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## Synthesis of Polyamides and Polyesters Having Various Functional Groups

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## Synthesis of Polyamides and Polyesters Having Various Functional Groups

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### ABSTRACT

Polyamides and polyesters having various functional groups have been synthesized either by the polycondensation of functional monomers having a high reactivity or by the modification of unsaturated polymers by means of suitable polymer reactions. Polyamides or polyesters having hydrophilic groups such as hydroxyl group have a high affinity for moisture adsorption and are applicable to membrane uses. Photosensitive polyamides or polyesters were also prepared.

### INTRODUCTION

All natural polymers, including cellulose or proteins, are condensation-type polymers in terms of chemical structures, and these natural polymers have excellent functionalities to maintain life metabolism. There has been considerable interest in synthesizing polymers having functionalities similar to those of natural polymers in terms of separation, transport of ions, and so on.

Most synthetic functional polymers are limited to olefinic polymers derived from the polymerization of functional monomers by free-radical or ionic polymerizations or the reaction of olefinic polymers to introduce functional groups into polymer chains after the olefinic polymers have been prepared. On the other hand, very few reports have been published on the synthesis of condensation polymers having functional groups. The reason for this may lie in the difficulty in polymerizing monomers having functional groups by conventional melt methods at elevated temperatures and in the difficulty in dissolving condensation polymers in common organic solvents for polymer reactions. For instance, polycondensation of hydroxyl diesters or dicarboxylic acids with diamines easily causes degradation at high temperatures above the melting point of the nylon salts formed from the acid and diamine, and no polymer having a high molecular weight is obtained.

Common polyamides or polyesters are quite insoluble in organic solvents such as benzene or alcohol except strong acids, and the modification of these polyamides or polyesters by suitable polymer reactions is very difficult because of the poor solubility.

It was found that the reactivity of diesters having a hetero atom or heterocyclic groups is greatly enhanced to such extent that the polycondensation reaction of these diesters can take place in solutions under mild conditions to form condensation polymers having various functional groups. Polyamides or polyesters having double bonds in the main chains are useful starting materials to introduce functional groups because various addition reactions to the double bond are available when the materials are soluble in common organic solvents.

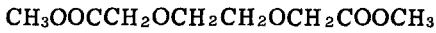
This paper describes new synthetic routes to obtain functional condensation polymers either by solution polycondensation of functional monomers or by the modification of condensation polymers by means of suitable polymer reactions of unsaturated polyamides or polyesters.

## SYNTHESIS OF FUNCTIONAL POLYAMIDES

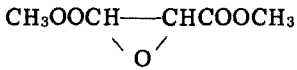
### Polycondensation of Diesters Having Various Functional Groups

It was found [ 1, 2 ] that diesters having hetero atoms such as oxygen or sulfur atoms at a position  $\alpha$  to the carbonyl group of the ester undergo a polycondensation reaction with diamines to form a corresponding polyamide under mild conditions in solution.

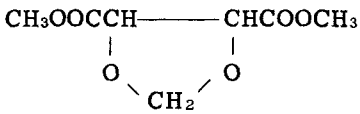
The diester monomers I-VIII were found to have a high reactivity toward polycondensation with diamines, and the corresponding polyamides could be obtained in solutions under mild conditions without heating.



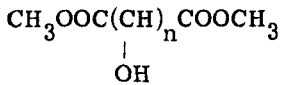
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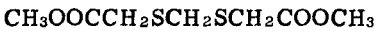
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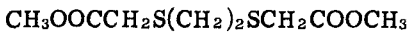
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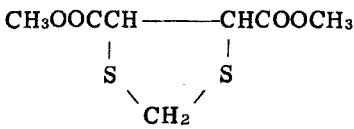
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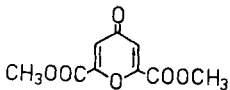
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VI



VII



VIII

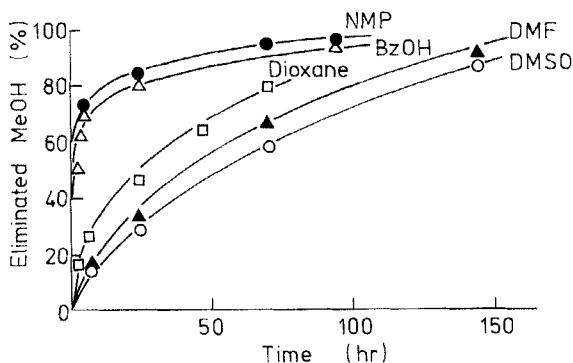


FIG. 1. Effect of solvent on the polycondensation of monomer I with hexamethylenediamine at 30°C; concentration 1 M.

Figure 1 indicates [3] the polycondensation of monomer I with hexamethylenediamine (HMD) in various solvents; the polycondensation reaction takes place at as low a temperature as 30°C, and a marked effect of solvent on the polycondensation rate is observed. The polycondensation proceeded even in methanol solution, provided that methyl ester was used as monomer, indicating that the equilibrium of the polycondensation was favorably shifted toward polymer formation.

Figure 2 indicates that the polycondensation of monomer I with HMD takes place even in aqueous solution; the polycondensation reaction occurs even at a temperature as low as 9.5°C.

Table 1 summarizes results of the polycondensation of monomer I with HMD in various solvents; yields of polymers obtained were determined by weight of the acetone-insoluble fraction.

Figure 3 indicates the polycondensation of various diesters having ether, formal [4, 5], or epoxy [5] groups at a position  $\alpha$  to the ester carbonyl group. It is seen that these three oxygen-bearing diesters have similar reactivities toward the polycondensation with HMD and the reactivity enhancement due to the oxygen atom is independent of either linear or cyclic derivatives in terms of monomer structure.

None of these polyamides derived from monomers I, II, and III has a distinct melting point, and all start to decompose on heating at temperatures above 230°C.

