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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: M. Audenaert (1985): New Conductivity Data on Bromine-Doped Trans-Polyacetylene, *Molecular Crystals and Liquid Crystals*, 117:1, 159-162

To link to this article: <http://dx.doi.org/10.1080/00268948508074615>

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NEW CONDUCTIVITY DATA ON BROMINE-DOPED TRANS-POLYACETYLENE

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Abstract We present new experimental results on the macroscopic transport properties of bromine-doped trans-(CH)_x. The mechanism of conduction which comes out of our detailed analysis of the data corresponds to a model of two resistances in series, the fibrillar resistance which is typical of an amorphous semiconductor and the interfibrillar resistance (Sheng's model). The evolution with time of the latter is correlated with the assumption that, due to the high chemical reactivity of bromine, this halogen adds to the double bond.

It is well known that bromine-doped polyacetylene has a maximum of conductivity ($\sim 1 \Omega^{-1} \text{cm}^{-1}$) at about 6mol% (Ref.1.). This system becomes a colourless insulator at high doping levels. Whatever the dopant concentration is, its conductivity decreases slowly with time, even under an argon atmosphere. Except for the observation of a Korringa relation $T_1 T = \text{const.}$, no metallic character has been reported.

As for AsF₅-doped (CH)_x (Ref.3.), we tried to find out whether a transition in $\sigma(T)$ could be observed as a function of dopant concentration and we limited our work to the investigation of trans-(CH)_x doped at concentrations below 6 mol%. Our measurements are characterized by a very low experimental error. Moreover, because of the high reactivity of bromine, the time between the preparation of the doped (CH)_x and the recording of $\sigma(T)$ was noted.

The method of analysis of our data has been reported elsewhere (Ref.3.). Only those experimental data which could be fitted according to this method were retained. In Fig.1., we present a typical curve obtained for (CHBr_{0.020})_x. Our data were fitted with the use

of the same model: $R(T) = R_{io} \exp(T_A/T)^{1/4} + R_{jo} \exp(T_1/T + T_1/T_0)$ where $R(T)$ is the overall resistance of the film, the first term of the right hand side of the equation is the intrinsic resistance of the fibrils and the second term is the resistance of the junctions between the fibrils⁴. The values of the different parameters, obtained for several samples, are shown in table 1.

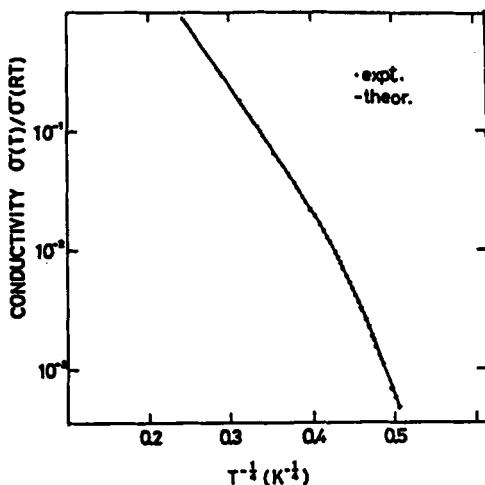


FIGURE 1

Typical fitted data obtained for $(\text{CHBr}_y)_x$, see text.

The data of a sample doped at 6 mol% could not be fitted at all, which suggests that a strong degradation occurs at such a concentration of dopant. We observed no transition in $\sigma(T)$ below and above this concentration. The intrinsic resistance is typical of a variable-range-hopping mechanism and the contribution of the junction resistance is more important than for iodine-doped $(\text{CH})_x^5$. The sample doped at 2 mol% has been kept for 3 days under an inert atmosphere of helium. As we can see from the data of table 1, T_1/T_0 increases with time, i.e. the barrier transparency decreases. From

the evolution of parameters λ and T_1 , we deduce that the barrier's volume increases by a factor of 2.7 (see ref.4.), in agreement with the assumption that bromine adds to the double bond¹. This is absolutely different from what happens for AsF_5 -doped $\text{trans}-(\text{CH})_x$ (Ref.3)

In Fig.2., we have plotted the evolution of $\sigma(\text{RT})$ as a function of time for both dopants. The samples were kept under an inert atmosphere in both cases. The decrease in conductivity is more rapid for bromine-doped $(\text{CH})_x$ than for the AsF_5 -doped samples.

TABLE 1

Values of the parameters for a fit with the model of two resistances in series (see text); N=number of expt. data; λ is a parameter which controls the magnitude of the correction to the rectangular barrier model; $e = ((1/N) \sum ((\sigma_i - f(T_i))/\sigma_i)^2)^{1/2}$ (see ref.3.); t=time after doping.

Sample	t	T_A (K)	T_1 (K)	T_0 (K)	λ	T_1/T_0	N	$\sigma_{RT} (\Omega^{-1} \text{cm}^{-1})$	e
$(\text{CHBr}_{0.009})_x$	1h	1.9×10^5	273	48.5	.0525	5.63	94	3.4×10^{-2}	.0099
$(\text{CHBr}_{0.020})_x$	3d	3.4×10^6	370	56.0	.10125	6.61	96	5.5×10^{-2}	.0160
idem	6d	3.5×10^6	528	75.5	.1225	6.99	94	1.6×10^{-2}	.0135
$(\text{CHBr}_{0.022})_x$	1h	1.9×10^6	450	70.0	.1130	6.43	96	2.2×10^{-2}	.0188

In this work, we have shown that some of the conductivity data, that we have obtained for bromine-doped $\text{trans}-(\text{CH})_x$, can be well fitted with the use of a model of two resistances in series, provided that the experimental error is kept very low. Other conductivity data obtained for this system could not be fitted with this model or any other plausible model, according to our method of analysis³. On the other hand, the evolution of $\sigma(T)$ and $\sigma(\text{RT})$ with time is consistent with an expected degradation of this system, by addition of the halogen to the double bond.

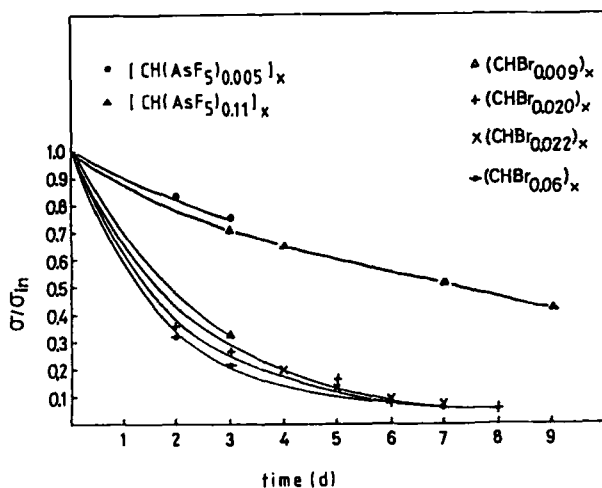


FIGURE 2

Evolution with time of σ (RT) for $(CH(AsF_5)_y)_x$ and $(CHBr_y)_x$.

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