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Dielectric response and a.c. conductivity of synthetic dopa-melanin polymer

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The dielectric spectra of dopa-melanin have been examined over the wide frequency range 100 Hz–1000 MHz at room temperature. Synthetic dopa-melanin was obtained by oxidative polymerization of *L*-3,4-dihydroxyphenylalanine. The purpose of the present study was to characterize polarization effects, the electrical conduction mechanism and structural arrangement of the units taking part in these processes as a basis for future biological applications. Real and imaginary components of the dielectric permittivity show an anomalous low-frequency dispersion. Values of the power-law exponents were interpreted in terms of the cluster model of potentially mobile charges and the structural arrangement of molecular units in melanin. The fractal circuit model (self-similar branched porous electrode system) was found to be equivalent to the cluster model in the description of the dielectric response in melanin. It has been shown that relations between cluster model parameters *p* and *n*, and fractal dimensionalities of melanin, are fulfilled very well. The presented results support the earlier findings based on d.c. conductivity measurements, that charge hopping is the main conduction mechanism, which contributes to the dielectric polarization in the low-frequency region. Dielectric spectra at frequencies above 10MHz show small β-relaxation features due to molecular polar segments and water molecules bound to melanin.

1. Introduction

The unique electronic properties of conducting organic polymers have attracted widespread research in their use as electroactive materials for different applications, including molecular electronics as well as biomaterials. Melanins are known as organic amorphous semiconducting biopolymers with important physico-chemical properties, including easy formation of charge-transfer complexes, strong cation binding, stable radical properties, phonon–photon coupling and wide spectral absorption [1–4]. Recently, it has been proposed to use melanin-containing hydrogels as biomaterials suitable for the manufacture of soft artificial intraocular lenses [5]. Williams *et al.* [6] reported a new class of site-specific magnetic resonance contrast agents containing gadolinium incorporated into an *L*-dopa melanin polymer. Semiconductor properties of melanin reported by many authors [7–10] and results of the electron exchange processes in the electrochemically deposited poly(5,6-dihydroxyindole) melanin film [11] have suggested that melanin polymer can be useful as a type of culture substratum. Studies performed on polypyrrole films showed that it was possible externally to change its properties and surface binding characteristics reversibly by using an applied electrical potential [12]. It has been found, that polypyrrole films can be useful as substrates for cell cultures, because their electroactivity provides a way to change reversibly their oxidation state and hence cell–substrate interaction.

Possible future applications of melanin polymer need detailed structural and charge-motion characteristics. Despite intensive investigations, the molecular structure and conduction mechanism in melanin have not been satisfactorily explained.

Melanins are polymers derived from the oxidation of such precursors as tyrosine, 3,4-dihydroxyphenylalanine (dopa), catecholamines or catechol [13, 14]. It has been shown that some or all of the intermediates in the eumelanogenesis pathway, e.g. dopa, dopaquinone, dopachrome, indole-5,6-quinone, can be incorporated into the final polymeric product [15, 16].

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However, it is usually assumed that the indole-5,6-quinone is the main monomeric unit [17]. As a result, a heteropolymer of irregular structure with the inability to be crystallized and chemical insolubility, is formed.

The presence of natural melanins in both illuminated (skin, hair, eye) and non-illuminated (substantia nigra of the brain, stria vascularis of the cochlea) areas, indicates that their biological function is not restricted to the photoprotective action only. Melanins are present in living organisms as granules containing a genetically determined amount of protein. In this study we have restricted the analysis to synthetic melanin obtained by autoxidation of *L*-3,4-dihydroxyphenylalanine. Previous studies on synthetic dopa-melanin have shown that its main structural and physical properties are very close to those of natural eumelanin [2].

It has been established that the d.c. conductivity of dopa-melanin strongly depends on the water content in the polymer structure [10]. In vacuum, where the humidity of melanin reaches a minimum value, the conductivity is of the order of 10^{-13} S cm^{-1} and rises as the temperature is increased, with an activation energy of about 0.7 eV. Thermopower measurements showed the p-type conductivity and the ability to maintain the polarized state induced by the temperature difference [18].