Since these polyamides contain hydrophilic ether, formal, or epoxy groups, some of them can dissolve in water, and most of them have a high affinity toward moisture. Figure 4 indicates the high moisture adsorption of the polyamide derived from monomer III (MT) and HMD in comparison with nylon 6.

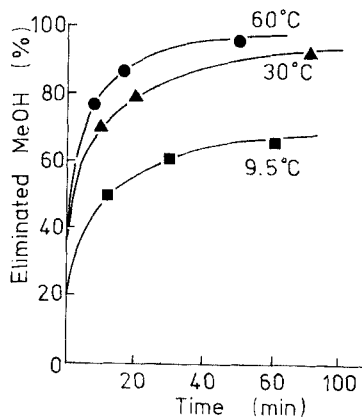


FIG. 2. Polycondensation of monomer I with hexamethylenediamine in water; concentration 0.05 M.

TABLE 1. Polycondensation of Monomer I with HMD in Various Solvents<sup>a</sup>

Solvent	Time (days)	Yield (%)	$\eta_{sp}/c$
MeOH	7	90	0.35
DMSO	7	77	0.19
Dioxane	5	39	0.20
BzOH <sup>b</sup>	7	39	0.33
NMP	7	39	0.21
CMF	7	14	0.14

<sup>a</sup> Monomer concentration, 1 M; temperature, 30°C.

<sup>b</sup> Benzyl alcohol.

Figure 5 shows the polycondensation of diethyl mucate [6], namely, diethyl 2,3,4,5-tetrahydroxyladipate, with HMD in various solvents, where a marked solvent effect on the polycondensation rate is observed. Since the polyamide from mucate and HMD did not dissolve in these solvents, the formed polyamide started to precipitate out of the solution. Therefore, the solvent effect may be ascribed to the reactivity change of ester or amino groups due to the polarity of the solvents, and also to the affinity of the solvents for the precipitating polyamide.

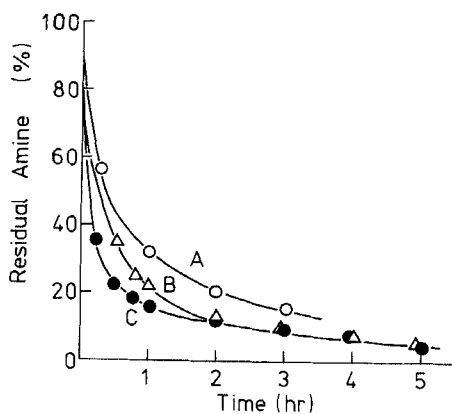


FIG. 3. Polycondensation of various diesters with hexamethylenediamine in MeOH at 30°C: (A)  $\text{MeOOCCH}_2\text{O}-\text{C}_6\text{H}_4-\text{C}(\text{CH}_3)_2\text{C}_6\text{H}_4-\text{OCH}_2-\text{COOMe}$ ; (B) monomer III; (C) Monomer II. Monomer concentration 1 M.

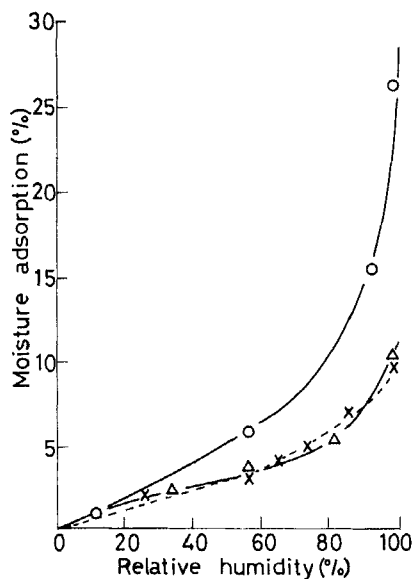


FIG. 4. Moisture adsorption of the polyamide from MT and HMD at 25°C: (○) polymer from MT; (△) polymer from L-tartrate; (×) nylon 6.

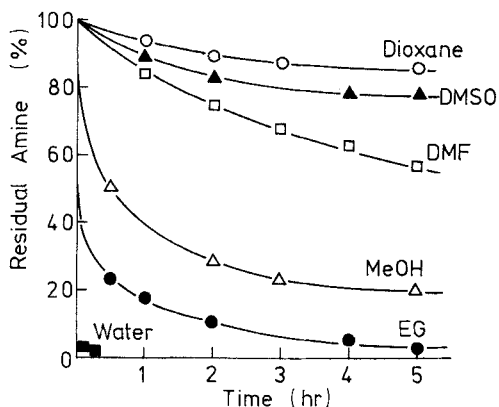


FIG. 5. Effect of solvent on the polycondensation of diethyl mucate with hexamethylenediamine at 30°C; concentration 0.05 M.

Dimethyl L-tartrate [7, 8] also underwent polycondensation with HMD in solutions at 30°C to form a polyamide having pendant hydroxyl groups, in which solvents had a great influence on the polycondensation rate. The polyamide from tartrate and HMD had a high crystallinity which disturbs the moisture adsorption. Therefore, the crystalline polyamide from tartrate and HMD did not have a high moisture adsorption as was expected from the hydrophilic character of pendant hydroxyl groups.

However, copolycondensation of tartrate and active diesters could modify the crystalline structure of the hydroxyl polyamide [9, 10]. Thus, amorphous copolyamide from tartrate and common diesters such as adipate had a high moisture adsorption.

Polycondensation of monomers V, VI, and VII, which contain sulfur atom, with HMD took place under mild conditions in solutions [2]. Figure 6 shows results of the polycondensation of monomer VI with HMD. The polycondensation reaction takes place at a much slower rate than the polycondensation of monomers having oxygen atoms. Transformation of the thioether group to a sulfone group by the oxidation with hydrogen peroxide leads to the enhancement of reactivity of the diesters (Fig. 6).

