Polymer Bulletin 10, 381–383 (1983)

Polymer Bulletin

A Chelating Polyamide

Synthesis, Characterization and Reaction with Cu(II) Ion

F. R. Diaz, L. H. Tagle and J. P. Olivares

Pontificia Universidad Católica de Chile, Facultad de Química, P.O. Box 114-D, Santiago, Chile

SUMMARY

A polyamide has been prepared by solution polymerization of 2,5-dihydroxyterephthaloyl dichloride and 4,4'-methylenedianiline. This polymer showed up chelating properties in presence of Cu (II) ion in aqueous solution.

INTRODUCTION

During the last few years some articles have been published (1,2) about the synthesis and application of polymers with chelating properties. Sugh et al. (3) reported the synthesis of a chelating polyacrylamidoxime capable of reacting with metal ions as Cu (II), Co (II), Zn (II) and Mn (II). Ramirez and Andrade (4) have reported the synthesis of derivative of polyacrolein chelating iron (III) which has an important application in cases of poisoning with this metal.

As a part of our work on the synthesis and characterization of polyamides (5-9) with different properties, the synthesis of a polyamide derived from the 2,5-dihydroxyterephthalic acid is reported as well as preliminary results on its chelating properties with Cu (II) ions.

EXPERIMENTAL

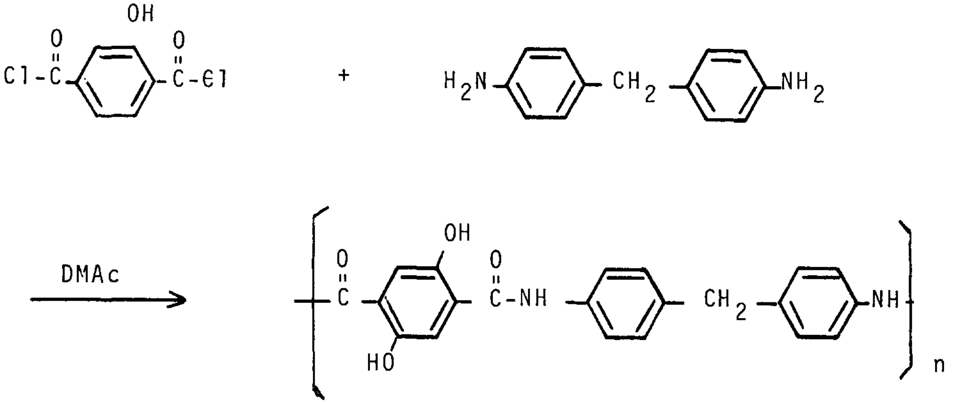
2,5-dihydroxyterephthaloyl dichloride was synthesized according to the following procedure: 1 g of 2,5-dihydroxyterephthalic acid(10) was refluxed with thionyl chloride for three hours, then the excess of thionyl chloride was evaporated and the solid was recrystallized from a benzene-petroleum ether mixture. The yield was 42%. N.M.R. spectrum (C_6D_6): 7,3δ (S, 2H, Arom.) and 8,34-8,92δ (wide band, 2H, OH). I.R. spectrum: 3350 cm^{-1} (C=0).

The polyamide was prepared by polymerization in solution according to the following procedure: 0,5 mmoles of the dichloride were added with stirring at -15°C to a solution of 0,5 mmoles of 4,4'-methylenedianiline and 1 mmol of triethylamine in 30 ml of N,N-dimethylacetamide (DMAc). The mixture was raised slowly up to 25°C. After 20 hours at this temperature the mixture was poured on water causing the polyamide to precipitate. The solid was separated by centrifugation and washed several times with water and acetone. Finally it was dried in vacuum at 50°C on P_2O_5. Calculated from $(C_{21}H_{16}O_4N_2)_n$: C: 69,99%;

H: 4,48%; N: 7,77%. Found: C: 69,29%; H: 5,18%; N: 7,12%.

RESULTS AND DISCUSSION

The polyamide was prepared by reaction of 2,5-dihydroxyterephthaloyl dichloride with 4,4'-methylenedianiline, in solution, according to the following polymerization scheme:

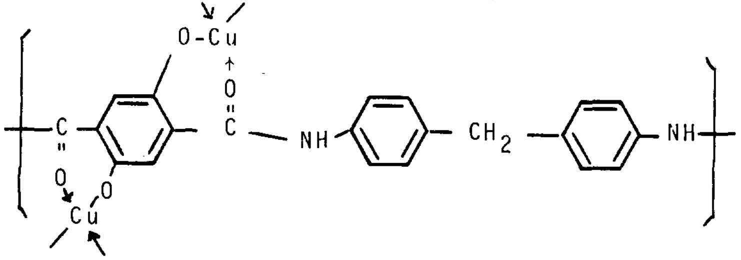


The polyamide was soluble in polar aprotic solvents such as DMAc, DMF and DMSO, but it was insoluble in ordinary organic solvents. The I.R. spectrum showed characteristic bands at 3330 cm^{-1} (C=O), 1600 and 1500 cm^{-1} (aromatic). As an estimation of the molecular weight the intrinsic viscosity $[\eta]$ was determined in DMSO at 25°C and it turned out to be 0,1 dl g^{-1}.

The results reported by Arpin and Strazielle (11) indicate that for the polyamide poly(p-phenylen-2,5-dimetoxyterephthalamide), the equation $[\eta]=KM^a$ ($K=2,1\cdot10^{-3}$, $a=1,16$), allows to conclude that the molecular weights fluctuate between 2.000 and 20.000. Furtheremore, this polymer presents a rigid configuration. By analogy, the polyamide described in this work should have similar dimensions.

The polyamide dissolved in DMSO was mixed with an aqueous solution of $CuSO_4$. A new product was obtained which was separated, washed and dried.

The I.R. spectrum showed a characteristic band at 3450 cm^{-1} corresponding to the -NH- group, whereas the wide band at 3300 cm^{-1} corresponding to the polyamide does not show up. The C=O group band presents a shift from 1645 cm^{-1} to 1630 cm^{-1} due to interaction in a chelate ring with Cu (II):



The polymer containing Cu (II) was refluxed with 10% HCl and the original polyamide and a Cu (II) solution were obtained. The concentration of Cu (II) in this solution was measured by atomic absorption indicating that the chelating capacity of the polyamide is 20,35 mg Cu (II)/ g polyamide.

Finally,it may be reported that the methoxylated polyamide has been prepared too, with an intrinsic viscosity $[\eta] = 0{,}25$ dl g^{-1} (DMSO, 25°C). Demethylation of this polyamide failed, in good agreement with the results of Rao et al. (12) on 2,5-dimethoxylated derivatives.

This work will be continued by testing the chelation of Cu (II) and other metal ions.

ACKNOWLEDGEMENT

The authors wish to thank the "Dirección de Investigación" of the Pontificia Universidad Católica de Chile for financial support.

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Accepted June 24, 1983

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