Short Communication

# Synthesis of a Hydroxyl Containing Polyamide by Ring-Opening Polyadditon of a Di- $\delta$ -valerolactone with Hexamethylenediamine

Mitsuru Ueda, Masayoshi Takahashi, and Yoshio Imai\*

Department of Polymer Chemistry, Faculty of Engineering, Yamagata University, Yonezawa, Yamagata 992, Japan

(Date of receipt: August 17, 1978)

### Introduction

Ring-opening polyadditions of four-membered di- $\beta$ -propiolactone compounds<sup>1</sup>) and five-membered di- $\gamma$ -butyrolactone compounds<sup>2</sup>) with diamines yielding the corresponding hydroxyl containing polyamides have been reported previously from this laboratory. It was known that phenylvalerolactone undergoes aminolysis by acyl-oxygen scission affording  $\delta$ -hydroxy amides<sup>3</sup>). This information promted us to study the synthesis of a new monomer containing two six-membered  $\delta$ -valerolactone rings (1) and the subsequent ring-opening polyaddition with a diamine 2 leading to a hydroxyl containing polyamide 3.



## **Results and Discussion**

The synthetic scheme for 5,5'-oxydi-*p*-phenylenedi- $\delta$ -valerolactone (1) is shown by the following equations:





The Friedel-Crafts reaction of diphenyl ether with ethyl 4-chloroformylbutyrate (mole ratio 1:2) in the presence of aluminium chloride, followed by alkaline hydrolysis, affords 4,4'-oxydi-4benzoylbutyric acid (4b). A direct synthesis of 4b by Friedel-Crafts reaction of diphenyl ether with glutaric anhydride (mole ratio 1:2) was unsuccessful; the isolated product was not 4b but 4-(*p*-phenoxybenzoyl)butyric acid. Reduction of 4b was accomplished with sodium borohydride to yield 5,5'-dihydroxy-5,5'-oxydi-*p*-phenylenedivaleric acid (5), which was used directly for subsequent cyclodehydration yielding monomer 1.

The ring-opening polyaddition of 1 with hexamethylenediamine (2) was carried out at elevated temperature in methanol, 1-methyl-2-pyrrolidone (NMP), or *m*-cresol. As it can be seen from Tab. 1, the polymer with an inherent viscosity of  $0.25 \text{ dl} \cdot \text{g}^{-1}$  was obtained in high yield.

Solvent	Polym	erization condit	Polymer		
	monomer conc. in wt-%	temp. in °C	time in days	yield in %	$\frac{\eta_{\rm inh}}{{\rm dl}\cdot{\rm g}^{-1}}^{\rm b}$
Methanol	19	65	10	98	0,15
Methanol	38	65	10	99	0,25
NMP	16	65	10	93	0,26
NMP	32	80	10	95	0,20
m-Cresol	22	80	2	94	0,25

Tab. 1.	Conditions	and	results	of	the	ring-opening	polyaddition	of	the	di- $\delta$ -valerolactone	1	with
hexameth	nylenediamin	1e ( <b>2</b> )										

<sup>a)</sup> Polymerization was carried out with 2 mmol of 1 and of 2.

<sup>b)</sup> Inherent viscosity was measured at a concentration of  $c = 0.5 \text{ g} \cdot \text{dl}^{-1}$  in NMP at 30 °C.

The structure of the polymer was confirmed by IR spectroscopy and elemental analysis. The spectrum was free of a lactone carbonyl absorption at  $1730 \text{ cm}^{-1}$  and showed the characteristic amide carbonyl band at  $1650 \text{ cm}^{-1}$ . Polyamide 3, containing hydroxyl groups, is soluble in DMF, NMP, pyridine, or hot *m*-cresol, and partially soluble or swelling in acetone, methanol, or water. The polymer has no melting or softening point below 400 °C.

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#### **Experimental** Part

#### Materials

4,4'-Oxydi-4-benzoylbutyric acid (**4b**): To a stirred solution of 31,0 g (0,17 mol) of ethyl 4-chloroformylbutyrate<sup>4)</sup> (obtained from glutaric anhydride) in 300 ml of 1,2-dichloroethane, 50,0 g (0,37 mol) of aluminium chloride were added at 5-10 °C, and stirring was continued until the aluminium chloride was dissolved. A solution of 13,6 g (0,08 mol) of diphenyl ether in 50 ml of 1,2-dichloroethane was added at 0-3 °C, dropwise with vigorous stirring. The reaction mixture was stirred at 0-5 °C for 4 h and then heated under reflux for 15 h. During this period, hydrogen chloride gas evolved. The mixture was poured on 500 g of ice containing 30 ml of conc. hydrochloric acid. Then the dichloroethane was steam-distilled. The precipitate which formed on cooling contained mainly the diethyl ester **4a**. The isolated precipitate was saponified with aqueous sodium hydroxide at 95 °C for 2 h and the resulting solution was again acidified with dil. hydrochloric acid to give a white product. Yield: 10,6 g (33%); m. p. 166-169 °C (Lit.<sup>5)</sup>: m. p. 168-170 °C).

IR (KBr): 1705 (vs.; C=O) and 1680 cm<sup>-1</sup> (vs.; C=O).

5,5'-Oxydi-p-phenylenedi- $\delta$ -valerolactone (1): To a solution of 24,0g (0,06 mol) of **4b** in 200 ml of 5% aqueous sodium hydroxide 2,3g (0,06 mol) of sodium borohydride were added and the resulting solution was stirred at room temperature for 24 h. Then, it was acidified with dil. hydrochloric acid and the precipitated 5,5'-dihydroxy-5,5'-oxydi-p-phenylenedivaleric acid (5) was collected by filtration and washed repeatedly with water. Then, 5 was heated in a flask at 110-120°C under reduced pressure (15 Torr) for 2 h. The crude product was recrystallized three times from benzene. White needles; m. p. 162-164°C. Yield: 2,2g (10%).

IR (KBr):  $1730 \text{ cm}^{-1}$  (vs.; C==O).

C22H22O5	(366,4)	Calc.	C 72,12	H 6,05
		Found	C 71,9	H 6,0

Reagent and solvent: Hexamethylenediamine (2), m-cresol, and 1-methyl-2-pyrrolidone (NMP. supplied by Mitsubishi Chemical Industries Ltd.) were purified by vacuum distillation before use.

#### Polymerization

Synthesis of polyamide  $3^{\circ}$ : To a solution of 0,232 g (2 mmol) of 2 in 2 ml of methanol 0,733 g (2 mmol) of 1 were added and the mixture was stirred at 65°C for 10 days. The solution was then evaporated i. vac. to dryness giving a solid polymer. Yield: 0,96 g (99%). Inherent viscosity: 0,25 dl  $\cdot$  g<sup>-1</sup> (in NMP,  $c=0.5 \text{ g} \cdot \text{dl}^{-1}$  at 30°C).

IR (KBr): 1 650 cm<sup>-1</sup> (vs.; C=O).

$(C_{28}H_{38}N_2O_5)_n$	(482,6) <sub>n</sub>	Calc.	C 69,68	Н 7,94	N 5,80
		Found	C 69,5	Н 7,7	N 6,3

The authors are indebted to Mr. Sadao Kato for the performance of the elemental analyses.

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<sup>\*)</sup> Systematic name: poly[oxy-1,4-phenylene-(1-hydroxy-5-oxopentamethylene)iminohexamethyleneimino-(1-oxo-5-hydroxypentamethylene)-1,4-phenylene].