Polyamides derived from these sulfur-containing monomers suffered degradation on heating and no clear melting points were observed.

Heterocyclic diesters containing pyrazine, pyridine, furan, or thiophene had a high reactivity toward polycondensation with HMD in solutions, as indicated in Fig. 7 and Table 2, and corresponding polyamides were easily prepared under mild conditions as shown in Table 2 [11].



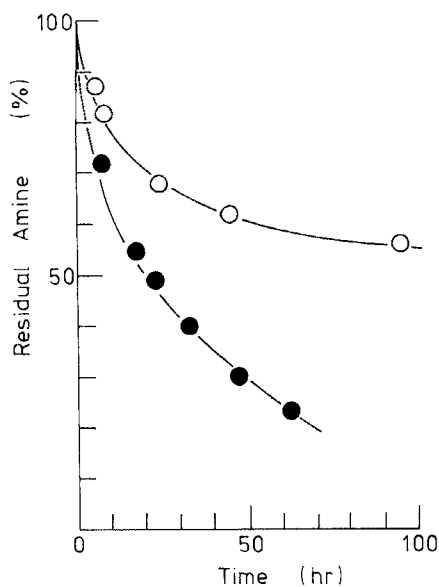


FIG. 6. Polycondensation of monomer VI with HMD in DMSO at 30°C: (○) monomer VI; (●) sulfone derivative of monomer VI. Monomer concentration 1 M.

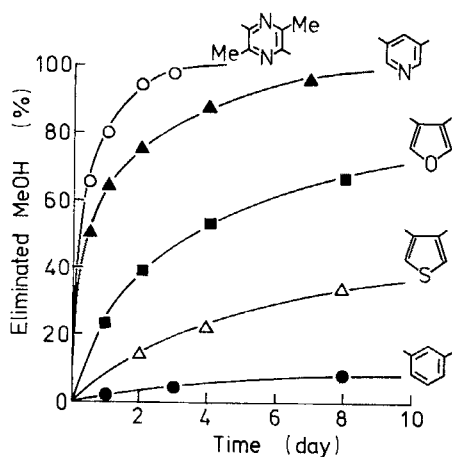













FIG. 7. Polycondensation of various dimethyl esters with hexamethylenediamine in HMPA at 60°C; concentration 1 M.

TABLE 2. Polycondensation of R''OOC-R-COOR'' with NH<sub>2</sub>-R'-NH<sub>2</sub>

-R-	-R'-	Temp (°C)	Time (hr)	$\eta_{sp}/c^a$	PMT (°C) <sup>b</sup>	Solubility <sup>c</sup>
	$(\text{CH}_2)_6$	120	46	0.19	180-192	-
	"	120	46	0.36	192-196	+
	"	100	24	0.29	230-235	-
	"	112	24	0.27	234 <sup>f</sup>	++
	"	100	46	0.31	134-140	++
	"	100	46	0.17	168-172	+
	"	112	46	0.21	114-120	+
	"	100	46	0.27	87-92	+++
	NH NH	120	20	0.08	145-152	+++
	"	120	20	0.09	174-179	+++
	$(\text{CH}_2)_6$	60	120	0.40	218-224	--

<sup>a</sup>0.10 g/10 ml in m-cresol at 30°C.

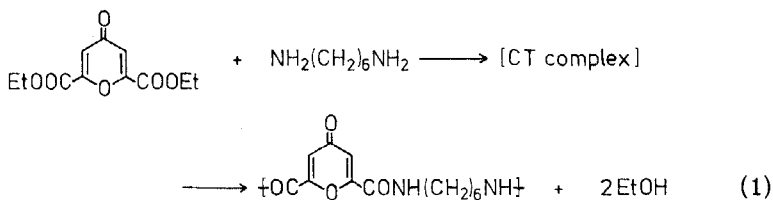
<sup>b</sup>Polymer melting temperature.

<sup>c</sup>Solubility in DMF at room temperature.

<sup>d</sup>Decomposition.

When the heterocyclic nucleus has a highly electron-accepting character to such extent that a charge-transfer complex is formed with amine, a very rapid polycondensation reaction takes place in solutions under mild conditions. Diethyl chelidonate [12, 13], which contains an electron-accepting  $\gamma$ -pyrone, underwent polycondensation with HMD in solutions to form polyamide via the formation of a charge-transfer complex at the reaction intermediate stage, and the polycondensation reaction was completed within 1 hr at 30°C to form polyamide.

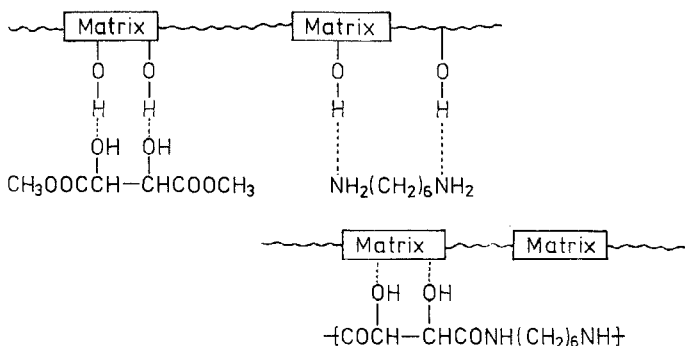
These heterocyclic polyamides have a strong affinity for heavy metal ions due to the chelation of the ions to the heterocyclic nuclei such as pyridine or  $\gamma$ -pyrone, and they can be used as scavengers of heavy metal ions, including mercury or cadmium ions.



### Matrix Polycondensation

As described previously, [14], diesters having oxygen or sulfur atoms have a high reactivity toward polycondensation in solution. Since oxygen or sulfur atoms easily form hydrogen bonds with compounds having a labile hydrogen such as amide or alcohol, it is expected that the polycondensation of these active diesters with HMD may be greatly enhanced by the presence of some polymer matrixes such as polysaccharides, polyvinylpyrrolidone, or poly(vinyl alcohol).

