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Interfacial Polymerization for the Preparation of Regularly Alternating Polyesteramides

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SUMMARY:

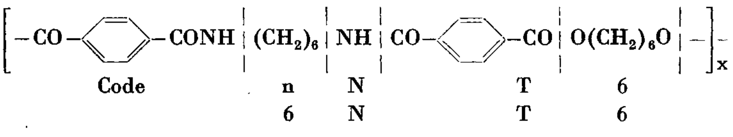
Polyesteramides have been prepared by interfacial condensation of hexamethylene glycol-1,6-bis(4-chlorocarbonylbenzoate) and various alkylenediamines. The melting points of these polyesteramides are compared with samples prepared previously by melt condensation of bisesteramides and glycols.

ZUSAMMENFASSUNG:

Mittels Grenzflächenkondensation wurden aus Hexamethylendiol-1,6-bis-(4-benzoesäurechlorid)ester und verschiedenen normalen α,ω-Alkylendiaminen Polyesteramide hergestellt. Die Schmelzpunkte dieser Polyesteramide werden mit jenen der Produkte verglichen, die durch Schmelzkondensation mit Diesteramiden und Glykolen erhalten wurden.

Introduction

Previous reports of preparations of regularly alternating polyesteramides described the melt-condensation polymerization¹⁾ of preformed bisesteramides²⁾ with various glycols. The condensations were conducted at 225–300 °C., a region in which ester stability and even amide stability are marginal. In most cases, such as 6NT6, where preparations were conducted below 275 °C., polymers with well-defined structures were obtained. 6NT6 was reported to crystallize in unit cells characteristic of the esteramide unit, rather than as terephthalate or terephthalamide structures. Difficulty was experienced in the preparation of other members of the 6NT series because the shorter-chained glycols produced polymers



m.p. 265 °C.

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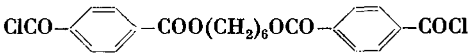
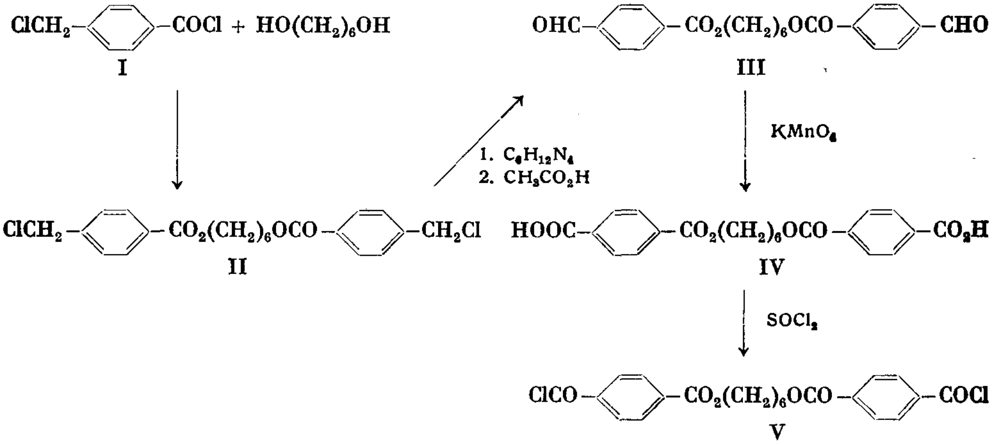
* Comm. No. 2346.

with melting points above 270 °C., and polycondensation was accompanied by pyrolysis of either the ester or the amide functions. In many cases, the polymers crystallized during preparation, and, despite the use of oil-bath temperatures in excess of 300 °C., low-molecular-weight, brittle, and often highly colored polymers resulted. It was therefore apparent that the members of the 6NT series melting above 275–280 °C. would not be obtained by the melt-polymerization method. Thus, it was decided to prepare and condense the bis-acid chloride, hexamethylene 1,6-bis(chlorocarbonylbenzoate) (V), with a number of bis-primary amines.

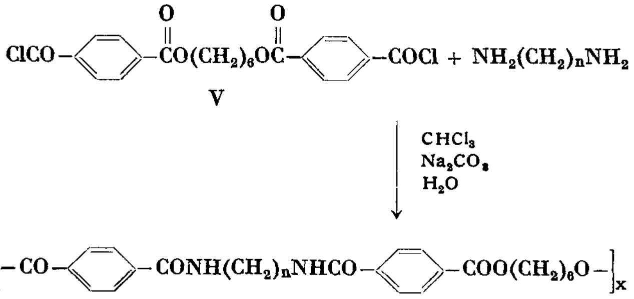


V

The bis-acid chloride (V) was prepared by the following synthetic route:



Polyesteramide preparation was conducted by the interfacial polymerization of V with alkylenediamines as illustrated below:



The physical data for various nNT6 polyesteramides prepared in this manner are summarized in Table 1.

