Beer's law and the Isosbestic Points in the Absorption Spectra of Conductive Polymers

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Beer's law and linear superposition of absorption spectra are known to be valid in dilute solutions. In this work it is shown with two examples that in a condensed phase conducting polymers are subject to the frequency-dependent local field of lightwave, also called dielectric effect, which influences the absorbance, the position of the absorption maximum, and the band width. The consequence is the apparent nonlinear behavior of absorption spectra and disappearance of isosbestic points in two-component systems. If the refractive index and absorbance as the function of wavelength are available, an appropriate correction can be made by using the Lorentz−Lorenz approximation for the local field. A nearly complete recovery of the isosbestic point is observed in the case of poly(3-methylthiophene) by using this local field approximation, casting some doubts on the conclusions previously drawn on the basis of these spectral data.

Introduction

In recent years electroactive polymers have attracted considerable attention in the literature due to the wide range of both potential and sometimes even practically realized applications of these materials in various devices based on electrochemical and spectroelectrochemical principles. Conductive polymers are conjugated, intensely light-absorbing macromolecular compounds with strong intermolecular interactions. Various optical phenomena such as thermochromism, solvatochromism, and electrochromism have been observed in these materials and explained by changes in the molecular interactions, conformations, and redox states. Correspondingly spectroscopic and spectroelectrochemical properties of conductive polymers are widely discussed in literature. One of the most significant characteristics of conductive polymers is their redox activity. In contact with a metallic conductor and electrolyte solution, the redox state of the polymer film can be changed by changing the potential of the metallic conductor vs. solution. A concurrent phenomenon is usually a very significant change in the optical absorption spectrum of the polymer film, which is the basis of many suggested applications of these materials. The electrochemical processes which cause these optical phenomena are known to be complicated and considerable efforts have been put forth for their studies. Polarons and bipolarons are assumed to be charge carriers in the oxidized polymer and their presence are claimed to be supported on the basis of different spectral methods as recently reviewed by Furukawa.[1]

Spectroelectrochemical investigation of electrochemically deposited thin films of conductive polymers on some transparent electrode material is a routine method when studying new polymers or redox mechanisms of "classical" polymers. In addition to the useful information obtained from the qualitative study of the set of absorption spectra recorded as the function of potential, quantitative information is considered to be obtained by studying the set of spectra as a linear manifold of vectors. The only assumption being the validity of Beer's law and the linear superposition of spectra, the number of independent light-absorbing species can be estimated from the number of basis vectors needed to span the entire experimental spectral vector set.[2] The method is an extension to the factor analytical method developed already nearly 30 years ago for dilute solutions of metal complexes.[3] If only two interchangeable species are present and their mutual proportions can be varied by varying a single parameter such as potential, pH, temperature, etc., one may expect the measured absorption spectra to intersect at one single wavelength, the isosbestic point, where the absorption coefficients of both species are equal. Hence, the existence of isosbestic points is a simple manifestation of Beer's law and the linear superposition of spectra. Very often the presence of an isosbestic point is observed also with thin films of conductive polymers when varying potential applied between the film and solution. However, equally often the spectra do intersect but not in a single point, and on this basis the presence of more than two species is customarily assumed. In dilute solutions this rationale is valid in most cases, but the message of this study is to show that when dealing with a highly absorbing condensed phase one should be more cautious when applying methods based on Beer's law and linear superposition of spectra.

It has long been recognized that the absorption of light by species in the condensed phase is significantly affected by electric field of lightwave. The importance of correcting spectra for this dielectric effect, particularly for strong bands, was emphasized and explained in detail by Bakhshiev and co-authors.[4,5] Although this effect has been reported to play an important role in many cases, such as molecules in solution,[6,7] liquid crystals,[8] and various Langmuir−Blodgett monolayers,[9−11] it seems that it has been largely neglected in the case of conductive polymers. Neglect of this factor may lead in many cases to misinterpretations in studies of spectra of conductive polymers. To show this, we consider the experimental data regarding poly(3-methylthiophene). The redox processes of this polymer are already a classical example of the polaron/bipolaron concept and these processes have been subjected to numerous studies where spectroelectrochemical methods have had a central role. In the present paper we shall show that the proper account of the dispersion of the effective field of the lightwave in a

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condensed medium helps to circumvent an incorrect interpretation of experimental data, such as the potential dependent shifts of spectral bands and the apparent nonexistence of the isosbestic point.