Figure 8 indicates the polycondensation of dimethyl tartrate with HMD in dimethyl sulfoxide (DMSO) in the presence of various polysaccharides having different molecular weights. As shown in Fig. 8, the polycondensation was greatly enhanced by the presence of polysaccharides, and the accelerating effect of polysaccharides was dependent on the molecular weight of the polysaccharide used as a matrix. Therefore, it is presumed that dimethyl tartrate and HMD may be drawn up in a line of polysaccharide molecules by hydrogen bonding, thus leading to the enhancement of the polycondensation.



Polycondensation of dimethyl tartrate with HMD in DMSO was also accelerated by the presence of poly(vinyl alcohol) (PVA), and a polymer complex which was insoluble in water was formed between

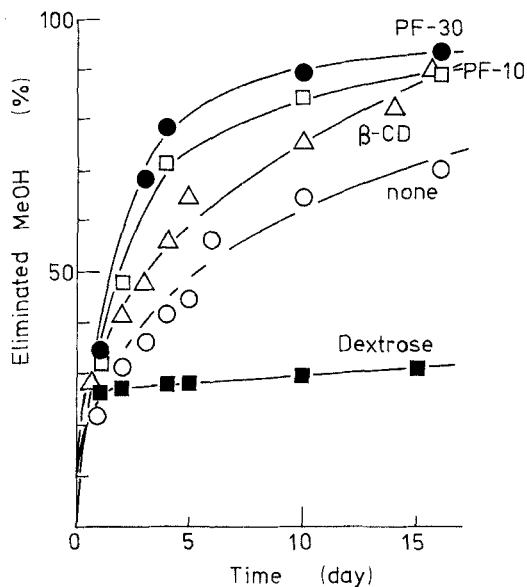


FIG. 8. Polycondensation of dimethyl tartrate with HMD in the presence of polymer (polysaccharide) matrices: (PF-30) Pluran, molecular weight 300,000; (PF-10) Pluran, molecular weight 100,000; ( $\beta$ -CD)  $\beta$ -cyclodextrin. Monomer concentration, 0.05 M; polymer matrix, 0.1 M.

the polyamide and PVA during the polycondensation. The formation of the polymer complex was dependent on the concentration of monomers and also PVA, and gelation of the solution took place at a certain concentration. Figure 9 shows the change in apparent viscosity of the DMSO solution during the polycondensation; gelation of the solution takes place at a monomer concentration of 0.3 mole/liter of dimethyl tartrate and HMD in the presence of a twice molar concentration of PVA (calculated as a repeating unit). The optimum molar ratio of monomers and PVA to form the polymer complex was found to be 1/2.

The polymer complex from the hydroxyl polyamide and PVA had a high affinity for water; it absorbed up to almost 5 times by weight as much water as the dried polymer, and a hydrogel was formed.

#### Application of the Ritter Reaction

Among the many routes for preparing polyamides, the Ritter reaction with dinitrile and formaldehyde is effective for syntheses

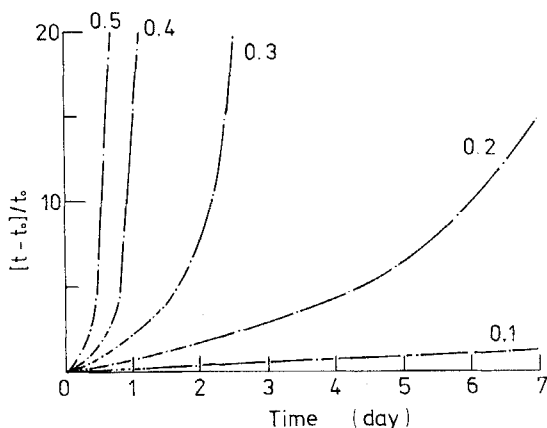
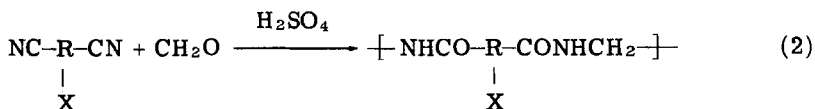


FIG. 9. Apparent viscosity change of the DMSO solution during the polycondensation of dimethyl tartrate with MND in the presence of PVA. Figures on curves indicate the molar concentration of monomer; temperature, 30°C; PVA is twice the molar concentration of the monomers.

at low temperatures. When dinitriles having such functional groups as hydroxyl, mercapto, or amino groups are subjected to the Ritter reaction in concentrated sulfuric acid at low temperature, functional polyamides having reactive groups X are expected to be obtained.



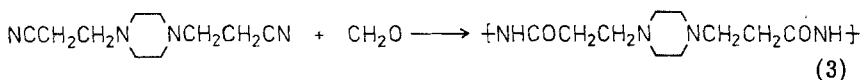
The polymerization of  $\beta$ -hydroxyglutaronitrile yielded [15] a water-soluble polyamide having a low molecular weight which might be ascribed to the participation of the hydroxyl group with the polymerization, while the polymerization of  $\beta$ -mercaptoglutaronitrile resulted in the formation of a crosslinked polyamide which was insoluble in common solvents. On the other hand, N,N'-bis(2-cyanoethyl)piperazine, which is a dinitrile having basic two imino groups [Eq. (3)], yielded a water-soluble polyamide having a high molecular weight (Table 3).