Table 1. Polyesteramides Prepared by Interfacial Condensation of Hexamethylene 1,6-Bis(4-chlorocarbonylbenzoate) (V) with Various Amines

n	Yield (%)	M. P. (°C.)	Inherent Viscosity[a]	Previous M. P. (°C.)[b]
2	70	319	0.24	274
3	55	278	0.20	256
4	78	302	0.26	290
5	75	252	0.21	238
6	68	265	0.27	265
7	69	234	0.21	
8	66	250	0.34	
9	44	217	0.26	
10	56	233	0.36	
11	64	204	0.24	
12	74	223	0.38	

[a] ln η_r/c; c = 0.25%.

[b] Melting points of polyesteramides prepared by melt polymerization.

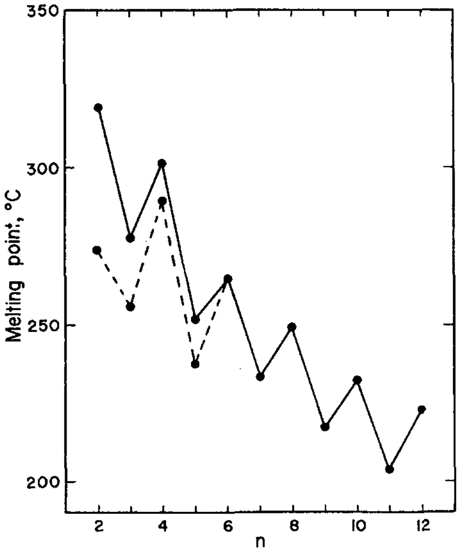


Fig. 1. Melting points of nNT6 polyesteramides with varying interamide alkylene linkages. Polyesteramides prepared by interfacial polymerization: ——; melt condensation: ----; n = number of methylene groups in an interamide alkylene linkage.

Fig. 1 shows the dependence of the melting points on the number of interamide methylene groups when n is varied from 2 to 12, as well as the comparable melting points for several samples prepared previously by the melt-condensation technique.

Although the inherent viscosities of the polymers prepared by the interfacial technique are not as high as those obtained by melt polymerization, they are in the range where the melting points of such polymers are independent of molecular weight. The viscosity values are dictated by the fact that even low-molecular-weight polyesteramides are insoluble in chloroform. We have noted the interesting phenomenon that the inherent viscosities of the polymers alternate in relation to the number of interamide methylene groups in a manner similar to that of the melting points of the polymers. Fig. 2 graphically represents this phenomenon which is dictated by the limited solubilities of the polyesteramides in chloroform during interfacial condensation.

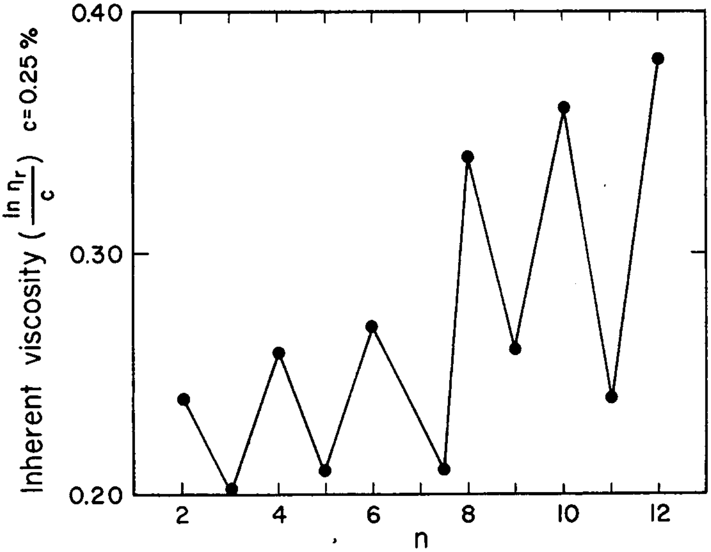


Fig. 2. Inherent viscosity of nNT6 polyesteramides with varying interamide alkylene linkages.

Conclusions

Interfacial preparation of polyesteramides from V and various diamines produces higher-melting, better-defined polymers than are produced by polycondensation of bisesteramides with glycols. The higher temperatures

required to prepare nNT6-type polymers where ethylene, propylene, butylene, and pentamethylenediamines are employed, lead, as suggested earlier[2), to side reactions and nonregular polyesteramides.

Experimental

Hexamethylene 1,6-Bis(4-chloromethylbenzoate) (II)

A mixture of 60 g. (0.32 mole) of *p*-chloromethyl benzoyl chloride[3) and 19 g. (0.16 mole) of 1,6-hexanediol in 100 ml. of benzene was refluxed for 4 hrs., and, after chilling, the solid was collected and recrystallized from ligroin (b.p. 90–120 °C.) to yield 51 g. of product, m.p. 73–74 °C.

