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Synthesis of New Thermally Stable Halopolyamides

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ABSTRACT

Several new thermally stable halopolyamides were prepared by low temperature solution polycondensation from some new diacid chlorides and a number of diamines, namely p-phenylenediamine (I), m-phenylenediamine (II), benzidine (III), 4,4'-diaminodiphenylmethane (IV), 4,4'-diaminodiphenyl sulfone (V), ethylenediamine (VI), hexamethylenediamine (VII), and 4,4'-diaminodicyclohexylmethane (VIII). The diacid chlorides were derived from two series of some new dicarboxylic acids: (A) 2-halo-(chloro-, bromo-, and iodo-)-4-carboxyphenoxyacetic acid (IX-XI); and (B) 2-halo-(chloro- and iodo-)hydroquinone-1,4-diacetic acid (XII and XIII). Dimethyl esters and diamide derivatives were prepared to confirm the structures of the diacid chlorides (IXa-XIIIa). Nylon salts of the new dicarboxylic acids (IX-XIII) were also prepared. Some of the factors affecting the reduced viscosity of the polymers such as the effect of the concentration of initial components, temperature, and duration time were studied. In the case of the polymerization of 2-chloro-4-chlorocarbonylacetyl chloride (IXa) with diamines I and VII as representatives of aromatic and aliphatic diamines, maximum viscosity values were obtained by the use of 0.5 mol/L at -10°C for both diamines, whereas the optimum time was 30 min for diamine VII and 45 min for I. No effect on reduced viscosities

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was observed with time in the case of reactions carried out at room temperature. The optimum conditions were then applied in the case of the other diacid chlorides (XIa, XIIa, and XIIIa) in order to obtain the corresponding halopolyamides. Study of the thermal stability using DSC showed that the halopolyamides obtained from the more rigid dicarboxylic acids series A have higher T_g values than those of the less rigid series B which carry more ether units. Halopolyamides derived from aliphatic diamines are less thermally stable than those derived from aromatic diamines. Films could be obtained from halopolyamides via either the solution or melt phase.

INTRODUCTION

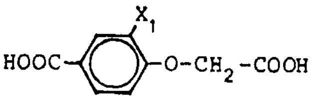
The low temperature solution polycondensation of diamines and diacid chlorides has become an increasingly important route to high melting polymers [1]. Heat-resistant polyamides were prepared from 1,4-bis-(chlorocarbonylmethoxy)benzene [2] with a variety of diamines, the condensation being carried out in N,N-dimethylacetamide (DMA). Optimum yields and viscosities were obtained at 0°C.

The diacid chlorides used in the present work have the same structure except for the presence of a halogen atom. The presence of halogen imparted fire-retardant or fire-resistant properties to the polymers [3].

From halogenated 2,4-diaminodiphenyl ether and isophthaloyl chloride and/or terephthaloyl chloride in DMA, self-extinguishing copolyamides were obtained [4].

In the present work, soluble or moldable thermostable halopolyamides were prepared using low temperature solution polycondensation of some new dicarboxylic acid chlorides with a number of aliphatic and aromatic diamines, namely p-phenylenediamine (I), m-phenylenediamine (II), benzidine (III), 4,4'-diaminodiphenylmethane (IV), 4,4'-diaminodiphenyl sulfone (V), ethylenediamine (VI), hexamethylenediamine (VII), and 4,4'-diaminodicyclohexylmethane (VIII).

Two new series, A and B, of dicarboxylic acids were prepared in the present work.



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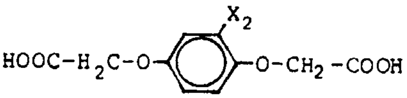


Series A

Series B

X_1 = Cl, 2-Chloro-4-carboxyphenoxyacetic acid (IX)
X_1 = Br, 2-Bromo-4-carboxyphenoxyacetic acid (X)
X_1 = I, 2-Iodo-4-carboxyphenoxyacetic acid (XI)
X_2 = Cl, 2-Chlorohydroquinone-1,4-diacetic acid (XII)
X_2 = Br, 2-Bromohydroquinone-1,4-diacetic acid (XIII)

These acids were identified by elemental analysis and molecular weight determination (neutralization), both of which agreed with the calculated molecular formulas. The diacid chlorides IXa-XIIIa of these new acids were prepared and their structures confirmed by conversion to the corresponding dimethyl esters and diamides. Further evidence of the structure of diacid chlorides was obtained by determination of their saponification equivalents.

Reaction of the new dicarboxylic acids IX-XIII with aliphatic diamines, hexamethylenediamine, 4,4'-diaminodicyclohexylmethane, and decamethylenediamine led to the formation of the corresponding nylon salts which are tabulated in Table 5.

In the present work, some of the factors which affect the reduced viscosity were studied such as the effect of the concentration of initial components, the effect of temperature, and the effect of duration time of the reaction at both room and low temperature.

For selected halopolyamides, thermal studies by DSC were carried out.