The basic polyamide which was water-soluble had a strong coagulation effect for colloidal solutions as a cation-type polymeric

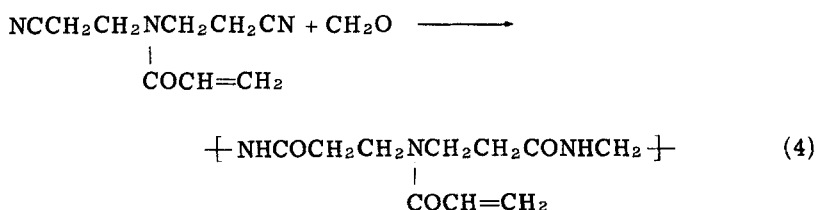
TABLE 3. Polymerization of N,N'-Bis(2-cyanoethyl)piperazine (BCEP) with Trioxane in 95% H<sub>2</sub>SO<sub>4</sub>

BCEP concn (mole/mole)	Time (hr)	Temp (°C)	Polymer	
			Yield (%)	$\eta_{sp}/c^a$
1/40	0.25	room	65	0.13
"	0.5	"	67	0.53
"	1	"	55	0.39
"	3	"	81	0.12
"	5	"	52	0.21
"	1	0	64	0.28
"	1	60	62	0.09
1/80	1	room	83	0.19
"	1	room	79	0.23

<sup>a</sup>Measured in water at 30°C.



flocculent. N,N'-Bis(2-cyanoethyl)acrylamide underwent [16] polymerization with formaldehyde to yield a water-soluble polyamide [Eq. (4)].



Since the pendant acryloyl group has photosensitivity, the water-soluble polyamide was a photosensitive polymer. When the aqueous solution of the polyamide was irradiated with a high-pressure mercury

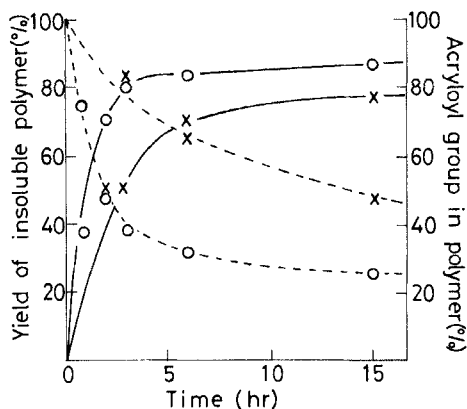
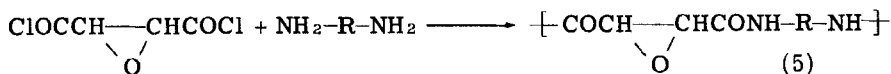


FIG. 10. Irradiation with light of (○) water-soluble polymer and (×) copolymer. Polymer concentration, 2 wt % in water; irradiation with 450 W high-pressure HG Hg lamp.

lamp, an insoluble polyamide started to precipitate out of the solution owing to the crosslinking reaction among acryloyl groups. Figure 10 indicates results of the irradiation of the aqueous solution of the water-soluble polyamide and copolyamide from *N,N'*-bis(2-cyanoethyl)acrylamide.

### Polymer Reactions of Epoxy Polyamides

Polyamides having epoxy groups are favorable for the modification of polyamide because the epoxy group can react with various reactants including amine or aminoalcohol to form various polyamide derivatives having both hydroxyl and amino groups as pendant side groups [17]. Interfacial polycondensation of a dicarboxylic acid chloride having an epoxy group with diamine is one method to prepare epoxy polyamide. Thus, 2,3-epoxysuccinyl chloride (ESC) was allowed to react with various diamines either by interfacial or solution methods [Eq. (5)]; results are summarized in Table 4.



Another route to prepare epoxy polyamides is to use an active di-ester having an epoxy group for the polycondensation because the

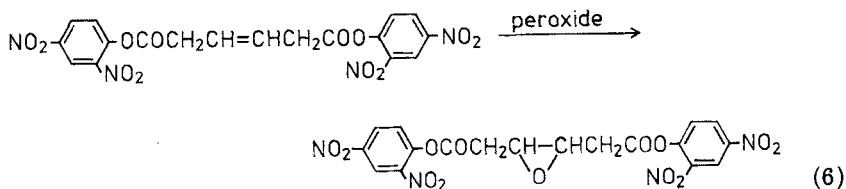
TABLE 4. Polycondensation of ESC with Diamine

Method	Diamine	Solvent	Polymer	
			Yield (%)	$\eta_{sp}/c$
Solution <sup>a</sup>	p-Phenylenediamine	Chloroform	77	0.13
	"	THF	71	0.12
	"	1,2-Dichloroethane	75	0.14
	m-Phenylenediamine	Chloroform	60	0.11
	"	THF	58	0.15
	"	1,2-Dichloroethane	56	0.12
Interfacial <sup>b</sup>	p-Phenylenediamine	1,2-Dichloroethane	55	0.15
	m-Phenylenediamine	"	40	0.14

<sup>a</sup> Monomer concn., 0.1 M; acid acceptor, Et<sub>3</sub>N.

<sup>b</sup> Monomer concn., 0.2 M; acid acceptor, NaOH.

synthesis of acid chloride having an epoxy group is usually difficult. The oxidation of the di-2,4-dinitrophenyl ester of 3,4-butenedicarboxylic acid with peroxide could afford di(2,4-dinitrophenyl)epoxy adipate (DNEA) in good yield [ Eq. (6) ].



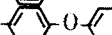
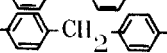


DNEA was allowed to react with various diamines in solution under mild conditions to form corresponding polyamides with satisfactory results [ Eq. (7) ].

