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Influence of polycrystalline structure on dielectric properties of some organic molecular crystals

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Abstract. The results of investigations on the influence of the polycrystalline structure on the low-frequency dielectric properties of aromatic hydrocarbons are presented. It is suggested that the dielectric losses in most polycrystalline structures of p-terphenyl and tetrabenzofulvalene below about 100 Hz are strongly influenced by scattering of charge carriers at inter-grain regions. The activation energy of the scattering is equal to about 0.2–0.3 eV and is one order of magnitude greater than the activation energy of the hopping transport inside grains. The spectral shape of the G/ω curve in the frequency region in which the scattering takes place is well described by a power law with the exponent -0.5 .

1. Introduction

The recent development of molecular electronics has given rise to increasing interest in systems in which single molecules preserve their individuality. Organic molecular crystals are good examples of such systems. The most often investigated representatives of the organic molecular crystals are comparatively simple aromatic hydrocarbons such as anthracene and p-terphenyl. Although much attention has been paid to investigations of electrical properties of aromatic hydrocarbons (Pope and Swenberg 1982, Silinsh 1980), some properties of the compounds have remained unclear. The influence of inhomogeneities of the polycrystalline structure on energy structure and transport of charge carriers belong to such poorly known phenomena in organic molecular crystals.

The results of investigations on the influence of the polycrystalline structure on the low-frequency dielectric properties of p-terphenyl and tetrabenzofulvalene single crystals and polycrystalline films are presented in this paper. Both these compounds are aromatic hydrocarbons. The structure of molecules of both p-terphenyl (pTPH) and tetrabenzofulvalene (TBF) are shown in the insets of figures 2 and 9, respectively.

The measurements presented in this paper were carried out using a Solartron frequency analyser 1191 with a pre-amplifier and measuring box. The measuring system has been described in detail elsewhere (Pugh 1984).

2. Dielectric properties of p-terphenyl single crystals

The single-crystal samples were obtained by vacuum evaporation of gold electrodes on pTPH single crystals. The measurements were carried out in a vacuum of 10^{-4} Torr.

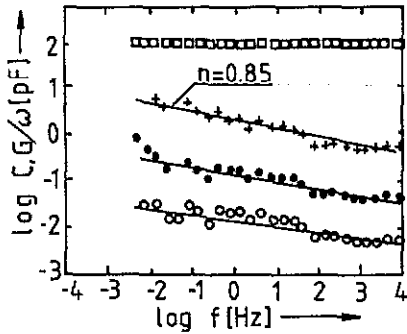


Figure 1. Dielectric response of pTPH crystals parallel to the c' axis where the structure of the crystal was comparatively perfect: \circ , G/ω , 270 K; \bullet , G/ω , 308 K; $+$, G/ω , 320 K; \square , C , 320 K. The points for 270 K are in their correct place. The other curves are displaced by an order of magnitude with respect to each other to avoid overcrowding.

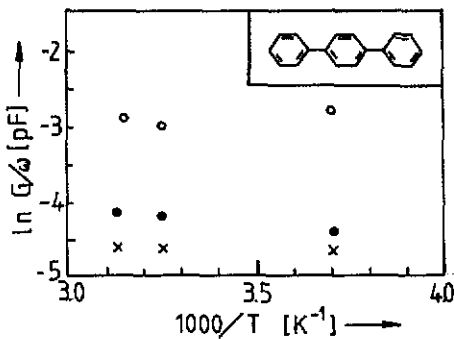


Figure 2. Temperature dependence of G/ω for a pTPH crystal at various frequencies (from figure 1): \circ , 10^{-1} Hz; \bullet , 56.2 Hz; $+$, 3160 Hz. The inset shows the pTPH molecule structure.

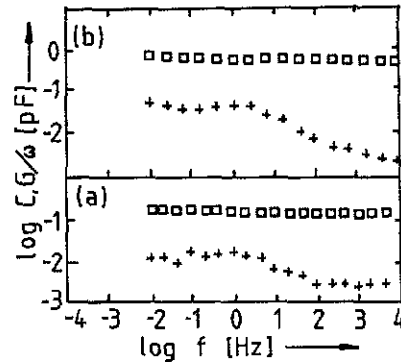


Figure 3. Dielectric response of more imperfect pTPH crystals showing (a) the response in the direction parallel to the c' axis ($T = 320$ K) and (b) the response in the direction perpendicular to the c' axis ($T = 340$ K): \square , C ; $+$, G/ω .

