JOURNAL OF MATERIALS SCIENCE 21 (1986) 4327–4330

Dielectric response of *p*-terphenyl

G. W. BAK
Institute of Physics, Technical University of Łódź, ul. Wólczańska 219, 93-005 Łódź, Poland

Dielectric properties of *p*-terphenyl crystals (large- and small-grained polycrystalline layers and compressed pellets) have been measured. An anisotropy of the dielectric properties of the crystals has been found. The dielectric losses in disordered *p*-terphenyl structures proved to be of injected carrier origin: a discontinuous change of dielectric losses in the disordered structures being found near 285 K.

1. Introduction

During the last 20 to 30 years a great deal of attention has been focused on the electrical properties of some aromatic hydrocarbons such as anthracene, tetracene and some polyphenyls which are considered to be model compounds for organic molecular crystals [1, 2]. *p*-Terphenyl is the counterpart of anthracene among polyphenyls. It consists of three benzene rings in a straight line (a diagram of its molecule is shown in the inset of Fig. 2).

Dielectric properties of materials can be described by their complex capacitance:

$$C^*(\omega) = C'(\omega) - iC''(\omega) = C(\omega) - iG(\omega)/\omega \qquad (1)$$

where $C'(\omega)$ and $C''(\omega)$ are the real and imaginary parts of the complex capacitance, respectively, $C(\omega)$ is the ordinary capacitance, $G(\omega)$ is the conductance and ω is the circular frequency.

The complex dielectric permittivity $\varepsilon^*(\omega)$ is related to C^* by a geometrical factor. The complex susceptibility may be obtained from that by subtracting the direct current conductivity, G_0/ω, and the high-frequency permittivity, C_∞ [3]:

$$\chi^*(\omega) = \chi'(\omega) - i\chi''(\omega) = G_f\{C'(\omega) - C_\infty - i[C''(\omega) - G_0/\omega]\} \qquad (2)$$

In the case of the "universal" dielectric relation, often found in solids, given by the power law:

$$\chi''(\omega) = \cot(n\pi/2)\chi'(\omega) \sim \omega^{n-1}, \qquad (3)$$

the ratio of $\chi''(\omega)$ and $\chi'(\omega)$ is frequency independent. The exponent n takes values in the range $0 < n < 1$. The real and imaginary parts of $\chi^*(\omega)$ must be compatible according to the well-known Kramers–Kronig (KK) relations.

It is possible to define [3], for the purpose of dielectric study of a given single polarization mechanism, α, in a limited region of frequency, a high-frequency permittivity, $\varepsilon_\infty^\alpha(v^\alpha)$ (or a high frequency capacitance, $C_\infty^\alpha(v^\alpha)$ multiplying by a geometrical factor):

$$\varepsilon(\omega) = \varepsilon_\infty^\alpha(v_v^\alpha) + \varepsilon_0\{\chi'^\alpha - i\chi''^\alpha\} \qquad (4)$$

where v^α is the upper limit of the considered frequency region. If $\varepsilon_\infty^\alpha$ can be defined in a given situation, i.e. if the higher-lying loss peaks are sufficiently far removed in frequency from the considered region, then it is possible to obtain the susceptibility $\chi'^\alpha(\omega)$ by subtracting $\varepsilon_\infty^\alpha(v^\alpha)$ from the measured values of the real part of $\varepsilon'(\omega)$. Testing the KK compatibility, we should take into account $\chi''(\omega) = \varepsilon''/\varepsilon_0$ and $\chi'^\alpha(\omega)$, because the constant value of $\varepsilon_\infty^\alpha$ is not included in the result of the KK transformation from $\chi''(\omega)$ to $\chi'(\omega)$, since the Hilbert transform of a constant is zero. The d.c. conduction is not taken into account by the KK relations either, because d.c. conduction does not contribute to the real part of the permittivity.

As we can see, the KK relations are very useful in ascertaining the magnitude of the d.c. conductivity and of the high-frequency permittivity and also in enhancing the reliability of dielectric measurements.

The real and imaginary components of the complex dielectric permittivity plotted in logarithmic coordinates against the frequency, as shown in the figures in this paper, often lend themselves to normalization, consisting in parallel translation laterally and vertically of data corresponding to individual temperatures until a single master curve is obtained [3]. If this procedure is possible, it implies that the spectral shape of the response remains invariant under variable temperature, while only the amplitude and the position in the frequency coordinate changes, so that the generalized response may be described by the relation:

$$C''(\omega, T) = A(T)\{F[\omega/\omega_p(T)]\} \qquad (5)$$

where $F(x)$ is the spectral function of the reduced frequency variable $x = \omega/\omega_p(T)$. The information contained in the master curve is complemented by the locus of translation of the individual curve in bringing them into coincidence in the master curve. The vertical translation of this locus gives the dependence $A(T)$ and its horizontal translation gives $\omega_p(T)$.