Table 5 summarizes results of the polycondensation of DNEA with various diamines in dimethylacetamide (DMAc) solution, where it is



TABLE 5. Solution Polycondensation of DNEA with Various Diamines<sup>a</sup>

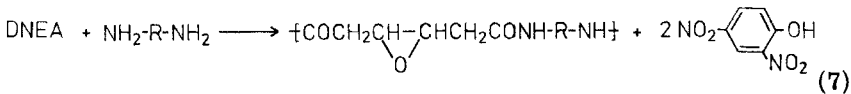
R in H <sub>2</sub> N-R-NH <sub>2</sub>	Temp (°C)	Time (hr)	Yield (%)	$\eta_{sp}/c^b$
-(CH <sub>2</sub> ) <sub>6</sub> -	30	2	73	0.42
-(CH <sub>2</sub> ) <sub>6</sub> -	60	2	74	0.48
-(CH <sub>2</sub> ) <sub>6</sub> -	90	2	71	0.45
	60	23	79	0.73 <sup>c</sup>
	60	23	100	1.67 <sup>c</sup>
	60	24	92	3.62 <sup>c</sup>
	60	24	114	Insoluble

<sup>a</sup> Monomer concn, 0.20 M; solvent, DMAc; acid acceptor:

Et<sub>3</sub>N.

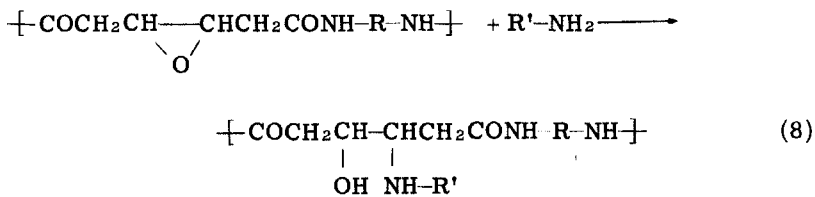
<sup>b</sup> 0.1g/10 ml in m-cresol at 30°C.

<sup>c</sup> 0.1 g/10 ml in DMAc-LiCl (5 wt %).



seen that a very high molecular weight polyamide is obtained from DNEA and aromatic diamines.

The epoxy polyamides can be used to obtain various derivatives of polyamides by the ring-opening reaction of the epoxy group with amine [Eq. (8)].



Figures 11 and 12 indicate the moisture adsorption of these various polyamides which were obtained by the ring-opening reaction of the epoxy group. Generally speaking, the moisture adsorption of these polyamide derivatives increased remarkably in comparison with that

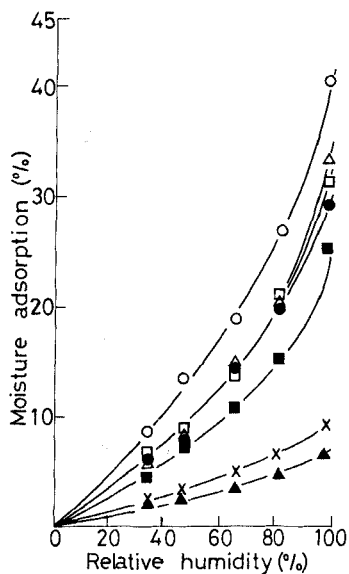


FIG. 11. Moisture adsorption of various polyamides at 22°C having the structure  $\text{[-OCCH}_2\text{CHOHCH(NHR)CH}_2\text{CONH(CH}_2\text{)}_6\text{NH-]}$ : (○) R = -NH<sub>2</sub>; (△) R = -CH<sub>2</sub>CH<sub>2</sub>NH<sub>2</sub>; (□) R = -CH<sub>2</sub>CH<sub>2</sub>OH; (●) R = -(CH<sub>2</sub>)<sub>6</sub>NH<sub>2</sub>; (■) R = n-Bu; (×) nylon 6; (▲) CNPEA-HMD.

of original polyamides. Particularly, the polyamides derived from the epoxy polyamide and ethanolamine had a high moisture adsorption. Apparent solution viscosities of these polyamide derivatives were not changed by the ring-opening reaction, except for the reaction with hydrazine. None of these polyamides had a distinct melting point, and all started to decompose on heating at around 200°C. They can be cast into films from solutions in DMAc or N-methyl- $\alpha$ -pyrrolidone (NMP) for a membrane application.

Polyamides having pendant hydroxyl and imino groups could be converted into photosensitive polyamides [18] by reacting the polyamides with cinnamoyl chloride so as to introduce cinnamoyl groups into the polyamide chains [Eq. (9)].

## SYNTHESIS OF FUNCTIONAL POLYESTERS

It is very difficult to prepare polyesters having various functional groups as pendant side groups because the reactivity of diols is not

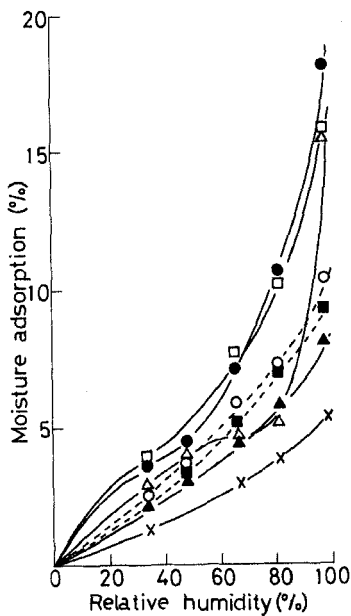
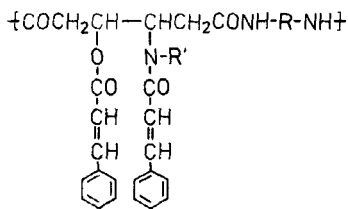
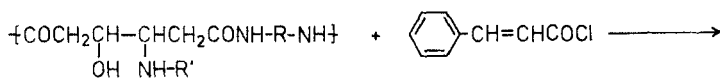
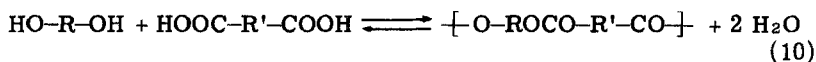


FIG. 12. Moisture adsorption at 22°C of polyamides having the structure:  $\text{[-COCHOHCH(NHR)CONH-C}_6\text{H}_4\text{-NH-]}$ : (●) R =  $-\text{CH}_2\text{CH}_2\text{OH}$ ; (□) R =  $-\text{CH}_2\text{CH}_2\text{NH}_2$ ; (△) R =  $-\text{NH}_2$ ; (▲) R =  $-(\text{CH}_2)_6\text{NH}_2$ ; (×) R = n-Bu; (○) MPD-ESC; (■) MPD-SC.



