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Syntheses and Properties of Some New Polyamides. Part II

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ABSTRACT

Interfacial condensation of decamethylenediamine and acid chlorides I, II, and III yielded polyamides the thermal stability of which decreased in the order III, I, II, a finding reasserted by calculating activation energy decomposition temperatures. Irradiation of these polyamides does not appreciably affect their properties, and thus they can be considered satisfactorily γ-irradiation resistant.

It appears that there are only few papers dealing with syntheses and properties of polyamidoarylates. Cleaver and Pratt [1] prepared polyamidoesters by the polymerization of bisoxazolones with glycols. Korshak and others [2], however, obtained a polyamidoester by the aminolysis of polyethylene-sebacate with hexamethylenediamine.

In a previous investigation [3] a few polyamidoarylates were obtained by the condensation of aminophenols with aromatic acid chlorides.

In this work we obtained some new polyamidoarylates by the interfacial condensation of equimolar ratios of decamethylenediamine with

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TABLE 1. Effect of Solvent on the Viscosity and Yields of Polyamides Synthesized from Decamethylenediamine and the Acid Chlorides I, II, and III[a]

		I		II		III		Copolymer (DMD + resorcinol, 1:1) with II	
Solvent	Solubility parameter	η_{red}	Yield %	η_{red}	Yield %	η_{red}	Yield %	η_{red}	Yield %
Nitrobenzene	10.0	0.61	95.3	0.50	86.3	0.59	76.9	0.15	73.8
Methylene chloride	9.7	0.56	94.5	0.46	88.1	0.64	83.6	0.19	76.8
Chloroform	9.3	0.52	86.3	0.38	81.2	0.60	73.9	0.18	77.5
Benzene	9.2	0.49	89.1	0.20	78.4	0.51	75.5	0.12	75.7
Carbon tetrachloride	8.6	0.16	56.9	0.18	62.8	0.29	66.0	0.11	73.4
n-Hexane	7.3	0.11	61.9	0.12	58.3	0.25	53.8	0.08	62.1

[a] η_{red} measured in concentrated sulfuric acid.

terephthaloyl chloride (I), 4,4'-bis-(chloroformylmethoxy) diphenyl (II), and bis-(4-chloroformylmethoxyphenyl) sulfone (III).

In our study of the solvent effect on these synthesized decamethylenediamine polyamides (Table 1), it was noticed that the highest viscosities and yields were obtained with those solvents having high solubility parameters [4], a concept previously verified by Burrell [5]. Further, the viscosities of these polyamides were also found to be acid-chloride-concentration and inherited-structure-dependent (Table 2). Thus, whereas for polydecamethylene-terephthalamide the viscosity decreases with an increase of the terephthaloyl chloride concentration, the viscosities of other polyamides from decamethylenediamine and acid chloride III, obtained under the same experimental conditions, were found to be directly proportional to the acid chloride concentration.

The copolymerization of acid chlorides I, II, and III with a mixture of decamethylenediamine and dihydric phenols led in most cases to soluble polymeric materials (Tables 3 and 4). However, a quinol-decamethylenediamine mixture with either I or II and a 4,4'-dihydroxydiphenyl-decamethylenediamine mixture with I yielded insoluble copolyamidoarylates. This can probably be correlated to the rigid structure repeating unit in the case of these two phenols since replacing quinol by the unsymmetrical resorcinol and inserting a sulfone group between two phenyl groups led to the expected solubilizing effect.

Careful study of Tables 3 and 4 reveals that for the copolyamidoarylates synthesized here, their viscosities vary directly with the decamethylenediamine percentage but inversely with the dihydric phenol and acid chloride concentrations. This criterion can be extrapolated to the higher decamethylenediamine reactivity toward the acid chlorides as compared with the dihydric phenols under the experimental conditions.

