

# Studies on the Electronic Transport and Optical Properties of Some New Chelate Modified Polysulfones in Thin Films

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**ABSTRACT:** The studied polymers (chelate modified polysulfones) have been prepared by the polycondensation reaction between chloro-end-capped polysulfones and bis(2,4-dihydroxybenzaldehyde)Cu<sup>2+</sup> in the dimethyl sulfoxide/dichloromethane system, in the presence of an aqueous sodium hydroxide solution. The temperature dependence of electrical conductivity and Seebeck coefficient of the respective polymers was investigated using thin-film samples, deposited from chloroform solutions onto glass substrates. The polymers under study have typical semiconducting properties. The values of some characteristic param-

eters of the investigated polymers (for example, activation energy of electrical conduction, ratio of carrier mobilities, etc.) have been determined. The nature of the electrical conduction mechanism is discussed. The values of the optical bandgap energy are determined from the absorption spectra. © 2005 Wiley Periodicals, Inc. *J Appl Polym Sci* 99: 100–106, 2006

**Key words:** absorption spectra; activation energy; charge transport; conducting polymers; thin films

## INTRODUCTION

In recent years, the study of the electronic transfer mechanism in semiconducting polymeric materials has been the object of many investigations.<sup>1–4</sup> Usually, the experimental results have been interpreted in terms of various conduction mechanisms, such as band conduction, variable-range hopping conduction, model based on polaron formation, trapping model, and so forth.<sup>1,5–8</sup>

Semiconducting polymers are increasingly important for many solid-state devices (organic solar cells, sensors, photodetectors, etc).<sup>5,9,10</sup> A large number of these devices are at present made by using the polymers in thin film form (generally, their thickness being less than 5 μm).

It is well known that the structure, electronic transport, and optical properties of semiconducting films strongly depend on the deposition method and preparation conditions.<sup>4,7</sup> Therefore, it is important to establish experimental conditions for obtaining thin film samples with stable structure and reproducible properties.

In a series of previous articles,<sup>4,11–13</sup> we have studied the electrical and thermoelectrical properties of a

great number of polymers showing their semiconducting characteristics. In this article we extend these investigations on some recently synthesized chelate modified polysulfones.

Some correlations between chemical structure of the polymers and their fundamental parameters were established. The nature of the mechanism of electrical conduction is also discussed.

## EXPERIMENTAL

### Synthesis of the polymers

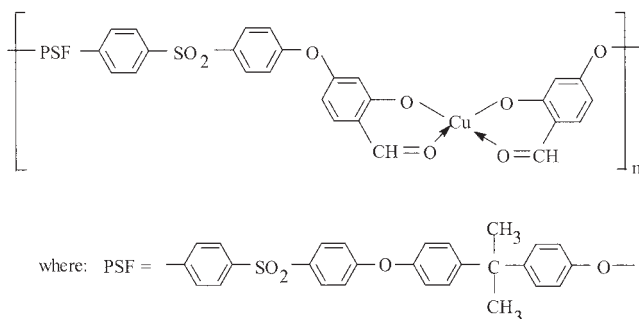
Chelate modified polysulfones were prepared by the polycondensation reaction between chloro-end-capped polysulfones and bis(2,4-dihydroxybenzaldehyde)Cu<sup>2+</sup> in the dimethyl sulfoxide/dichloromethane system, in the presence of an aqueous sodium hydroxide solution. The resulting polymers have lower values of the reduced viscosities than the chelate modified polysulfones previously obtained.<sup>14,15</sup>

The prepared polymers have the general formula shown in Scheme 1. Some characteristic parameters of studied polymers are listed in Table I. The preparation procedure of polymers has been described previously.<sup>14,15</sup>

### Sample preparation and measurements

The electronic transport properties of the polymers were investigated on thin-film samples deposited onto

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Scheme 1

glass substrates from chloroform solutions. The experimental conditions for obtaining samples with compact structure and uniform thickness have been described in detail in other articles.<sup>4,12,13</sup> During the film preparation, the substrates were maintained at approximately 325 K for a slow solvent evaporation.

The thickness of polymeric films (measured by an interferometric method<sup>12</sup>) ranged between 0.43 and 2.85  $\mu\text{m}$ .