Polaron hopping as a possible charge-transport mechanism has been proposed on a basis of the d.c. conductivity and electron spin resonance (ESR) measurements performed on synthetic dopa-melanin doped with Cu^{2+} ions [9].

In this work, we studied the a.c. dielectric properties of melanin polymer over the wide frequency range 100 Hz–1000 MHz. Dielectric spectroscopy can provide information on the structural arrangement of the molecular units in the polymer, as well as on the electrical conduction mechanism. On the other hand, melanin exists as an organic semiconductor in biological systems and its response to the alternating electric field has not been investigated before. Kirkpatrick *et al.* [19] have reported results of melanin–water–ion dielectric interactions performed on aqueous melanin suspensions at different pH. They concluded that the high dielectric constant was due to a collective interaction between melanin, water and ions, so the dielectric response of melanin polymer alone was not investigated.

2. Experimental procedure

2.1. Preparation of synthetic dopa-melanin

Synthetic dopa-melanin was obtained by oxidative polymerization of *L*-dopa (*L*-3,4-dihydroxyphenylalanine, Reanal Hungary). The solution of *L*-dopa in tris-HCl buffer (0.005 mol l^{-1}, pH = 7.4) was aerated at 22 °C for 72 h. After acidification with concentrated hydrochloric acid to a final pH of 2.0, the precipitated melanin was separated by centrifugation (1500 g, 20 min). The melanin sediment obtained was washed with distilled water until it yielded a negative chloride reaction, and then it was dried over phosphorous pentoxide.

2.2. Dielectric measurements

Powdered and dried melanin was pressed at 500 MPa into pellets 0.7–1 mm thick and 5 or 10 mm in diameter, at room temperature.

Measurements were performed using two impedance analysers: a HP 4192A impedance analyser in the frequency range 100 Hz–10 MHz and a HP 4191RF impedance analyser in the range 1–1000 MHz. We could not perform measurements at frequencies below 100 Hz, because this fell outside the recommended capacitance range of the dielectric test fixture HP 16451B. In the high-frequency range, the coaxial test chamber was used, where the sample pellet was a part of the inner conductor of the measurement cell. Before measurements, circular electrodes were painted on both sides of the sample using conductive silver paint.

The measured values of capacitance, C, conductance, G, and susceptance, B, were used to calculate the conductivity as well as the real, ε', and imaginary, ε'', parts of the complex permittivity using the equations

$$\sigma = G(d/A) \tag{1}$$

$$\varepsilon' = C(d/A\varepsilon_0) \tag{2}$$

$$G/B = \tan\delta = \varepsilon''/\varepsilon' \tag{3}$$

where A is the electrode area and d is the thickness of the sample.

3. Results and discussion

Fig. 1 presents real and imaginary parts of the complex dielectric permittivity versus frequency on a log/log scale for synthetic dopa-melanin in the frequency range 100 Hz–10 MHz. The real part, ε', has been diminished by the high-frequency dielectric constant, ε_∞, equal to ~ 9 at 1000 MHz. According to Fig. 1, both components decrease with increasing frequency in the range 100 Hz–10 MHz. Behaviour of this type, identified as anomalous low-frequency dispersion, has been found in a wide variety of materials with potentially mobile charges [20–23]. According to this model, the real and imaginary components follow the frequency dependence of the type

$$\varepsilon'(\omega) - \varepsilon_\infty \sim \varepsilon''(\omega) \sim \omega^{-p} \quad \text{for } \omega < \omega_c \tag{4}$$

$$\varepsilon'(\omega) - \varepsilon_\infty \sim \varepsilon''(\omega) \sim \omega^{n-1} \quad \text{for } \omega > \omega_c \tag{5}$$

where the exponents p and n can have values between 0 and 1, and ω_c is the crossover frequency, which indicates two regimes of relaxation at low ($\omega < \omega_c$) and high ($\omega > \omega_c$) frequencies.

