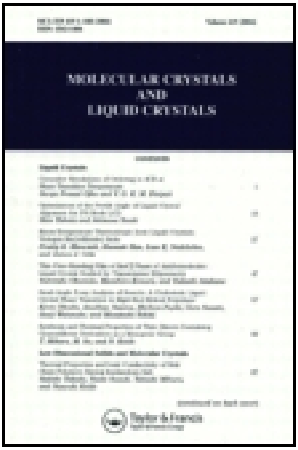

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

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To cite this article: H. Münstedt, H. Naarmann & G. Köhler (1985): Electrical Conductivity of Modified Poly-Acetylenes and Polypyrroles, Molecular Crystals and Liquid Crystals, 118:1, 129-136

To link to this article: http://dx.doi.org/10.1080/00268948508076200

Mol. Cryst. Liq. Cryst. 1985, Vol. 118, pp. 129-136
0026-8941/85/1184-0129/$15.00/0

Printed in the United States of America

ELECTRICAL CONDUCTIVITY OF MODIFIED POLYACETYLENES AND POLYPYRROLES

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Abstract A partial stabilization of the conductivity of undoped polyacetylene has been reached by chemical modifications. No stabilizing effect was obtained, however, in the iodine doped state. The influence of various comonomers and counterions on the conductivity of polypyrrole and its stability to air is reported. By a treatment of polypyrrole with alkalines and acids a chemical shifting of the conductivity and an improvement of the stability has been achieved.

AGEING OF POLYACETYLENE

It is well established that polyacetylene in the doped and undoped state becomes very unstable if exposed to air. One result of this instability is the decrease of the electrical conductivity. An example of such a behaviour is represented in Fig.1. The conductivity of an electrochemically oxidized polyacetylene with BF_4 as counterion drops dramatically on air. A conductivity decrease, although smaller than on air, is observed, however, under an argon atmosphere of high purity, too. This result makes it clear that not only reactions with oxygen but with the doping agent itself are responsible for the instability of polyacetylene. These findings gave rise to the idea to chemically saturate those sites of the polyacetylene chain which preferably react with oxygen or the counterion.

MODIFIED POLYACETYLENES IN THE NON-DOPED STATE

N-bromosuccinimide (NBS) has been used as one of the modifying agents. The bromine radical and the

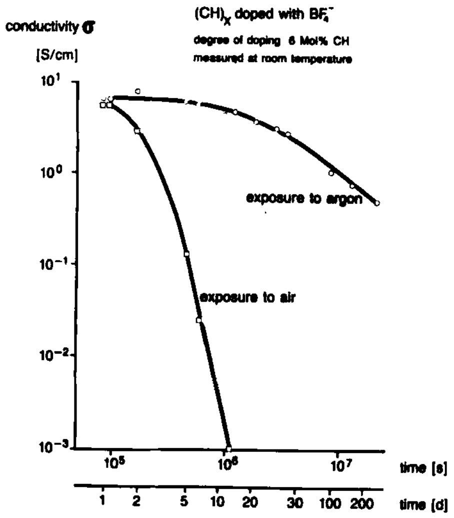

FIGURE 1 Ageing of $(CH)_x$ with BF_4 as counterion

succinimide react with the $(CH)_x$-chain (Fig.2). Besides that, the existence of Br_3^- becomes evident from the IR-spectrum indicating a partial oxidation of the polyacetylene. The latter reaction explains the higher conductivity of 10^{-4} S/cm compared to 10^{-5} S/cm as the maximum value of unmodified $(CH)_x$ if exposed to air (Fig.3). Besides the higher conductivity a better stability is reached by the NBS-modification. The conductivity of the NBS-modified $(CH)_x$ remains unchanged over nearly one day on air. After that time the conductivity begins to drop similarily to the unmodified product but it has still been found significantly higher over the measured period. An

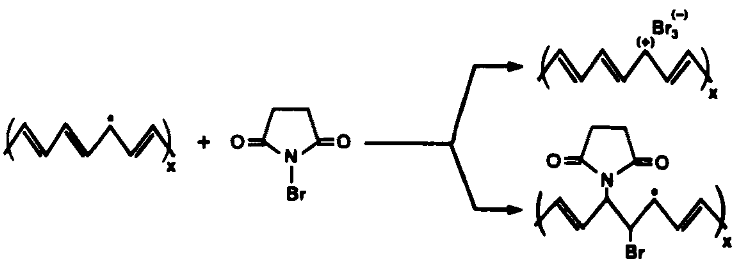

FIGURE 2 Reaction scheme of $(CH)_x$ with NBS

obvious reason for the better stability lies in the smaller oxygen uptake of the modified sample (Fig.3).

