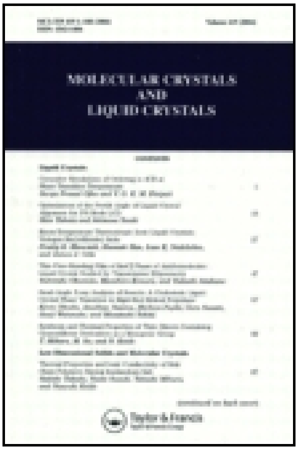

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Doping of Novel Phenylene Derivative Polymers Relating to Electrical Conductivity

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Version of record first published: 17 Oct 2011.

To cite this article: D. R. Rueda , T. A. Ezquerra , M. E. Cagiao , F.J. Balta Calleja & J. Alonso-lopez (1985): Doping of Novel Phenylene Derivative Polymers Relating to Electrical Conductivity, Molecular Crystals and Liquid Crystals, 118:1, 263-266

To link to this article: http://dx.doi.org/10.1080/00268948508076221

Mol. Cryst. Liq. Cryst. 1985, Vol. 118, pp. 263-266
0026-8941/85/1184-0263/$10.00/0

Printed in the United States of America

DOPING OF NOVEL PHENYLENE DERIVATIVE POLYMERS RELATING TO ELECTRICAL CONDUCTIVITY

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Abstract Poly-p-phenylene, prepared in this laboratory, commercial poly-p-phenylene sulphide and two new high temperature thermoplastic polymers (polyarylethersulphone and polyaryletherketone) have been doped by means of $SbCl_5$. Measurements of electrical conductivity at room temperature carried out in situ as a function of doping time are reported.

INTRODUCTION

The electrical conductivity of doped polymers can take-up characteristic features of semiconductors and metals depending on the specific reaction of dopant with the polymer and on the dopant concentration[1]. Conducting polymers like polyacetylene, poly-p-phenylene and polypyrrol, exhibiting highest conductivity levels, are, however, neither soluble nor melt processable. In the present study we report preliminary data on the doping aspects of two new commercial, melt processable polymers - Polyarylethersulphone (PES) and Polyaryletherketone (PEEK) - in relation to their electrical conductivity levels reached. Antimony pentachloride, $SbCl_5$, a relatively weak electron acceptor dopant, was used. Poly-p-phenylene (PPP), and poly-p-phenylene sulphide (PPS), were additionally investigated owing to the lack of data for this dopant, and used as reference systems.

EXPERIMENTAL

PES and PEEK are melt processable, aromatic polymers having outstanding properties at high temperatures. Their formulae are:

$[-\phi-SO_2-\phi-O-]_n$ (PES) and $[-\phi-CO-\phi-O-\phi-O-]_n$ (PEEK) where ϕ denotes a phenylene ring. PES is an amorphous polymer with a softening point of 235°C. PEEK is a crystalline polymer with a high melting point (334°C)[2]. Both PES and PEEK were crystallized into films of 80 μm thick from the melt. The sample of poly-p-phenylene, PPP, was prepared following the Kovacic method[3]. Both PPP and commercial PPS (Ryton) were sintered in the form of 300 μm thick films at room temperature and 0.75 GPa. Doping with $SbCl_5$ was carried out within a glass cell under 10^{-2} torr static vacuum at room temperature. Conductivity measurements were carried out in situ. All the samples were cut into parallelepipeds of 10x5xt mm with two Pt wires attached at their shortest edges using electroconductive cement. A Keithley source of dc current was employed. The relative weight uptake, infrared spectroscopy and wide angle X-ray diffractometry were used to a first characterization of doped samples.

RESULTS AND DISCUSSION

The IR spectra from the surface of PPP and PPS films (using KBr method) and of PES' solution cast film (<10 μm thick) do not exhibit appreciable changes after doping with $SbCl_5$. The wide angle X-ray diffractograms show, in contrast, a dramatic loss of peak intensity as a function of doping time (Fig. 1). This is due to the high mass-absorption coefficient (800 $cm^2.g^{-1}$) of the dopant intercalated within the polymer. By removing a thin 10 μm surface layer of the treated polymer the initial diffracted intensity is totally recovered. This result implies that doping takes place preferentially at the surface and that diffusion of the dopant into the sample proceeds slowly. Fig. 2 illustrates the evolution of the conductivity, σ, for PPP and PPS with doping time. For PPP σ rises instantly (~1 min) some twelve orders of magnitude. It shows a maximum after 8 min and finally levels off to a nearly constant value after 5 h. Under application of a vacuum of 10^{-2} torr a decrease of about 2 decades after 16 h is observed. In the case of