Theory

In discussing the effects of intermolecular interactions on molecular spectra in a condensed medium one should clearly distinguish between two separate phenomena.[5a,e] The well-known "medium effect" is usually considered as the effect caused by the different polarities of the ground state and excited state of a molecule and the consequent different energies of interaction with the media of different polarity. A typical example is solvatochromism[12] due to, for example, conformational changes induced by solvents on the molecule. The other phenomenon, which is much less known, is the local field effect of lightwave, also called dielectric effect. This is a purely physical phenomenon which does not involve any changes in the molecular conformation or short-range interactions. These phenomena can be further illustrated by the concepts of "true spectrum" and "observed spectrum". The true spectrum is connected with the energy level diagram of a molecule in a state with no external field. In this case the spectrum can be described by energy differences and corresponding Einstein coefficients of induced absorption $B(\nu)$. The first-mentioned medium effect is connected with the change of Einstein coefficients and energy levels with the change of medium. The latter phenomenon, the local field effect or dielectric effect, deals with the connection between the true and observed spectra (i.e., with the link between the Einstein coefficient $B(\nu)$ and the observed absorption coefficient $K(\nu)$). Although the theory has been presented before,[4,5] it is briefly presented also here in relevant parts.

The decrease in intensity of radiation as it penetrates a distance dl is proportional to I, the radiation intensity, and to the path length dl. Using the Lambert−Bouguer absorption coefficient $K(\nu)$ we may write

$$-\mathrm{d}I = K(\nu)I\mathrm{d}l \tag{1}$$

On the other hand, this can be expressed by using the Einstein coefficient:[13]

$$-\mathrm{d}I = B\rho h\nu N'\mathrm{d}l \tag{2}$$

Here N' is the number of absorbing species in a unit volume and ρ is the energy density (i.e., the energy per unit volume that is irradiated by the electromagnetic radiation of frequency ν). Equations 1 and 2 lead to an expression

$$B(\nu) = \frac{K(\nu)I}{\rho h\nu N'} \tag{3}$$

In gas phase we can simply write

$$I = c\rho \tag{4}$$

because I is the energy flowing through a unit cross section in a unit time with a velocity c. In a condensed medium the situation is different. The energy density ρ is proportional to the square of the amplitude of the electromagnetic field. Due to the polarization of the medium, the field which affects on the transition of a molecule is not the macroscopic average field $\mathbf{E}$ but the local or effective field $\mathbf{E}_{\mathrm{loc}}$. On the other hand, the rate of energy flow in a condensed phase is not the same as in vacuum but lower by a factor of n, the refractive index. In

order to preserve the general form of eq 3 we write

$$B(\nu) = \frac{K(\nu)c}{h\nu N'}\Theta(\nu) \tag{5}$$

where the correction factor $\Theta(\nu)$ is, according to the reasoning presented above

$$\Theta(\nu) = n(\nu)\left|\frac{\mathbf{E}}{\mathbf{E}_{\mathrm{loc}}}\right|^2 \tag{6}$$

The problem is now on the estimation of the local field $\mathbf{E}_{\mathrm{loc}}$.

The local field at any molecule inside the dielectric can be written as the sum of various contributions, such as the external field, depolarization field resulting from polarization charges on the outer surface of the specimen, polarization charges on the fictitious cavity around the molecule, and dipoles within the cavity. Various models have been devised for estimating the local field, the most common of them being the Lorentz−Lorenz model. This is the simplest model in which the shape, size, and polarizability of the light-absorbing species are neglected. In spite of its simplicity, the Lorentz−Lorenz model has been found to be quite adequate for estimating the local field in the case of strong absorption bands in condensed phases. In the present case, we have no real alternative because the microscopic parameters of the light-absorbing species, such as the size and polarizability, required for the more advanced models, are completely unknown for conductive polymers. The Lorentz−Lorenz equation relates the effective, local (or "internal") field $\mathbf{E}_{\mathrm{loc}}$ to the macroscopic field $\mathbf{E}$:

$$\mathbf{E}_{\mathrm{loc}} = \mathbf{E} + (4\pi/3)\mathbf{P} \tag{7}$$

Here $\mathbf{P}$ is the polarization of the dielectric:

$$\mathbf{P} = \frac{\hat{\epsilon} - 1}{4\pi}\mathbf{E} \tag{8}$$

where $\hat{\epsilon}$ $(= \epsilon' - i\epsilon'')$ is the complex dielectric constant.