EXPERIMENTAL

Materials

Preparation of 3-Chloro-4-hydroxybenzoic Acid [5]

This acid was prepared by the method of Gray and Jones [5] except that sulfuryl chloride was used in place of chloramine T. Sulfuryl chloride (3.2 mL, 1 mol) was dropped into a solution of p-hydroxybenzoic acid (5 g, 1 mol) in 20 mL of glacial acetic acid containing benzoyl peroxide (0.001 g). After complete addition the reaction mixture was refluxed until evolution of hydrogen chloride ceased, poured into ice-cold water, and the solid filtered, washed with water, and recrystallized from hot water to give 3-chloro-4-hydroxybenzoic acid (5 g, 85%) as colorless needles, mp 172°C.

Preparation of 3-Iodo-4-hydroxybenzoic Acid [6]

3-Iodo-4-hydroxybenzoic acid which had been prepared from 3-amino-4-hydroxybenzoic acid by Sandmeyer reaction [6] could be obtained in high yield by direct iodination of p-hydroxybenzoic acid by adding a solution of iodine monochloride (5.8 g, 1 mol) in 10 mL of glacial acetic acid to a solution of p-hydroxybenzoic acid (5 g, 1 mol) in 20 mL of glacial acetic acid and refluxing until no more hydrogen chloride gas evolved. After cooling and pouring into ice-cold water, a solid separated which was filtered, washed with water, and recrystallized from hot water to give the acid, 3-iodo-4-hydroxybenzoic acid (8 g, 85%), which was separated as colorless needles, mp 176°C.

3-Bromo-4-hydroxybenzoic acid [5] was prepared similarly.

General Procedure for the Preparation of 2-Halogeno-4-carboxyphenoxyacetic Acids (IX-XI)

3-X-4-hydroxybenzoic acid (1 mol; X = Cl, Br, or I) was dissolved in aqueous sodium hydroxide solution (500 mL, 2 mol). A solution of sodium chloroacetate (1 mol) in 500 mL of water was then added to the stirred solution and the reaction mixture brought to the reflux temperature. After 1 h a second mole of sodium chloroacetate in 250 mL of water was added and the mixture refluxed for an additional 3 h. After cooling and acidifying with 10% hydrochloric acid, 2-halogeno-4-carboxyphenoxyacetic acids IX, X, and XI separated in 80% yield. The acids were purified by recrystallization. Results are tabulated in Table 1.

General Procedure for the Preparation of 2-Halogenohydroquinone-1,4-diacetic Acids (XII and XIII)

2-X-hydroquinone (1 mol, X = Cl [7] or Br [7]) was dissolved in 500 mL ice-cold of (2 N) sodium hydroxide solution, 500 mL of (2 N) sodium chloroacetate solution (2 mole) was added, and the reaction mixture refluxed for 1 h. A second 500 mL portion of (2 N) sodium chloroacetate was added, and refluxing was continued for a further 3 h. After cooling and acidifying with dilute hydrochloric acid (1:1), 2-halogenohydroquinone-1,4-diacetic acid (XII or XIII) separated. The acid was filtered, washed with water, and crystallized from hot water.

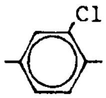
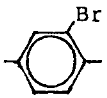
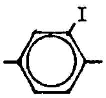
All dicarboxylic acids (IX-XIII) were identified by molecular weight determination, elemental analyses (Table 1), and their IR spectra (KBr) at ν 1720-1700 cm^{-1} (C=O), and 1240-1220 cm^{-1} (OCH_2).

General Procedure for The Preparation of Dicarboxylic Acid Chlorides (IXa, XIa, XIIa, and XIIIa)

The dicarboxylic acid was refluxed with an excess of thionyl chloride until a clear solution was obtained (5-6 h). In the case of IX, after being refluxed for 1 h, a mixture of 0.01 mL of pyridine and 5 mL of thionyl chloride was added to the reaction mixture. Excess thionyl chloride was then removed under reduced pressure. In case of dicarboxylic acids IX and XI, the oily residue was crystallized from benzene-n-hexane (1:1). In case of dicarboxylic acids XII and XIII, the crude oil was dissolved in benzene which was then removed under reduced pressure. The residue was dissolved in dry ether, the mixture filtered, and the ether distilled. Treatment with ether was repeated three times with final cooling in an ice chest. The diacid chlorides XIIa and XIIIa were obtained crystalline in this way.

TABLE 1. Properties of Dicarboxylic Acids IX-XIII

Compound	Formula	Crystallization solvent	MP (°C)	Yield (%)	MW		Elemental analysis			
					Obs	Calc		C (%)	H (%)	X (%)
HOOC–R_1–OCH_2–COOH (IX)	$C_9H_7O_5Cl$	Ethanol	324-326	80	229.7	230.6	R.	46.88	3.06	15.39
							F.	46.62	3.40	15.37
HOOC–R_2–OCH_2–COOH (X)	$C_9H_7O_5Br$	Acetone	330-332	80	273.5	275.1	R.	39.29	2.56	29.05
							F.	39.00	2.80	29.20
HOOC–R_3–OCH_2–COOH (XI)	$C_9H_7O_5I$	Ethanol or acetone	317	85	320.9	322.1	R.	33.56	2.19	39.40
							F.	33.90	2.60	39.00
R_1(–OCH_2–COOH$)_2$ (XII)	$C_{10}H_9O_6Cl$	Water	228-230	85	262.1	260.6	R.	46.09	3.48	13.60
							F.	45.80	3.80	13.50
R_2(–OCH_2–COOH$)_2$ (XIII)	$C_{10}H_9O_6Br$	Water	227-228	82	305.0	305.1	R.	39.37	2.97	26.19
							F.	39.61	2.70	26.30

Where R_1 = , R_2 = , R_3 = .

