TEMPERATURE AND FREQUENCY DEPENDENCES OF MICROWAVE CONDUCTIVITY OF ISOTROPIC RETICULATE DOPED POLYMERS

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Abstract

Frequency dependence of conductivity for reticulate doped systems is observed at room temperature only around 1 GHz and even so it is relatively weak. The temperature dependence of conductivity is characteristic of the CT complex used and not of the polymer matrix. For the system containing TTF-TCNQ, for which the d.c. conductivity has a maximum at c. 230 K (i.e. metal-like behaviour at higher temperatures), this maximum becomes more pronounced and shifts towards lower temperatures with increasing frequency in the GHz range. The temperature dependence of the microwave conductivity is weaker than that of the d.c. conductivity. Such behaviour can be described by a modified Maxwell–Wagner model if an appropriate shape factor for the conducting inclusions is introduced, and if a relatively high conductivity of the continuous phase is assumed. We conclude that charge-carrier transport in reticulate doped polymers is not controlled by insulating barriers. The disorder within microcrystals plays a fundamental role, while the CT complex crystalline network is continuous in spite of very low concentration.

1. Introduction

Measurements of microwave (m.w.) conductivity of heterogeneous systems at sufficiently high frequencies are believed to give insight into the discrete properties of the various components. In multicomponent microsystems consisting of conducting and insulating phases, charge-carrier transport is usually limited by insulating barriers separating conducting grains. Therefore, temperature dependences of the d.c. conductivity are determined mainly by the height and width of the barriers rather than by the intrinsic conducting properties of the conducting phase. For a.c. conductivity measurements, the barriers are progressively shunted by capacitive coupling between conducting grains as the frequency increases. Subsequently, conductivity

increases with increasing frequency. Most models predict a $\sigma \propto \omega^s$ dependence in some frequency ranges above and below which the conductivity is frequency independent (see e.g. ref. 1). The low-frequency value is equivalent to the d.c. conductivity; the high-frequency value approaches the bulk conductivity of the conducting phase.

Reticulate doped polymers are very specific heterogeneous conducting systems in which the conducting phase is made of fine dendrite microcrystals of quasi-one-dimensional organic metals (e.g. TTF-TCNQ) grown *in situ* in polymer matrices [2]. Diffusion-limited correlated crystallization of the organic metals leads to formation of the continuous conducting networks at extremely low concentrations, even below 0.003 vol. fraction in certain cases [3].

Charge-carrier transport in these materials has been the subject of various investigations [4 - 7]. The main conclusions drawn from these investigations were that the connectivity and perfectness of the network are very high and that the properties of a given system are characteristic of the organic metal used rather than of the polymer matrix [4, 5]. A.c. conductivity measurements up to 10 MHz in the temperature range 90 - 300 K show no dispersion unless some discontinuities in the crystalline conducting network are intentionally introduced [6, 7].

The aim of the present work was to find the frequency range in which dispersion is observed for reticulate doped systems and whether above this range the conductivity shows temperature dependences typical of organic metals.

2. Experimental

The preparation of reticulate doped polymers has been described elsewhere for both amorphous [2, 8] and semicrystalline matrices [9]. Two highly conducting charge-transfer (CT) complexes were used for reticulate doping: tetrathiotetracene–tetracyanoquinodimethane (TTT-TCNQ) and tetrathiofulvalene–TCNQ (TTF-TCNQ).

D.c. and m.w. conductivity measurements were carried out for following systems:

    (1) polycarbonate (PC) + 1 wt.% TTT-TCNQ;
    (2) polymethylmethacrylate (PMMA) + 1 wt.% TTT-TCNQ;
    (3) polypropylene (PP) + 1 wt.% TTT-TCNQ;
    (4) polyethylene (PE) + 1 wt.% TTT-TCNQ;
    (5) PE + 1 wt.% TTF-TCNQ.

Samples 1 - 3 were cast from *o*-dichlorobenzene and samples 4 and 5 were cast from chlorobenzene. The films were c. 20 μm thick, uniform and isotropic. The morphologies of the crystalline CT complex networks are different in each case; the common feature is dendrite-like branching. Descriptions of the morphologies and micrographs of these systems have been given in previous papers [8, 9].