The experiments presented in this paper were carried out on five kinds of *p*-terphenyl samples: large- and small-grained polycrystalline layers, compressed pellets and crystals parallel and perpendicular to the *c*-axis. The layers were obtained by vacuum evaporation and then some were annealed at about 415 K to obtain the large grained samples. The thickness of the layers was between 2.5 and 11 μm; the thickness of the compressed pellets was about 1.5 mm. The crystal samples

0022–2461/86 $03.00 + .12

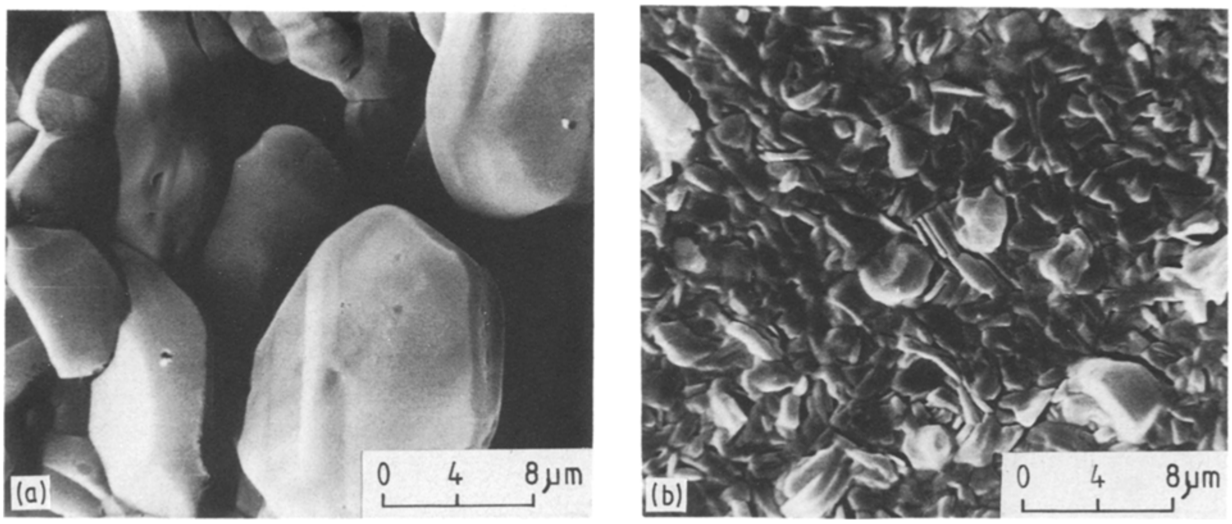

Figure 1 Scanning electron micrographs of (a) a large-grained and (b) a small-grained *p*-terphenyl polycrystalline layer.

were plates also about 1.5 mm thick. The high-frequency relative dielectric permittivity $\varepsilon_r(\infty)$ of all the samples was found to be equal to 3.2 ± 0.2 and may be assumed to be the same for all the samples within experimental error. The areas of the crystal samples were between 25 and 40 mm^2.

2. Results and discussion

Dielectric properties of *p*-terphenyl (*p*TPh) crystals, polycrystalline layers and compressed pellets have been measured. Some of the polycrystalline layers consisted of comparatively large crystallities (see Fig. 1a), some of them consisted of much smaller crystallities (Fig. 1b).

The dielectric properties of *p*TPh crystals were measured parallel and perpendicular to the *c*-axis. Fig. 2 shows the dielectric response of *p*TPh crystal in the direction parallel to its *c*-axis: the a.c. conduction can be well described by the power law with $n \cong 7/8$. The a.c. conduction at lower frequencies proved to be a little more sensitive to temperature, which amounts to a temperature dependence of the exponent n, but the dependence is rather weak.

Fig. 3 shows the dielectric response of *p*TPh crystal measured perpendicular to the *c*-axis. The results differ significantly from the previous ones. The measurements show a temperature-dependent peak of losses, shifting towards higher frequencies with increasing temperature. After subtracting $C_\infty(\nu = 10^4\,\text{Hz})$ from the real part of capacitance we obtain a $C'-C_\infty$ curve which turns out to be KK compatible to the C'' curve and confirms the existence of the peak.