The film resistance was measured with a digital electrometer (Keithley Model 6517) in a coplanar configuration with Ag (or In) electrodes (at an internal width of 2–3 mm and length 6–8 mm) evaporated onto substrate before the deposition of the polymeric films.

The measurements were performed by applying static electric fields of low intensity ( $E < 10^2$  V/cm). Under these conditions, the current-voltage characteristics are ohmic (Fig. 1).<sup>16</sup>

The Seebeck coefficient,  $S$ , was measured by using the method of thermal-probe electrodes.<sup>17,18</sup> Temperature difference between electrodes was of 8–10 K. The Seebeck voltage was measured with a Keithley Model 6517 electrometer.

Experimental details and methods of determining the characteristic parameters were described in our previous articles.<sup>4,11,12,16</sup>

TABLE I  
Reduced Viscosity, Softening Point and Glass Transition Temperature for Studied Polymers

Polymer	$\eta_{\text{red}}$ (dL/g)	Softening point (K)	$T_g$ ( $^{\circ}\text{C}$ )
PSU.RC1	0.298	515–547	428
PSU.RC2	0.165	479–492	430
PSU.RC3	0.277	464–466	440
PSR.13RC	0.174	465–475	445
PSR.11RC	0.171	419–422	444
PSR.09RC	0.115	438–453	434

Reduced viscosity ( $\eta_{\text{red}}$ ) of polymer solutions (0.2% w/v) at 300 K in N-methyl-2-pyrrolidone measured with a Ubbelohde viscosimeter.

Glass transition temperature ( $T_g$ ) determined by DSC measurements, with a rate of 20 K/min.

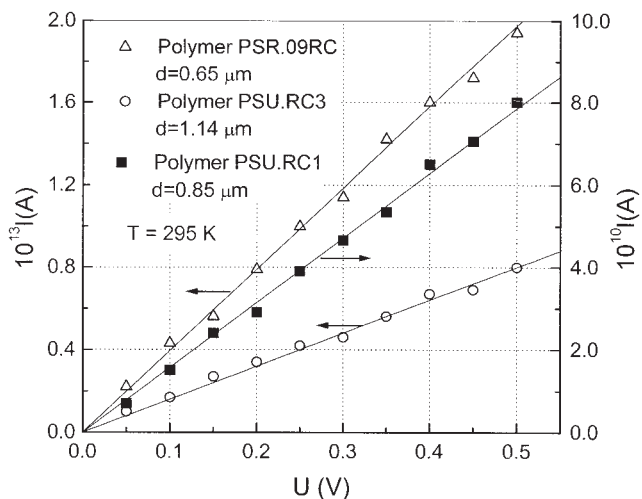


Figure 1 Current-voltage characteristics.

The reflection and transmission coefficient were recorded at room temperature using a PMQ-II type spectrophotometer and an ETA-STC spectrometer.

The absorption coefficient,  $\alpha$ , was calculated according to eq. (1)<sup>19–21</sup>:

$$\alpha = \frac{1}{d} \ln \left[ \frac{(1-R)^2}{T} \right] \quad (1)$$

where  $d$  is film thickness and  $R$  and  $T$  are reflection and transmission coefficient, respectively.

## RESULTS AND DISCUSSION

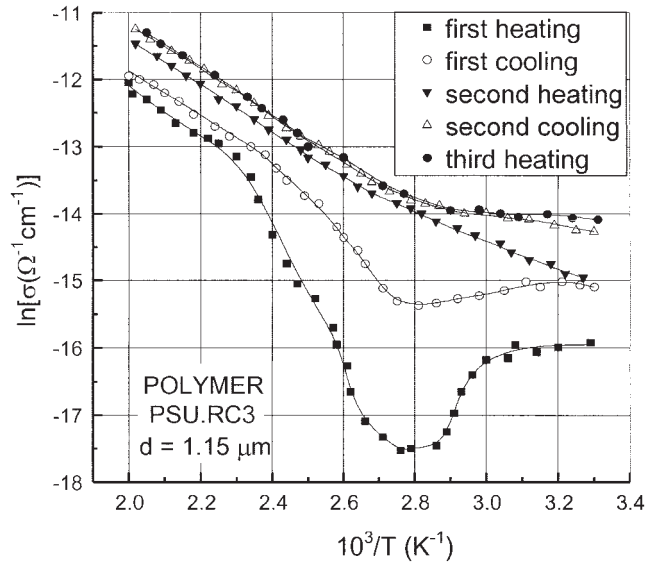
It was experimentally established that samples with stable structure can be obtained by submitting them, after preparation, to a heat treatment consisting of 2–4 successive heating/cooling cycles within a certain temperature range,  $\Delta T$ , characteristic for each polymer (Table I). The polymers show a good thermal stability in respective temperature ranges.<sup>14,15</sup>

Figure 1 illustrates the static current-voltage characteristics for heat-treated polymeric films measured at room temperature. It can be observed that these dependences are ohmic.