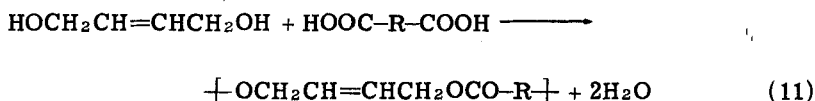
(9)

sufficiently high enough to carry out the polycondensation under mild conditions and the equilibrium of the polycondensation is not favorable for formation of polyesters in comparison with the formation of polyamides.



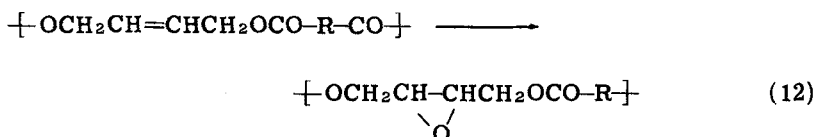
Therefore, the polycondensation reaction to form polyesters must be carried out at elevated temperatures (above 200°C) under a very high vacuum so as to shift the equilibrium toward the formation of polyester. Under such severe conditions, thermal degradation or crosslinking reactions easily occur when diols or dicarboxylic acids contain functional groups such as hydroxyl or amino groups.

Interfacial polycondensation is available to prepare polyesters under mild conditions. However, as acid chlorides are quite reactive, it is difficult to prepare linear polyesters having functional groups which can also react with the acid chloride. Consequently, functional polyesters were prepared [19] by polymer reactions of unsaturated polyester. Conventional melt polycondensation of 1,4-butanediol with aliphatic dicarboxylic acid afforded unsaturated polyester which was used as a precursor polymer to introduce various functional groups into the polyester.



### Epoxidation of Unsaturated Polyester

Epoxidation of the unsaturated polyester was carried out [19] successively in benzene or chloroform by using cumene hydroperoxide in the presence of molybdenum trioxide [Eq. (12)].



It was found that little epoxidation of the trans double bonds in the unsaturated polyester took place, and the degree of the epoxidation

TABLE 6. Unsaturated Polyesters having Diol Groups

Polyester	C=C content (%)		Diol content (mole %)	Mp (°C)	$\eta_{sp}/c$
	cis	trans			
Poly(butylene adipate)	25	70	5	34-35	0.49
"	14	70	16	34-36	0.49
Poly(butylene isophthalate)	19	79	2	68-69	0.09
"	16	79	5	83-84	0.16

depended on the content of cis double bonds in the unsaturated polyester. Hydrolysis of the epoxy groups led to the formation of polyester having a pendant hydroxyl group which can modify the moisture affinity of the original polyester. Thus, hydrolysis of the epoxy polyester was carried out by using an excess of sulfuric acid; results are summarized in Table 6. Little difference between the epoxy and diol derivatives in the melting point of the aliphatic polyesters was observed.

#### Hydroformylation of Unsaturated Polyester

It has been reported previously [20] that hydroformylation of olefinic polymers by use of carbon monoxide and hydrogen takes place easily under mild conditions in the presence of a rhodium catalyst. This technique could be used to incorporate formyl groups into the unsaturated polyester, and these formyl groups in the modified polyester could then be converted to alcohol or aldoxime groups and finally to amino derivatives by means of suitable polymer reactions [Eqs. (12)].

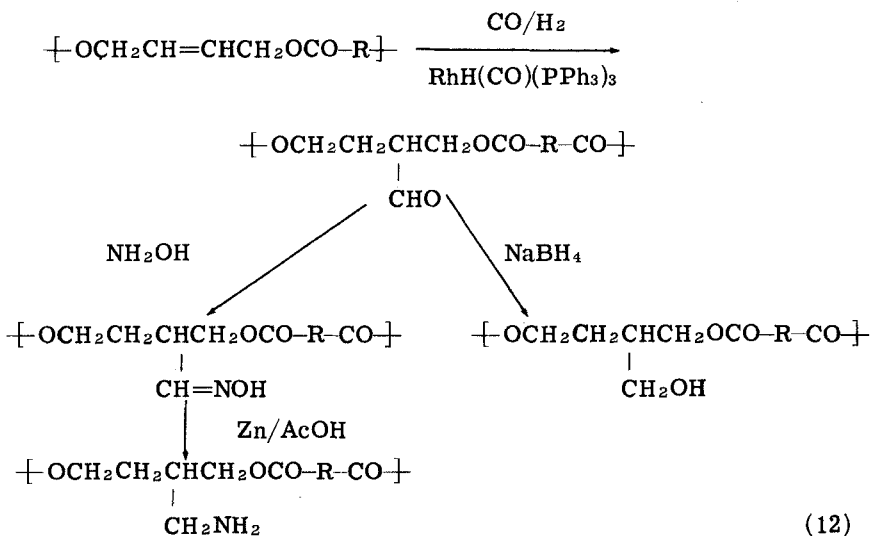
The hydroformylation of the unsaturated polyester with  $\text{RhH}(\text{CO})(\text{PPh}_3)_3$  was carried out under mild conditions as described in Table 7. It was possible to control the amount of combined formyl group from less than 1 mole % to about 90 mole % by proper selection of reaction conditions.