Further elucidation of the structure of the polyamidoarylates and copolyamidoarylates synthesized was attested to by a study of their thermal properties (Table 5). A careful study of Table 5 reveals that the decamethylenediamine polyamides obtained from I, II, and III show decreasing stability temperature in the order III > I > II, the same sequence previously noted for poly- and copolyarylates [3]. Yet the thermal stabilities and intensive decomposition temperatures for the polyamides were found to be higher than those of the corresponding polyarylates. This is quite evident as exemplified by those copolyamidoarylates (cf. Table 5) obtained from a mixture of decamethylenediamine and 2,2-bis-(4-hydroxyphenyl) propane with terephthaloyl chloride when compared with the corresponding polyarylates [3]. The higher thermal stabilities of polyamidoarylates over the polyarylates is undoubtedly due to the presence of the amide linkage increasing hydrogen bonding interactions, a criterion not existing in the arylates [6].

Calculations of the intensive decomposition activation energies

TABLE 2. Effect of Acid Chloride Concentration on the Viscosity and Yields of Polyamidoarylates from Decamethylenediamine with Acid Chlorides I and III (1:1)[a]

Acid chloride concentration (mol/L)	Solvent (mL)	I		III			
		Nitrobenzene		Nitrobenzene		Methylene chloride	
		η_{red}	Yield %	η_{red}	Yield %	η_{red}	Yield %
0.33	7.5	0.61	92.6	0.59	76.9	0.63	83.6
0.17	15.0	0.65	90.0	0.48	72.5	0.54	78.3
0.11	22.5	0.69	89.9	0.38	68.0	0.48	75.5
0.08	30.0	0.73	89.5	0.34	65.0	0.45	67.8
0.07	37.5	0.78	91.8	0.30	62.7	0.42	63.7

[a] η_{red} measured in concentrated sulfuric acid.

TABLE 3. Effect of Acid Chloride Concentration on Viscosity and Yields of Copolyamidoarylates Synthesized from Acid Chlorides I, II, and III with an Equimolar Mixture of Decamethylenediamine and Different Bisphenols[a]

2,2-Bis-(4-hydroxyphenyl) propane in 37.5 mL of nitrobenzene			Resorcinol in 7.5 mL of methylene chloride				
Acid chloride concentration (mol/L)	I		Acid chloride concentration (mol/L)	II		III	
	η_{red}	Yield %		η_{red}	Yield %	η_{red}	Yield %
0.034	0.30	38.5	0.17	0.34	46.1	0.40	34.8
0.67	0.20	88.8	0.33	0.19	78.2	0.27	71.3
0.100	0.18	68.7	0.50	0.16	74.5	0.24	65.2
0.134	0.16	58.9	0.66	0.14	68.3	0.18	62.5
0.200	0.12	50.3	0.99	0.11	61.7	0.14	60.7

[a] η_{red} measured in concentrated sulfuric acid.

TABLE 4. Effect of Initial Reactants Percentage Composition on Viscosity and Yields of Copolyamidoarylates Synthesized from Acid Chlorides I, II, and III with a Mixture of Decamethylenediamine and Bisphenols (IV-VIII)[a]

% mixture composition		Quinol (IV)		Resorcinol (V)		2,2-Bis-(4-hydroxyphenyl) propane (VI)		Bis-(4-hydroxy phenyl) sulfone (VII)		4,4'-Dihydroxy-diphenyl (VIII)	
DMD	Phenol	η_{red}	Yield %	η_{red}	Yield %	η_{red}	Yield %	η_{red}	Yield %	η_{red}	Yield %
		Terephthaloyl Chloride (I) (in 37.5 mL of Nitrobenzene)									
75	25	Insoluble	85.2	0.34	87.8	0.37	92.8	0.26	95.2	Insoluble	96.3
50	50	"	80.3	0.16	83.7	0.21	88.6	0.18	86.9	"	92.1
25	75	"	73.8	0.10	80.2	0.11	76.6	0.09	80.0	"	89.4
		4,4'-Bis(chloroformylmethoxy) Diphenyl (II) (in 7.5 mL of Methylene Chloride)									
75	25	Insoluble	79.9	0.26	82.7	0.24	85.6	0.22	82.3	0.21	88.0
50	50	"	75.7	0.19	76.8	0.16	77.3	0.15	79.1	0.12	81.3
25	75	"	73.8	0.08	74.5	0.05	75.8	0.06	77.0	0.04	79.3
		Bis-(4-chloroformylmethoxyphenyl) Sulfone (III) (in 7.5 mL of Methylene Chloride)									
75	25	0.31	72.3	0.33	84.2	0.27	80.9	0.33	81.5	0.21	85.8
50	50	0.29	68.2	0.27	71.3	0.12	72.8	0.22	74.6	0.13	80.4
25	75	0.07	57.2	0.09	54.7	0.07	59.9	0.04	64.7	0.05	68.7

[a] η_{red} measured in concentrated sulfuric acid. DMD = decamethylenediamine.