In our previous articles<sup>4,11,13</sup> related to the electronic transport properties of some polymers with similar molecular structure (chelate-modified polysulfones, aromatic polysulfones, etc.), we showed that the temperature dependence of the electrical conductivity,  $\sigma$ , can be written as<sup>6,7,22,23</sup>:

$$\sigma = \sigma_0 \exp(-\Delta E/2kT), \quad (2)$$

where  $\Delta E$  denotes the thermal activation energy of electrical conduction,  $\sigma_0$  is a parameter depending on the polymer nature, and  $k$  is Boltzmann's constant.



**Figure 2** Temperature dependence of the electrical conductivity during heat treatment.

Consequently, the shape of the  $\ln\sigma = f(10^3/T)$  dependences was studied for a large number of samples of different thicknesses.

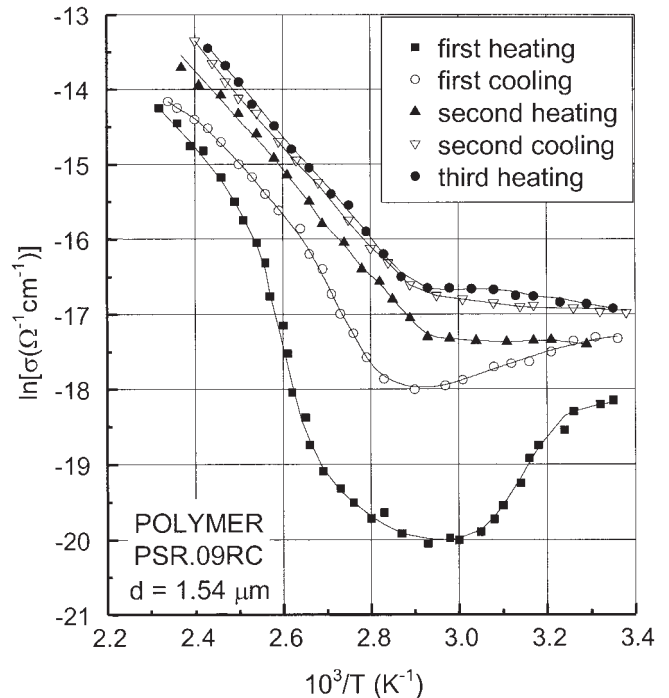
The analysis of the  $\ln\sigma = f(10^3/T)$  curves during the heat treatment provided valuable information on the processes taking place in the samples. The removal of adsorbed and/or absorbed gases, residual solvent molecules, and so forth (introduced during polymer synthesis and preparation of thin-film samples)<sup>4,11</sup> and also some structural changes in the polymeric films may occur during respective heat treatments.<sup>12,13</sup> These factors strongly influence the transport properties of organic polymers in thin films.<sup>24–26</sup>

In Figures 2 and 3, the typical temperature dependence of the electrical conductivity during the heat treatment are presented.

It can be observed that after the heat treatment, the temperature dependence of the electrical conductivity becomes reversible. This fact shows that the sample structure becomes stable in the respective temperature range.

The metallographic investigations showed that the polymeric films have a granular structure. Figure 4 shows an optical micrograph of the film surface, after the heat treatment, for a sample of polymer PSU.RC3. It can be observed that the film has a discrete microstructure. There are many large grains (probably formed in the film during solvent evaporation) limited by grain boundaries with small thickness and compact structure. In these conditions it can be assumed that grain boundaries have a small influence on the mechanism of electrical conduction.<sup>4,11,27,28</sup>

Figure 5 depicts the variation of dc conductivity,  $\sigma$ , with the reciprocal temperature,  $10^3/T$ , for six heat-treated samples.

