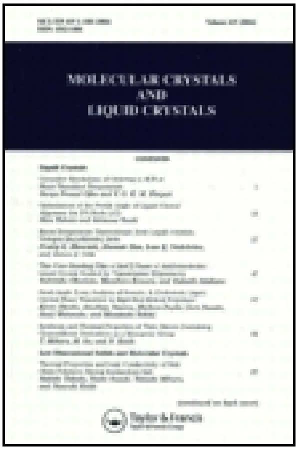

Molecular Crystals and Liquid Crystals

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

Thermal Properties of Polyacetylene

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Version of record first published: 17 Oct 2011.

To cite this article: R. J. Schweizer, K. Menke, W. Göhring & S. Roth (1985): Thermal Properties of Polyacetylene, Molecular Crystals and Liquid Crystals, 117:1, 181-184

To link to this article: http://dx.doi.org/10.1080/00268948508074620

Mol. Cryst. Liq. Cryst. 1985, Vol. 117, pp. 181-184
0026-8941/85/1174-0181/$10.00/0

THERMAL PROPERTIES OF POLYACETYLENE

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Abstract Data of specific heat and thermal conductivity of three types of polyacetylene samples are presented: (i) undoped, (ii) highly conducting AsF_5 doped, (iii) $(CH_3)_2NH$ compensated into the insulting state after AsF_5-doping. The specific heat of doped and undoped polyacetylene shows an anomalous behaviour below 1 K. Below 10 K the thermal conductivity of the compensated samples is higher than that of the doped samples and even much higher than that of the undoped ones.

Polyacetylene[1] (PA) has become a very interesting substance because of its high electrical conductivity after doping[2]. There are many precise measurements about the electrical behaviour[3] of doped PA but thermal investigations[4-8] are very scarce. A complete understanding of the influence of the inserted ions to thermal properties is still missing, particularly the effect of mobile charge carriers to thermal conductivity is not known. Therefore we have decided to investigate the influence of AsF_5 doping in more detail. We have compared not only AsF_5 doped and undoped samples but in addition samples which have been compensated after doping, so that they have become insulating again.

PA was polymerized using the Shirakawa method[9]. Doping was performed by exposure to AsF_5 vapour with intermitted pumping cycles. The doping concentration was determined by weight uptake measurments. By exposing doped PA to $(CH_3)_2NH$ vapour we obtained again insulating samples. A weight uptake during counter doping corresponds to an incorporation of 4 mol% of $(CH_3)_2NH$ if no AsF_5 has left the polymer matrix during this process.

The specific heat was measured with a heat pulse method[10] and the thermal conductivity with a reversed four-probe-technique[11] and the modified Ångström method[11].

Figure 1 shows the specific heat data of undoped polyacetylene. The data above 2 K were measured by Guckelsberger et al.[6]. Below 2 K we observe a behaviour of the specific heat like $C(T) = \gamma T + \beta T^3$, the sum of a 3d phonon part and a linear part, the latter being due to the amorphous intercrystallites in PA.

Figure 2 shows the specific heat data for doped and for compensated polyacetylene below 2 K. The solid line corresponds to a $(\gamma T + \beta T^3)$-behaviour, fitted between 1 K and 2 K to the data of the doped sample. We observe a large excess specific heat in both samples which is plotted separately in Figure 3 and fitted by a Schottky-behaviour

$$C(T)-\gamma T-\beta T^3 = N\cdot S(\Theta) = N\cdot R(\Theta/T)^2 \exp(\Theta/T) \left[1+\exp(\Theta/T)\right]^{-2}$$

(S: Schottky-function, R: gas constant, Θ: characteristic temperature, N: number of excitations.)

In Figure 4 the thermal conductivity of doped and of compensated polyacetylene is compared to that of the undoped sample. Below 12 K the thermal conductivity increases with doping. To check if this increase is due to a contribution of charge carriers (Wiedemann-Franz law) we have measured an insulating compensated sample which is also plotted in Figure 4. This sample shows an even higher thermal conductivity at low temperatures, quite in contrast to the expectations from the Wiedemann-Franz law. Therefore we can not explain the additional conductivity of doped polyacetylene by an effect of charge carriers and must attribute it - at least in part - to a change in the phonon contribution which is caused by the intercalation of the dopant and counter-dopant.

