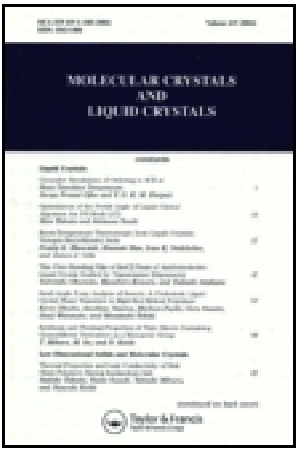


Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl17

Electrical and Infrared Properties of a Polyheterocycle Structurally Related to Poly(p-Phenylene Sulfide)

Franco Bertinelli [a], Paolo Costa Bizzarri [b], Carlo Della Casa [b] & Maurizio Fiorini [b]

[a] Dipartimento di Chimica Fisica ed Inorganica, 40136, Bologna, ITALY

[b] Dipartimento di Chimica Industriale e dei Materiali, 40136, Bologna, ITALY

Version of record first published: 22 Sep 2006.

To cite this article: Franco Bertinelli, Paolo Costa Bizzarri, Carlo Della Casa & Maurizio Fiorini (1990): Electrical and Infrared Properties of a Polyheterocycle Structurally Related to Poly(p-Phenylene Sulfide), Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics, 187:1, 241-247

To link to this article: http://dx.doi.org/10.1080/00268949008036048

Mol. Cryst. Liq. Cryst., 1990, vol. 187, pp. 241–247
Reprints available directly from the publisher
Photocopying permitted by license only

Printed in the United States of America

ELECTRICAL AND INFRARED PROPERTIES OF A POLYHETEROCYCLE STRUCTURALLY RELATED TO POLY(P–PHENYLENE SULFIDE)

FRANCO BERTINELLI
Dipartimento di Chimica Fisica ed Inorganica, 40136 Bologna, ITALY

PAOLO COSTA BIZZARRI, CARLO DELLA CASA, MAURIZIO FIORINI
Dipartimento di Chimica Industriale e dei Materiali, 40136 Bologna, ITALY

Abstract A comparison between a thianthrenic polymer and the parent poly(p–phenylene sulfide) is presented on the basis of electrical and infrared properties. Evidence that the polyheterocycle has a higher conductivity after doping with different amounts of $SbCl_5$ is reported. In this doped polymer significant spectral modifications are also observed, mostly around 1100 cm^{-1}. On the contrary the spectral profile of poly(p–phenylene sulfide) remains nearly unchanged at all doping concentrations.

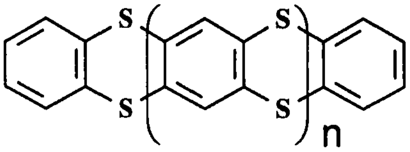
INTRODUCTION

In recent years extensive research has been carried out on the role of sulfur atoms in the electrical conduction of poly(p–phenylene sulfide) (PPS). There are some indications that sulfur links provide p orbitals for continuous orbital overlap along the pristine polymer chain[1]. In the complexed PPS the overlapping seems to increase with doping[2] and a conjugate system extended over the sulfur atoms is suggested[3,4]. Also the formation of a delocalized structure induced by heavy doping mainly by intramolecular crosslinking (benzothiophene units) has been proposed[1,5].

In this paper, we report some results on electrical and infrared properties of a doped polymer structurally related to PPS, with extra sulfur bridges along the chain, i.e. containing thianthrene units. This structure would emphasize the role of sulfur linkages and prevent intrachain condensation. A comparison is made with similarly doped PPS, taken as an obvious reference system.

ELECTRICAL CONDUCTIVITY

Thianthrenic polymers with the following structure



can be synthesized starting from sulfurated molecular or polymeric materials with a phenylene backbone, such as PPS itself, in the presence[6,7] of $AlCl_3$. High–temperature bulk polycondensation of diphenylsulfide gives a thianthrenic polymer (TAP) with regular, ribbon–like fully cyclized thianthrenic segments corresponding to a ladder structure. These segments are limited by defective units, mainly 1,2,4–trithiosubstituted benzenes, as indicated by a detailed infrared analysis[8]. The pristine polymer, partially crystalline, is an insulator with $\sigma = 2.8 \times 10^{-15}$ S/cm at room temperature. By complexation of powders with a $SbCl_5$ solution in dried $CHCl_3$ the conductivity is enhanced by 9 orders of magnitude.