The investigations on the dielectric properties of pTPH single crystals have shown that the spectral shape of their dielectric response depends on the single-crystal quality (Bak 1988). The dielectric properties of pTPH single crystals with few defects are shown in figure 1. The spectral shape of the G/ω curve may be well described by

$$C'' = G/\omega \propto \omega^{n-1} \quad (1)$$

where $n = 0.85$. In the frequency range 10^{-2} – 10^4 Hz the crystals are low-loss material and no relaxation mechanism has been found, as no loss peak is visible in figure 1. The temperature dependence of the imaginary part of capacitance is shown in figure 2. As we see, the AC conduction almost does not depend on temperature.

As far as more imperfect single crystals are concerned, measurable relaxation phenomena in such crystals take place (figure 3). Figure 3(a) shows the dielectric response of a pTPH crystal in the direction parallel to the c' axis. This imperfect crystalline sample was obtained by putting a pressure parallel to the top surface of the crystal. The light transparency of the crystal became much worse at that moment, which may be regarded as evidence of structure worsening. The response in the direction perpendicular to the c' axis is shown in figure 3(b). In the second case we consider an even worse crystalline

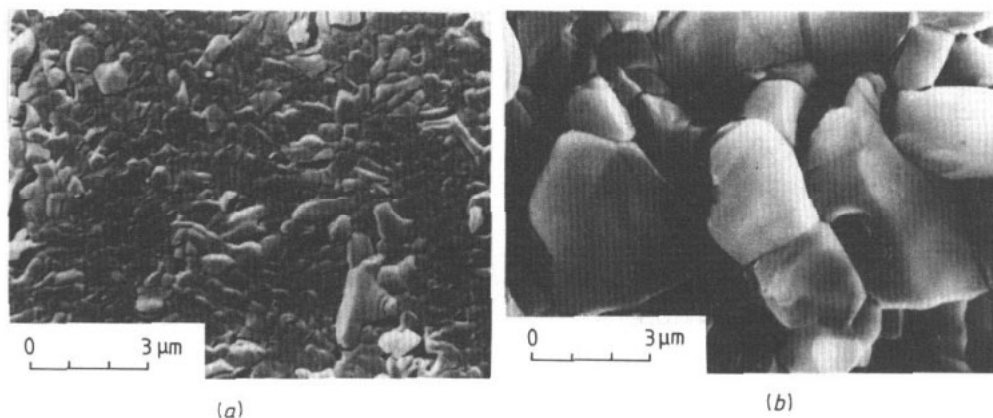


Figure 4. Electron micrographs of (a) small-grained and (b) large-grained polycrystalline pTPH films.

structure than in the first case, because it is not easy to cut off such a crystal in order to get a sample with electrodes parallel to the c' axis and many defects are produced during sample preparation. Easily detectable peaks of dielectric losses are on the G/ω curves. The activation energy of the frequency of peak maximum is equal to about 0.65 eV (Bak 1987, 1988). As was shown earlier, the loss peak is probably caused by relaxation of charge carriers between traps 0.65 eV deep (Bak 1987). The traps are supposedly connected with defects in the crystalline structure and the trap number increases with decreasing quality of crystalline structure (Bak 1988).

3. Dielectric properties of polycrystalline systems

Small-grained and large-grained polycrystalline pTPH films were used for the dielectric measurements. The small-grained films were prepared by vacuum evaporation on a glass substrate covered with a gold electrode and the top electrodes were also evaporated in vacuum. The large-grained layers were obtained by recrystallization consisting in annealing the small-grained films for a few hours at a temperature of about 415 K. The average diameters of grains in the small-grained and large-grained films were 2 μm and 7 μm, respectively. Micrographs of small-grained and large-grained pTPH polycrystalline films are shown in figures 4(a) and 4(b), respectively. In the case of all the film samples their thicknesses were measured with an interferometer microscope to check whether the electrodes were parallel, and unsuitable samples were rejected. Polycrystalline TBF films were obtained by melting TBF powder on a glass substrate covered with a conducting SnO₂ electrode and the top gold electrodes were evaporated in vacuum. The range of diameters of the grains in TBF was very much larger than that shown by pTPH films. The dielectric properties of compressed pTPH pellets were also investigated. The pellets were about 10⁻³ m thick. The dielectric constants (measured with a signal frequency of 1 MHz) for both polycrystalline and single-crystal samples were the same within the experimental error and equal to 3.2 which suggests that the continuity of material in polycrystalline samples may be considered to be satisfactory.

