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Publisher: Taylor & Francis

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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: Show-An Chen & Wu-Chung Chan (1985): Sorption Mechanism of Iodine in Polyacetylene, *Molecular Crystals and Liquid Crystals*, 117:1, 117-120

To link to this article: <http://dx.doi.org/10.1080/00268948508074608>

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SORPTION MECHANISM OF IODINE IN POLYACETYLENE

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Abstract Simultaneous measurements of weight uptake and conductivity variation with time for cis- and trans-rich polyacetylene (PA) during sorption and desorption of iodine indicate a pore diffusion characteristic. In the earlier stage, sorption occurs on the fibrillar surface. In the later stage, diffusion of iodine into the interior of the fibrils is appreciable for cis-rich PA and insignificant for trans-rich PA.

INTRODUCTION

For iodine vapor doping in PA, Kiess et al (1), Benoit et al (2) and Danno et al (3) measured weight uptake vs time and gave diffusion coefficients of 10^{-14} , 10^{-7} and 10^{-9} cm²/sec respectively. None of them pointed out the pore diffusion characteristic of the iodine vapor sorption despite the fibrillar structure of the PA. This work reports experimental results on weight uptake and conductivity variation during sorption and desorption of iodine, which reflect the pore diffusion characteristic.

EXPERIMENTAL

PA films were prepared using the Shirakawa technique. Characterization of these films are given in the previous paper (4). The PA produced without treatment contains 90% cis. The trans-PA (90% trans) was obtained by heating in argon.

Simultaneous measurements of weight uptake using a quartz

spring and conductivity using a two probe method are made in a vacuum line which allows controls of iodine vapor pressure and temperature of the sample cells.

RESULTS AND DISCUSSION

Figs. 1 and 2 for cis-rich PA and Fig.3 for trans-rich PA show variations of reduced weight uptake M_t/M_∞ and conductivity with time during sorption and desorption of iodine at 50°C under iodine vapor pressures of 2.54, 0.201 and 2.54 torr respectively. For cis-rich PA, weight uptake and conductivity increase rapidly during the initial stage. During the later stage, weight uptake increases slowly and conductivity decreases from the maximum by 6-13 folds after one day. During desorption, for the case of higher iodine vapor pressure in Fig. 1, both weight uptake and conductivity increase in the first 16 min and then drop slowly; and for the case of lower iodine vapor pressure in Fig. 2, both decrease slowly from the beginning. For trans-rich PA, weight uptake varies in the same way as that of cis-rich PA, but conductivity increases first and then remains unchanged.

The rapid increase in weight uptake and conductivity together with the fibrillar structure of the PA would indicate a pore diffusion type sorption, by which adsorption of iodine is on the fibrillar surface during the initial stage. The increase in weight uptake during initial stage of desorption also supports this pore diffusion mechanism. For high iodine vapor pressure, there are appreciable amount of iodine suspended in the pores of PA. This iodine can condense on the PA fibrillar surface during the initial stage of desorption.

Another evident for the pore diffusion mechanism is given below. For cis-rich PA after pressing under a pressure of 4×10^4 psi, its surface area reduces from $62 \text{ cm}^2/\text{g}$ to $31 \text{ cm}^2/\text{g}$ and the diffusion coefficient of the earlier stage sorption reduces from 6.19×10^{-8} to $1.41 \times 10^{-8} \text{ cm}^2/\text{sec}$ at 50°C and 2.54 torr as calculated using the Fick's law.

The drops of conductivity of cis-rich PA during later stage in Figs. 1 and 2 are attributed to that appreciable iodine diffuses into the interior of the fibril in molecular state, imparting a resistance to conductivity. For the case of trans-rich PA, the conductivity remain unchanged. This is attributed to its more densely packed structure, which is more difficult for iodine to diffuse in.