D.c. conductivity measurements in the temperature range 10 - 300 K were performed under reduced pressure using a Cryosystems LTS-21 closed cycle refrigerator system. A linear four-probe technique was used. Electrical contacts were made using four thin conducting graphite foil strips which were pressed to the sample between two sapphire plates. Good thermal contact between the cryostat cold finger and the sample holder was obtained through indium foil. A dual heat-shield system was used to prevent heat flow by radiation. Measurements were carried out through an interface with an Apple IIe microcomputer. Results were in good agreement with those obtained previously for some of the investigated materials using free-mounted probes in a gas-exchange cryostat [4].

For microwave conductivity measurements, disc-like samples (diameter 2 mm) were punched from the films and put into the maximum of the electric field strength (field direction parallel to the diameter) of the microwave cavities. The complex permittivity and thus the microwave conductivity were determined by the usual cavity perturbation technique [10]. A re-entrant coaxial cavity (4.6 GHz) and a rectangular waveguide cavity (23.5 GHz) were used when working in the temperature range 80 - 300 K. A cylindrical cavity was used in the temperature range 4 - 300 K. The measurement of the frequency dependence of the conductivity at lower frequencies (0.3 - 2.5 GHz) was carried out in a coaxial line using a standing-wave detector. In this case the film was inserted between line segments covering the whole cross section of the line.

3. Results

Figure 1 shows the temperature dependence of the m.w. conductivity at 10.3 GHz for different polymers reticulate doped with 1 wt.% TTT-TCNQ or
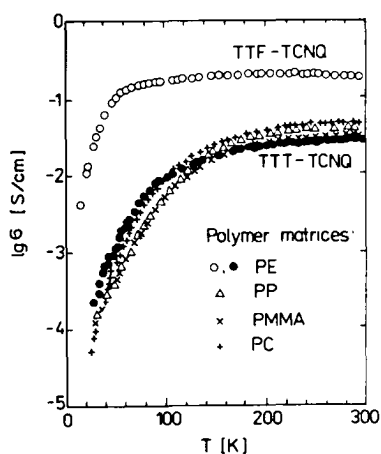

Fig. 1. Temperature dependences of the m.w. conductivity at 10.3 GHz for different polymers reticulate doped with 1 wt.% of TTF-TCNQ or TTT-TCNQ, as indicated in the Figure.

TTF-TCNQ. The plots for all the systems with TTT-TCNQ are very similar and almost coincide, showing a continuous decrease of the conductivity with decreasing temperature. The behaviour of the system with TTF-TCNQ is very different: the plot is almost flat down to $c.\,60\,K$ (even with a weak maximum) and it suddenly decreases below this temperature.

Analogous differences in behaviour of the TTT-TCNQ system as compared with the TTF-TCNQ system are observed also for m.w. conductivity measured at 4.6 and at 23.5 GHz, as illustrated in Fig. 2. For each system the plots obtained at different frequencies are very similar. We should also remember that it is difficult to compare the absolute values of the conductivity for a given system obtained from independent experiments at different frequencies. In fact, it was found from the investigations of the PC + 1 wt.% TTT-TCNQ system that in the range between d.c. and 20 GHz some frequency dependence is observed only around 1 GHz. It is seen in Fig. 3 that in this range the conductivity increases $c.$ four times. These results indicate that between 4 and 20 GHz the room temperature conductivity is practically frequency independent. This means that for each system the plots in Fig. 2 obtained at different frequencies should be slightly shifted vertically towards each other, yielding practically two curves: one for the TTF-TCNQ system and another for the TTT-TCNQ system. Some small, but symptomatic, variations of $\sigma(T)$ with frequency for the system with TTF-TCNQ in the region of the conductivity maximum are shown in Fig. 6 and will be discussed later.

Although the m.w. conductivity at room temperature is only slightly higher than the d.c. conductivity, their temperature dependences differ very strongly. In Figs. 4 and 5 one can compare the Arrhenius plots for d.c. and m.w. (at 10.3 GHz) conductivity for systems having the same polymer matrix
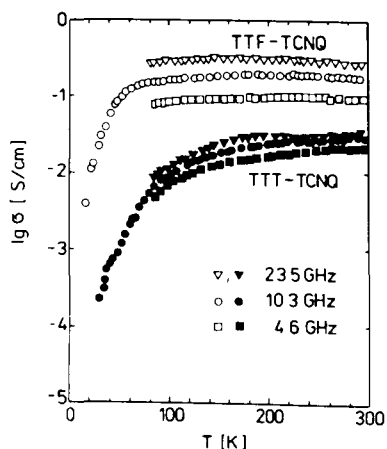