Combining eqs 7 and 8 we have

$$\mathbf{E}_{\mathrm{loc}} = \frac{\hat{\epsilon} + 2}{3}\mathbf{E} \tag{9}$$

which gives with eq 6

$$\Theta(\nu) = \frac{9n(\nu)}{|\hat{\epsilon}(\nu) + 2|^2} \tag{10}$$

For the optical region we can use Maxwell's relation $\hat{\epsilon} = \hat{n}^2$, where $\hat{n}$ $(= n - i\kappa)$ is the complex refractive index. Equation 10 becomes then

$$\Theta(\nu) = \frac{9n}{(n^2 - \kappa^2 + 2)^2 + 4n^2\kappa^2} \tag{11}$$

This expression was derived by Bakhshiev et al.[5b] and later independently in a slightly different form by Clifford and Crawford.[14]

The relationship between the absorption index κ and absorption coefficient $K(\nu)$, is

$$K(\nu) = 4\pi h\nu\kappa(\nu) \tag{12}$$

By comparing eqs 5 and 12 we see that the function $\kappa(\nu)\Theta(\nu)$ is similar in the line shape to the spectrum of the Einstein coefficient $B(\nu)$. Hence the analysis of the dispersion of the
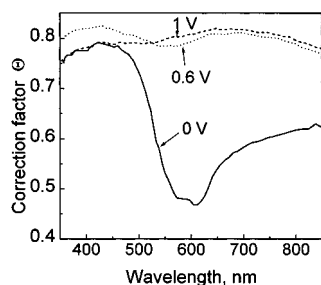
Figure 1. Calculated (eq 11) correction factors Θ for the reduced (—), partially oxidized (0.6 V, $\cdots$), and oxidized (1 V, $--$) film of poly-(3-methylthiophene). Experimental data for the refractive and absorption indexes from ref 15.

effective field of the lightwave can be carried out either on the basis of the correlation between $\kappa(\nu)$ and $\kappa(\nu)\Theta(\nu)$, or the correlation between the Lambert–Bouguer absorption coefficient $K(\nu)$ and its corrected value $K(\nu)\Theta(\nu)$.[4]

The correction of line shape for the dielectric effect has been made possible by the recent availability of spectroellipsometric data of certain conductive polymers.[15–17] In those cases when the corresponding spectroellipsometric data are presented in terms of ϵ' and ϵ'', the relations to n and κ are:[18]

$$\epsilon' = n^2 - \kappa^2 \tag{13}$$

$$\epsilon'' = 2n\kappa \tag{14}$$

For convenience from here on we use the representation of corresponding functions as related to wavenumbers ($\tilde{\nu}$, cm^{-1}) and wavelength (λ, nm).

Spectral Correction and Discussion

The Bakhshiev correction factor (eq 11) attains practically significant values only at high values of κ.[4] In this respect conjugated polymers are excellent examples for demonstrating the dielectric effect. The derivatives of polythiophene are thoroughly studied polymers and plenty of relevant data are available in the literature. Two examples of poly(3-methyl-thiophene) from the literature are taken, and the correction procedure for the dielectric effect is carried out in order to show that the effect is significant and cannot be ignored.

The spectroellipsometric investigation of poly(3-methylthio-phene) has been carried out by Chao et al.[15] The values of the complex dielectric function ϵ' and ϵ'' given in that work were used to calculate the corresponding values n and κ through eqs 13 and 14 and values of the correction factor $\Theta(\lambda)$ by eq 11. These data correspond to poly(3-methylthiophene) film doped at several potential values (vs. SCE) in acetonitrile solution of 0.2 M LiClO$_4$. Especially we consider the case of the film with the deposition charge of $Q = 13.6$ mC cm^{-2} (curves F of Figures 12–14 of the work[15]).