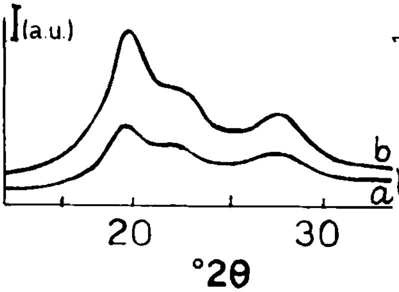

Fig. 1

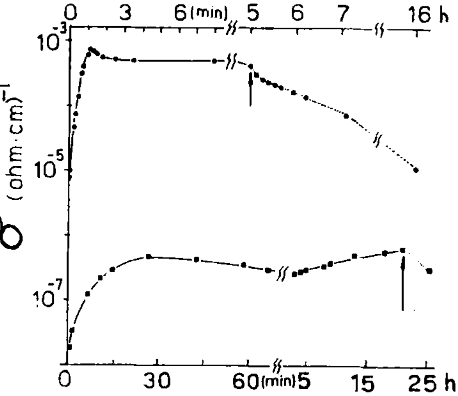

Fig. 2

Fig. 1. WAXD diffractograms using CuK$_\alpha$ radiation, a) from a sintered film (750 µm thick) of PPP doped with $SbCl_5$ for 3 h (relative weight increase of ~3%), b) the same sample after peeling off a thin 10 µm layer.

Fig. 2. Electrical conductivity of $SbCl_5$ doped PPP (●) and PPS (■) as a function of doping time. Arrows indicate when dynamic vacuum was applied.

PPS the initial rise in σ is slower than for PPP and after 30 min shows a rather broad maximum. Here the σ level is 3 orders of magnitude smaller than for PPP. For t>3 h a gradual further increase in σ is detected.

Fig. 3 illustrates the variation of σ for PES and PEEK as a function of doping time. In case of PES σ reaches a maximum ($10^{-7}ohm^{-1}cm^{-1}$) and drops again to insulating levels after 6 min. However, we noted that the relative weight increase after 30 min doping was ~15%. After heating the $SbCl_5$ glass vessel at 66°C σ reaches again a well defined maximum, one order of magnitude higher, and levels off to $10^{-7}ohm^{-1}cm^{-1}$ after 22 min. In the case of PEEK the level of σ at room temperature is nearly undetectable. σ shows a maximum after 2 min of doping. By heating of $SbCl_5$ at 62°C this sample reaches a σ value of $10^7ohm^{-1}cm^{-1}$. Here the increasing rate of σ is much slower than for PES and a very broad maximum is observed. The appearance of a σ maximum could be

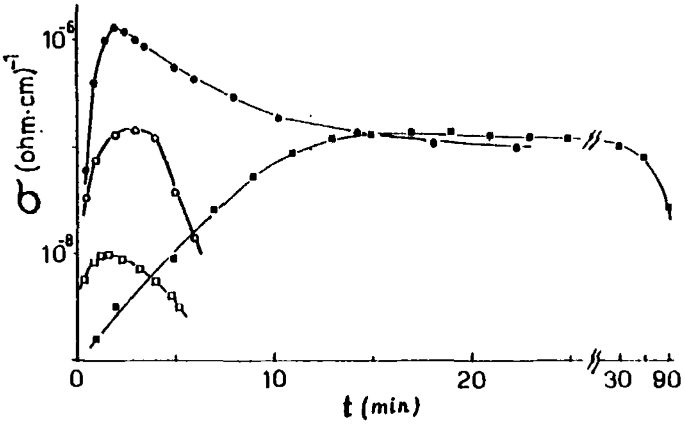

Fig. 3. Room temperature σ of $SbCl_5$ doped PES (O) and PEEK (□) as a function of doping time. Full symbols refer to σ of the same samples after heating the $SbCl_5$ vessel (see text).

related to the presence of new ionic species for the dopant.

Summarizing, while further additional information to explain satisfactorily the kinetics of σ for PES and PEEK is required, the present preliminarly results and the levels of σ previously reported for PPP, PPS and PPO treated with other related doping agents (AsF_5, SbF_5)[4,5] open up avenues for these aromatic processable polymers, after doping, as thermoplastic semiconducting materials. Indeed, one can expect that PES could reach σ values similar to PPS and that the σ level for PEEK could lie between PPS and PPO.

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