To determine the power-law exponents p and n, we used the relations [24]:

$$(\varepsilon'(\omega) - \varepsilon_\infty)/\varepsilon''(\omega) = \tan((1-p)\pi/2) \quad \text{for } \omega < \omega_c \tag{6}$$

$$(\varepsilon'(\omega) - \varepsilon_\infty)/\varepsilon''(\omega) = \tan(n\pi/2) \quad \text{for } \omega > \omega_c \tag{7}$$

Fig. 2 illustrates the plot of $(\varepsilon' - \varepsilon_\infty)$ as a function of ε''. One can notice three distinct slopes of the curve. The slope 0.1 at low frequencies ($\omega < \omega_c$) corresponds

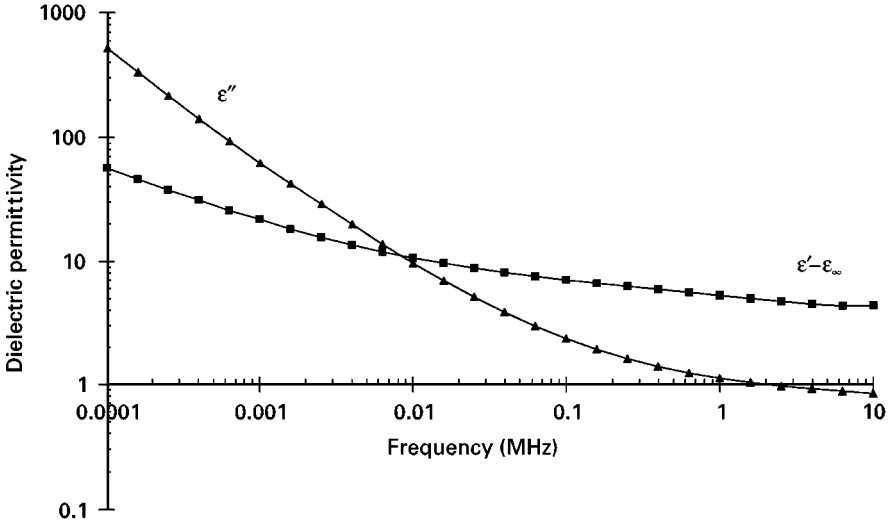

Figure 1 Real and imaginary parts of the complex dielectric permittivity versus frequency on a log/log scale for synthetic dopa-melanin. The crossover frequency is 8.5 kHz.

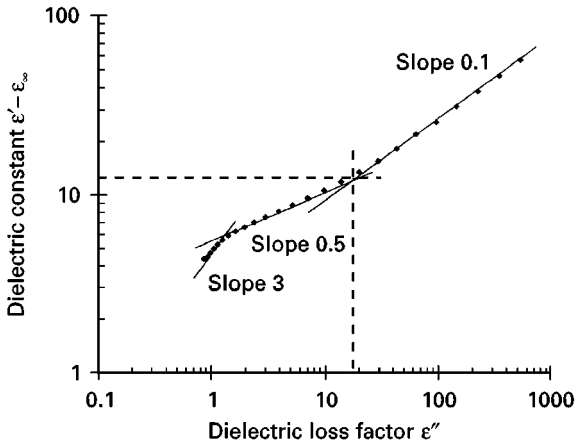

Figure 2 Plot of $(\varepsilon' - \varepsilon_\infty)$ as a function of the dielectric loss factor, ε'', for the determination of the exponents p and n according to the Equations 6 and 7. The straight lines represent the best linear fits to the experimental points. (– – –) Two frequency regions, $(\omega < \omega_c)$ with the slope of 0.1, and $(\omega > \omega_c)$ with the slopes of 0.5 and 3.