Fig. 4 shows the dielectric properties of polycrystalline layers consisting of large crystallities. The properties proved to be very similar to those of crystals with the *c*-axis parallel to the measuring electric field. The dielectric response of small-grained *p*TPh polycrystalline layers is shown in Fig. 5a. The response differs from that of the large-grained layer shown in Fig. 4. It should be noted that it is possible to normalize the curves at 250 and 270 K as well as at 295 and 310 K, but it is impossible to normalize the two master curves (Fig. 5b). The impossibility of normalization is evidence of a discontinuous change of dielectric properties of disordered *p*TPh structures between 280 and 295 K, which turned out to be reversible. A new relaxation process may be supposed to begin between the two temperatures. The discontinuous change of dielectric properties will be confirmed later by the

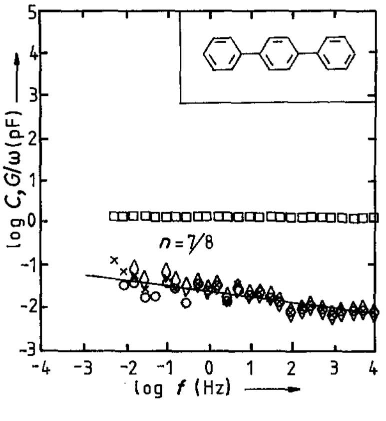

Figure 2 Dielectric response of a *p*-terphenyl crystal; *c*-axis parallel to the measuring electric field. G/ω: (○) 270 K, (+) 308 K, (◇) 320 K. C: (□) 308 K. The inset shows the structure of the *p*-terphenyl molecule.

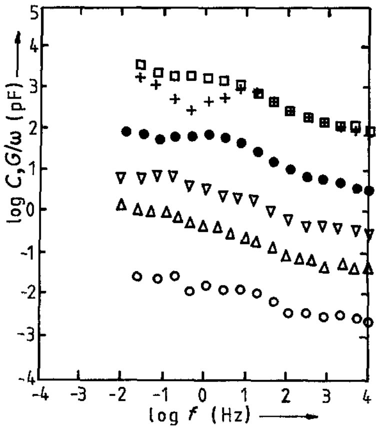

Figure 3 Dielectric response of a *p*-terphenyl crystal; *c*-axis perpendicular to the measuring electric field. G/ω: (○) 270 K, (△) 295 K, (▽) 310 K, (●) 340 K, (+) 370 K. C: (□) $C' - C_\infty(\nu = 10^4\,\text{Hz})$. The curve for 270 K is in its correct place. The other curves are displaced with respect to one another by an order of 10 to avoid overcrowding.

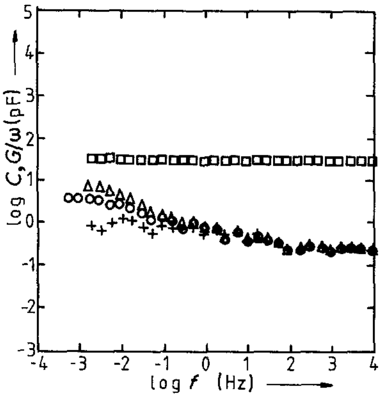

Figure 4 Dielectric response of a large-grained *p*-terphenyl polycrystalline layer. G/ω: (+) 205 K, (○) 295 K, (△) 353 K. C: (□) 353 K.

results obtained on *p*TPh pellets. It should be mentioned at this point that a similar reversible transition has been found in tetrabenzofulvalene [4].

Fig. 6 shows typical results of dielectric measurements on *p*TPh compressed pellets. There exists a temperature-dependent loss peak, which appears above 280 K. The capacitance of the samples shows a strong dispersion at low frequencies. The low-frequency dispersion is similar to that found in polycrystalline small-grained *p*TPh layers and may be suggested to be characteristic of less-perfect *p*TPh structures. Fig. 6 shows the $C' - C_\infty$ curves after subtracting the values of capacitances which result from the dielectric phenomena at frequencies higher than 10^4 Hz, in the first case, and 3×10^{-1} Hz, in the second. Both results are KK compatible, though in the second case the range of frequencies is too small to draw final conclusions. Nevertheless the results obtained suggest that the influence of the d.c. phenomena on the dielectric losses in *p*TPh pellets can be neglected even at very low frequencies.