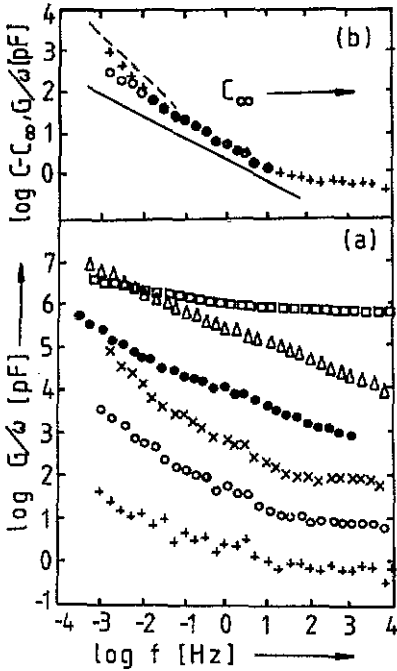


Figure 5. (a) Dielectric response of a pTPH small-grained film: +, G/ω , 230 K; O, G/ω , 250 K; ×, G/ω , 270 K; ●, G/ω , 295 K; Δ, G/ω , 310 K; □, C_∞ , 310 K. The points for 230 K are in their correct place. The other curves are displaced by an order of magnitude with respect to each other to avoid overcrowding. (b) Analysis of the dielectric response at 270 K: +, G/ω ; O, $C - C_\infty$. C_∞ is the capacitance resulting from polarization faster than 31.6 Hz. The slope of the full curve is -0.5 , and that of the broken curve is -1 .

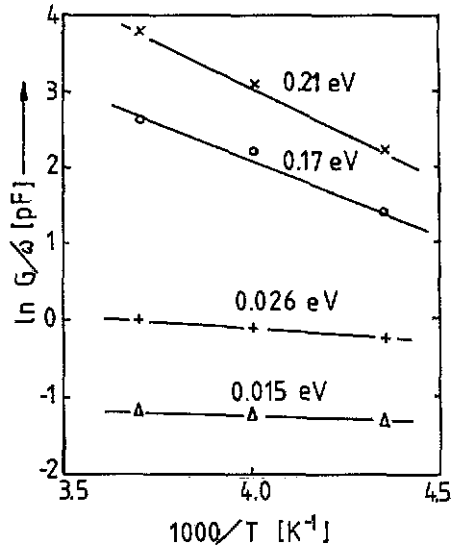


Figure 6. Temperature dependence of G/ω in pTPH small-grained films at various frequencies: Δ, 10^3 Hz; +, 10^2 Hz; O, 3.16×10^{-1} Hz; ×, 3.16×10^{-2} Hz. The curve at 10^3 Hz is displaced by an order of magnitude to avoid overcrowding. The temperatures of the measurements are 230 K, 250 K and 270 K.

The dielectric response of small-grained pTPH films is shown in figure 5. The spectral shape of the G/ω curve changes at 295 K, because of the loss peak which is known to appear at this temperature (Bak 1987). As was shown earlier, the peak results from the relaxation of charge carriers between traps 0.65 eV deep (Bak 1987), just as in the case of the more imperfect pTPH crystals. The spectral shape of the G/ω curve without the loss peak (at 270 K) is analysed in figure 5(b). As we see, the G/ω curve at 270 K consists of three parts. The high-frequency part is similar to that found in comparatively good crystals and may be described with a coefficient n close to unity. As is shown in figure 6 the temperature dependence of this part of the G/ω curve is very weak, just as for pTPH crystals (see figure 1). It has been suggested that such an AC conduction may be interpreted in terms of hopping transport of charge carriers in a narrow band of localized states at the Fermi level (Bak *et al* 1979).