We examined the behaviour, as regards to conductivity of TAP, as a function of dopant concentration in comparison with that of PPS. The latter polymer, purchased by Aldrich, was purified by Soxhlet extractions before doping. It was found that for both polymers σ increases steadily over many orders of magnitude for a low dopant concentration (Fig. 1). The conductivity of TAP tends to saturate gradually at high dopant levels, above approximately a mole ratio of $y = 0.06$ for $[C_6H_{2.5}S_{1.6}(SbCl_5)_y]_x$, reaching the semiconductor range of 10^{-5} S/cm. This fact suggests a transition in transport properties from an insulator to a semiconductor regime. On the other hand the curve of PPS displays a more gradual change in slope around $y = 0.04$ for $[C_6H_4S(SbCl_5)_y]_x$, that does not seem to coincide with any defined transition. Moreover a low conductivity of only 1.6×10^{-8} S/cm corresponds to the maximum amount of dopant incorporated into PPS ($y = 0.19$). However, for this polymer the slope of the curve suggests that higher doping levels would lead to larger σ values. We can speculate that one of the reasons for the relatively small doping effect may be due to the choice of the solvent used for the $SbCl_5$ solution. Indeed the diffusion of Lewis acids into PPS seems to be strongly affected by the doping media utilized[9,10].

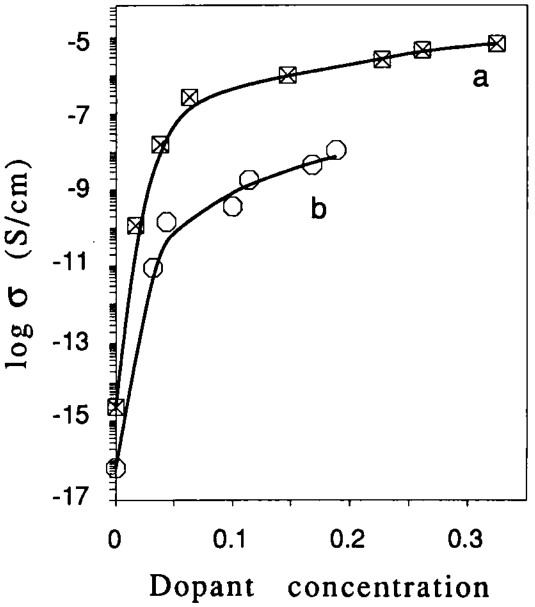


FIGURE 1 Room temperature conductivity (pressed pellets) of $SbCl_5$ doped (a) TAP and (b) PPS as a function of dopant concentration.

Over the whole range of dopant concentrations examined for PPS, the conductivity of the thianthrenic polymer is at least two orders of magnitude higher than that of the parent polymer. This is indicative of the importance of the extra sulfur linkage between aromatic nuclei.

INFRARED SPECTROSCOPY

A comparison of infrared spectra of $SbCl_5$–doped samples of the thianthrenic polymer and poly(p–phenylene sulfide) was made. Typical profiles are shown in Fig. 2. The IR spectrum of the pristine TAP[8] was used to investigate that of the corresponding $SbCl_5$–doped polymer. To this purpose the IR spectrum of the thianthrene–$SbCl_5$ (1:1) molecular complex also was taken into consideration. The assignment of the IR absorptions of S–Ø–S or C–S–C groups in pristine PPS is available[11]. In our assignment of the whole spectrum[12] we referred in particular to the spectrum of p–dichlorobenzene due to its remarkable correlations with that of PPS. For minor details we also referred to diphenylsulfide.

