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Low-frequency dielectric dispersion in some aromatic hydrocarbons

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The dielectric properties of polycrystalline structures of p-terphenyl and tetrabenzofulvalene and amorphous tetrabenzofulvalene layers have been measured. Two kinds of low-frequency dispersion in the samples have been found. It is suggested that the low-frequency dispersion is due to the releasing of charge carriers from deep traps. In addition the kinetics of retrapping are suggested to have an influence on the arising and scale of low-frequency dispersion in these materials.

1. Introduction

The electrical properties of organic materials have been investigated extensively for the last 30 years because they are of great importance from a biological point of view. It is rather difficult to study basic phenomena in very complicated organic molecules, so some simple aromatic hydrocarbons (first of all anthracene, tetracene and their phenyl counterparts p-terphenyl and p-quaterphenyl) were chosen as model substances for investigations.

Tetrabenzofulvalene (TBF) is an aromatic hydrocarbon which can be easily obtained and exist in the amorphous state at room temperature. TBF and p-terphenyl (PTPH) were chosen as representatives for the dielectric study of aromatic hydrocarbons.

It is convenient to describe the dielectric response of solid samples on a double logarithmic scale, using the complex dielectric capacitance

$$C^* = C' - \mathrm{i}C'' = C - \mathrm{i}(G/\omega) \qquad (1)$$

where C is the ordinary electric capacitance and $G(\omega)$ is the total conductance at angular frequency ω given by

$$G(\omega) = G_{\mathrm{a.c.}}(\omega) + G_0 \qquad (2)$$

$G_{\mathrm{a.c.}}(\omega)$ being the alternating-current conductance and G_0 being the direct-current conductance.

For the study of a single dielectric process α separated in frequency it is convenient to write Equation 1 in the form [1]

$$(C - C_\infty) - \mathrm{i}\left(\frac{G(\omega)}{\omega} - \frac{G_0}{\omega}\right) = G_{\mathrm{f}}\varepsilon_0(\chi'_\alpha - \mathrm{i}\chi''_\alpha) \qquad (3)$$

where C_∞ is defined as the "high-frequency" capacitance due to dielectric phenomena faster than the high-frequency limit of the considered frequency region, G_{f} is a geometrical factor, and χ'_α and χ''_α are the real and imaginary parts of the dielectric susceptibility, respectively, describing the α process under consideration. Both parts of the dielectric susceptibility should be Kramers–Kronig (KK) compatible.

The most common frequency dependence in solids of the a.c. conduction is of the form [1]

$$G_{\mathrm{a.c.}}(\omega) \propto \omega^n \qquad (4)$$

The smaller the value of the coefficient n is, the faster the imaginary part of complex capacitance G/ω increases with decreasing frequency (under the assumption that the G_0/ω part is negligible). If additionally C_∞ becomes negligible in comparison to C, then an increase in G/ω is accompanied by an increase in capacitance according to the KK relations.

It is often observed in solids that the G/ω curve at low frequencies is described by $n \leqslant 0.5$ [1, 2] and accompanied by an increase in electric capacitance. Such a phenomenon was found both in PTPH and TBF non-crystalline structures and will be described in this paper.

PTPH is a typical simple aromatic hydrocarbon. Its molecular structure is shown in the inset of Fig. 1 below. The PTPH films were obtained by vacuum evaporation under a pressure of the order of 10^{-5} torr. The PTPH pellets were obtained by compression. The molecular structure of TBF is shown in the inset of Fig. 3. The TBF samples were obtained by melting TBF powder between two glass plates covered by conducting SnO_2 or gold films. Rapid cooling of the system resulted in amorphous TBF samples, while slow cooling resulted in polycrystalline ones. The amorphous phase was detected by means of X-ray diffraction [3].

2. Low-frequency dispersion in p-terphenyl

The dielectric properties of PTPH crystals, small-grained and large-grained layers and pellets have been measured, and no detectable low-frequency dispersion (LFD) in PTPH crystals and large-grained layers has been found [4, 5]. Fig. 1 shows the dielectric response of small-grained PTPH layers at various temperatures. It may be shown that the spectral shape of the G/ω curve changes between 270 and 295 K [4]. The change of spectral shape is due to a loss peak appearing at 295 K [4]. The loss peak was interpreted by thermally activated jumps among traps about 0.65 eV