The slope of the middle part of the G/ω curve in figure 5(b) is very close to -0.5 , i.e. the value of n is about 0.5. If equation (1) is fulfilled, the Kramers-Kronig (KK) relations give the following expression:

$$\chi''(\omega)/\chi'(\omega) = C''(\omega)/[C'(\omega) - C_\infty] = \cot(n\pi/2). \quad (2)$$

The above equation can be used to test the KK compatibility of dielectric data in a given frequency region provided that the influence of faster dielectric phenomena represented by C_∞ is subtracted.

From equation (2) it results that the distance between the $C''(\omega)$ and $C'(\omega) - C_\infty$ curves is equal to $\log[\cot(n\pi/2)]$ on a $\log(C' - C_\infty, C'')$ versus $\log \omega$ plot. If $n = 0.5$, then $\log[\cot(\pi/4)] = 0$, i.e. the distance between the two curves is zero in this case. As we see in figure 5(b), $C - C_\infty$ and G/ω are compatible from the KK relations point of view, which means that there is no measurable influence of the DC phenomena at the frequencies at which $n = 0.5$. These considerations are based on the assumption that the middle part of the G/ω curve is a straight line on the double-logarithmic scale and C_∞ was taken to be equal to the measured capacitance at about 2 Hz to subtract the influence of all faster polarization phenomena. The activation energy of this part of the G/ω curve is much greater than in the case of the high-frequency part and is equal to about 0.2 eV (figure 6).

The slope of the low-frequency part of the G/ω curve becomes close to -1 which may suggest that the DC phenomena have a measurable influence at low frequencies.

The change in slope of the G/ω curve from very small at high frequencies to -0.5 takes place between 10 and 100 Hz. The distance travelled by a charge carrier during half the period of a sinusoidal electric field depends on the frequency of that field. This distance in pTPH small-grained films becomes equal to the diameter of the grain at about a few tens of hertz (taking typical values of the drift mobility $\mu = 10^{-9} \text{ m}^2 \text{ V}^{-1} \text{ s}^{-1}$ (Lipinski *et al* 1980), the amplitude of the measuring field $V_0 = 2 \text{ V}$ and the sample thickness $d = 2.9 \mu\text{m}$). This means that at frequencies below about 100 Hz the scattering in the inter-grain regions should have an outstanding influence on dielectric losses. This is more probable since the activation energy of the middle part of the G/ω curve (figure 5) is much greater than that of the high-frequency part.

In order to verify the suggestion that the scattering in the inter-grain regions has an influence on the dielectric response, computer simulation of dielectric losses in an inhomogeneous hopping system has been carried out (Bak 1986). The following three assumptions are the foundations of the simulation.

(1) The dielectric response of the system is dominated by the movement of charge carriers which are injected from electrodes. The permanent dipole moment of a pTPH molecule equals zero. This means that the low-frequency dielectric phenomena should be caused by movement of charge carriers in a sample. In order to verify the influence of injected charge carriers on dielectric losses in polycrystalline pTPH structures, dielectric measurements on two kinds of compressed pellet have been carried out. The first kind was a pellet supplied with gold injecting electrodes, and the second was a pellet with a thin insulating silicone oxide film between metal electrodes and the sample bulk. Comparison of the dielectric properties of such pTPH pellets is shown in figure 7. As we see, the dielectric losses in the insulated pellet are some one to two orders of magnitude smaller than those in the sample with injecting electrodes. This means that the first assumption is justified when interpreting dielectric losses in polycrystalline pTPH films.

(2) Scattering at inter-grain barriers has an essential influence on the movement of charge carriers. Both the above estimation of the frequency at which the slope of the G/ω curve changes from close to zero to -0.5 and the remarkable increase in the activation energy (figure 6) support this assumption of the simulation.