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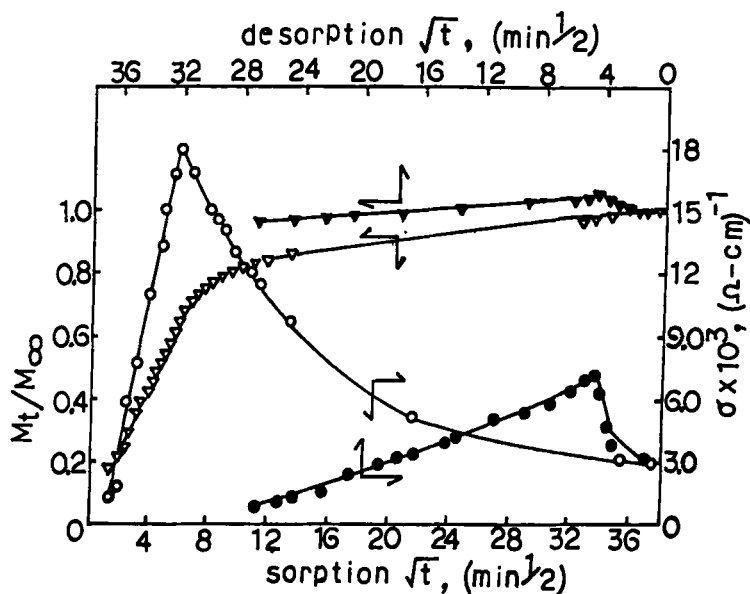


Fig. 1. Cis-rich PA, weight uptake and conductivity vs square root of time during sorption and desorption of iodine at 50°C and 2.54 torr of iodine.

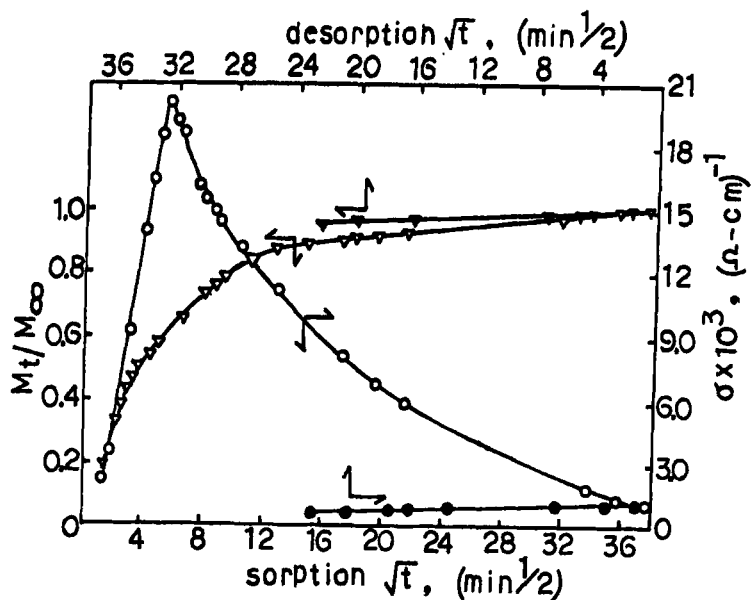


Fig. 2. Cis-rich PA, weight uptake and conductivity vs square root of time during sorption and desorption of iodine at 50°C and 0.201 torr of iodine.

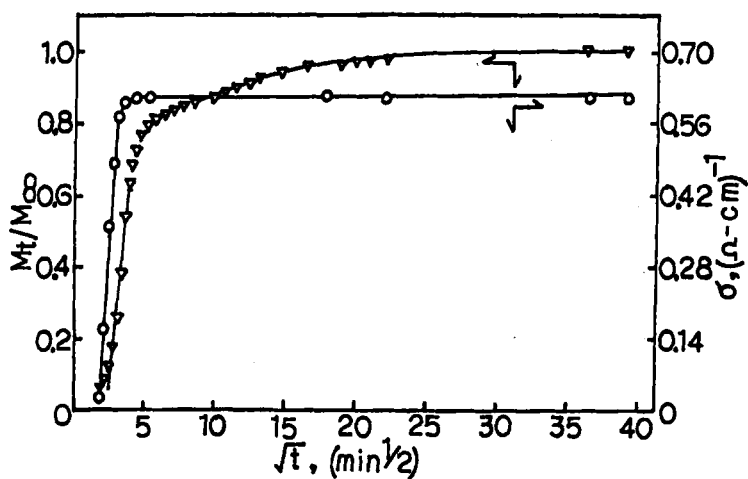


Fig. 3. Trans-rich PA, weight uptake and conductivity vs square root of time during sorption of iodine at 50°C and 2.54 torr of iodine.