An effect similar to the reaction with NBS has been found for other modifying agents. Detailed results are given elsewhere.[1]

NBS-MODIFIED POLYACETYLENE DOPED WITH IODINE

The stabilizing effect of the above modification in the undoped state is not reflected, however, in the ageing behaviour of the NBS-modified sample doped with iodine (Fig.4). The time dependence of the conductivity decrease is nearly the same for the unmodified and modified sample. The conductivity of the NBS-modified $(CH)_x$ exposed to air for one day and doped afterwards with iodine is smaller by a factor of two in comparison to the unmodified sample having undergone the same treatment. After an air exposure of six days before iodine doping the result is reverse: The NBS-modified $(CH)_x$ can be doped to a higher conductivity than the unmodified product. The time dependence of the ageing, however, is very much the same. An interpretation of this behaviour and similar results on other modified samples are given elsewhere.[1]

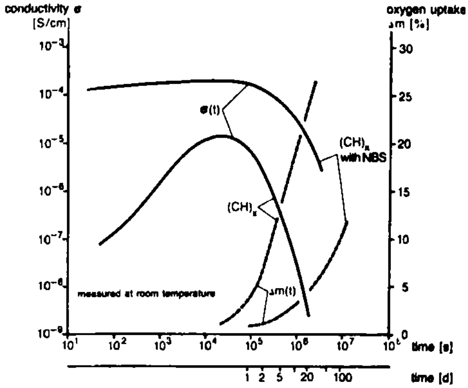

FIGURE 3 Conductivity and oxygen uptake under air

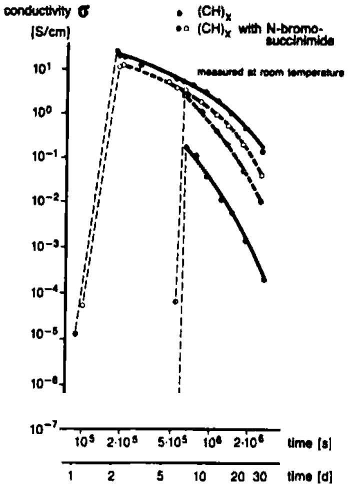

FIGURE 4 Ageing of iodine doped samples

CONCLUSIONS

The modification results in two improvements:

1. The initial conductivity and the stability against oxygen in the non-doped state increase.
2. The conductivity in the iodine-doped state after an extensive previous air exposure increases.

The two improvements are not effective enough, however, for opening up promising applications to polyacetylene.

POLYPYRROLE WITH DIFFERENT COMONOMERS AND COUNTERIONS

Electrochemically prepared polypyrrole is more stable to air than doped polyacetylene. Whereas the conductivity of polyacetylene doped with iodine decreases by a factor of 1000 within 30 days on air, polypyrrole with benzenesulfonicacid as counterion looses only 10% of its initial conductivity under the same ambient conditions within 200 days. For many applications, however, this stability of polypyrrole is not sufficient. Therefore, further improvements of the stability of polypyrrole are desirable.

Of interest in this connection is the question whether the stability of the conductivity can be increased by copolymerization of pyrrole with various monomers. Fig.5 shows the conductivity as a function of time at

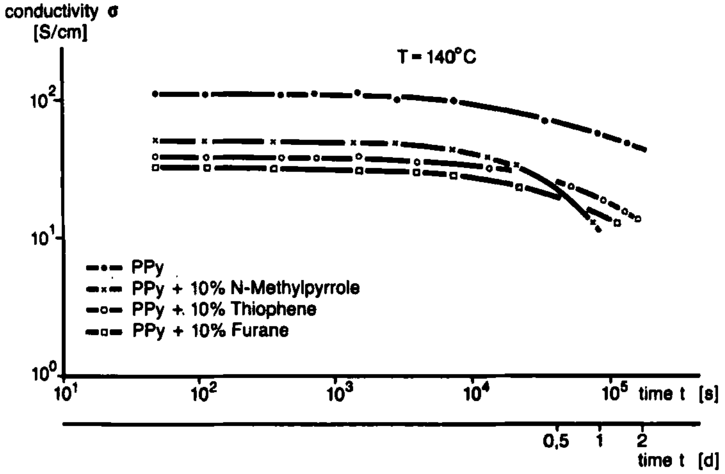

FIGURE 5 Ageing of polypyrroles with various comonomers

140 °C for polypyrroles of different composition. In order to accelerate the ageing process to an extent that a few weeks instead of several months are sufficient for characterizing the stability of a product the conductivity measurements have to be carried out at elevated temperatures. For none of the copolymers a significantly higher stability is found than for the unmodified polypyrrole. Besides that, all the copolymers show a lower conductivity.

