA and EDA were found to have much higher affinities for moisture than the original polyamide having epoxy groups, as expected.

However, the polyamides prepared by the ring-opening of the epoxy group with HMD and *n*-BA have lower affinities for moisture than the original polyamide, in spite of the fact that the modified polyamide molecule has numerous hydrophilic pendent groups.

On the other hand, the polyamide modified with HH had almost the same amount of moisture adsorption as that modified with HMD at low relative humidity, while at high relative humidity it had a higher affinity for moisture. It is clear from these results that the moisture adsorption of the modified polyamides, as well as that of the modified polyesters reported in a previous paper,⁴ depends on the character of the hydrophilic pendent groups. That is, an appropriate distance between the main chain and hydroxyl or amino groups incorporated into the polyamide seems to be required for the effective action of the hydrophilic group toward the water molecule.

The moisture adsorptions of the modified copolyamides at various relative humidities are shown in Figure 2, where that of the starting copolyamide in the ESC/AC-MPD series is compared. The copolyamide modified with EDA had

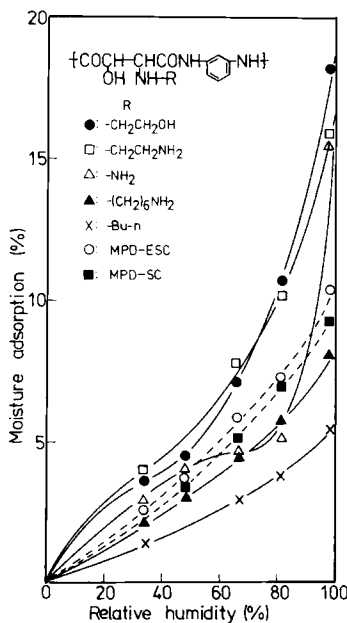


Fig. 1. Moisture adsorption of polyamides at 22°C.

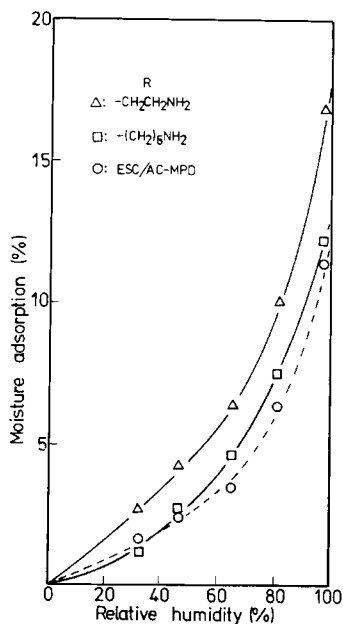


Fig. 2. Moisture adsorption of copolyamides at 22°C.

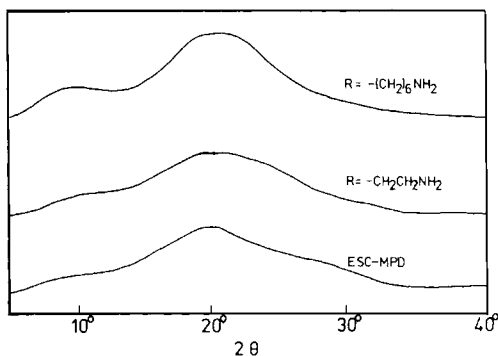


Fig. 3. X-Ray diffraction patterns of polyamides in the ESC-MPD series.

a higher affinity for moisture than that modified with HMD as well as the polyamide mentioned above.

The x-ray diffraction patterns of the modified polyamides are shown in Figure 3, which indicates that the polyamides are almost amorphous. Consequently, the difference in the moisture adsorption seems to be independent of the difference in crystallinity.

TABLE VII
BET Surface Area of Polyamides

Polyamide R	Surface area, m ² /g
ESC-MPD	28.7
H ₂ NCH ₂ CH ₂ -	23.4
H ₂ N(CH ₂) ₆ -	10.2

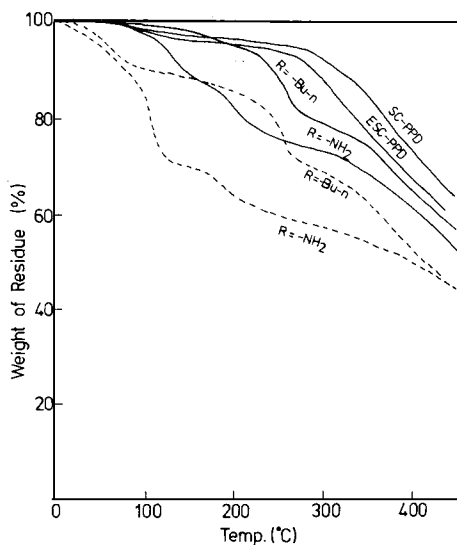


Fig. 4. TGA curves for polyamides in the ESC-PPD series: (—) dried for 36 hr at 70°C; (- - -) after adsorption of water.

The BET surface area of the polyamides is summarized in Table VII. The surface area of the polyamide modified with HMD is smaller than that modified with EDA. This might be related to the low affinity of the HMD-modified polyamide for moisture.

Figure 4 shows the TGA curves for the modified polyamides in the ESC-PPD series, which indicates that the thermal stabilities of the polyamides modified with *n*-BA and HH are lower than those of the original polyamide having epoxy groups and the polyamide from SC and PPD.

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