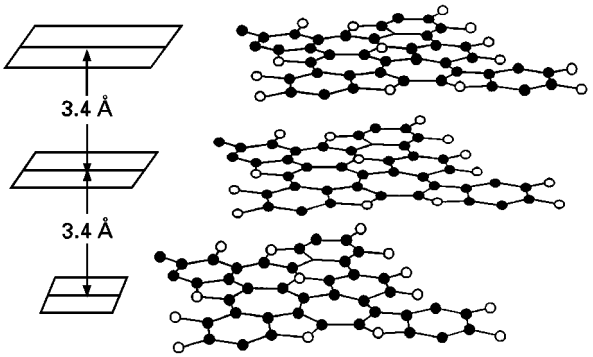

Figure 3 Three-dimensional molecular model of the melanin local structure as the three stacked sheets, according to Zajac *et al.* [17]. A single sheet is the random linkage of 5,6-indolequinone monomers.

to the exponent $p = 0.93$. The slopes 0.5 and 3 correspond to the two different values of the exponent n in the high-frequency region $(\omega > \omega_c)$, the values being 0.3 and 0.8, respectively.

According to the cluster model of the dielectric response [20] at high frequencies $(\omega > \omega_c)$ potentially mobile charges correlate their individual displacements to generate a coherent charge displacement identified as a polarized cluster. Two values of the index n obtained for synthetic dopa-melanin can be attributed to the formation of two different clusters as the frequency is changed. The low value of $n = 0.3$ indicates a highly irregular cluster with low correlation between charge movements. When the frequency is increased and the exponent n becomes equal to 0.8, high correlation between displacing charges occurs. The value near unity for $p(p = 0.93)$ in the low-frequency region indicates a quasi-d.c. process, in which charge movement between clusters takes place relatively freely with a large path length between jumps.

Recent results concerning the melanin structure can support the presented interpretation of the dielectric response. It has been established using X-ray diffraction techniques [15, 16] and scanning tunnelling microscopy [17] that in amorphous dopa-melanin local atomic arrangements take place, which account for the short and intermediate range order. These local structures consist of ~ 2 nm lateral extent and ~ 1 nm high stack of approximately three to four planar sheets composed mainly of indole-quinone monomer units with an interlayer spacing of about 0.34 nm (Fig. 3). Other monomers, such as dopa, dopaquinone and dopachrome can also be incorporated into the planar network. There is extensive π-delocalization within the individual polymeric sheets. According to Cheng *et al.* [16] melanin granules are clusters formed by such building blocks with alternate bonding across them to produce larger structures. We suggest that charge displacements are constrained to the finite-sized clusters of polarization by the existence of both planar structures and three-dimensional stacking of the layers.

Melanin granules are porous aggregates formed in the colloidal melanin suspension upon reducing pH. Huang *et al.* [25] used light-scattering techniques to

study the dynamics of the aggregation. They found a fractal structure of aggregates and two regimes of aggregation, one corresponding to the diffusion-limited aggregation with fractal dimension of $d_s = 1.8$ and the other one corresponding to the reaction-limited aggregation with fractal dimension of $D_p = 2.2$.

Analytically solvable fractal circuit models, e.g. the self-similar branched porous electrode system, are found to be equivalent to the cluster model [26]. According to this model, the clusters are to be taken as the internally self-similar pores and the cluster distribution refers to the fractal arrangement of the pore cross-section. This seems to be the correct way to describe the fractal regimes of relaxation in melanin.

Assuming that d_s is related to the surface dimensionality of the pore system in melanin, and according to the porous electrode model, we can express the index p as follows [26]

$$p = |1 - d_s| \tag{8}$$

For melanin, p and d_s are equal to 0.93 and 1.8, respectively, so that equation 8 is fulfilled quite well.

In the high-frequency limit ($\omega > \omega_c$), the index n can be expressed by the relation [26]

$$n = 3 - D_p \tag{9}$$

where D_p is the fractal dimensionality of the internal pore surface. Taking $D_p = 2.2$, we found that $n = 0.8$, which is in very good agreement with one of the indexes, n, obtained from the dielectric response. On the basis of the recent data concerning the fractal nature of melanin, it is difficult to interpret the second value of the index $n = 0.3$. However, more than a single value of n is allowed in the fractal model of the low-frequency dielectric response [26].