The calculated $\Theta(\lambda)$-functions for several oxidized states of the polymer are shown in Figure 1. One can see that for both highly and partially oxidized forms of poly(3-methylthiophene) (1 and 0.6 V) the correction factor $\Theta(\lambda)$ remains approximately constant, but for the reduced film (0 V) it exhibits significant dispersion. This dispersion leads to the difference between the experimentally observed spectrum $\kappa(\lambda)$ and the true spectrum (i.e., the one corrected for the dielectric effect $\kappa(\lambda)\Theta(\lambda)$) as it is shown in Figure 2. In the case of reduced poly(3-methyl-thiophene) the value of κ of the absorption maximum (533 nm) is significant and reaches a value 0.63. In line with this one can see from Figure 2 that the corrected $\kappa(\lambda)\Theta(\lambda)$-spectrum is different from $\kappa(\lambda)$-spectrum in all characteristics, such as the
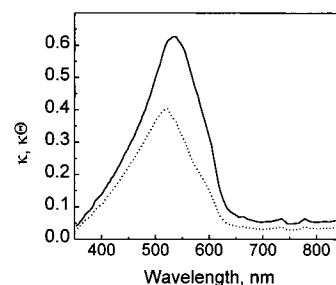

Figure 2. Experimental (—) and corrected ($\cdots$) absorption spectrum of reduced poly(3-methylthiophene). Recalculated experimental data have been taken from ref 15.

TABLE 1: Influence of Bakhshiev Correction on the Spectral Parameters of Reduced Poly(3-methylthiophene) Film

parameter	observed spectrum[a]	corrected spectrum
height of maximum	0.63	0.40
wavelength, nm	533	523
half-width, cm^{-1}	4980	5530

[a] Recalculated experimental data taken from ref 15.

height of maximum, the wavelength of maximum, and band half-width. The parameters of the spectra are given in Table 1. This example illustrates that the dispersion of the effective field of the lightwave has a profound influence in the case of line-shape analysis of intense absorption bands.

The mechanism of electrochemical oxidation of poly(3-methylthiophene) has been discussed in literature in a number of reports[19–21] and a number of important conclusions were based on UV–vis spectra, but yet without considering the influence of the local field effect. An example of spectra of poly(3-methylthiophene) (PMT), taken from an earlier work[20b] is given in Figure 3a. These data correspond to the absorbance changes of poly(3-methylthiophene)/ClO$_4^-$ film during anodic doping in acetonitrile solution. The original spectra have been modified by applying polynomial baseline subtraction and increasing slightly the spectral region. From the absorbance change during the electrooxidation of the polymer one can see a blue shift for the $\pi-\pi^*$ transition (and the reverse red shift during the reduction) and no isosbestic point. The lack of an isosbestic point is a fact of great importance, because it seemingly implies the coexistence of more than two kinds of species (i.e. the existence of two redox processes) that seems to support the polaron/bipolaron conception. Potential depend-ent shift of the $\pi-\pi^*$ transition was assumed to be connected with the participation of species with different effective conjugation lengths in the redox reaction.

Due to the paucity of experimental data, the system of a thin film of PMT was simulated by creating artificial data. The purpose is to show that by using reasonable values of param-eters, experimental results can be reproduced and conclusions can be drawn on the different effects on the band shapes and positions. Especially we are interested in the fate of the isosbestic point during the dielectric correction procedure.

Let us assume the Gaussian profiles for the "true" spectra of species (i.e., for the Einstein coefficient $B(\tilde{\nu})$ for each of two transitions). Since $\kappa(\tilde{\nu})\Theta(\tilde{\nu})$-function is similar in line shape to the spectrum of the Einstein coefficient, we can write:

$$\kappa(\tilde{\nu})\Theta(\tilde{\nu}) = xa_0 \exp(-d_0^2(\tilde{\nu} - \tilde{\nu}_0)^2) +$$
$$(1 - x)a_1 \exp(-d_1^2(\tilde{\nu} - \tilde{\nu}_1)^2) \tag{15}$$

Here the band centers are denoted by $\tilde{\nu}_0$ and $\tilde{\nu}_1$, and the line