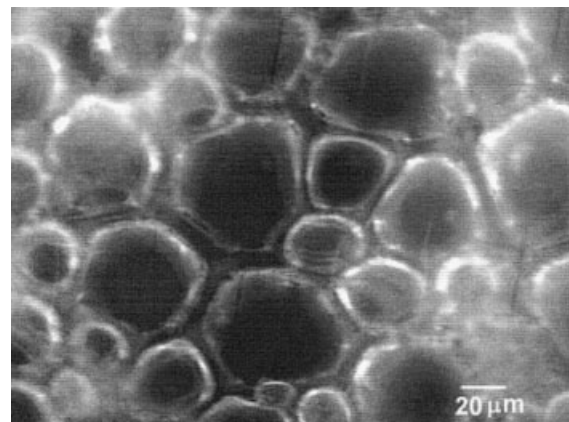


**Figure 3** Temperature dependence of the electrical conductivity during heat treatment.

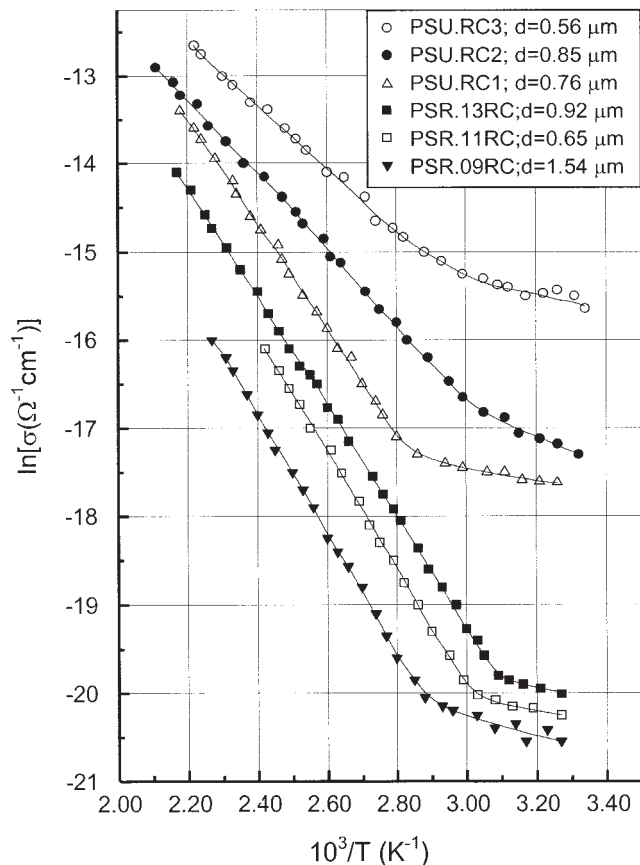
It is observed that  $\ln\sigma = f(10^3/T)$  dependences cannot be approximated by a single activation energy within the investigated temperature range. We suggest that the curves show that two types of mechanisms of electrical conduction contribute to the temperature dependence of electrical conductivity. These dependences can be expressed as a sum of activated mechanisms of the form<sup>23,24</sup>

$$\sigma = \sigma'_0 \exp(-\Delta E_{\text{imp}}/2kT) + \sigma_0 \exp(-\Delta E/2kT) \quad (3)$$

where the symbols have their usual meaning.  $\Delta E_{\text{imp}}$  is the thermal activation energy for the extrinsic conduction domain.<sup>6,23</sup>



**Figure 4** Optical micrograph of film surface for PSU.RC3 polymer ( $d = 1.55 \mu\text{m}$ ).



**Figure 5** Temperature dependence of the electrical conductivity after the heat treatment for six investigated samples.

The experimental data indicate that the thermal activation energy,  $\Delta E$ , calculated from the slope of these linear portions, are dependent on film thickness (Table II).

They are characterized by two distinct parts: a part with a smaller slope (within the lower temperature

range), where probably the extrinsic conduction is predominant, and a part with a larger slope (within the higher temperature range), where it may be supposed that the polymer possesses an intrinsic conduction. A series of experimental facts confirm this last supposition: the intrinsic conduction domain begins at a certain temperature  $T_c$  (characteristic for every sample), which, during heat treatment, shifts to the range of lower temperatures (this fact indicates a decrease in the concentration of impurities and structural defects in the sample); in the higher temperature range the slope of the  $\ln\sigma = f(10^3/T)$  curves remains practically unchanged, and so forth.<sup>4,13</sup>

The linearity of  $\ln\sigma = f(10^3/T)$  curves indicates that in the higher temperature range intrinsic conduction predominates and consequently, these dependences are described by eq. (2).