Fig. 4 shows the a.c. conductivity, σ_{ac}, of melanin measured in the frequency range 100 Hz–10 MHz. The increase of σ_{ac} with frequency follows the Jonscher's power law [21, 27]

$$\sigma_{ac}(\omega) = b \cdot \omega^s \tag{10}$$

where b is a temperature-dependent parameter and s is an exponent varying in the range $0 < s < 1$. Presenting the data on a log/log scale, one can determine values of the exponent s by fitting straight lines to the appropriate portions of the plot. Taking into account the relation [21]

$$\sigma(\omega) = \sigma_{dc} + \sigma_{ac} = \sigma_{dc} + \omega\varepsilon_0\varepsilon''(\omega) \tag{11}$$

where ε_0 is the permittivity of free space (8.85×10^{-12} F m^{-1}), we note that the dielectric indexes p and n calculated earlier correspond very well to the conductivity behaviour. In the low-frequency limit ($\omega < \omega_c$) the slope is equal to 0.1 and gives again a value of the index $p = 0.9$. In the high-frequency range ($\omega > \omega_c$), two slopes of the plot are attributed to the two values of the index n, 0.4 and 0.85, which are in good aggrement with the values obtained earlier.

The variable-range hopping model (VRH) involving interaction with phonons is the most frequently used conduction mechanism to interpret a variation of the a.c. conductivity proportional to ω^s with $s < 1$ [27]. Our results confirm the earlier findings from d.c. conductivity, according to which the VRH model can describe the motion of charge carriers in melanin [9, 10]. It is well established that charge hopping contributes to the polarization processes [20, 22]. For dopa-melanin, it seems to be the main mechanism involved in the dielectric response at low frequencies.

Measurements of the dielectric permittivity for synthetic dopa-melanin have also been performed at very high frequencies. Fig. 5 presents the dispersion curves of ε' and ε'' in the frequency range 4 MHz–1000 MHz. The dielectric loss factor ε'' shows two relaxation peaks at $\sim$15 and $\sim$600 MHz, respectively. The latter is very broad and probably consists of several overlapping relaxation peaks. These peaks are probably attributable to the β-relaxation of molecular polar segments in an externally applied field, without a change in the orientation of the whole macromolecule. For dopa-melanin, dipole moments can be

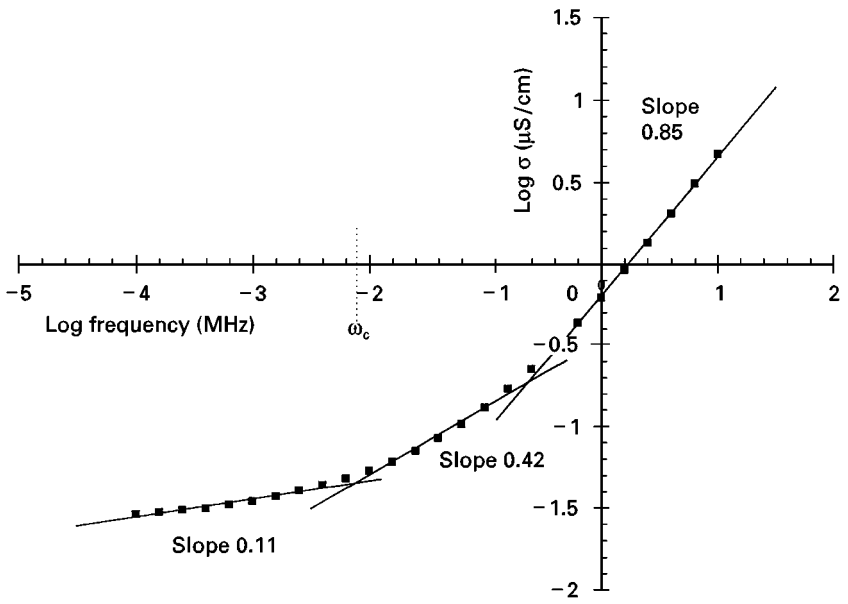

Figure 4 Frequency-dependence of conductivity for synthetic dopa-melanin on a log/log scale. (——) The best linear fits to the appropriate portions of the log/log plot. (– – –) The position of the crossover frequency, ω_c.