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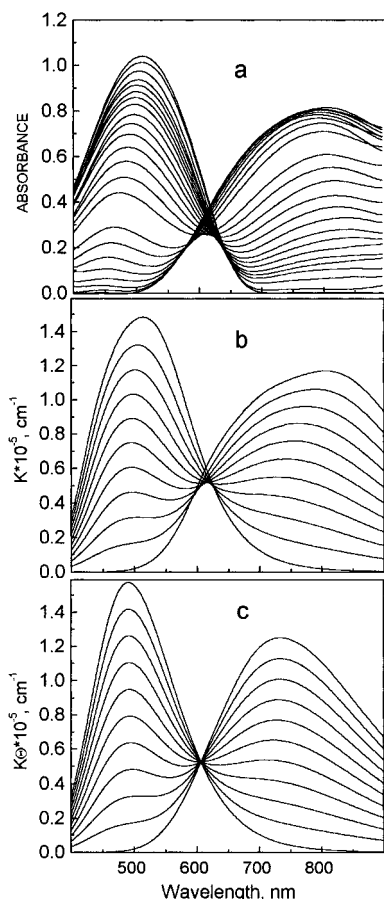*J. Phys. Chem. B, Vol. 102, No. 7, 1998* **1139**

Figure 3. (a) Spectral changes during the anodic doping of poly(3-methylthiophene) film in acetonitrile/tetrabutylammonium perchlorate. Experimental data taken from ref 20b subjected to polynomial base line subtraction. Simulated "uncorrected" (b) and "corrected" (c) absorption spectra corresponding to the anodic doping of poly(3-methylthiophene).

widths $\Delta\tilde{\nu}_{1/2}$ by $2\sqrt{\ln 2}/d_i$; a_0 and a_1 are parameters describing the intensities of the bands, and x is the fraction of the reduced species denoted by a subscript 0. It implies that during the electrooxidation process the value of x decreases and the corresponding fraction of oxidized species tends to unity. The system has an isosbestic point (Figure 3c).

To find the refractive index n as a function of frequency we apply the Kramers−Kronig (K−K) transform,[22] which relates the frequency variation of refraction with the frequency variation of absorption for any medium:

$$n(\tilde{\nu}) - 1 = \frac{1}{\pi} \int_{-\infty}^{\infty} \frac{\kappa(t)}{t - \tilde{\nu}} dt \qquad (16)$$

The lack of data for the refractive indices and their calculation by applying the K−K transform to the absorbance data is the main reason why we assume a functional form such as Gaussian for the experimental data. The K−K transform requires the infinite integration limits and this can be only achieved by assuming some functional form for the spectral shapes.

The problem of calculating the functions $\kappa(\tilde{\nu})$, $n(\tilde{\nu})$, and $\Theta(\tilde{\nu})$ is now completely defined by eqs 11, 15, and 16. Finally, by using eq 12, one can obtain the spectra of absorption coefficient $K(\tilde{\nu})$, assumed to correspond to the experimental data, and the spectra $K(\tilde{\nu})\Theta(\tilde{\nu})$ (i.e. the spectra corrected for the dielectric effect). This system of equations has been solved numerically by using the iterative procedure described in the Appendix.

By a proper choice of the parameters the calculated $K(\lambda)$-spectra (Figure 3b) and real experimental data presented in Figure 3a can be made very similar in their shapes (see Appendix). From the absorbance change during the simulated electro-oxidation of the polymer ($x \rightarrow 0$) one can see a blue shift for the 0-band (corresponding to the $\pi-\pi^*$ transition of poly-(3-methylthiophene)) and no isosbestic point in either cases. But the comparison of $K(\lambda)$-spectra (Figure 3b) and $K(\lambda)\Theta(\lambda)$-spectra (Figure 3c) reveals clearly that the spectral shifts and the lack of isosbestic point appear to be artifacts due to the dielectric effect. The corrected $K(\lambda)\Theta(\lambda)$-spectra show no band shift, and they have a clear isosbestic point. Hence the evidence for the presence of more than two species based on the lack of the isosbestic point is of very doubtful value unless the Bakhshiev correction for the dielectric effect is made. Although the present study is basically instrumental and not specifically devoted to the polaron/bipolaron problem, it may be said that the newly interpreted old experimental data[20b] do not support the presence of more than two redox species in partially oxidized poly(3-methylthiophene) within the potential region studied. This is in concordance with some other spectrochemical results[1] for polythiophene where the existence of bipolaron is questioned. On the other hand, more recent measurements at a wider potential range using not only voltammetry and spectroelectrochemistry but also in situ conductimetry and electrochemical quartz crystal microbalance support the presence of more than two electroactive species.[23]