Diacid chlorides IXa, XIa, XIIa, and XIIIa were identified by their melting points and saponification equivalents (Table 2) and also by the preparation of dimethyl esters and diacid amides which were identified by their melting points and elemental analyses (Tables 3 and 4).

General Technique for the Preparation of Nylon Salts

The aliphatic diamines, hexamethylenediamine (VII), 4,4'-diaminocyclohexylmethane (VIII), or decamethylenediamine (XIV) (1 mol), were dissolved in ethanol and 1 mol of the appropriate dicarboxylic acid (IX-X) was added, followed by a few drops of water until the amine salt dissolved. The reaction mixture was boiled, filtered, cooled, and the nylon salt which separated was recrystallized from ethanol-water. Results are tabulated in Table 5.

Attempts to convert the nylon salts to high molecular weight halopolyamides by melt polycondensation failed because of decomposition at the temperatures required to induce polycondensation or the formation of low molecular weight polyamides.

Technique for Low Temperature Solution Polycondensation

In a three-necked flask equipped with a mechanical stirrer and a thermometer, a solution of the diamine in N,N-dimethylacetamide (DMA) was cooled to and held at a specific temperature for a definite period of time. After complete reaction the soluble or swollen polymer was diluted with about 100 mL of water with continuous stirring. The polymer was then filtered through a sintered glass funnel and washed several times with boiling ethanol and boiling acetone to remove unreacted monomers. The polymer was dried for 24 h in a vacuum desiccator.

Viscosity Measurements

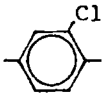
The viscosities of 0.5% solutions of the polymers in appropriate solvents were measured at 30 + 0.1°C, using the Ubbelhode suspended level viscometer as modified by Ravikov [8, 9]. The viscometer used had solvent flow times ranging from 60 to 80 s.

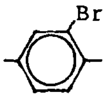
Determination of Melting Point

Melting points were determined on a Kofler block and are uncorrected.

TABLE 2. Properties of Diacid Chlorides IXa, XIa, XIIa, and XIIIa

Compound	Formula	Crystallization solvent	MP (°C)	Yield (%)	Saponification Eq.	
					Found	Required
ClOC–R$_1$–OCH$_2$–COCl (IXa)	$C_9H_5O_3Cl_3$	Benzene-n-hexane	56-58	80	25.5	26.5
ClOC–R$_3$–OCH$_2$–COCl (XIa)	$C_9H_5O_3Cl_2I$	Benzene-n-hexane	58-60	75	20.0	19.9
R$_1$(–OCH$_2$–COCl)$_2$ (XIIa)	$C_{10}H_7O_4Cl_3$	See p. 420	32-34	80	23.0	23.8
R$_2$(–OCH$_2$–COCl)$_2$ (XIIIa)	$C_{10}H_7O_4BrCl_2$	See p. 420	28-30	70	21.6	20.7

Where R_1 = 

, R_2 = 

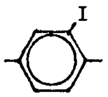
, R_3 = 

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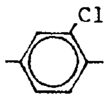
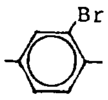
TABLE 3. Properties of Dimethyl Ester Derivatives of Dicarboxylic Acids IX-XIII

Compound	Formula	Crystallization solvent	MP (°C)	Yield (%)	Elemental analysis			
						C (%)	H (%)	X (%)
$H_3C{-}OOC{-}R_1{-}OCH_2{-}COOCH_3$ (IXb)	$C_{11}H_{11}O_5Cl$	Ethanol	115-117	80	R.	51.07	4.29	13.70
					F.	51.30	4.70	14.10
$H_3C{-}OOC{-}R_2{-}OCH_2{-}COOCH_3$ (Xb)	$C_{11}H_{11}O_5Br$	Ethanol	116-118	70	R.	43.59	3.66	26.36
					F.	43.30	3.80	26.50
$H_3C{-}OOC{-}R_3{-}OCH_2{-}COOCH_3$ (XIb)	$C_{11}H_{11}O_5I$	Ethanol	120-122	70	R.	37.74	3.17	36.25
					F.	38.00	3.60	36.60
$R_1({-}OCH_2{-}COOCH_3)_2$ (XIIb)	$C_{12}H_{13}O_6Cl$	Ethanol or benzene	65-68	70	R.	49.93	4.54	12.28
					F.	50.10	4.40	12.70
$R_2({-}OCH_2{-}COOCH_3)_2$ (XIIIb)	$C_{12}H_{13}O_6Br$	Ethanol or benzene	68-70	70	R.	43.27	3.93	23.99
					F.	42.90	4.10	24.10