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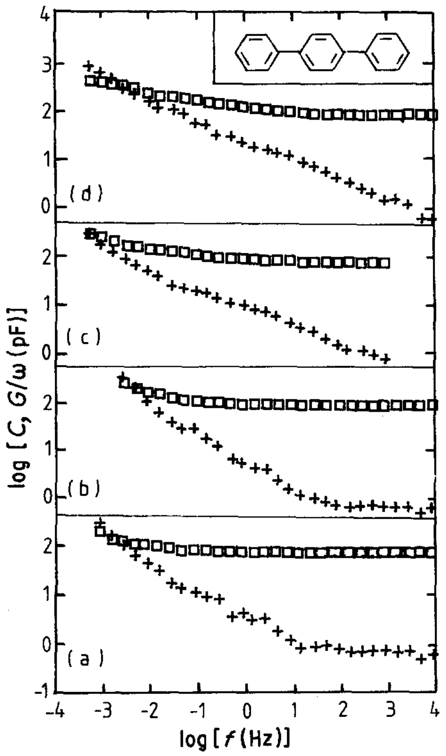

Figure 1 Dielectric response of small-grained p-terphenyl layer: (□) capacitance, (+) G/ω. (a) 250 K, (b) 270 K, (c) 295 K, (d) 310 K. The inset shows PTPH molecular structure.

deep [5]. The low-frequency dispersion in small-grained PTPH layers takes place and increases gradually with increasing temperature.

The dielectric response of PTPH pellets (Fig. 2) is similar to that of small-grained films. The loss peak appearing between 283 and 310 K is accompanied by LFD which increases gradually with increasing temperature.

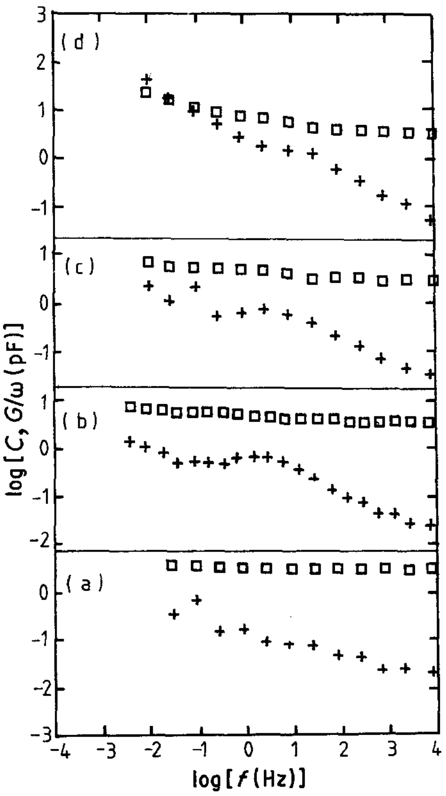

Figure 2 Dielectric response of p-terphenyl pellet: (□) capacitance, (+) G/ω. (a) 283 K, (b) 310 K, (c) 333 K, (d) 373 K.

In order to find the influence of injected charge carriers on the existence of LFD, dielectric measurements on PTPH pellets with insulating SiO thin films between metal electrodes and the bulk of the sample were carried out. The comparison of dielectric properties between such an insulated sample and an ordinary one shows that the injected carriers play a significant role in dielectric phenomena in metal–PTPH–metal systems. In particular the existence of LFD depends on charge-carrier injection from the electrodes [4, 6].

3. Low-frequency dispersion in tetrabenzofulvalene

The dielectric response of TBF crystals is similar to that of PTPH crystals in the direction perpendicular to the *c* axis [5]. A loss peak in TBF crystals is observed [7]. The loss peak may be interpreted in terms of thermally activated jumps of charge carriers among traps about 0.73 eV deep [7]. No detectable LFD in TBF crystals has been found.

Fig. 3 shows the dielectric properties of polycrystalline TBF samples. The slope of the G/ω curve below 340 K is equal to -0.5 which corresponds to $n = 0.5$. Starting from 340 K the slope of the G/ω curve changes gradually down to about -1 to 373 K. The change of dielectric response is reversible. It is not possible to find a value of C_∞ for which the G/ω and $(C - C_\infty)$ curves at 373 K would be KK compatible,