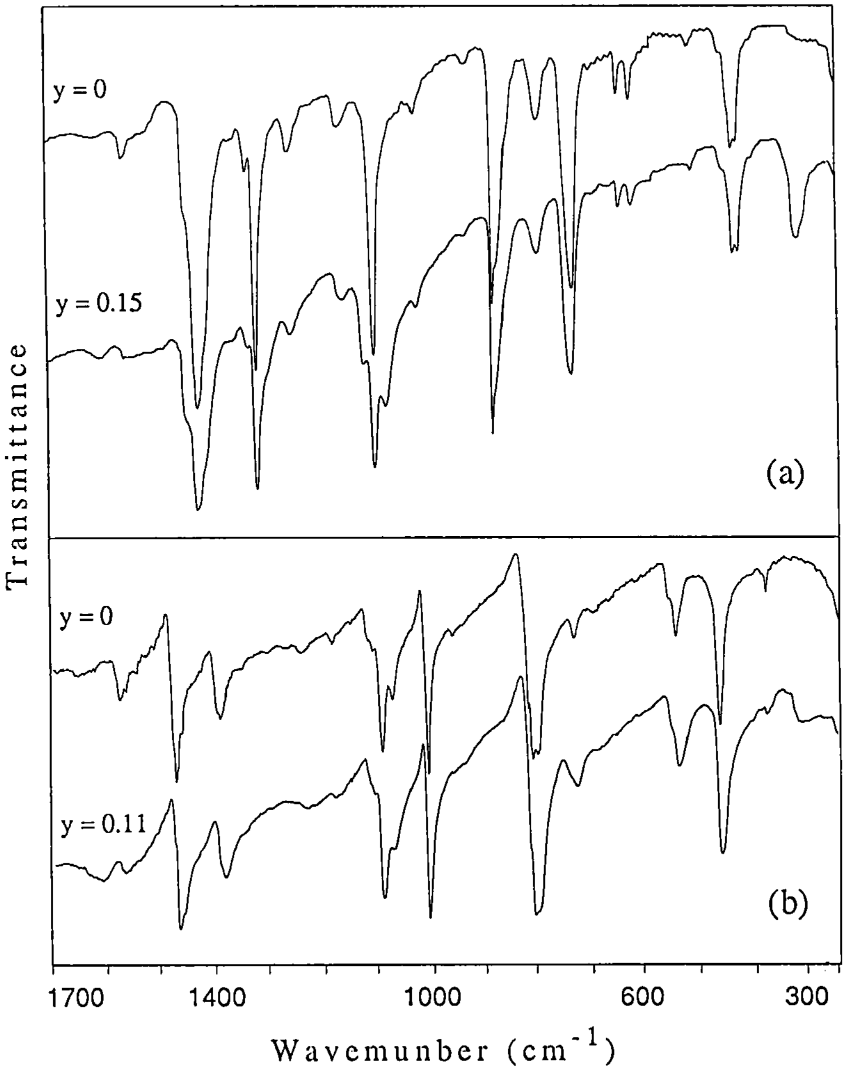


FIGURE 2 IR spectra (KBr pellets) of (a) TAP and (b) PPS, before and after doping.

Obvious differences between the spectra of the two polymers appear at first glance, due to the different number of substitutions in each chemical repeat unit and to the different geometries of their relative arrangements in the chain. However the most significant comparison could be made after the change induced by the doping. In general, in doped TAP one can observe spectral modifications even at low dopant concentrations. On the contrary, except for very minor details, the spectral profile of doped PPS does not change significantly at all doping levels.

Complexation of TAP mainly affects C–S–C bridges without affecting ring motions (identified on pure polymer). In any case no chemical change seems to take place in this polymer with doping. Around 1100 cm^{-1} we observe three distinct absorptions at 1103, 1120, and 1088 cm^{-1}. The first shows an intensity that remains constant with doping. It is assigned to an IR allowed stretching mode of C–S–C groups. The other two, both extremely weak in pure polymer and rapidly increasing with doping, could be interpreted as due to originally IR forbidden C–S–C stretching modes which become allowed when the repeat units are partly subjected to some internal distortion as a consequence of the $SbCl_5$ complexation[13]. We note that the two absorptions vanish reversibly when the doped samples are washed with a solvent. In this region the IR spectrum of doped PPS also shows three distinct peaks. However their intensities remain constant in pure and doped samples at all doping levels. In the pure polymer one of them, at 1075 cm^{-1}, has been explained as due to amorphous regions and the other two by ordinary repeat unit selection rules[11].