In conclusion, the low-temperature specific heat of doped samples and of samples compensated after doping shows a Schottky-anomaly at about 1 K, corresponding to about 10^{-4} states/mol. No correlation of this anomaly to electrical or thermal transport properties is observed. The low-temperature thermal conductivity increases in the sequence undoped - doped - doped and compensated and in contrast to the Wiedemann-Franz law, is not correlated with the electrical conductivity. Therefore from measurements of the thermal conductivity of conductive polymers no conclusions on an "intrinsic" electrical conductivity can be drawn.

We want to thank Dr. H. Grimm for fruitful discussions and the Stiftung Volkswagenwerk for financial support.

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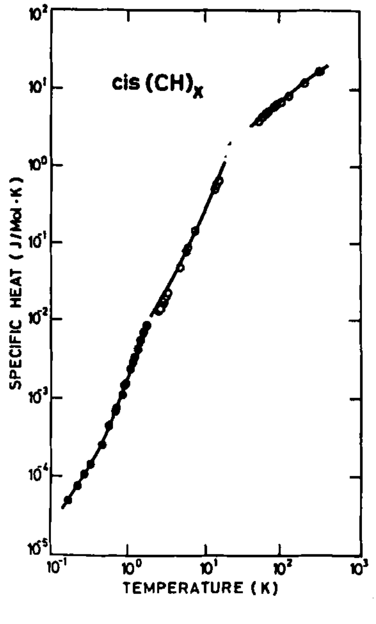

Figure 1: Specific heat of undoped cis-polyacetylene (o... Ref.[6])

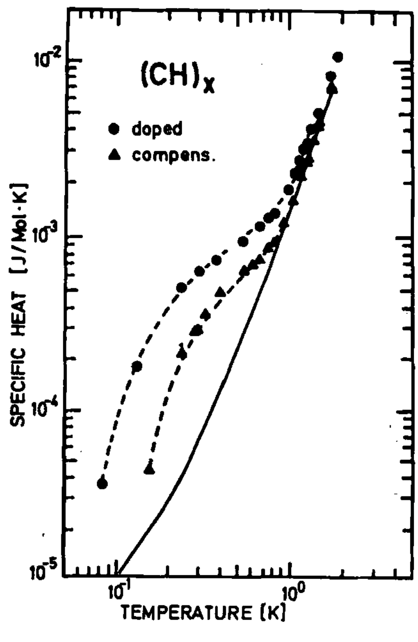

Figure 2: Specific heat of doped and of compensated PA below 2K. Solid line ... $\gamma T + \beta T^3$

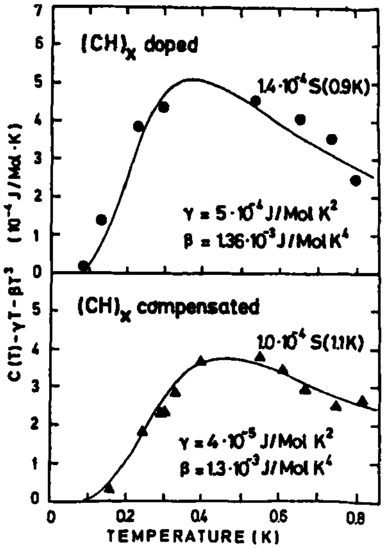

Figure 3: Specific heat anomaly of doped and of compensated PA with Schottky-function N•S(Θ) fitted

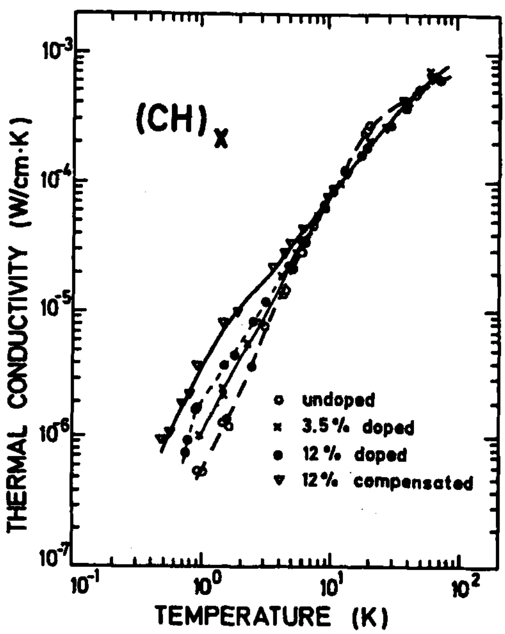

Figure 4: Thermal conductivity of undoped, of doped, and of compensated PA