Another way of trying to improve the stability of polypyrroles lies in the use of different counterions. In Fig.6 the conductivity as a function of time is plotted for polypyrroles with benzenesulfonicacid, benzenedisulfonicacid, ClO_4^-, BF_4^-, and PF_6^- as counterions. The measurements were carried out at 140 °C. The polypyrrole with benzenedisulfonicacid shows the highest stability. In 150 days the conductivity drops by 50% at 140 °C. The corresponding data are 1.4 days for the product with benzenesulfonicacid, 1.4 days for polypyrrole with ClO_4^-, 15 days for that with BF_4^-, and 1.9 days for that with PF_6^-. The ageing behaviour at other temperatures is not yet available. For the ageing of the polypyrroles with various comonomers an Arrhenius-type behaviour has been found between room temperature and 140 °C. The activation energy governing the ageing process depends on the composition of the sample. Therefore, predictions of the ageing of the polypyrroles with different counterions at room temperature from the results at 140 °C have to be made with precaution. With

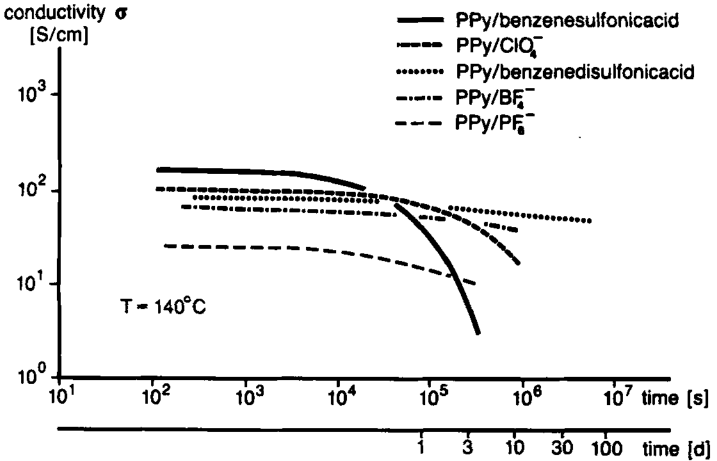

FIGURE 6 Ageing of polypyrroles with different counterions

the exception of PF_6^- only a small influence of the counterion on the initial value of the conductivity has been found for the samples investigated. An explanation of the effect of the counterion on the ageing behaviour of polypyrrole cannot be given at the moment.

POLYPYRROLE MODIFIED BY CHEMICAL AFTER-TREATMENTS

The conductivity of polypyrrole with benzenesulfonic-acid as counterion can be reduced by exposing it to a NaOH-solution. Fig.7 shows the decrease of conductivity as a function of concentration after a treatment of 10 min. The conductivity drops steeply at low concentrations, runs through a broad minimum, and rises again. For NaOH-concentrations higher than 35% one gets again the initial value of conductivity. The decrease in conductivity is connected with a loss of mass of the sample (Fig.7). According to measurements of the sulfur distribution by energy dispersive X-ray analysis the loss in conductivity and mass can be related to a disappearance of the benzenesulfonicacid counterion.

The NaOH-treatment has an astonishing effect on the long-term stability of the conductivity. Fig.8 shows