TABLE 5. Activation Energy and Intensive Decomposition Temperatures of Some Irradiated Polyarylates, Polyamides, and Copolyamidoarylates[a]

		I + DMD (1:1) (IX)	II + DMD (1:1)	III + DMD (1:1)	I + mixture of VI and DMD (1:1) (X)	VI + mixture of I (60%) and III (40%) (XI)	I + VI (1:1) (XII)
Intensive decomposition temperature, °C	Unirradiated	415	355	430	440	400	420
	Solid irradiated[b]	415			380	365	425
	Solution irradiated[b]	420			350	355	360
Activation energy, kcal/mol	Unirradiated	15.56	13.12	21.25	12.39	19.60	20.17
	Solid irradiated[b]	12.12			8.09	14.99	17.88
	Solution irradiated[b]	9.22			6.47	12.28	15.58

[a] DMD = decamethylenediamine

[b] Irradiated at 220.8 Mrad.

TABLE 6. IR Spectra (in cm $^{-1}$) of Some Decamethylenediamine Polyamides and Copolyamidoarylates Synthesized from Various Compounds[a]

	NH	C=O	–O–
Terephthaloyl chloride (I)	3500s	1640s	-
4,4'-Bis-(chloroformylmethoxy) diphenyl (II)	3300s	1660s	1120m
Bis-(4-chloroformylmethoxyphenyl) sulfone (III)	3350s	1660s	1120s
Bis-(4-chloroformylmethoxyphenyl) sulfone + a mixture (1:1) of DMD and 4,4'-dihydroxydiphenyl	3350s	1760s 1660s	1110s
Bis-(4-chloroformylmethoxyphenyl) sulfone + a mixture (1:1) of DMD and 2,2-bis-(4-hydroxyphenyl) propane	3400s	1760s 1670s	1120s 1150m
Bis-(4-chloroformylmethoxyphenyl) sulfone + a mixture (1:1) of DMD and bis-(4-hydroxyphenyl) sulfone	3400s	1770s 1660s	1120s

[a] s = strong, m = medium.

(Table 5) reattest the relationship between polymer thermal stability and the irregularities of the molecular structure repeating units.

The IR spectra of these polyamides (Table 6) show an NH band at 3300-3400 cm^{-1}. A strong band at 1660-1640 cm^{-1} can be attributed to an amide carbonyl group. With copolyamidoarylates this band was noticed to occur at a higher frequency, 1760-1660 cm^{-1}. A strong band at 2900 cm^{-1} is evidently due to CH absorption.

In the present investigation some of the polyamides and copolyamides prepared as well as some previously prepared arylates were subjected to γ-irradiation in both the solid state and in solution. Although γ-irradiation of a variety of polymeric classes has been thoroughly investigated by several workers [7-9], information on high energy irradiation effects on polyesters is nearly absent. Irradiation of Polymers IX, X, XI, and XII (Table 5) in the solid state in air and at five different doses (55.2, 110.4, 165.6, 220.8, and 276 Mrad) indicated that all investigated polymers could be adequately considered radiation resistant (Figs. 1 and 2). This conclusion is based on the limited data changes observed in their viscosities compared with those known before irradiation. Irradiation of a chloroformic polymer solution, however, led to more pronounced viscosity changes

