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SYNTHESIS AND CONDUCTIVITY OF COPOLYMER OF 4-4'-DIAMINODIPHENYLAMINE AND TEREPHTHALOYL CHLORIDE

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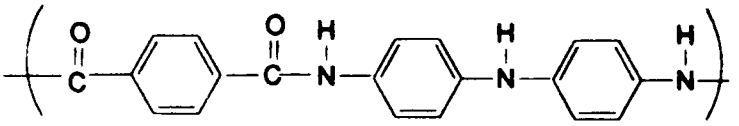
ABSTRACT

The synthesis of the copolymer of 4-4' diaminodiphenylamine sulfate with terephthaloyl chloride, (a copolymer of polyamide and polyaniline), is reported. After doping with SO_3 the conductivity of this copolymer approaches that of salts of polyaniline derivatives.

The chemical structure and conductivity of polyaniline are of interest.[1, 2] Attempts to improve its mechanical properties can be made through the formation of copolymers of polyaniline with other polymers, such as polyamide, which are known to possess desireable mechanical properties. In this paper we report the preparation of the copolymer of 4-4' diaminodiphenylamine sulfate with terephthaloyl chloride and its conductivity with SO_3 doping. The mechanical properties are left to further investigation.

The sample was synthesized using the following procedure. Two solutions were prepared, the first being 0.2 grams of 4-4'-diaminodiphenylamine sulfate (Aldrich) in 50 ml. of 0.01 M NaOH. The second solution was composed of 0.25 grams of terephthaloyl chloride (Aldrich) in 20 ml. of chloroform. The *chloroform solution was added dropwise to the first*, while stirring, until a yellow-green polymer with a structure



was formed. This solution was then stirred for 20 minutes. The polymer was isolated by suction filtration with a succession of wash solutions. These were, in order, 1.0 M HCl, carbon tetrachloride, and a final rinse with methanol to remove any unreacted remnants. The polymer was then dried using a dynamic vacuum. The conductivity of the polymer was determined by the resistance of a thin film of the polymer, prepared by dissolving the polymer in concentrated sulfuric acid, then casting the polymer solution onto a substrate and subsequently submersing it in water thereby forming a thin

(100 μm) film. The resulting film was then washed with water to remove any remaining acid. Two probes were attached to the sample for monitoring the conductivity. The film was placed into an SO_3 atmosphere for doping. The resistance, monitored with a multimeter, was found to decrease as time elapsed, figure 1. This increase in conductivity may be due to a successful doping of amine nitrogen atoms of the polymer backbone. The doped form of the polymer is not stable in air likely due to the strong electron-withdrawing properties of the ketone functional group.

Acknowledgment. This research has been supported in part by the Defense Advanced Research Projects Agency through a contract monitored by the U.S. Office of Naval Research.