Fig. 2. Temperature dependences of the m.w. conductivity at different frequencies indicated in the Figure for polyethylene doped with 1 wt.% of TTF-TCNQ or TTT-TCNQ.
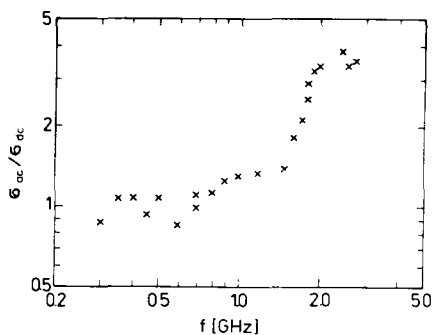
Fig. 3. Relative changes of the m.w. conductivity with frequency in the GHz range at room temperature for polycarbonate doped with 1 wt.% TTT-TCNQ.
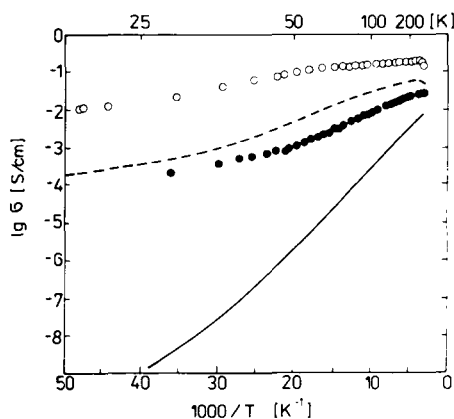

Fig. 4. Arrhenius plots of the m.w. conductivity at 10.3 GHz (circles) and of d.c. conductivity (lines) for polyethylene doped with 1 wt.% of TTF-TCNQ (open circles and broken line) or of TTT-TCNQ (full circles and full line).

(PE) but different CT complexes, and also systems having the same CT complex (TTT-TCNQ) but different polymer matrices (PE or PC).

For the system with TTF-TCNQ (Fig. 4), the m.w. conductivity plot has a kink at c. 55 K, above which the activation energy is very small (below 4 meV), the conductivity saturates and exhibits a weak maximum above 200 K (more pronounced in Arrhenius coordinates than in the plot shown in Fig. 1 for the same system). At lower temperatures one can distinguish two regions with different activation energies: c. 7 meV (25 - 55 K) and 4 meV (below 25 K). The plot for d.c. conductivity also has a sigmoidal character with a weak maximum at high temperatures. The estimated activation energy is c. 15 meV in the temperature range 45 - 100 K, c. 11 meV in the range 30 - 45 K and decreases to c. 4 meV below 20 K.
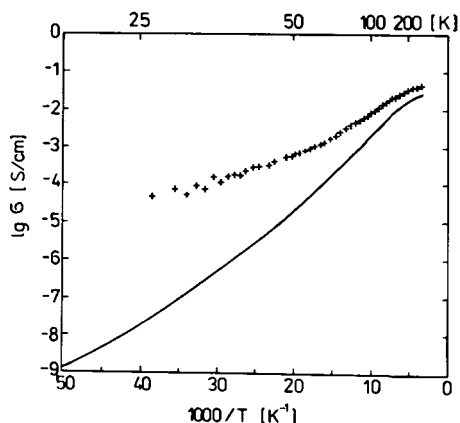
Fig. 5. Arrhenius plots of the m.w. conductivity at 10.3 GHz (crosses) and of the d.c. conductivity (line) for polycarbonate doped with 1 wt.% TTT-TCNQ.

For the system with TTT-TCNQ, for both PE (Fig. 4) and PC (Fig. 5) matrices, the log σ versus $1/T$ plots of d.c. and m.w. conductivities also exhibit a sigmoidal shape, but they are steeper and without any maxima. In spite of the fact that the room temperature conductivity of the PC system is higher than that of the PE system, the temperature dependences are very similar. M.w. conductivity saturates above 170 K; in the temperature range 50 - 170 K it has an activation energy of c. 18 meV for PE and 23 meV for PC, and below 50 K of c. 8 meV for PE and 13 meV for PC. D.c. conductivity saturates above 200 K; in the temperature range 40 - 170 K it has an activation energy of c. 40 meV and in the temperature range 25 - 40 K of c. 30 meV for both systems.