Where R_1 = 

, R_2 = 

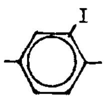
, R_3 = 

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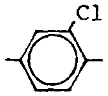
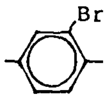
TABLE 4. Properties of Diamide Derivatives of Dicarboxylic Acids IX-XIII

Compound	Formula	Crystallization solvent	MP (°C)	Yield (%)	Elemental analysis			
					C%	H%	X%	N%
$H_2NOC-R_1-OCH_2-CONH_2$ (IXc)	$C_9H_9O_3N_2Cl$	Ethanol-water	260-262	85	R. 47.29 F. 47.26	3.97 4.48	15.51 15.50	12.25 11.83
$H_2NOC-R_2-OCH_2-CONH_2$ (Xc)	$C_9H_9O_3N_2Br$	Ethanol-water	264-266	80	R. 39.58 F. 39.45	3.22 3.38	29.26 28.97	10.26 9.98
$H_2NOC-R_3-OCH_2-CONH_2$ (XIc)	$C_9H_9O_3N_2I$	Ethanol-water	267-269	75	R. 33.77 F. 34.10	2.83 3.20	39.64 39.90	8.75 8.30
$R_1(-OCH_2-CONH_2)_2$ (XIIc)	$C_{10}H_{11}O_4N_2Cl$	Water	247-248	82	R. 46.43 F. 46.83	4.29 4.20	13.70 13.35	10.83 10.30
$R_2(-OCH_2-CONH_2)_2$ (XIIIc)	$C_{10}H_{11}O_4N_2Br$	Water	230-233	76	R. 39.63 F. 39.10	3.66 4.00	26.36 26.00	9.24 8.96

Where R_1= 

, R_2= 

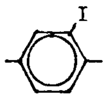
, R_3= 

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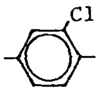
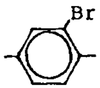
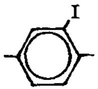
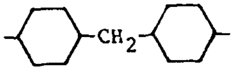
TABLE 5. Nylon Salts of Dicarboxylic Acids IX-XIII

Nylon salts	Formula	Mp (°C)	Yield (%)	Elemental analysis C (%)	H (%)	X (%)	N (%)
$HOOC{-}R_1{-}O{-}CH_2{-}CO\bar{O}$ $\overset{+}{N}H_3{-}(CH_2)_6{-}NH_2$	$C_{15}H_{23}O_5N_2Cl$	235-238	80	R. 51.95 F. 51.76	6.68 6.30	10.22 10.60	8.08 7.60
$HOOC{-}R_1{-}O{-}CH_2{-}CO\bar{O}$ $\overset{+}{N}H_3{-}R_4{-}NH_2 . 2H_2O$	$C_{22}H_{37}O_7N_2Cl$	282-284, decomp	66	R. 55.40 F. 55.50	7.82 7.35	7.43 7.50	5.87 5.40
$HOOC{-}R_2{-}O{-}CH_2{-}CO\bar{O}$ $\overset{+}{N}H_3{-}R_4{-}NH_2 . 0.5H_2O$	$C_{22}H_{34}O_{5.5}N_2Br$	298-300	60	R. 53.45 F. 53.93	6.93 7.08	16.16 15.80	5.67 5.90
$HOOC{-}R_2{-}O{-}CH_2{-}CO\bar{O}$ $\overset{+}{N}H_3{-}(CH_2)_{10}{-}NH_2 . 0.5H_2O$	$C_{19}H_{34}O_{5.5}N_2Br$	152-155	86	R. 50.00 F. 50.20	7.08 6.69	17.51 17.70	6.14 6.50

$HOOC-R_3-O-CH_2-COO^-$ $\overset{+}{N}H_3-(CH_2)_6-NH_2$	$C_{15}H_{23}O_5N_2I$	224	96	R. F.	41.11 41.65	5.24 5.50	28.95 28.54	6.39 6.20
$HOOC-R_3-O-CH_2-COO^-$ $\overset{+}{N}H_3-(CH_2)_{10}-NH_2.1.5H_2O$	$C_{19}H_{34}O_{5.5}N_2I$	85-86	85	R. F.	43.77 43.76	6.57 5.99	24.34 23.98	5.37 5.37
$HOOC-H_2C-OR_1-OCH_2COO^-$ $\overset{+}{N}H_3-(CH_2)_6-NH_2$	$C_{16}H_{25}O_6N_2Cl$	246-248	80	R. F.	51.00 50.80	6.69 6.50	9.41 9.50	7.43 7.20
$HOOC-H_2C-OR_2-OCH_2COO^-$ $\overset{+}{N}H_3-(CH_2)_{10}-NH_2.0.5H_2O$	$C_{20}H_{34}O_{6.5}N_2Br$	200-203	88	R. F.	49.39 49.31	7.05 6.99	16.43 16.08	5.76 5.60
$HOOC-H_2C-OR_2-OCH_2COO^-$ $\overset{+}{N}H_3-R_4-NH_2.H_2O$	$C_{23}H_{37}O_7N_2Br$	276-280, decomp	65	R. F.	51.78 51.60	6.99 6.60	14.99 15.10	5.25 4.79

Where R_1 =  , R_2 =  , R_3 =  , and R_4 =  .