As is shown in Fig. 7, the temperature dependence of the a.c. conduction changes above 280 K. The lower the frequency is, the more distinct the change of temperature dependence of the dielectric losses becomes. The change seems to be associated with the change of spectral shape of the response shown in Figs 5b and 6.

In order to estimate the influence of injected carriers on dielectric properties of *p*TPh pellets, a pellet with insulating SiO films between electrodes and bulk of sample was measured. As shown in Fig. 8 the dielectric losses in the insulated sample proved to be an order of magnitude smaller at higher frequencies and two orders of magnitude smaller at lower frequencies.

The results suggest the following conclusions:

1. Dielectric properties of *p*TPh crystals along the *c*-axis and large-grained polycrystalline layers are very similar. This is not surprising taking into account that the crystallities in oriented polycrystalline layers of polyphenyls show a tendency to grow with the *c*-axis perpendicular to the surface of the substrate [5]. The temperature dependence of dielectric losses at lower frequencies is a little stronger than that at higher frequencies. This suggests that there may exist a very slow polarization process of a different nature to that at higher frequencies.
2. There is a temperature-dependent peak of losses in a direction perpendicular to the *c*-axis. This means that there exists a very slow relaxation mechanism in *p*TPh crystals in this direction. Molecules of *p*-terphenyl are not permanent dipoles. This suggests that the relaxation process should be carrier-related, i.e. it may be regarded as a limited-in-space hopping of charges. In other words, the samples may be considered to consist of a number of clusters, inside which the hopping process takes place. The very slow intercluster transitions may give rise to the low frequency peak and losses. It should be mentioned at this point that the existence of so-called "difficult" transitions was suggested previously in connection with drift mobility results in simple aromatic hydrocarbons [6–8]. It has been shown recently by means of computer simulation [9] that the dielectric losses in a hopping system containing "difficult" transitions should be very similar to the losses found in *p*TPh disordered structures. On the other hand, there exists another "cluster" approach to the low-frequency losses in solids [10]. A common feature of both approaches is a discontinuous electronic structure of the dielectric system in a non-stationary state.
3. Both small-grained polycrystalline samples and

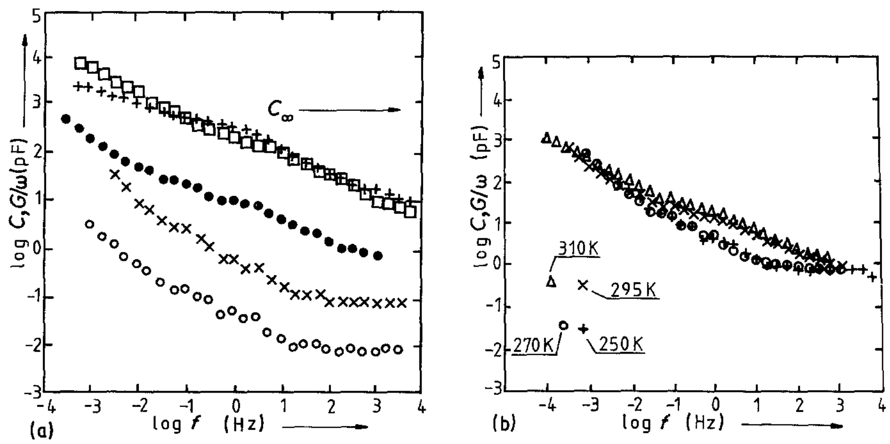

Figure 5 (a) Dielectric response of a small-grained polycrystalline *p*-terphenyl layer. G/ω: (○) 250 K, (x) 270 K, (●) 295 K, (□) 310 K. (+) $C - C_\infty(\nu = 0^4\,\mathrm{Hz})$. The curve for 250 K is in its correct place. The other curves are displaced with respect to one another by an order of 10 to avoid overcrowding. The C_∞ arrow relates to the G/ω curve at 310 K. (b) The master curve of the imaginary part of the capacitance of *p*-terphenyl small-grained polycrystalline layer.