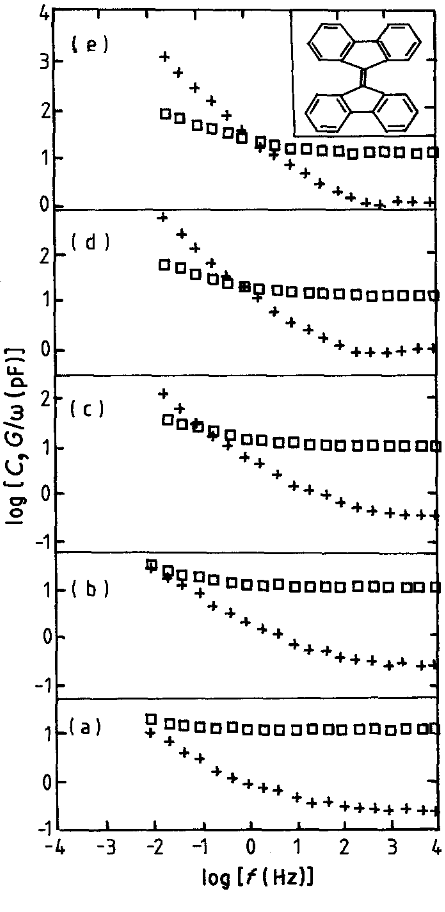

Figure 3 Dielectric response of polycrystalline TBF layer: (□) capacitance, (+) G/ω. (a) 300 K, (b) 320 K, (c) 340 K, (d) 360 K, (e) 373 K. The inset shows TBF structure.

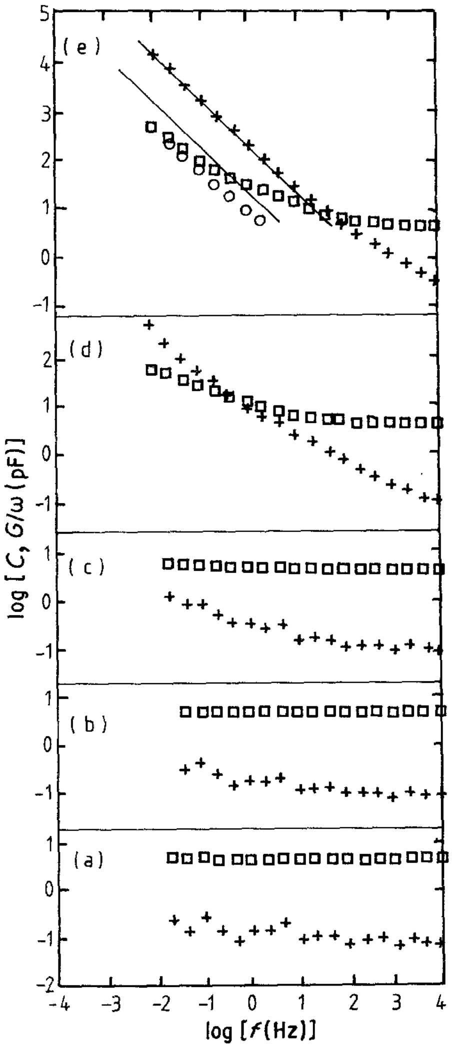

Figure 4 Dielectric response of TBF pellet: (□) capacitance, (+) G/ω. (a) 250 K, (b) 300 K, (c) 320 K, (d) 340 K, (e) 360 K. (○) $(C - C_\infty)$ curve at C_∞ $(f = 4\,\mathrm{Hz})$.

so it may be suggested that the gradual change of slope of the G/ω curve is due to an increasing influence of d.c. phenomena. The low-frequency dispersion increases gradually with increasing temperature, similarly to that in PTPH films and pellets.

The dielectric properties of compressed TBF pellets are shown in Fig. 4. Starting from 340 K an instantaneous change of dielectric response takes place. The dielectric losses increase suddenly between 320 and 340 K and a remarkable LFD appears. The LFD increases with increasing temperature. The G/ω curve at 360 K may be well described by $n = 0.1$. The two full lines in Fig. 4e are KK compatible. The hypothetical $(C - C_\infty)$ curve in Fig. 4e differs significantly from the real $(C - C_\infty)$ $(f = 4\,\mathrm{Hz})$ curve (obtained after subtraction of C_∞ $(f \geqslant 4\,\mathrm{Hz})$ due to "high-frequency" phenomena; the change of the slope of G/ω curve starts between 1 and 10 Hz). This suggests that d.c. phenomena have a measurable influence on the losses. On the other hand the strong LFD proves that there must exist remarkable dielectric (or a.c.) phenomena in TBF pellets in the frequency range 10^{-2} to 10 Hz. Some suggestions on a possible mechanism of the phenomena will be presented in Section 4 of this paper.

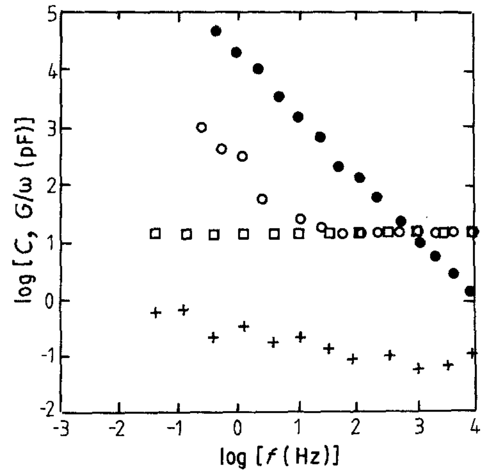

Figure 5 Dielectric response of amorphous TBF sample at 250 K: (□) C, (+) G/ω and at 300 K: (○) C, (●) G/ω.