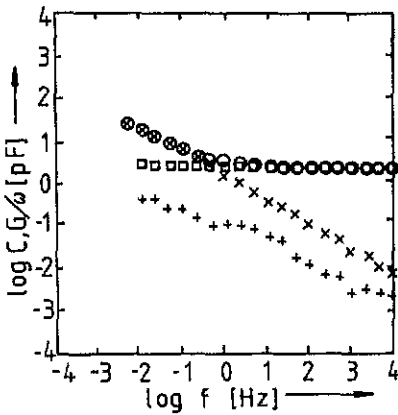


Figure 7. Comparison of the dielectric properties of pTPH pellets with injecting gold electrodes (O, C; ×, G/ω) and with insulating silicon oxide films between the metal electrodes and bulk of sample (□, C; +, G/ω) ($T = 300$ K). The thickness of the pellets was equal to about 10^{-3} m.

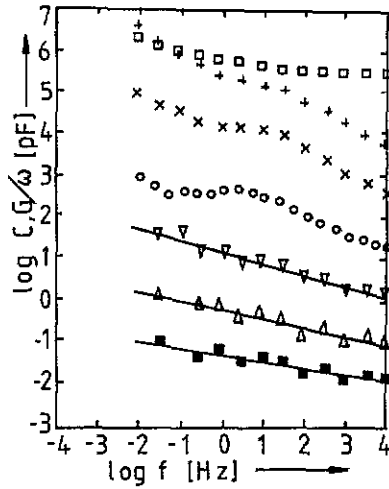


Figure 8. Dielectric response of a pTPH pellet with gold electrodes at various temperatures: ■, G/ω , 233 K; △, G/ω , 263 K; ▽, G/ω , 283 K; ○, G/ω , 310 K; ×, G/ω , 333 K; +, G/ω , 373 K; □, C, 373 K. The curve at 233 K is in its correct place. The other curves are displaced by an order of magnitude with respect to each other to avoid overcrowding.

(3) The concentration of hopping carriers is much smaller than the concentration of localized states. Discussion of this assumption is rather difficult from the methodological point of view. In order to compare the two concentrations, one should estimate both using credible methods. The credible calculation of the concentration of localized states might be carried out if a widely accepted theory of AC hopping transport in organic molecular organic crystals were to exist. Such an accepted theory does not actually exist. The estimation of concentration of localized states by means of Mott's hopping theory gives $N = 10^{17} - 10^{18} \text{ cm}^{-3}$ (Bak *et al* 1979, 1980). If we assume the suggestion of Eley and Parfitt (1955, 1960) that a moving charge carrier is localized at every molecule in its way, then the concentration of localized states becomes even greater whereas the concentration of injected charge carriers estimated from DC measurements is of the order of 10^{14} cm^{-3} .

As a result of computer simulation of dielectric losses in such an inhomogeneous hopping system, $n = 0.45$ has been obtained (Bak 1986). The value of n is very close to that from the presented measurements (figure 5).

The dielectric response of a pTPH compressed pellet is shown in figure 8. As in the small-grained films, a loss peak appears at 310 K. The difference between the dielectric responses of pellets and small-grained films is the lack of a frequency value at which a change in slope of the G/ω curve takes place. Instead of such a change in slope we have a continuous change in slope over the whole G/ω curve with increasing temperature (see figure 8). This is understandable if we take into account the fact that the size of grains of polycrystalline structure of pellets spans a comparatively wide range contrary to the small-grained films in which the size of grains is comparatively well defined. In

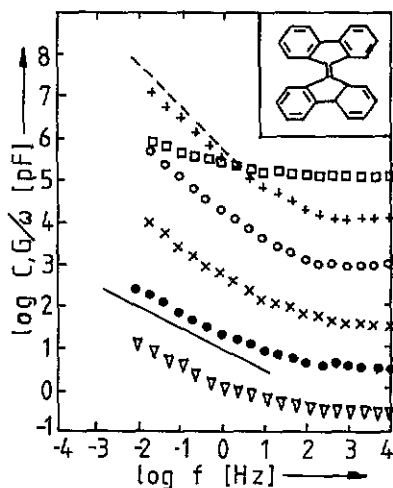


Figure 9. Dielectric response of TBF polycrystalline film at various temperatures: ∇ , G/ω ; 300 K; \bullet , G/ω ; 320 K; \times , G/ω ; 340 K; \circ , G/ω ; 360 K; $+$, G/ω ; 373 K; \square , C ; 373 K. The curve at 300 K is in its correct place. The other curves are displaced by an order of magnitude with respect to each other to avoid overcrowding. The inset shows TBF molecule structure.