Thermal Properties

The thermal properties of selected polyamides were examined under a nitrogen atmosphere by DSC on a Perkin-Elmer DSC-1B instrument with a heating rate of 20°C/min and by microscopy [(Leitz, Model-Ortholux) equipped with cross-polarizers and a hot stage (Mettler's FP-2 Model)].

IR spectra were recorded on a Unicam SP 200 spectrophotometer (KBr). Microanalyses were carried out by the microanalytical laboratory, Faculty of Science, Cairo University.

RESULTS AND DISCUSSION

A recent modification of polycondensation is the low temperature solution polycondensation which has been used in the synthesis and fabrication of nearly all aromatic polyamides [1, 10, 11].

In the present work, low temperature solution polycondensation of 2-chlorocarboxyphenoxyacetyl chloride IXa with a variety of aromatic and aliphatic diamines was carried out by application of the same techniques and procedures used for nitropolyamides [12] derived from 2-nitrohydroquinone-1,4-diacetyl chloride.

The effects of various factors such as initial reactant concentrations, reaction temperature, and time duration which were found in the earlier work to affect the reduced viscosity values were also found to be of importance in the present work.

The results of halopolyamides derived from diacid chloride IXa with diamines I and VII are summarized in Tables 6-9 and depicted in Figs. 1-3.

It was found that the most critical concentration for polycondensation is the use of 0.5 mol/L of each of the diamines and the diacid chloride at -10°C. The optimum time for the reaction was 30 min for hexamethylenediamine VII and 45 min for p-phenylenediamine I. However, at room temperature the reduced viscosity values were not found to vary with time. Taking into consideration the optimum data values obtained for low temperature solution polycondensation of diacid chloride IXa with diamines I and VII, the polycondensation of the diacid chlorides XIa, XIIa, and XIIIa was attempted by applying the same optimum conditions. Thus 0.5 mol/L of the diacid chloride was added dropwise during a time ranging from 30 min for aliphatic diamines to 45 min for aromatic diamines to a solution of 0.5 mol/L of the diamine in 5 mL of DMA cooled at -10°C. After complete addition of reactants, stirring was continued for a further 30 min for aromatic diamines and 1 h for aliphatic diamines. Upon diluting the reaction mixture with water, the expected polyamide was precipitated in the case of aromatic diamines. The solution of the polyamides derived from aliphatic diamines was allowed to stand overnight at room temperature for complete coagulation whereby a good

TABLE 6. Effect of Initial Concentration on Low-Temperature Solution Polycondensation of Diacid Chloride IXa with Diamines I and VII

Concentration of reactants (mol/L)	Diamine I		Diamine VII	
	Yield (%)	η_{red}[a]	Yield (%)	η_{red}
0.25	30	0.25	23	0.16
0.50	97	0.32	31	0.22
1.00	97	0.25	38	0.13
1.50	94	0.19	41	0.10

[a] Reduced viscosity was measured in concentrated sulfuric acid.

TABLE 7. Effect of Temperature on the Solution Polycondensation of Diacid Chloride IXa with Diamines I and VII

Temperature (°C)	Diamine I		Diamine VII	
	Yield (%)	η_{red}[a]	Yield (%)	η_{red}
-15	97	0.19	20	0.13
-10	97	0.32	31	0.22
-5	100	0.28	44	0.16
0	81	0.25	35	0.13
10	94	0.19	29	0.10

[a] Reduced viscosity was measured in concentrated sulfuric acid.

TABLE 8. Effect of Time Duration on the Low Temperature Solution Polycondensation of Diacid Chloride IXa with Diamine I and VII

Time (min)	Diamine I		Diamine VII	
	Yield (%)	η_{red}[a]	Yield (%)	η_{red}
15	85	0.19	23	0.16
30	97	0.32	31	0.22
45	100	0.52	50	0.22
60	100	0.52	31	0.22

[a] Reduced viscosity was measured in concentrated sulfuric acid.

TABLE 9. Effect of Time Duration on the Room Temperature Solution Polycondensation of Diacid Chloride IXa with Diamines I and VII

	Diamine I		Diamine VII	
Time (min)	Yield (%)	η_{red}[a]	Yield (%)	η_{red}
Zero time at room temperature	97	0.52	15	0.22
30	100	0.52	23	0.22
60	100	0.52	33	0.22
120	100	0.52	36	0.22

[a] Reduced viscosity was measured in concentrated sulfuric acid.