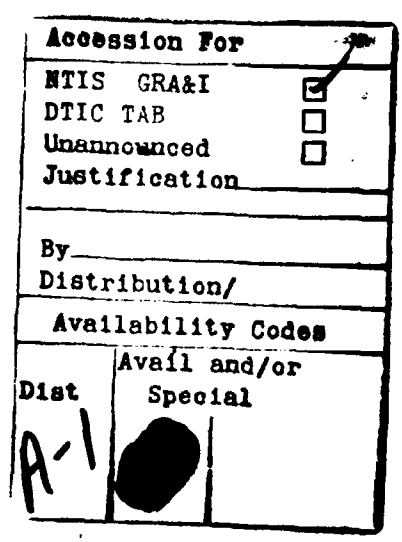
References

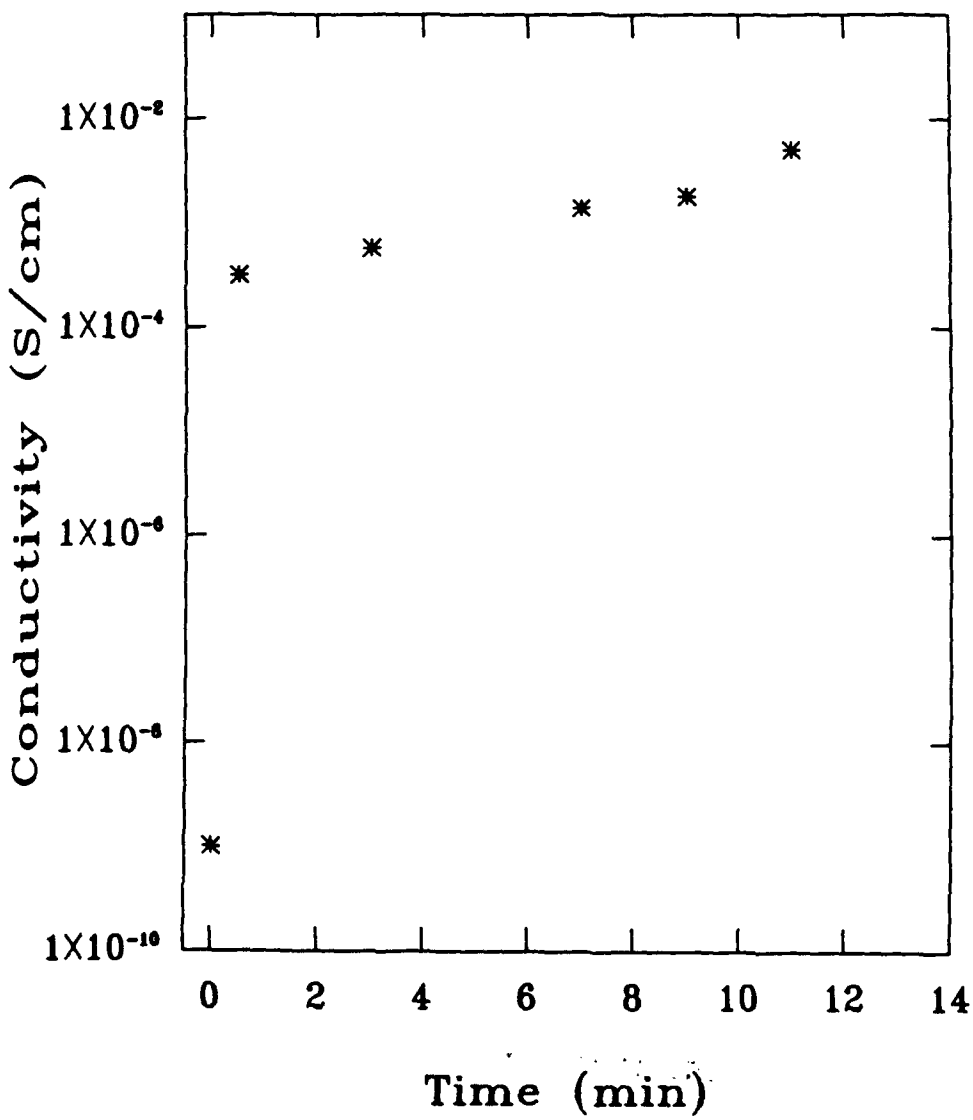
[1]See, for examples, Proc. Int. Conf. on Sci. & Tech. of Synth. Met., Tübingen, Germany, 2~9 Sept. 1990 *Synth. Met.* **1991** 41-43; and Sante Fe, NM 25 June ~ 2 July 1987 *Synth. Met* **1989** *27-29.*

[2]MacDiarmid, A. G.; Epstein, A. J. *Faraday Discus. Chem. Soc.* **1989**, *88*, 317.

Figure Caption

The conductivity of the polymer as a function of doping time in SO_3 gas atmosphere.




Conductivity (S/cm)
1X10⁻²
1X10⁻⁴
1X10⁻⁶
1X10⁻⁸
1X10⁻¹⁰
0
2
4
6
8
10
12
14
Time (min)