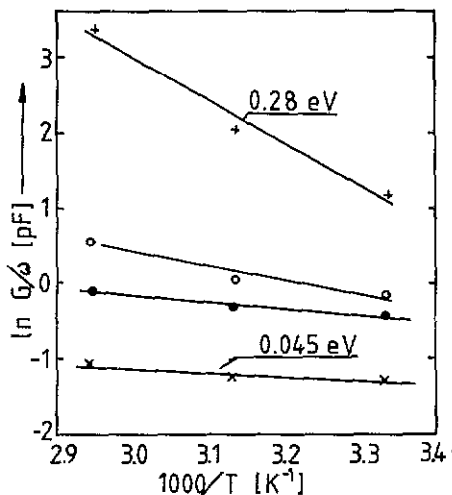


Figure 10. Temperature dependence of G/ω in polycrystalline TBF films at various frequencies: \times , 10^4 Hz; \bullet , 10^3 Hz; \circ , 10^2 Hz; $+$, 0.1 Hz. The curves at 10^4 Hz and 0.1 Hz are in their correct places. The two other curves are displaced upwards by an order of magnitude to avoid overcrowding.

this situation the frequency at which the distance travelled in half the period of the electric field is equal to the diameter of grains cannot be precisely defined.

Figure 9 shows the dielectric response of a polycrystalline TBF layer at various temperatures. The activation energy of the high-frequency part of the G/ω curve is small and is equal to about 0.045 eV (figure 10). As in the small-grained pTPH films the activation energy increases by about one order of magnitude with decreasing frequency and equals 0.28 at 0.1 Hz. The slope of the low-frequency part of the G/ω curve is about -0.5 . Taking into account this slope and the increase in the activation energy we suggest that the scattering at inter-grain inhomogeneities plays a significant role at the frequencies below 10 Hz. Unfortunately, in the case of TBF polycrystalline films it is rather impossible to estimate the limiting frequency at which the change in slope of the G/ω curve should take place, because the drift mobility of charge carriers in polycrystalline TBF turned out to be field dependent (Haladyj and Bak 1987).

Recrystallization of the small-grained pTPH films results in a significant enlargement of the size of grains (see figure 4). In such large-grained films the average diameter of grains becomes greater than the film thickness. In this situation it may be expected that no influence of inter-grain barriers should be detected. This is confirmed in figure 11 where the G/ω curve does not have a part with a slope close to -0.5 .

4. Conclusions

The influence of inhomogeneities in the polycrystalline structure on the dielectric properties of the two investigated aromatic hydrocarbons can be summarized as follows.

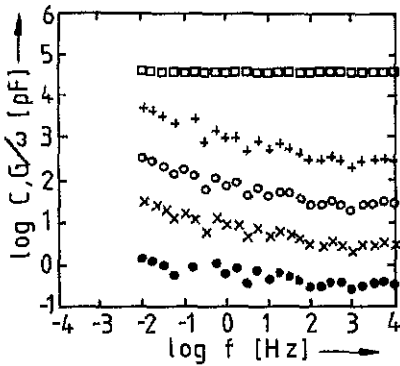


Figure 11. Dielectric response of a pTPH large-grained film at various temperatures: ●, G/ω , 205 K; ×, G/ω , 295 K; ○, G/ω , 310 K; +, G/ω , 353 K; □, C , 353 K. The curve at 205 K is at its correct place. The other curves are displaced upwards by a decade to avoid overcrowding.

(1) A peak of dielectric losses is detected in less perfect structures (crystals with more defects, and also small-grained pTPH films and pellets). The peak is due to relaxation of the charge carriers between traps.

(2) Hopping transport between localized states and scattering at inter-grain barriers also takes place in polycrystalline structures of hydrocarbons. Hopping transport may be assumed to take place in a narrow band of localized states at the Fermi level as its temperature dependence proved to be comparatively weak. The scattering becomes dominant at lower frequencies. The slope of the G/ω curve resulting from the scattering is very close to -0.5 . The activation energy of the scattering is much greater than that of hopping transport and is equal to about 0.2–0.3 eV.

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