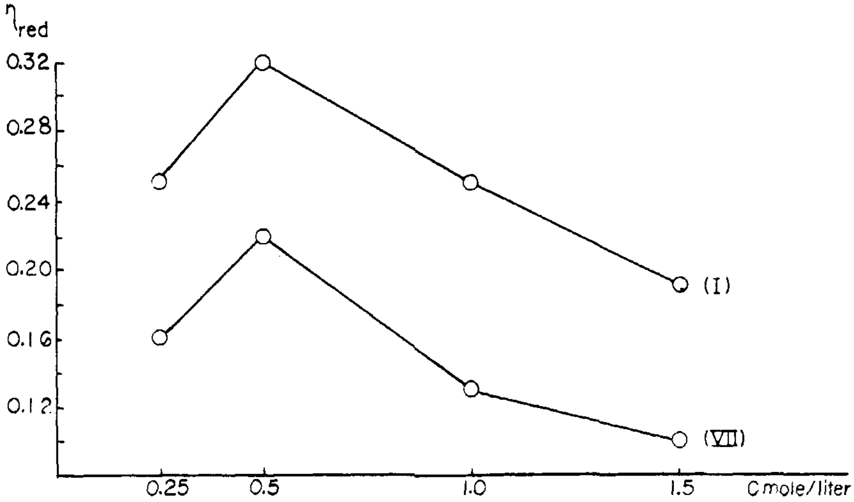


FIG. 1. Effect of initial concentration on low temperature solution polycondensation of diacid chloride IXa with diamines I and VII.

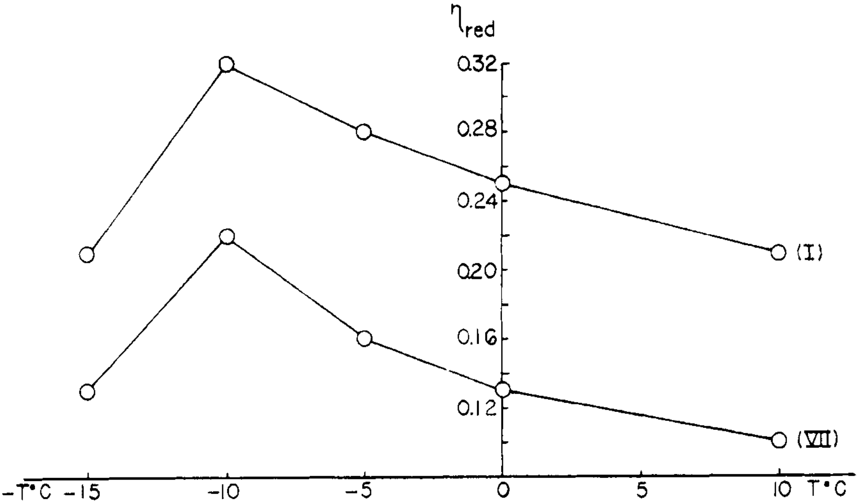


FIG. 2. Effect of temperature on solution polycondensation of diacid chloride IXa with diamines I and VII.

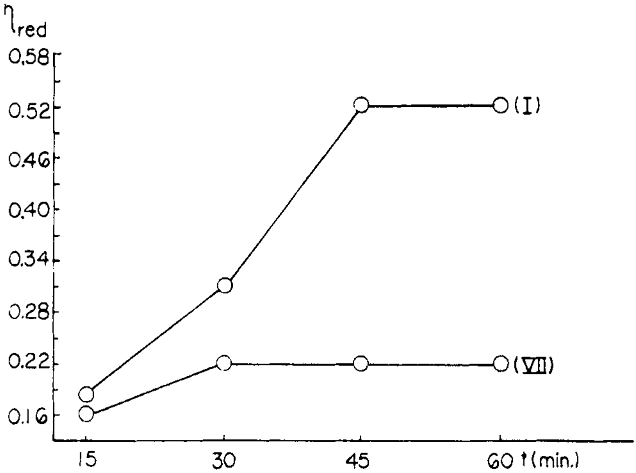


FIG. 3. Effect of time duration on low temperature solution polycondensation of diacid chloride IXa with diamines I and VII.

yield of the polymer was obtained. After filtration of the halopolyamide, it was washed with boiling ethanol, followed by boiling acetone, and dried under high vacuum for 24 h at room temperature.

Properties of the halopolyamides are tabulated in Tables 10-13. Infrared spectra of the halopolyamides supported the assigned structures.

As in previous studies in our [12] and other laboratories [13, 14], the highest yields and highest molecular weights were obtained under vigorous stirring.

It was found during the snythesis of halopolyamides that the addition of diacid chlorides IXa, XIa, XIIa, and XIIIa to the reaction mixture leads to the primary formation of an oligopolymer which separated. With further addition of reactant the polymer chain formation increases and high molecular weight polymers were obtained which swelled in DMA. This may be taken as evidence that the presence of the halogen atom along with the ether linkage improves solubility of polyamides. This is in harmony with other examples reported in the literature, showing that polyamides obtained from acid monomers having ether linkages directly attached to aromatic ring exhibit improved properties such as solubility, lowering of softening point, and thermal stability [15].

It was also found that the substitution of oxygen in the polyamide main chain increases chain flexibility and lowers the melting temperature [15]. In addition, the melt temperature of the polymer is influenced by the distance between the polar groupings present in the polymer chain [16-19]. The effect on melt temperature is most pronounced when an aliphatic unit is replaced by a p-substituted aromatic ring. For example, when adipic acid segments are replaced by terephthalic units, the melt temperatures of the corresponding polymers is raised by 100-170°C [20]. When the ring substituent is not conjugated with the amide carbonyl, the melt temperature is raised about 50-70°C. In general, introduction of aromatic rings decreases the flexibility and solubility of polyamides. Several studies [21, 22] have reported that symmetry is an important factor affecting the melt temperature in ring-containing polymers. Polyamides obtained from para isomers have higher melting points than those from meta isomers, and trans-1,4-cyclohexane rings are as effective as aromatic rings [23].