Measurements on amorphous TBF above room temperature cannot be carried out because it recrystallizes above room temperature. The dielectric response of amorphous TBF is shown in Fig. 5. A strong LFD in amorphous TBF appears at 300 K. The slope of G/ω curve is very close to -1, which may suggest a predominant influence of d.c. phenomena. The KK relations cannot be used in this case to confirm the influence of direct current, because the distance between the G/ω and $(C - C_\infty)$ curves is too sensitive to changes of n at n close to zero. No detectable LFD was found in the amorphous TBF at 250 K (Fig. 5).

Fig. 6 shows the dielectric response of insulated amorphous TBF samples at 300 K (i.e. with insulating SiO thin films between metal electrodes and the TBF layer). As we see, the LFD in amorphous TBF samples is of injected carrier origin too. All the dielectric measurements presented are linear, i.e. independent of amplitude of the measuring sinusoidal signal in the range 1 to 10 V.

4. Discussion

Comparing the results of measurements on polycrystalline PTPH films and pellets, polycrystalline TBF films and pellets, and amorphous TBF samples it may be noticed that there exist two different kinds of LFD. The features of the two kinds of LFD are summarized in Table I.

In the case of small-grained PTPH films and pellets

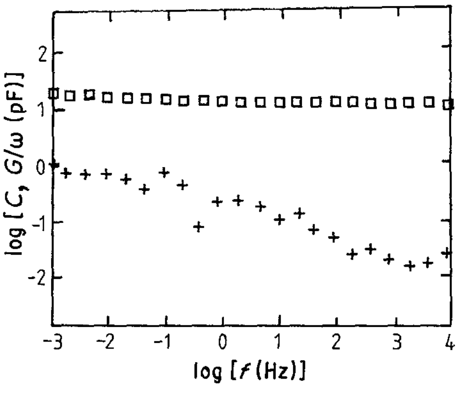

Figure 6 Dielectric response of insulated amorphous TBF sample at 300 K: (□) capacitance, (+) G/ω.

TABLE I Low-frequency dispersion in PTPH and TBF

Type of LFD	Features	Samples
1st kind	1. n is close to 0.5 and increases gradually as a result of d.c. influence 2. Increase in capacitance is smaller than one order of magnitude 3. LFD increases gradually with temperature 4. LFD depends on injection of carriers from electrodes	1. Small-grained polycrystalline PTPH 2. PTPH compressed pellets 3. Polycrystalline TBF films
2nd kind	1. n is close to zero 2. Detectable (or presumable in amorphous TBF) influence of d.c. phenomena 3. Increase in capacitance is greater than one order of magnitude 4. Discontinuous change of both G/ω and C curves at a certain temperature 5. LFD depends on injection of carriers from electrodes	1. TBF compressed pellets 2. TBF amorphous samples

there exists a discontinuous change of spectral shape of the G/ω curve. The change is accompanied by a gradual increase in capacitance. In the case of TBF pellets the instantaneous change of spectral shape of the G/ω curve is accompanied by an equally instantaneous increase in capacitance. It has been shown that there exists a trapping level about 0.62 eV deep in polycrystalline PTPH structures [8]. The loss peak in the small-grained polycrystalline PTPH layers and less perfect PTPH crystals was interpreted by thermally activated relaxations among the traps [5]. The depth of the trapping level found from the dielectric measurements is equal to 0.65 eV [5]. The temperature of the thermally stimulated current (TSC) peak is equal to 293 K [8] and it was shown that the shape of the G/ω curve changes a little above this temperature [4].

The TSC measurements on polycrystalline TBF layers show that there exists a TSC peak at about 269 K [9]. The shape of the TSC peak suggests that retrapping processes do not play a significant role in the layers [9]. The depth of trapping level calculated by the authors is between 0.73 and 0.77 eV, depending on the method used for calculations [9]. On the other hand, as mentioned above, the depth of the trapping level was found to be about 0.73 eV from dielectric measurements [7].

