Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

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Version of record first published: 17 Oct 2011.

To cite this article: M. Ogasawara , K. Funahashi & K. Iwata (1985): Enhancement of Electric Conductivity of Polypyrrole by Stretching, Molecular Crystals and Liquid Crystals, 118:1, 159-162

To link to this article: http://dx.doi.org/10.1080/00268948508076204

Mol. Cryst. Liq. Cryst. 1985, Vol. 118, pp. 159-162
0026-8941/85/1184-0159/$10.00/0

Printed in the United States of America

ENHANCEMENT OF ELECTRIC CONDUCTIVITY OF POLYPYRROLE BY STRETCHING

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Abstract Polypyrrole films with improved elongation at break were prepared electrochemically at low temperature. Mechanical stretching of the film gave highly oriented film with improved conductivity. Maximum conductivity was measured to be $\sigma_{//}$ = 1005 S/cm. Anisotropy of conductivity was observed ($\sigma_{//}/\sigma_{\perp}$ = 4.9).

INTRODUCTION

Increasing attention has been paid on polypyrrole since the first preparation by Kanazawa and coworkers of the flexible film by electrochemical oxidation.[1] This polymer is characteristic not only in its high conductivity ($\sigma \sim 100$ S/cm) but also in its high stability. However, since its first introduction, the conductivity level has remained unchanged in spite of various efforts.[2,3] We supposed that the structural disorder suggested by Street and coworkers[4,5] impeded the improvement of the conductivity.

The present paper reports successful preparation of highly stretchable film of polypyrrole and the effect of stretching.

EXPERIMENTAL

Polypyrrole films were prepared by the electrochemical oxidation of pyrrole. The cell contained 0.06 M of pyrrole and 0.1 M of tetraethylammonium perchlorate. A platinum plate was used as an anode and a copper foil as a cathode. The current was set to

0.125 mA/cm^2. The films were stretched with a hand-made apparatus and subsequently subjected to heat-set at 150°C for 5 min.

RESULTS AND DISCUSSION

Figure 1 shows the electrical conductivity of polypyrrole films prepared at various temperatures. The conductivity increased with

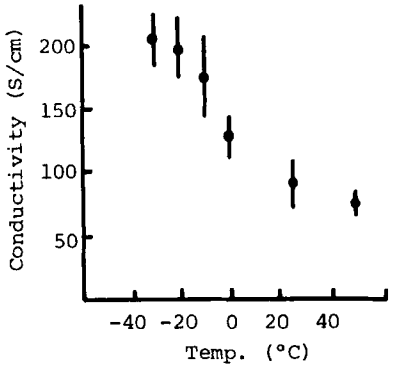


FIGURE 1 Conductivity vs. preparation temperature of polypyrrole.

the decreasing preparation temperature. Typically, a film prepared at +20°C showed a conductivity of 97 S/cm. On the other hand, a film prepared at -20°C showed a conductivity of 287 S/cm. Elemental analysis of these films gave compositions of $C_{4.00}H_{3.48}N_{1.00}(ClO_4)_{0.38}$ and $C_{4.00}H_{3.48}N_{1.01}(ClO_4)_{0.38}$, respectively, indicating no substantial difference between them.

In order to elucidate the structural difference, the ESR spectra were compared. The line widths of the ESR spectra of the films prepared at + and -20°C were measured to be 5.1 and 2.0, respectively. The narrow line width of the film prepared at -20°C indicates extended space for free electron. These results suggested higher conjugation in the polymer backbone.

The mechanical property of the films was also contrasting. The elongation of the film prepared at +20°C was measured to be 6% which was comparable to the data obtained by Diaz and coworkers.[6] In contrast, the film prepared at -20°C exhibited a higher

elongation to 70%. Sometimes, the elongation exceeded 100%.

Based on the data, we stretched the film prepared at -20°C. The stretching was carried out in the following three types of media including air at room temperature or organic solvents at 40°C and vapor of boiling solvents. After stretching, the film was subjected to heat-set at 150°C for 5 min in air. Table I summarizes the data.

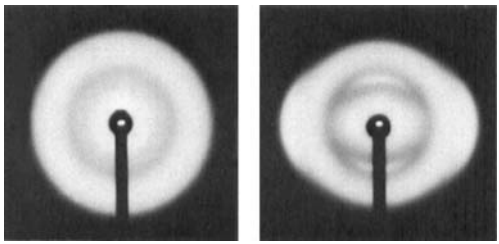
TABLE I Conductivity of polypyrrole film stretched in various media.

Media		Temp.	Stretched ratio: $\sigma_{//}$ (S/cm) 1	1.5	2.0	2.2
Air		r.t.	-	708	896	-
PC[a)]	Liq.	40	300	740	860	1005
CH_3CN	Vap.	82	-	774	960	-
	Liq.	40	350	730	890	-
$n\text{-}C_6H_{14}$	Vap.	69	340	540	805	-
	Liq.	40	-	-	783	-

a) propylene carbonate

The films prepared at -20°C could be stretched up to twice of the original length irrespective of the media. The highest stretched film was obtained with propylene carbonate as a medium. The conductivity of the films dramatically increased by stretching. The film stretched up to twice ranged 783–960 S/cm. Maximum conductivity was measured to be $\sigma_{//}$ = 1005 S/cm with the film stretched 2.2 times. The high conductivity was attributable to the oriented structure of the polymer.

This idea was supported by the X-ray analysis as given in Figure 2. The unstretched film showed only halo rings indicating no ordered structure. In contrast, the stretched film showed broad but distinguishable patterns on both equatorial and meridian directions.



Unstretched Stretched (1.8)

FIGURE 2 X-Ray diffraction pattern of unstretched and stretched films.

When a polypyrrole film with a conductivity of 330 S/cm was stretched up to 1.9 times, the conductivity in the direction of stretch increased up to 752 S/cm. On the other hand, the conductivity perpendicular to the direction of stretch decreased to 155 S/cm. The ratio was 4.9. The stretched film showed almost the same temperature dependence of conductivity as the unstretched one.

Acknowledgement

This work was performed under the management of the Research Association for Basic Polymer Technology for Future Industries sponsored by Agency of Industrial Science and Technology, Ministry of International Trade and Industry.

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