Halogen-containing polyamides, studied in the present work, were found to melt without decomposition in most cases. This is contrary to analogous polymeric substances bearing nitro groups [12] in place of the halogen atom. This supports the idea that halogens improve thermal stability of the polymer chains [3].

As found in the case of nitropolyamides [12], thermal stability of the halopolyamides depends on the structure of both dicarboxylic acid and diamine residues. Halopolyamides obtained from dicarboxylic acids of Series B, which bear an additional ether function, lead to lower T_g values than those derived from the more rigid dicarboxylic

TABLE 10. Properties of Halopolyamides Derived from Diacid Chloride IXa with Diamines I-VIII.

Structure of repeat unit	Yield (%)	η_{red}	Solubility in DMA	Mp (°C)	Tg (°K)	Tm (°K)	Decomp (°K)
$[-OC-R_1-OCH_2-CONH-R_5-NH-]_n$	100	0.52[a]	Insoluble	>330	439.9	470.8	>630
$[-OC-R_1-OCH_2-CONH-R_6-NH-]_n$	93	0.24	Soluble	270-275	398.0		540
$[-OC-R_1-OCH_2-CONH-R_7-NH-]_n$	81	0.38[a]	Insoluble	>330	490.0		>660
$[-OC-R_1-OCH_2-CONH-R_8-NH-]_n$	90	0.29	Soluble	>330	481.7	612.0	630
$[-OC-R_1-OCH_2-CONH-R_9-NH-]_n$	99	0.24	Soluble	310	494.5	580.0	620
$[-OC-R_1-OCH_2-CONH-(CH_2)_2-NH-]_n$	13	0.16	Soluble	195-200			
$[-OC-R_1-OCH_2-CONH-(CH_2)_6-NH-]_n$	50	0.22	Soluble	205-210	349.7		520
$[-OC-R_1-OCH_2-CONH-R_4-NH-]_n$	28	0.21[a]	Insoluble	250-255			

[a] Reduced viscosity was measured in concentrated sulfuric acid.

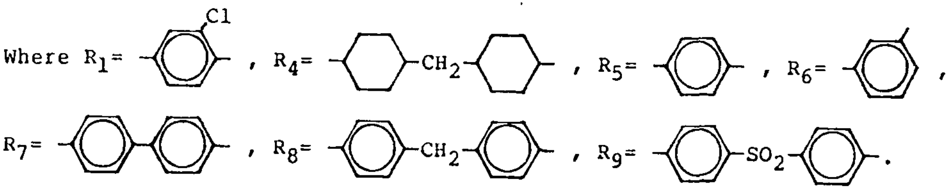


TABLE 11. Properties of Halopolyamides Derived from Diacid Chloride XIa with Diamines I-VIII

Structure of repeat unit	Yield (%)	η_{red}	Solubility in DMA	Mp (°C)	T_g (°K)	T_m (°K)	Decomp (°K)
$[-OC-R_3-OCH_2-CONH-R_5-NH-]_n$	70	0.34	Soluble	>300	430.7	462.8	>630
$[-OC-R_3-OCH_2-CONH-R_6-NH-]_n$	50	0.25	Soluble	280, decomp	367.9		530
$[-OC-R_3-OCH_2-CONH-R_7-NH-]_n$	95	0.45[a]	Insoluble	300-305			
$[-OC-R_3-OCH_2-CONH-R_8-NH-]_n$	81	0.29	Soluble	280-285	489.5		>510
$[-OC-R_3-OCH_2-CONH-R_9-NH-]_n$	96	0.21	Soluble	300	492.1		510
$[-OC-R_3-OCH_2-CONH-(CH_2)_2-NH-]_n$	17	0.14	Soluble	210			
$[-OC-R_3-OCH_2-CONH-(CH_2)_6-NH-]_n$	20	0.16	Soluble	160-165			
$[-OC-R_3-OCH_2-CONH-R_4-NH-]_n$	38	0.17	Soluble	250	435.0		510

[a] Reduced viscosity was measured in concentrated sulfuric acid.

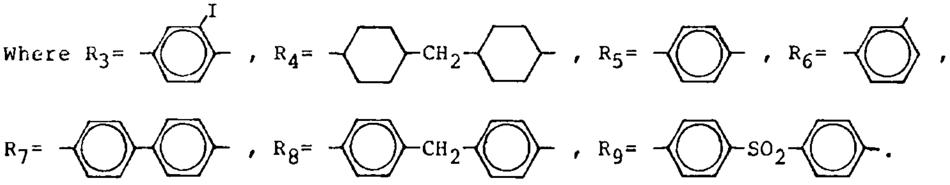


TABLE 12. Properties of Halopolyamides Derived from Diacid Chloride XIIa with Diamines I-VIII