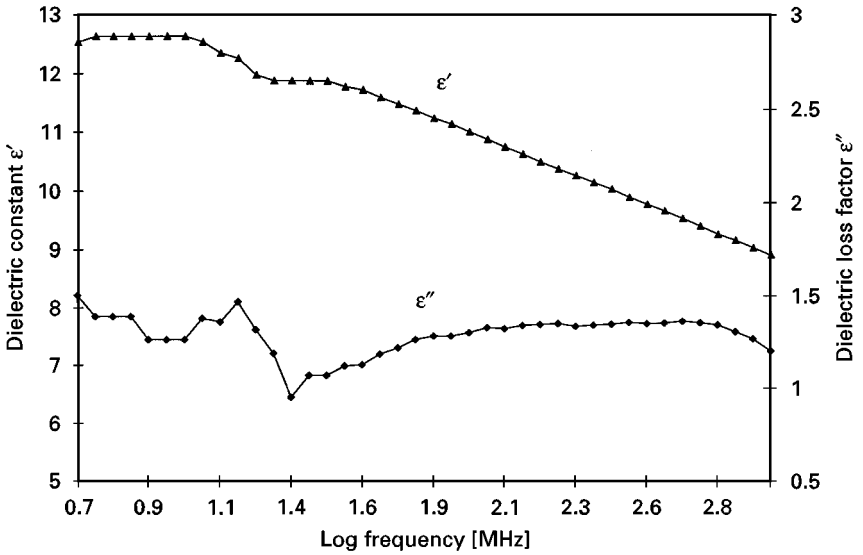

Figure 5 Dispersion curves of the real and imaginary parts of the dielectric permittivity in the frequency range 4 MHz–1000 MHz for synthetic dopa-melanin.

associated with hydroxy and carboxy groups bound to the most common monomer units present in melanin, such as 5,6-dihydroxyindole or dopachrome. Such orientation processes usually have a wide distribution of the relaxation time values and the corresponding dielectric loss is therefore smaller and of much wider frequency range than in the case of small molecules. The broad peak at ~ 600 MHz seems to be attributable also to the relaxation of water molecules bound to melanin. According to the spatial model of the melanin structure mentioned earlier [15–17], it has been postulated, that water molecules can be present between the layers composed of the planar monomer units and form water bridges or hydrogen bonds between carboxy, hydroxy and amino groups of melanin. The measurements of Rayleigh scattering of Mössbauer radiation [2] performed on dried pressed synthetic dopa-melanin pellets indicate that water molecules bound to melanin have a relatively high mobility.

4. Conclusions

The presented analysis of the experimental data has demonstrated that synthetic dopa-melanin shows anomalous low-frequency dispersion and the cluster model of potentially mobile charges provides a good description of the dielectric response. Recent results concerning the melanin structure support the interpretation of the dielectric behaviour. It has also been found, that relations between the cluster model parameters p and n and fractal dimensionalities expressed on the basis of the self-similar branched porous electrode system, are fulfilled very well for dopa-melanin. These results provide one additional piece of evidence of the fractal nature of the cluster model dielectric relaxation. According to the earlier findings from d.c. conductivity measurements, charge hopping is proposed to be the main conduction mechanism, which contributes to the dielectric polarization in the low-frequency region.

These results may contribute to the research effort in the field of conducting organic polymers with respect to the possibilities of using them as the biomaterials for culture substratum, as well as possibly assisting in the studies of the influence of radio frequencies on the melanin polymer in biological systems.

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