Figure 6 shows relative changes of d.c. and a.c. conductivity at different frequencies for the PE + 1 wt.% TTF-TCNQ system in the high temperature
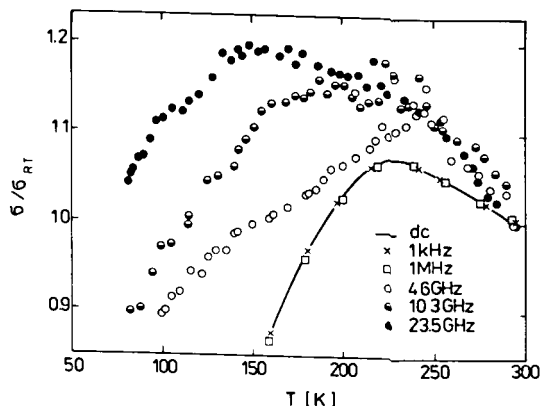

Fig. 6. Relative changes of d.c., a.c. and m.w. conductivities at different frequencies indicated in the Figure for polyethylene doped with 1 wt.% TTF-TCNQ.

region, where a maximum of conductivity has been observed. The differences between plots obtained for 4.6, 10.3 and 23.5 GHz, poorly visible in Fig. 2, are here better exposed because of an enlargement of the conductivity scale, in spite of a scattering of the experimental points. While a.c. conductivity up to 1 MHz shows the same temperature dependence as d.c. conductivity, with a weak maximum around 230 K [7], at microwave frequencies the maximum increases and shifts towards lower temperatures with increasing frequency.

4. Discussion

The structure of reticulate doped polymers (conducting crystals embedded in an insulating matrix) suggests that their electrical properties at m.w. frequencies could be described by two-phase models concerning the Maxwell–Wagner effect [11]. A simple approach to this problem, assuming that the mixture consists of an insulating matrix with low concentration of conducting, spherical inclusions, yields an expression for the relaxation frequency, f_r

$$f_r = \sigma_2/2\pi\varepsilon_0(2\varepsilon_1 + \varepsilon_2) \tag{1}$$

where ε_0 is the permittivity of the vacuum; σ is the conductivity; and ε is the permittivity of the components where subscripts 1 and 2 denote the matrix and the conducting filler respectively [11].

This model predicts that the conductivity increases continuously with increasing frequency as ω^2, starting from d.c. up to the f_r frequency, above which it is constant. Taking for our system PC + 1 wt.% TTT-TCNQ: $\sigma_1 = 0$, $\sigma_2 = 10$ S/cm [12], $\varepsilon_1 = 3$ and $\varepsilon_2 = 1000$ [13], one obtains $f_r > 1000$ GHz. Therefore, according to this simplest model for interfacial polarization, the conductivity should be frequency dependent as ω^2 over the entire investigated range. This is in obvious contradiction to the experimental findings for two main reasons: the conducting CT complex inclusions are long needles and not spheres; and the d.c. conductivity is not zero (in fact, it is quite high) because of the continuity of the conducting network.

More appropriate seems to be a model originally employed in a description of the dielectric relaxation behaviour of dislocations in semiconductors [14]. In this model a shape factor for the conducting phase is introduced and needle-like inclusions of different aspect ratios are considered. Additionally, by assuming a small conductivity for the matrix, non-zero d.c. conductivity is allowed. For such a system the conductivity with increasing frequency is initially constant (and equal to the d.c. value) up to some frequency and then increases as ω^2 up to the relaxation frequency f_{r1} given by

$$f_{r1} = D_{c\|}(1 - v_2)\sigma_2/2\pi\varepsilon_0\varepsilon_1 \tag{2}$$

where v_2 is the volume fraction of the conducting phase; $D_{c\|}$ is the depolarization coefficient for the direction parallel to the long axis of the inclusion with

length l and diameter d, which for $l \gg d$ is expressed by an approximation:

$$D_{c\parallel} = (d/l)^2(\ln 2l/d - 1) \tag{3}$$

For the PC + 1 wt.% TTT-TCNQ system, the relaxation frequency found experimentally is c. 2 GHz (Fig. 3); then, taking $\sigma_2 = 10$ S/cm, $v_2 = 0.01$ and $\varepsilon_1 = 3$, it is easy to show from eqns. (2) and (3) that the aspect ratio, l/d, should be of the order of 100. Recent results of electron microscope investigations for this system show that the CT complex forms very long, thin whiskers and their aspect ratio is very high [15]. Considering the increase of m.w. conductivity in the range 1 - 2 GHz (Fig. 3), assuming a $\sigma \propto \omega^s$ dependence, the value of s can be estimated only to lie between 1 and 3.5 because of strong scattering of the experimental points. However, taking into account that when the frequency increases twice (from c. 1 to 2 GHz) the conductivity increases approximately four times, the value $s = 2$, as predicted by the model, seems to be reasonable.