$C_{22}H_{24}Cl_2O_4$ (422)	Calcd.	C 62.5	H 5.7	Cl 16.6
	Found	C 62.3	H 5.9	Cl 17.0

Hexamethylene 1,6-Bis(4-formylbenzoate) (III)

A mixture of 42 g. (0.1 mole) of the 1,6-hexanediol ester of *p*-chloromethylbenzoic acid and 28 g. (0.2 mole) of hexamethylenetetramine in 250 ml. of chloroform was refluxed on the steam bath for 4 hrs., cooled, and the salt collected (yield, 60 g.). A mixture of the salt and 300 ml. of water was heated on the steam bath for 3 hrs., the water decanted from the solid, and the solid dried *in vacuo*. The solid was dissolved in 150 ml. of warm acetic acid. The solution was cooled to room temperature, diluted with water and chilled in a refrigerator to yield 18 g. of the product, m.p. 80 °C. A small sample of this material was converted to the 2,4-dinitrophenylhydrazone derivative, m.p. 275 °C.

$C_{34}H_{30}N_8O_{12}$ (742)	Calcd.	C 55.0	H 4.1	N 15.1
	Found	C 55.5	H 4.4	N 15.0

Hexamethylene 1,6-Bis(4-carboxybenzoate) (IV)

To a solution of 7 g. (0.0183 mole) of the terephthalaldehydic ester in 50 ml. of dioxane was added slowly, with stirring, a solution of 3.86 g. (0.0244 mole) of potassium permanganate in 300 ml. of water. The reaction mixture was maintained at a p_H of 7 by the addition of potassium carbonate solution. The reaction mixture was filtered, the manganese dioxide was washed with 100 ml. of 5% sodium bicarbonate solution, and the filtrates were acidified with hydrochloric acid. The white solid was collected and recrystallized from a mixture of tetrahydrofuran and petroleum ether (b.p. 30–60 °C.) to yield 4.2 g. of product, m.p. 240 °C., with decomposition (bubbling).

$C_{22}H_{22}O_8$ (414)	Calcd.	C 63.7	H 5.3
	Found	C 63.3	H 5.0

Hexamethylene 1,6-Bis(4-chlorocarbonylbenzoate) (V)

A mixture of 4 g. of the 1,6-hexanediol ester of terephthalic acid, 25 ml. of benzene, 2.7 g. of thionyl chloride and 5 drops of dimethylformamide was refluxed for 2 hrs., diluted with petroleum ether (b.p. 30–60 °C.) and chilled to yield 3.8 g. of acid chloride, m.p. 91–92 °C. (from benzene-petroleum ether).

$C_{22}H_{20}Cl_2O_6$ (450)	Calcd.	C 58.7	H 4.4	Cl 15.5
	Found	C 59.0	H 4.5	Cl 15.2

The interfacial condensations were conducted by the procedure which is described for the preparation of 6NT6: A solution of 0.5 g. ($4.6 \cdot 10^{-3}$ mole) of sodium carbonate and 0.13 g. of $NH_2(CH_2)_6NH_2$ ($1.11 \cdot 10^{-3}$ mole) in 20 ml. of cold water was rapidly agitated in a water-jacketed Waring-type blender. There was then added in one portion a solution of 0.5 g. ($1.11 \cdot 10^{-3}$ mole) of hexamethylene 1,6-bis(4-chlorocarbonylbenzoate) in 40 ml. of dry chloroform.

The aqueous layer was saturated with sodium chloride and the polymer separated by filtration. The polymer was washed several times by resuspension in water and then finally washed on the filter with methanol. The polymer was then dried *in vacuo*. The physical data for the polyesteramides prepared in this work are tabulated in Table 1.

Inherent Viscosity Measurements ($\ln \eta_r/c$)

Inherent viscosities were calculated from the relative viscosities determined in 0.25% olutions of the polymers in a 50:50 phenol-chlorobenzene mixture at 25°C.

Melting-Point Determinations

Melting-point determinations were made using a hot-stage, low-power, polarizing microscope. The temperatures at which polarization colors completely disappeared were taken as the melting points.

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1) J. L. R. Williams, T. M. Laakso, and L. E. Contois, J. Polymer Sci. **61** (1962) 353.

2) J. L. R. Williams, T. M. Laakso, K. R. Dunham, D. G. Borden, J. Van Den Berghe, J. A. Van Allan, and D. D. Reynolds, J. org. Chemistry **25** (1960) 817.

3) F. F. Blicke and W. M. Lilienfeld, J. Amer. chem. Soc. **65** (1943) 2282.