Conclusions

There are several phenomena which may cause apparent deviation from Beer's law when measuring absorption spectra in a condensed phase. The main goal of this work is to emphasize the influence of one of these effects, the frequency-dependent local field. It is shown that on the basis of this effect certain apparent deviations from Beer's law and linear additivity of spectra can be explained without resorting to the presence of additional absorbing components. Hence the correction of spectra taken in a condensed phase is necessary in those cases where quantitative interpretation is attempted. The best instrument for spectral recording is a spectroellipsometer which allows to record in situ also refractive indices as a function of wavelength. In this case all the necessary parameters are available and the use of Kramers−Kronig transform is not needed. Although the present study is based on the elementary Lorentz−Lorenz approximation of the local field, surprisingly good conformity with the experimental data is obtained. It may well be that this is so far the best clear-cut experimental evidence on the applicability of the local field approximation and correction on the spectra in a condensed phase.

Obviously the phenomena discussed in this work are not restricted to conductive polymers. It is only that in these materials the dielectric effect is most strikingly manifested. Nor is the effect restricted within absorptiometric measurements. Equally well the spectral deformations due to the dispersion of the local field can be observed in the emission measurements, such as, for example, the electroluminescence of conductive polymers.

It is obvious that the consideration of the dispersion of the effective field of the lightwave is of fundamental importance in spectroanalytical studies of highly absorbing condensed materials. Especially in case of conductive polymers it is crucial to make the appropriate corrections along the lines described in this paper if any conclusions on the number of absorbing species are to be made on the basis of spectroelectrochemical measurements.

TABLE 2: Parameters Used for the Simulation of Spectroelectrochemical Data of Redox Processes of Poly(3-methylthiophene)

parameter	value
$\tilde{\nu}_0$, cm^{-1}	20000
$\tilde{\nu}_1$, cm^{-1}	13200
$\tilde{\nu}_{1/2,0}$, cm^{-1}	10500
$\tilde{\nu}_{1/2,1}$, cm^{-1}	9000
a_0	0.62
a_1	0.74

Appendix

Iterative Correction of Spectra. Let j be the number of some iteration step, and at this step let the set of $\kappa_j(\tilde{\nu})$-, $n_j(\tilde{\nu})$-, and $\Theta_j(\tilde{\nu})$-functions be known. For the fixed $\kappa(\tilde{\nu})\Theta(\tilde{\nu})$-profile, given by eq 15, the following simultaneous recurrence equations were used for the iteration

$$\kappa_{j+1}(\tilde{\nu}) = \frac{\kappa(\tilde{\nu})\Theta(\tilde{\nu})}{\Theta_j(\tilde{\nu})} \tag{A1}$$

$$n_{j+1}(\tilde{\nu}) - 1 = \frac{1}{\pi}\int_{-\infty}^{\infty} \frac{\kappa(t)\Theta(t)}{(t - \tilde{\nu})\Theta_j(t)}\, dt \tag{A2}$$

$$\Theta_{j+1}(\tilde{\nu}) = \frac{9n_j(\tilde{\nu})}{(n_j(\tilde{\nu})^2 - \kappa_j(\tilde{\nu})^2 + 2)^2 + 4n_j(\tilde{\nu})^2\kappa_j(\tilde{\nu})^2} \tag{A3}$$

Iteration was started at $j = 0$ and $\Theta_0(\tilde{\nu}) = 1$, $\kappa_0(\tilde{\nu}) = 0$, $n_0(\tilde{\nu}) = 1$. The iteration appeared to be convergent in no more than seven steps to produce the optical functions $\kappa(\tilde{\nu})$, $n(\tilde{\nu})$, and $\Theta(\tilde{\nu})$, fitting to the $\kappa(\tilde{\nu})\Theta(\tilde{\nu})$-profile given by eq 15.

Other parameters used in the calculation are given in Table 2. They were adjusted to reflect as far as possible the image of the real experimental spectra (i.e. band positions, half-widths, and their relative intensities (see Figure 3b)). The proper attention was given to fit the calculated values of κ for the 0-band close to the experimental κ-value 0.63 for reduced poly-(3-methylthiophene) as determined by Chao et al.[15]

All the calculations including the K−K transform were done by using the program Mathcad+ 6.0.

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