Two points should be discussed concerning the applicability of the present model to reticulate doped systems. First, the formalism has been elaborated for parallel oriented needle-like inclusions, while in the reticulate doped systems the CT-complex whiskers are randomly oriented. It was shown, however, that in the discussed model the needles oriented perpendicularly have a very slight influence on the conductivity, and the main contribution to the observed m.w. conductivity behaviour comes from the needles oriented along the electric field. This means that the effective content of the conducting phase active in the relaxation frequency range is lower than 1%, but it does not change the qualitative conclusions. Secondly, the low-frequency, constant conductivity is introduced into the model by an assumption of some low conductivity of the continuous phase. In reticulate doped systems, the polymer matrices are good insulators and high d.c. conductivity is assured by the continuity and high connectivity of the CT-complex network. It follows that this network could be visualized as a mixture of highly and poorly conducting bonds with different temperature dependences of conductivity. The highly conducting bonds give rise to the high-frequency relaxation, while the poorly conducting bonds control the d.c. conductivity behaviour, especially at low temperatures.

Other results presented in this paper are also consistent with such a picture. Temperature dependences of the m.w. and d.c. conductivities are independent of the polymer matrix but depend on the CT complex used, because they are determined by characteristic internal properties of the continuous conducting network. The observed much higher activation energies of d.c. conductivities as compared with m.w. conductivities (Figs. 4 and 5) result from an increasing number of poorly conducting bonds at lower temperatures. At a high enough frequency they are shunted and therefore they influence the m.w. conductivity much less than the d.c. conductivity.

The most spectacular results confirming the proposed model are presented in Fig. 6 for a system containing TTF-TCNQ. The behaviour of the

d.c. and low-frequency a.c. conductivity is essentially equivalent to that found for polycrystalline compaction of TTF-TCNQ [16]. The presence of many defective microcrystals causes smearing out of the conductivity maximum, which for perfect single crystals is very sharp and occurs below 60 K, as it is associated with the Peierls transition. However, for microwave conductivity above the relaxation frequency, because of capacitive coupling between highly conducting regions, the response of more perfect microcrystals becomes dominant, resulting in a maximum of the conductivity which is higher and shifted towards lower temperatures with increasing frequency. The slight kink visible in Fig. 4 in the Arrhenius plot of the m.w. conductivity of the TTF-TCNQ system at c. 55 K marks the metal–insulator transition of the most perfect microcrystals in the network.

Finally, we should like to point out that such $\sigma(\omega)$ behaviour as observed for PC + 1 wt.% TTT-TCNQ (i.e. dispersion at c. 1 GHz) could be also predicted by pair approximation or extended-pair approximation for transport in localized states, if one assumes a high enough state density and characteristic hopping frequency of the order of $10^{12}\,\mathrm{s}^{-1}$ (cf. Fig. 6 in ref. 17). Thus, this explanation would be similar to that proposed by Epstein *et al.* [18] for polyacetylene, that charge carriers are localized in states between which there is a fast transfer rate rather than large barriers. Therefore, a disorder within microcrystals would play a fundamental role in determining both the d.c. and a.c. conductivity behaviour while the crystalline network is continuous. This last statement is in fact analogous to the conclusion drawn from the previously discussed model.

5. Conclusions

Microwave conductivity measurements of reticulate doped systems demonstrate that, in spite of very low concentrations, the conducting phase forms a continuous network consisting of CT-complex microcrystals of different perfection. At room temperature the conductivity is frequency independent up to a relaxation frequency at c. 1 GHz. The m.w. conductivity behaviour at frequencies above the relaxation frequency bears the characteristics of the CT-complex crystals. Defects and disorder within the microcrystals constituting the conducting network play a fundamental role in determining the electrical properties of reticulate doped polymers.

Acknowledgement

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