A change of spectral shape of the dielectric response usually takes place when the temperature changes from lower than the TSC peak temperature to higher than the TSC peak temperature [4, 5]. The spectral shape for TBF pellets does not change at 269 K [10], but it changes remarkably between 320 and 340 K (see Fig. 4). If we assume that a strong retrapping in TBF pellets takes place (the role of retrapping phenomena may be supposed to increase because of a greater concentration of traps in more disordered TBF pellets than in polycrystalline TBF layers) than the TSC peak temperature may be estimated by means of the simplified Bube method as

$$E_t = nkT_{\max} \qquad (5)$$

where E_t is the depth of the trapping level (0.73 eV), n is a constant between 20 and 25 (approximately equal to 25 in simple aromatic hydrocarbons), k is the Boltzmann constant and $T_{\max}$ is the TSC peak temperature. The TSC peak temperature estimated from Equation 5 is equal to 338 K, so it is inside the range 320 to 340 K in which the rapid change of dielectric response takes place. In this situation it may be suggested (see Table II for details) that the discontinuous change of dielectric properties of both PTPH and TBF is related to the releasing of charge carriers from the traps, because all the changes take place above the peak temperature of the TSC curve (measured in PTPH [8] and calculated from Equation 5 in the case of TBF pellets).

In other words, the temperature of change of the spectral shape of the dielectric response is suggested to be equal to the temperature of the TSC peak, and the latter is dependent on the kinetics of retrapping phenomena. Thus the temperature of change of the dielectric response should be dependent on the role of retrapping phenomena.

No similar comparison for the amorphous TBF

TABLE II Link between TSC peak and dielectric response

Type of sample	TSC peak temperature (K)	Low loss response (K)	Detectable change of G/ω curve (K)	Type of change of G/ω curve	Kind of LFD
PTPH small-grained film	293	250 270	295 310	Loss peak appears at 295 K	First
PTPH pellet	293*	233† 263† 283	310 333 353† 373	Loss peak appears	First
TBF pellet	338 (calculated)	250 300 320	340 360	n decreases drastically	Second

*TSC measurements on PTPH pellets have not been carried out. TSC measurements on PTPH small-grained layers showed that strong retrapping takes place, so it is suggested that the kinetics of trapping phenomena in PTPH pellets and small-grained films are similar.
†Results for these temperatures are not shown in Fig. 2 to simplify the figure.

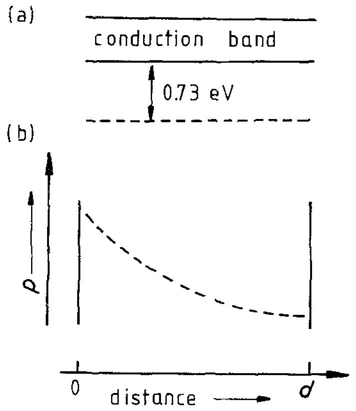

Figure 7 (a) Simple model of energetic structure of disordered TBF structure. (b) Schematic diagram of trap occupation probability as a function of distance from electrodes. p = probability of occupation of traps, d = sample thickness.

samples can be made, because there is no information about is energetic structure. However, it may be supposed that some shallower trapping levels should exist in amorphous TBF as is usually the case in other amorphous materials. Such shallower traps might give rise to a lower TSC peak temperature, resulting in a rapid change of dielectric response below 300 K.

Fig. 7a shows a simple model of the energetic structure of polycrystalline TBF (the corresponding model for PTPH would be similar, but the depth of the trapping level would be 0.65 eV). Below the TSC peak temperature the trapped electric charge is frozen in. Above the TSC peak temperature the trapped charge may be released and retrapped if the probability of retrapping is high enough. If the potential difference between electrodes equals zero, the probability of occupation of traps is independent of the distance from the electrodes. If the potential difference differs from zero (the potential may be varying in time slowly with a period much longer than the thermally activated hopping time between traps) then the occupation of traps becomes asymmetrical (Fig. 7b). The greater number of localized states at the electrodes may be an additional factor giving rise to an asymmetry of spatial distribution of trapped charge carriers. This asymmetry may give rise to a remarkable increase in capacitance. The relaxation time of such spatially trapped charge should be much greater than the relaxation time between two neighbouring traps if a large number of individual excitations between traps is required to travel a distance comparable with the thickness of the sample.

5. Summary

The results presented may be summarized as follows:

1. LFD in PTPH and TBF does not exist in monocrystalline structures, but it takes place in less perfect structures like small-grained polycrystalline layers, pellets and amorphous films.
2. There are two kinds of LFD in PTPH and TBF. The first one is accompanied by the G/ω curve described by $n \cong 0.5$. In the second case the G/ω curve is described by n close to zero and strong LFD takes place. The strong retrapping seems to be in favour of strong LFD in TBF.
3. There is a link between the injection of charge carriers from the electrodes and LFD. No LFD was detected in the insulated samples.
4. The release of charge carriers from traps has a significant influence on the dielectric properties of the two organic compounds.

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