Short Communication

Weakly conducting poly(α-methylheptyl isocyanide) films

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Abstract

Poly(α-methylheptyl isocyanide) films were prepared from solution. Both neutral and acid-treated films were doped with iodine and displayed an electrical conductivity of 3×10⁻⁴ ohm⁻¹ cm⁻¹; the latter showed a much faster rate of doping. Doping with arsenic pentafluoride was less effective, giving a conductivity value of 8.3×10⁻⁶ ohm⁻¹ cm⁻¹.

Introduction

Poly(isocyanides) can be prepared from isocyanides in the presence of protonic acids, Lewis acids or Ni(II) salts as catalysts [1–3].

[R—N=O] → [Ni(II)]
(or acids)

The main chain of these polymers forms a rigid rod helix because of a restricted rotation around the single bonds connecting the main chain carbon atoms [1, 4]. Liquid crystalline properties were observed in concentrated solutions of poly(isocyanides) or in solid films [2, 5]. Poly(isocyanides) also showed evidence of accumulated dipole coupling of the orthogonal double bonds of the vicinal imines [2]. These features suggest that these polymers may display interesting electrical properties.

Poly(isocyanides) turn from a light to a dark color upon acidification. It was proposed that this was caused by the isomerization of poly(isocyanides) to highly conjugated poly(cyanides) [1] or to the protonation of poly(isocyanides) on nitrogen [5]. The conducting properties of the neutral and acidified poly(isocyanides) in the form of compressed pellets have been
studied [1, 5]. A resistivity of $10^{14}$ ohm cm for the neutral polymer and $10^{10}$ ohm cm for the acidified polymer was observed. It should be noted, however, that these polymers were not doped.

We report here the preparation of neutral and acid-treated poly(a-methylheptyl isocyanide) (1) films and their doping with iodine or arsenic pentafluoride to a black, weakly conducting form.

\[
\begin{align*}
\text{CH}_3 & - \text{CH} \\
& \quad \text{C}_n \text{H}_{13}
\end{align*}
\]

Experimental

\(\alpha\)-Methylheptyl isocyanide was synthesized and polymerized with 0.35 mol% of NiCl\(_2 \cdot 6\text{H}_2\text{O}\) in methanol as described previously ([\(\eta\)] of compound 1 0.39 dl/g, \(M_w 65,000\)) [6]. Light yellow, transparent, flexible polymer films of compound 1 were cast from 10 wt.% solutions of compound 1 in chloroform.

A doping apparatus comprised a sample chamber with four platinum probes and an iodine chamber as reported by Chien [7]. A piece of the polymer film (1.5 \times 0.3 cm) was mounted on the four probes with the aid of Electrodag (Acheson 502). The chamber containing iodine crystals was then cooled in a dry ice bath and the system was evacuated for 1 h using dynamic vacuum. After the chamber was warmed to room temperature, the iodine vapors slowly diffused into the sample chamber and the conductivity slowly increased. The conductivity, monitored by a multimeter (Fluke 8024B) from the four-probe arrangement reached a maximum after four days.

Results

The undoped film was found to be an insulator ($10^{-9}$ ohm\(^{-1}\) cm\(^{-1}\)). After doping with iodine, the film became black with a metallic luster and showed an electrical conductivity of $3.5 \times 10^{-4}$ ohm\(^{-1}\) cm\(^{-1}\). The doping of the film with iodine was also evidenced by an increase of 61 wt.%. The conductivity was gradually lost in air after several hours.

Arsenic pentafluoride (30 Torr, 3 days, 28 °C) doping of the neutral polymer gave a lower conductivity value of $8.3 \times 10^{-5}$ ohm\(^{-1}\) cm\(^{-1}\).

In order to study the electrical properties of the acidified film, a piece of the film was dipped into concentrated hydrochloric acid in a test tube and left overnight. The film turned dark brown. It was then removed and
dried under vacuum for several hours. This undoped, acid-treated film was found to be an insulator ($10^{-9} \text{ ohm}^{-1} \text{ cm}^{-1}$). The film was then doped as described previously. A much faster rate of increase in conductivity was observed. After only several hours it reached the same conductivity as the doped neutral film. However, only slightly higher conductivity could be obtained by further doping.

In conclusion, a new type of weakly conducting organic polymer has been discovered.

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References