Taking into account eq. (2), the activation energy values  $\Delta E$  were calculated for the intrinsic conduction domain. These values are given in Table II. In this Table the values for other characteristic parameters of the respective samples are also listed.

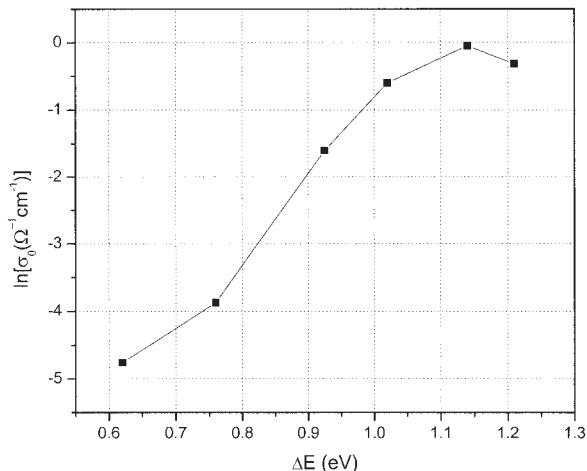
The semiconducting properties of the studied polymers are due to their molecular structure, which affords extended conjugation of the electrons in the polymer chain. Incorporation of chelate units into the polymer chain will lead to a decrease in flexibility of the backbone and, thus, will bring about the transfer charge carrier along the macromolecular chain.<sup>7,11</sup>

In the intrinsic conduction domain, according to the band model,  $\Delta E$  corresponds to the energy gap between the conduction band and the valence band. In the case of extrinsic conduction, thermal activation energy gives the distance of donor levels to the conduction band or of acceptor levels to the valence band. The observation of two values for thermal activation energy indicates the existence of those two mecha-

**TABLE II**  
Additional Characteristic Parameters for the Studied Polymers

Polymer	d ( $\mu\text{m}$ )	$\sigma_c$ ( $\Omega^{-1}\text{cm}^{-1}$ )	$\Delta T$ (K)	$\sigma_T$ ( $\Omega^{-1}\text{cm}^{-1}$ )	$T_s$ (K)	$\Delta E$ (eV)
PSU.RC1	0.76	$8.53 \times 10^{-9}$	300–463	$1.96 \times 10^{-8}$	354	0.93
PSU.RC1	2.05	$1.20 \times 10^{-8}$	300–460	$6.15 \times 10^{-8}$	365	0.92
PSU.RC2	0.85	$7.12 \times 10^{-9}$	293–475	$3.07 \times 10^{-8}$	335	0.76
PSU.RC2	1.64	$8.32 \times 10^{-9}$	296–465	$6.15 \times 10^{-8}$	342	0.74
PSU.RC3	0.56	$2.44 \times 10^{-8}$	300–454	$1.68 \times 10^{-7}$	340	0.62
PSU.RC3	1.15	$1.12 \times 10^{-7}$	300–458	$1.24 \times 10^{-6}$	350	0.60
PSR.13RC	2.25	$5.02 \times 10^{-7}$	296–455	$6.76 \times 10^{-6}$	355	0.63
PSR.13RC	0.92	$4.60 \times 10^{-10}$	300–465	$2.06 \times 10^{-9}$	328	1.02
PSR.13RC	1.86	$1.10 \times 10^{-9}$	295–460	$8.15 \times 10^{-9}$	333	1.00
PSR.11RC	0.65	$5.90 \times 10^{-10}$	300–415	$1.6 \times 10^{-9}$	338	1.14
PSR.11RC	1.26	$3.96 \times 10^{-10}$	296–415	$4.83 \times 10^{-9}$	340	1.12
PSR.09RC	0.62	$3.76 \times 10^{-10}$	300–444	$1.13 \times 10^{-9}$	347	1.22
PSR.09RC	1.54	$1.25 \times 10^{-8}$	293–435	$4.12 \times 10^{-8}$	345	1.20
PSR.09RC	2.10	$1.12 \times 10^{-8}$	300–440	$8.25 \times 10^{-8}$	348	1.20

d, film thickness;  $\sigma_c$  and  $\sigma_T$ , electrical conductivity at room temperature before and after the heat treatment, respectively;  $T_s$ , characteristic temperature for each sample;  $\Delta E$ , activation energy of electrical conduction.