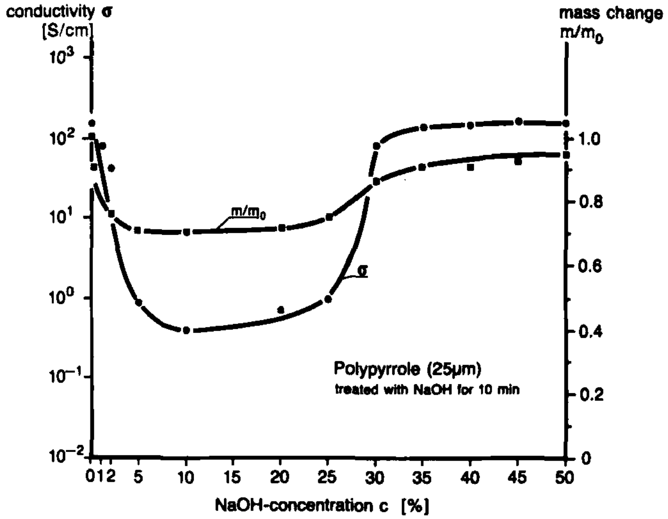

FIGURE 7 Conductivity and mass changes by NaOH-treatment

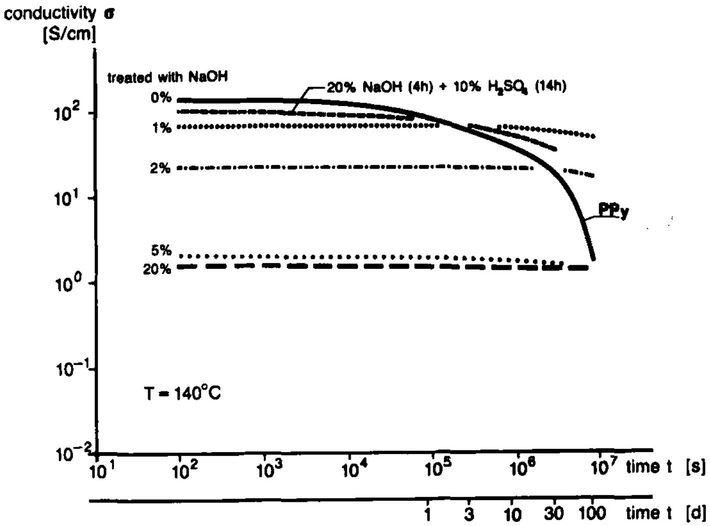

FIGURE 8 Ageing of NaOH-treated polypyrrole

the conductivity as a function of time at an ageing temperature of 140°C for the untreated polypyrrole film and the films exposed for 240 min to NaOH-solutions of various concentrations. The conductivity drop as a function of time of all the NaOH-treated samples is much smaller than that of the initial untreated film. Even an exposure to a solution of only 0.2% NaOH which reduces the conductivity marginally effects a distinct improvement of the stability.

The conductivity decrease by exposing polypyrrole to a NaOH-solution can be reversed if the sample is treated with sulfuric acid. In Fig.8 an example is given for the polypyrrole previously exposed to a 20% NaOH-solution. Treating such a sample for 14 h with 10% H_2SO_4 leads to a conductivity increase from 1.6 S/cm to 110 S/cm which is very close to the conductivity of the initial sample. The stability of this twofold modified sample is still superior to that of the original film.

The shifting of the conductivity by chemical modification can be repeated several times as demonstrated by Fig.9. Connected with the conductivity loss by a treatment with a 10% NaOH-solution is a decrease of sample mass and thickness. The rise in

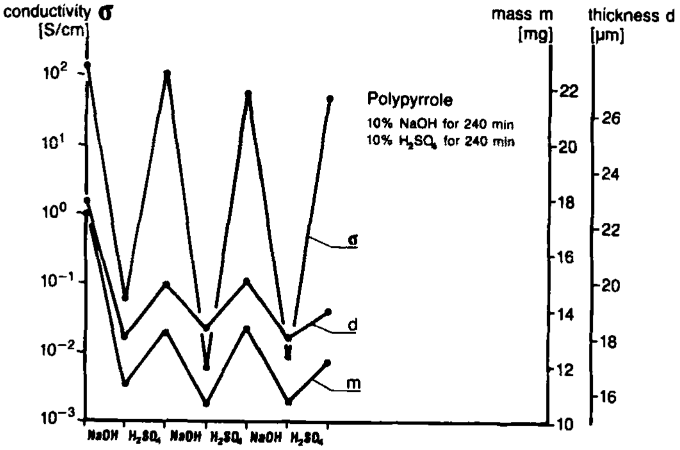

FIGURE 9 Conductivity shifting and mass and thickness changes by alkaline and acid treatments

conductivity by a following treatment with 10% H_2SO_4 is accompanied by an increase in mass and thickness. The initial values are not reached, however. More detailed results on these effects are given elsewhere.[2]

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2. H. Münstedt, in preparation