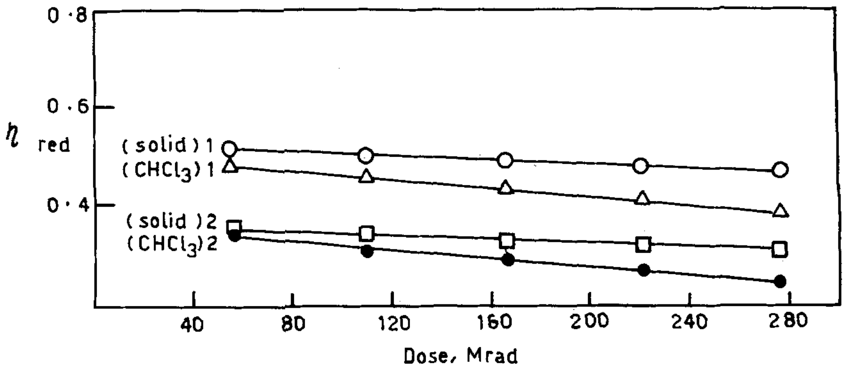

FIG. 1. Effect of γ-irradiation on (1) poly-[2,2-(4-hydroxyphenyl) propane] terephthalate and on (2) poly-[2,2-(4-hydroxyphenyl) propane-bis-(4-chloroformylmethoxyphenyl) sulfone (40%) + terephthaloyl chloride (60%)].

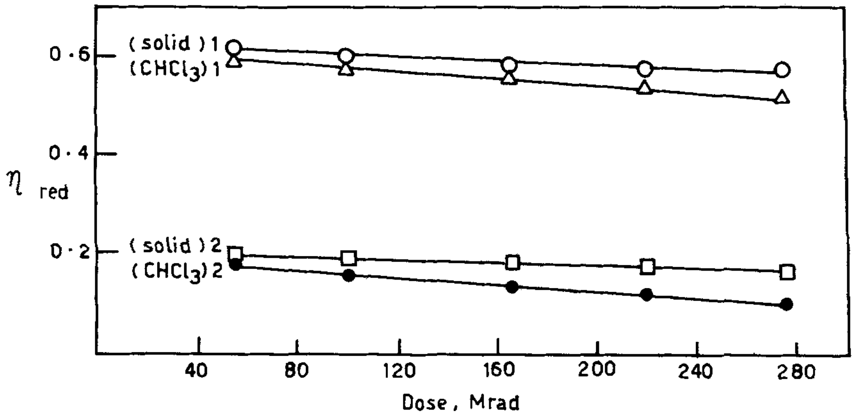

FIG. 2. Effect of γ-irradiation on (1) poly(decamethylene-diamine-terephthalamide) and (2) poly[decamethylenediamine (50%) + 2,2-(4-hydroxyphenyl) propane and terephthaloyl chloride (50%)].

(Table 5). The differences obtained in the latter case are probably due to indirect γ-irradiation effects in addition to the solvent radiolysis products [10].

Careful examination of Table 5 demonstrates that unirradiated polymers have higher intensive decomposition temperatures and activation energies than the corresponding irradiated ones. The stability decreasing order of polymers can thus be depicted as unirradiated > solid irradiated > solution irradiated. Polyarylates from acid chloride I can be satisfactorily considered the most irradiation stable polymer, being capable of withstanding high energy irradiation doses.

EXPERIMENTAL

Infrared measurements were run on a Unicam SP 200. Thermomechanical, thermogravimetric, and differential thermal analysis were run on a drivatograve "Paulk-Paulk and Erdi, Budapest, Hungaria." Samples of about 0.12-0.14 g were heated in carbon dioxide-free dry air from room temperature to 1000° C at a rate of 10° C/min.

General Procedure for Polyamide Synthesis

The acid chloride (1 mol) was dissolved in 75 mL of a dry organic solvent and was then added within 3 min to a vigorously stirred suspension of decamethylenediamine (1 mol) in 15 mL of water. Stirring was continued for a further 20 min. The separated polymer was then filtered, washed with water until chloride free, and then with an appropriate organic solvent to remove unreacted monomers. The purified polymer was then dried in high vacuum at 50° C to constant weight.

Irradiation Technique

An 8000 Curie source of ^{60}Co in a lead shield was used to give dose rates of 8×10^5, 6.4×10^4, and 6×10^5 Rontengen/h depending on the position of the sample. The polymer samples were irradiated in small glass vials in case of air-irradiation. Sealed ampules containing the polymer solution were used in the case of solution irradiation. The glass vials or the ampules were placed at a standard distance from the γ-irradiation source. During irradiation, the temperature was kept at 50° C.

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