**Figure 6** The dependence of  $\ln\sigma_0$  on the thermal activation energy  $\Delta E$ .

nisms of electrical conduction (intrinsic and extrinsic) in the different temperature ranges.

In a large number of investigations on organic semiconductors, a common interest is centered particularly on the nature of the pre-exponential factor,  $\sigma_0$ , in the standard eq. (2).

It is experimentally established that in many organic compounds,<sup>6,7,29,30</sup>  $\sigma_0$  varies exponentially with the activation energy  $\Delta E$  (or  $\Delta E/2k$ ):

$$\sigma_0 = \sigma'_0 \exp(\Delta E/2kT_0) \quad (4)$$

where the parameter  $\sigma'_0$  and characteristic temperature  $T_0$  (compensation temperature) are temperature independent.

Equation (4) indicates a linear relationship between  $\ln\sigma_0$  and  $\Delta E$ :

$$\ln \sigma_0 = \ln\sigma'_0 + \frac{1}{2kT_0} \Delta E \quad (5)$$

$$\ln \sigma_0 = \beta + \gamma\Delta E \quad (6)$$

where parameters  $\beta = 1/2kT_0$  and  $\gamma = \ln\sigma'_0$  depend on the individual classes of the compounds with similar molecular structure.<sup>6,29,30</sup>

Equation (6) shows the compensation effect (rule) in the electrical conduction mechanism and is verified by a large number of experimental data.<sup>29,30</sup>

The values of  $T_0$  (K) have been obtained from the  $\ln\sigma_0$  versus  $\Delta E$  plots. Equation (6) is verified by our experimental data (Fig. 6). For the class of investigated polymers, the parameters  $\beta$  and  $\gamma$ , calculated from the linear dependence presented in Figure 6, have the following values:  $\gamma = 8.5 \text{ eV}^{-1}$  and  $\beta = -9.9$ .

To obtain some new information on the mechanism of electrical conduction in the studied polymers, the

temperature dependence of the Seebeck coefficient,  $S$ , was investigated for a great number of samples. In Figure 7 are presented the  $S = f(10^3/T)$  curves for seven of them.

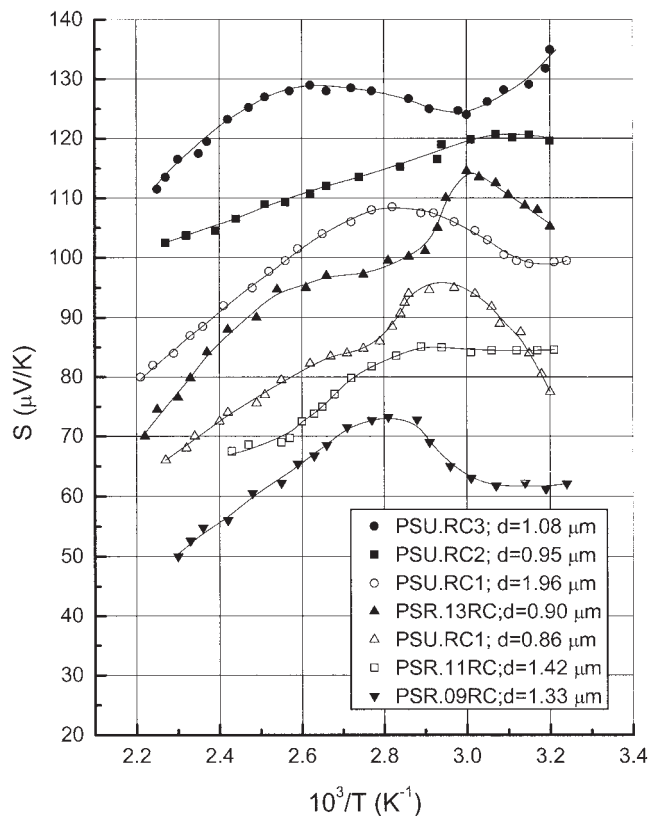
It is known that within the intrinsic domain, the temperature dependence of the Seebeck coefficient can be written in the following form<sup>17,23</sup>:

$$S = - \frac{k}{|e|} \left[ \frac{b-1}{b+1} \left( A_s + \frac{\Delta E}{2kT} \right) \right] \quad (7)$$

where  $b$  denotes the ratio of the carrier mobilities ( $b = \mu_e/\mu_h$ , where  $\mu_e$  denotes the electron mobility and  $\mu_h$  is the hole mobility),  $e$  is the electron charge, and  $A_s$  is the scattering factor depending on the nature of the carrier scattering mechanism that is predominant in the investigated samples.<sup>7,23</sup>

Equation (7) is deduced for a nondegenerate semiconductor with scalar effective masses of charge carriers.

According to eq. (7), the dependence of the Seebeck coefficient as a function of reciprocal absolute temperature must be linear. The Seebeck coefficient was found to be positive, and it can be observed from Figure 7 that the  $S = f(10^3/T)$  curves are linear in the intrinsic domain. Therefore, we may suppose that the



**Figure 7** Temperature dependence of the Seebeck coefficient for seven investigated samples.

TABLE III  
Some Characteristic Parameters of the Studied Polymers

Polymer	d ( $\mu\text{m}$ )	$\Delta E$ (eV)	$m_e/m_0$	b	$n_i$ ( $\text{cm}^{-3}$ )	$\sigma_i$ ( $\Omega^{-1}\text{cm}^{-1}$ )	$E_g$ (eV)
PSU.RC1	0.83	0.94	0.87	0.85	$5.03 \times 10^{13}$	$2.63 \times 10^{-7}$	—
PSU.RC1	1.96	0.92	-	0.75	$6.72 \times 10^{13}$	$3.74 \times 10^{-7}$	2.45
PSU.RC2	0.95	0.75	0.92	0.88	$7.90 \times 10^{14}$	$4.34 \times 10^{-7}$	2.00
PSU.RC3	1.08	0.63	0.85	0.68	$4.50 \times 10^{15}$	$1.37 \times 10^{-6}$	2.75
PSR.09RC	1.33	1.20	0.83	0.85	$1.16 \times 10^{12}$	$2.16 \times 10^{-8}$	2.56
PSR.11RC	1.42	1.12	0.90	0.90	$3.70 \times 10^{12}$	$8.76 \times 10^{-8}$	3.10
PSR.13RC	0.90	1.05	0.94	0.80	$1.02 \times 10^{13}$	$1.12 \times 10^{-8}$	2.90

$m_e$ , the effective mass of charge carriers ( $m_0$  is free electron mass); b, the ratio of carrier mobilities;  $n_i$  and  $\sigma_i$ , carrier concentration and electrical conductivity, respectively, at temperature  $T = 400$  K (where the polymers show an intrinsic conduction).

model based on band-gap representation could be suitable in the study of the electronic transfer mechanism through the investigated polymers.<sup>7,23</sup>

In this connection, some value of the characteristic parameters of the respective polymers have been estimated based on  $\ln\sigma = f(10^3/T)$  and  $S = f(10^3/T)$  dependences. The methods of determining these parameters are described in detail in other articles.<sup>4,11,29</sup>

The effective scalar masses of the charge carriers have been determined using static current-voltage characteristics for the thin-film sandwich system of the metal/polymer/metal type for higher values of intensity of the electric field ( $E \approx 10^5$ – $10^6$  V/cm).<sup>16</sup>

It can be observed from Table III that the values of b are lower than unity. Generally, for semiconductor materials,  $b > 1$ ; but for several inorganic semiconductors (PbSe, PbTe, etc.) and organic semiconductors (anthracene, pyrene, etc.), the b values are smaller than 1. This behavior can be explained by supposing that the conduction band of these compounds consists of two overlapping bands.<sup>31–33</sup>

An important semiconductor device based on the temperature dependence of electrical resistance is the thermistor, which is frequently used for measurements of temperature and radiation.<sup>18,34</sup>

The temperature dependence of the electrical resistance of a semiconductor material in the intrinsic conduction domain can be expressed as<sup>18,34</sup>:

$$R_T = R_\infty \exp(-B/T) \quad (8)$$

where  $R_T$  is the electrical resistance at absolute temperature  $T$ ,  $R_\infty$  is a parameter depending on the semiconductor nature ( $R_\infty$  formally denotes the resistance at  $T \rightarrow \infty$ ), and  $B$  is the temperature sensibility of the semiconductor ( $B = \Delta E/2k^{18}$ ).