Structure of repeat unit	Yield (%)	η_{red}	Solubility in DMA	Mp (°C)	T_g (°K)	T_m (°K)	Decomp (°K)
$[-OC-H_2C-O-R_1-OCH_2-CONH-R_5-NH-]_n$	97	0.38[a]	Insoluble	>330	428.5	630.0	>630
$[-OC-H_2C-O-R_1-OCH_2-CONH-R_6-NH-]_n$	79	0.13[a]	Insoluble	Decomp >260	346.8		500
$[-OC-H_2C-O-R_1-OCH_2-CONH-R_7-NH-]_n$	66	0.38[a]	Insoluble	330	460.0	656.0	660
$[-OC-H_2C-O-R_1-OCH_2-CONH-R_8-NH-]_n$	73	0.36	Soluble	260	412.0	542.5, 494.7	610
$[-OC-H_2C-O-R_1-OCH_2-CONH-R_9-NH-]_n$	66	0.26	Soluble	210-215			
$[-OC-H_2C-O-R_1-OCH_2-CONH-(CH_2)_2-NH-]_n$	16	0.16	Soluble	110			
$[-OC-H_2C-O-R_1-OCH_2-CONH-(CH_2)_6-NH-]_n$	17	0.20[a]	Insoluble	140			
$[-OC-H_2C-O-R_1-OCH_2-CONH-R_4-NH-]_n$	42	0.21[a]	Insoluble	180	385.0		420

[a] Reduced viscosity was measured in concentrated sulfuric acid.

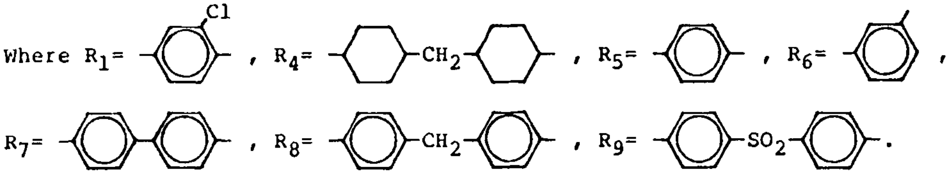
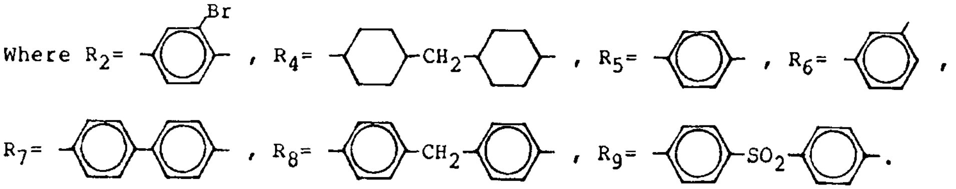


TABLE 13. Properties of Halopolyamides Derived from Diacid Chloride XIIIa with Diamines I-VIII

Structure of repeat unit	Yield (%)	η_{red}	Solubility in DMA	Mp (°C)	T_g (°K)	T_m (°K)	Decomp (°K)
$[-OC-H_2C-O-R_2-OCH_2-CONH-R_5-NH-]_n$	52	0.21[a]	Insoluble	>300			
$[-OC-H_2C-O-R_2-OCH_2-CONH-R_6-NH-]_n$	46	0.17[a]	Insoluble	Decomp >300			
$[-OC-H_2C-O-R_2-OCH_2-CONH-R_7-NH-]_n$	69	0.38[a]	Insoluble	>300	430.0	493.0 434.0	640
$[-OC-H_2C-O-R_2-OCH_2-CONH-R_8-NH-]_n$	58	0.23	Soluble	300			
$[-OC-H_2C-O-R_2-OCH_2-CONH-R_9-NH-]_n$	50	0.23	Soluble	235-240	335.2	425.8	600
$[-OC-H_2C-O-R_2-OCH_2-CONH-(CH_2)_2-NH-]_n$	19	0.17[a]	Insoluble	150	335.2	459.8	600
$[-OC-H_2C-O-R_2-OCH_2-CONH-(CH_2)_6-NH-]_n$	16	0.17[a]	Insoluble	135-140	327.8	421.2, 375.0	>500
$[-OC-H_2C-O-R_2-OCH_2-CONH-R_4-NH-]_n$	41	0.20[a]	Insoluble	75-80			

[a] Reduced viscosity was measured in concentrated sulfuric acid.



acids of Series A. In addition, polymers derived from aliphatic diamines are less stable thermally than those derived from aromatic diamines as expected on the basis of the rigidity of the backbone. Finally, halopolyamides derived from diamines III, IV, and V were shown to resist decomposition, thus reflecting the rigidity of their backbone.

The T_m values obtained after second heating of the polymers derived from dicarboxylic acid IX with diamine I, and from dicarboxylic acid XIII with diamines III, V, and VII are 491.2 K (broad melting), 555 K (broad melting), 473.8 K (sharp melting), and 430 K, respectively. These melting points are reversible because they are higher than those obtained after the initial heating. The rest of the polyamides are not crystallizable from their melts at the usual cooling rate. In addition, halopolyamides derived from various dicarboxylic acids and diamines II or VIII cannot be crystallized as shown by the fact that no melting was observed in the case of those polymers.

The soluble halopolyamides gave films from their solution in DMA while the insoluble materials gave films from their melts in a nitrogen atmosphere. Such films are worthy of further investigation.

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