In TAP a very strong peak appears at 886 cm^{-1}. In the pristine polymer it has been assigned to a regularity band[8,14], supporting a picture of polymeric chains made up of regular segments of intramolecularly fully cyclized thianthrenic units, characterized by translational symmetry. This peak remains nearly unaltered after doping, suggesting that the dopant interacts with C–S–C groups mainly around defective sites in the chemical stucture. In PPS there is no evidence at all of the existence of similar sharp peaks both in pure and doped powder samples.

Another significant feature of the spectrum of doped TAP is a band around 335 cm^{-1} which is very strong in the thianthrene–$SbCl_5$ molecular complex. This absorption band increases in intensity with doping nearly in the same way as the bands at 1120 and 1088 cm^{-1} do, without however reaching the same intensity. We attribute its origin to a Sb–Cl stretching mode of an ionic species produced by the dopant. However these spectral data, which only partially agree with a $SbCl_6^-$ anion, provide little information about the nature of the counterion.

No spectral modifications of particular relevance were observed in the doped PPS samples, in spite of a change in conductivity up to about 8 orders of magnitude shown by the sample with the highest dopant content. Minor details, common to all doped samples, are for example an increase of background on the higher frequency side explained either by free charge carriers or scattering, a flattening of the spectral profile around 750–700 cm^{-1}, and an apparent blue–shift of a band originally at 733 cm^{-1} and shifted to 747 cm^{-1}. This region is typical of ring modes [IR forbidden β(CCC) and γ(CC) modes of g character]. A shoulder around 770 cm^{-1} disappears. Only one new absorption, broad and weak, appears around 335cm^{-1}, in strict analogy with that observed on doped TAP and probably due to the same counterion. It is reduced by washing with a solvent and the spectral profile becomes practically the same as that of the pristine polymer. We can conclude that, even more clearly than for the thianthrenic polymer, no chemical change occurs at the doping levels examined. On the other hand, very large changes in conductivity take place on doped PPS chains without any spectroscopically appreciable modifications in their vibrational dynamics.

ACKNOWLEDGEMENT

This work was supported by the Ministero della Pubblica Istruzione of Italy.

REFERENCES

1. L. Elsenbaumer and L. W. Shacklette, in Handbook of Conducting Polymers, edited by T. A. Skotheim (Marcel Dekker, New York, 1986), Vol. 1, Chap. 7, pp. 213–263.
2. J. Tsukamoto and S. Fukuda, Synth. Met., 17, 673 (1987).
3. J. E. Frommer, Acc. Chem. Res., 19, 2 (1986).
4. T. Sugano and M. Kinoshita, Synth. Met., 17, 685 (1987).
5. L. W. Schacklette, R. L. Elsenbaumer, R. R. Chance, H. Eckardt, J. E. Frommer, and R. H. Baughman, J. Chem. Phys., 75, 1919 (1981).

6. P. Costa Bizzarri and C. Della Casa, Mol. Cryst. Liq. Cryst., 118, 245 (1985).
7. P. Costa Bizzarri, C. Della Casa, M. Fiorini, and W. Porzio, J. Polym. Sci., Part A: Polym. Chem., 24, 255 (1988).
8. F. Bertinelli, P. Costa Bizzarri, C. Della Casa, and M. Fiorini, J. Polym. Sci., Part B: Polym. Phys., 26, 2203 (1988).
9. Li Shijin, Jao Yangshen, and Li Xiaochang, Abstracts of International Conference on Science and Technology of Synthetic Metals, Kyoto, Japan, 1986, p. 233.
10. S. Radhakrishnan and S. G. Joshi, J. Macromol. Sci.–Phys., B27, 291 (1988).
11. P. Piaggio, C. Cuniberti, G. Dellepiane, E. Campani, G. Gorini, E. Masetti, M. Novi, and G. Petrillo, Spectrochim. Acta, in press.
12. F. Bertinelli, P. Costa Bizzarri, and C. Della Casa, unpublished data.
13. An analysis of the systems at 479–455 and 425 cm^{-1} also lead to the conclusion that not all the C–S–C groups are complexed.
14. G. Zerbi, Adv. Chem. Ser., 203, 487 (1983).