The temperature coefficient of the resistance can be calculated from the formula<sup>18</sup>:

$$\alpha_T = \frac{1}{R} \frac{dR}{dT} = -\frac{B}{T^2} \quad (9)$$

The values of  $\alpha_T$  (at 375 K) and  $B$  are indicated in Table IV for some heat-treated samples. It can be seen from this Table that the studied polymers are advantageous in the technology of different types of thermistors.

By studying the optical properties (particularly reflection, transmission, and absorption spectra) of polymeric films, very useful information can be obtained about the energy gap, characteristics of optical transitions, and position of the localized energy levels.<sup>25,26,33</sup> In Figure 8 the transmission spectra, reflection spectra, and absorption spectra of one sample in the spectral range 400–1000 nm are presented.

For allowed direct transitions (neglecting exciton effects), according to Tauc's law,<sup>26,33</sup> the absorption coefficient,  $\alpha$ , near the fundamental absorption edge can be expressed as<sup>11–21,23,35</sup>:

$$\alpha h\nu = A_a(h\nu - E_g)^{1/2} \quad (10)$$

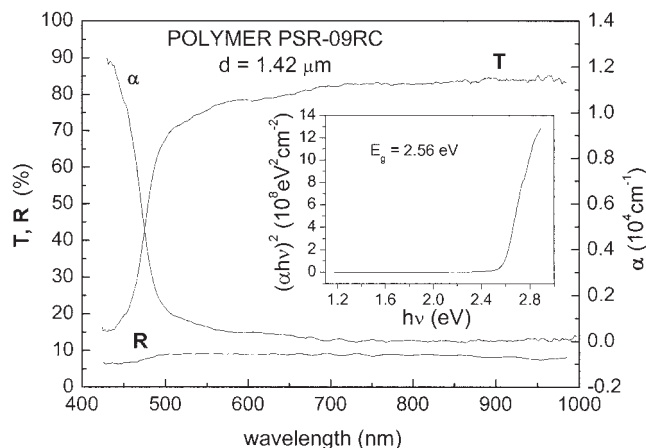
where  $h\nu$  denotes the photon energy,  $A_a$  is a characteristic parameter (independent of photon energy) corresponding to respective transitions, and  $E_g$  is the energy bandgap.

Equation (10) shows that  $(\alpha h\nu)^2$  linearly depends on the photon energy  $h\nu$ . Therefore, by extrapolating the linear portions of  $(\alpha h\nu)^2 = f(h\nu)$  curves to  $(\alpha h\nu)^2 \rightarrow 0$ ,

TABLE IV  
Film Thickness, Thermal Coefficient of Electrical Resistance, and Temperature Sensibility of the Studied Polymers

Polymer	d ( $\mu\text{m}$ )	$\alpha_T$ ( $\text{K}^{-1}$ )	B (K)
PSU.RC3	0.56	-0.025	3570
PSU.RC2	0.85	-0.030	4269
PSU.RC1	0.76	-0.042	5962
PSR.13RC	0.92	-0.044	6213
PSR.11RC	0.65	-0.047	6623
PSR.09RC	1.54	-0.048	6719

d, film thickness;  $\alpha_T$ , thermal coefficient of electrical resistance; B, temperature sensibility.



**Figure 8** Spectral dependence of transmission, reflection, and absorption coefficients.

the values of  $E_g$  can be determined (see the inset in Fig. 8). The evaluated values of  $E_g$  are listed in Table III.

It can be observed that these values are larger than those of the thermal activation energy,  $\Delta E$ , calculated from  $\ln \sigma = f(10^3/T)$  curves in the intrinsic conduction domain. This fact can be explained by taking into account the polycrystalline structure of the films.

## CONCLUSIONS

The results obtained by studying the temperature dependence of the electrical conductivity and the Seebeck coefficient (thermoelectrical power) can lead to the conclusion that the band conduction model could explain the electron transfer mechanisms through the investigated polymers in thin films.

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