It was also found [19] that a crosslinking reaction occurred rapidly when the solution of the polyester having pendant formyl groups was allowed to stand for a day in contact with air. Therefore, the reaction mixture was better treated immediately with sufficient hydroxylamine or sodium borohydride to convert the formyl groups to the corresponding aldoxime or hydroxylmethyl groups, respectively. The

TABLE 7. Hydroformylation of Unsaturated Polyesters<sup>a</sup>

Polyester	H <sub>2</sub> /CO	Temp (°C)	Time (hr)	CHO (mole %)
Poly(butylene adipate)	20/10	38	24	67
Poly(butylene sebacate)	30/15	40-44	25	90
"	30/15	43	2	25
"	30/15	46	4	45
"	30/15	49-50	8	88
Poly(butylene isophthalate)	30/15	70-71	2	14
"	30/15	80-82	4	22
"	30/15	80	6	33

<sup>a</sup>Reaction conditions: polymer concentration, 50 g/liter; solvent, benzene; catalyst, RhH(CO)(PPh<sub>3</sub>)<sub>3</sub>.



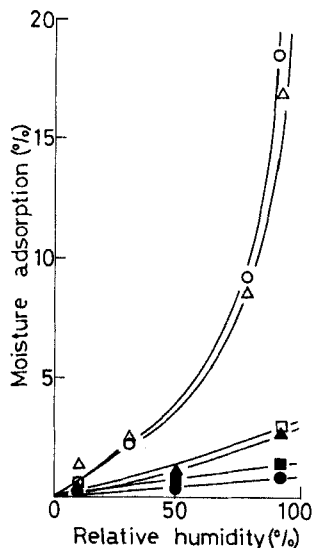


FIG. 13. Moisture adsorption of functional polyesters: ( $\circ$ ) PS-CH<sub>2</sub>NH<sub>2</sub>; ( $\Delta$ ) PS-CH<sub>2</sub>OH; ( $\square$ ) PS-CH=NOH; ( $\blacktriangle$ ) PI-CH<sub>2</sub>OH; ( $\blacksquare$ ) PS-CH=NOH; ( $\bullet$ ) PS; where PS denotes poly(butylene sebacate) and PI denotes poly(butylene isophthalate).

modified polyesters having these pendant functional groups have a high affinity for moisture, and the moisture adsorption of the aliphatic polyester having 50 mole % of pendant hydroxymethyl or aminomethyl groups is about 20 times as high as that of the strating polyester, as shown in Fig. 13.

### Phosphorylation of Unsaturated Polyester

It was reported [21] that a phosphorylation reaction of unsaturated polyolefins such as poly(pentenamer) takes place by use of dialkyl phosphate in the presence of a radical initiator [Eq. (13)]. This phosphorylation reaction was extended to the unsaturated polyester in order to obtain a phosphorylated polyester [22].

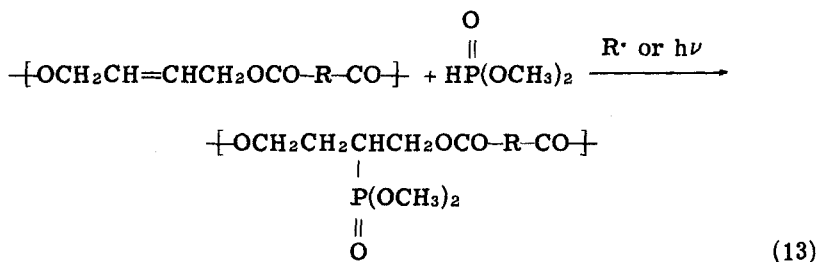
The phosphorylation reaction of poly(2,3-butylene adipate) (PBA) took place in dimethyl phosphate (DMP) solution in the presence of azobisisobutyronitrile at 85-90°C, and about 30 mole % of the double bond of PBA were phosphorylated after 24 hr. However, the solution viscosity of the phosphorylated polyester was drastically reduced,

TABLE 8. Phosphorylation of PBA with DMP

Initiator	Reaction time (hr)	Polymer				
		$\eta_{sp}/c$	$T_d$ ( $^{\circ}\text{C}$ )	$T_g$ ( $^{\circ}\text{C}$ )	$T_m$ ( $^{\circ}\text{C}$ )	Combined P (mole %)
BPO <sup>a</sup>	0	1.37	346	-	-	0
	15	0.28	276	-	-	19
	19	0.26	268	-	-	22
	24	0.15	258	-	-	31
UV irradiation <sup>b</sup>	0	1.37	346	-86	52	0
	7	1.30	278	-39	32	11
	21	1.07	258	-39	-	30

<sup>a</sup>PBA, 9 g; DMP, 360 g; temperature 88 $^{\circ}\text{C}$ ; BPO, 300-500 mg.

<sup>b</sup>PBA, 0.5 g; DMP, 6 g; benzene, 3 g; benzophenone, 0.1 g; UV lamp, 450 W; room temperature.



presumably due to degradation caused by a transesterification of PBA with DMP at elevated temperatures, as shown in Table 8. Therefore, UV irradiation was used to catalyze the phosphorylation of PBA under mild conditions in the presence of a sensitizer. Results are summarized in Table 8, where it is seen that the degradation of PBA was prevented and a significant amount of phosphonate group was introduced into the double bond of PBA. As the amount of phosphonate group attached to PBA increased, the  $T_g$  increased and the  $T_m$  decreased. The thermal stability of the phosphorylated PBA was inferior to that of the original PBA, and this may be ascribed to the transesterification between ester groups in the main chains and phosphonate groups at elevated temperatures. On the other hand, the flame



resistance of the polyester increased with increasing amount of the grafted phosphonate group and a self-extinguishing character in air was provided for the phosphorylated polyester.

The adsorption capacity of the phosphorylated PBA for cupric ion was proportional to the amount of grafted phosphonate group in PBA and decreased with decreasing pH of the solution. It is expected that the phosphorylated polyester may be applicable to membrane uses, including separation of metal ions in aqueous solution.

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