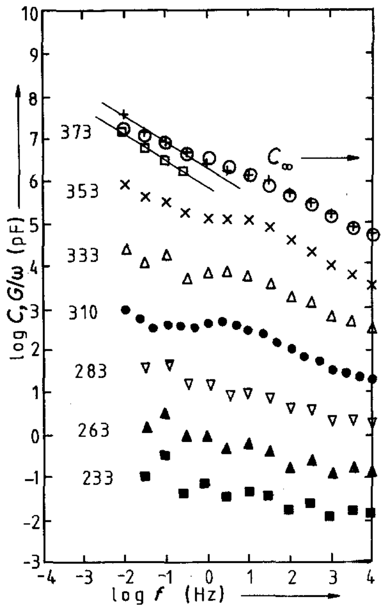

Figure 6 Dielectric response of *p*-terphenyl pellet. G/ω: (■) 233 K, (▲) 263 K, (▽) 283 K, (●) 310 K, (△) 333 K, (x) 353 K, (+) 373 K. (○) $C' - C_\infty(\nu = 10^4\,\mathrm{Hz})$, (□) $C' - C_\infty(\nu = 3 \times 10^{-1}\,\mathrm{Hz})$. The two lines are drawn to show the KK compatibility at low frequencies. The curve for 233 K is in its correct place; the other curves are displaced with respect to one another by an order of 10 to avoid overcrowding. The C_∞ arrow relates to the G/ω curves at 373 K.

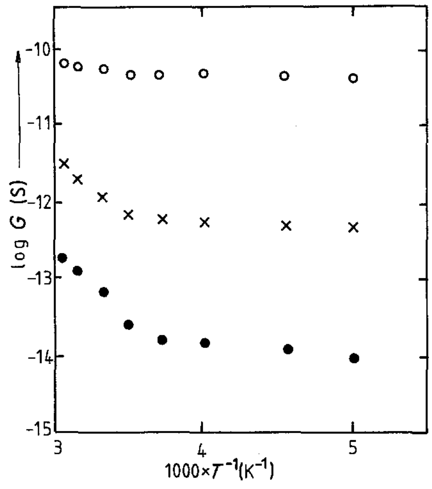

Figure 7 Temperature dependence of a.c. conductance of *p*-terphenyl pellets at various frequencies. (●) 0.03 Hz, (x) 3 Hz, (○) 300 Hz.

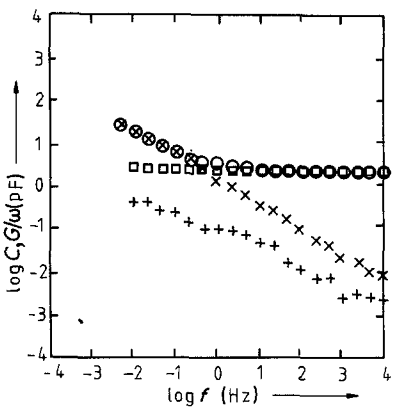

Figure 8 Comparison of dielectric response of a pellet with insulating SiO film between the electrodes and the bulk of the sample ((□) capacitance, (+) G/ω) with a pellet covered with gold electrodes ((○) capacitance, (x) G/ω). The thicknesses of the two samples were the same (within experimental error) and equal to about 1.5 mm.

pellets show a trace of a loss peak at about 10 Hz and strong dispersion at very low frequencies, i.e. below 1 Hz. The low frequency dispersion proved to be carrier-related, so it may be interpreted in terms of hopping of carriers between localized states of comparatively small concentration. It suggests that there should exist bands of localized states in strongly disordered structures of *p*-terphenyl, which do not exist in more perfect structures.

4. The structure of simple aromatic hydrocarbons plays a significant role in their dielectric properties at very low frequencies, i.e. below 10 Hz.

Acknowledgements

The measurements were carried out at Chelsea College, University of London, under the Leverhulme Trust sponsorship. This work was partially carried out under the CPBP 01.06 Project.

References

1. E. A. SILINSH, "Organic Molecular Crystals" (Springer-Verlag, Berlin, Heidelberg, New York, 1980).
2. M. POPE and C. E. SWENBERG, "Electronic Processes in Organic Crystals" (Clarendon, Oxford, 1982).
3. A. K. JONSCHER, "Dielectric Relaxation in Solids" (Chelsea Dielectrics, London, 1983).
4. G. W. BĄK, A. SZYMAŃSKI and A. K. JONSCHER, *J. Chem. Soc., Faraday Trans. 2* **81** (1985) 1053.
5. S. KANIA, W. MYCIELSKI and A. LIPIŃSKI, *Thin Solid Films* **61** (1979) 229.
6. G. W. BĄK, *ibid.* **105** (1983) 177.
7. *Idem, ibid.* **105** (1983) 183.
8. *Idem, Polym. Bull.* **11** (1984) 443.
9. *Idem, J. Phys. C*, in press.
10. L. A. DISSADO and R. M. HILL, *Proc. Roy. Soc.* **A390** (1983) 131.

Received 15 November 1985
and accepted 14 March 1986