

Conduction Mechanism in H-Type Polysiloxane–Polypyrrole Block Copolymers

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ABSTRACT: Conducting polymers of polysiloxane–polypyrrole were synthesized by electropolymerization of the pyrrole monomer through pyrrole moieties in *N*-pyrrole-terminated polysiloxanes. Sodium paratoluene sulfonate was used as the electrolyte. Scanning electron microscopy (SEM) was used to determine the surface morphology of the films. The room-temperature conductivity values of the films were found to be in the range of $1.9\text{--}4.4 \times 10^{-4} (\Omega \text{ cm})^{-1}$, depending on the supporting electrolyte concentration. The temperature dependence of the dc conductivities of the copolymers having different dopant concentrations was investigated within the temperature range of 100–320 K. The evaluated parameters showed that the electrical transport is dominated by variable range hopping. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 85: 52–56, 2002

Key words: conducting polymers; polypyrrole; conductivity; hopping

INTRODUCTION

Interest in electrically conductive polymers such as polyacetylene, polypyrrole (PPy), polythiophene, and polyaniline has been growing since the 1960s due to their potential applications in optoelectronics and microelectronics.^{1,2} The charge-transport mechanism in these conducting polymers is yet to be understood from various transport measurements.^{3,4} The common feature of these conducting polymers is the delocalized π electrons in their backbone. In particular, PPy is a polymer having nondegenerate ground states and charge transport occurs via polarons and, predominantly, bipolarons.⁵ The conduction process in doped PPy may follow $T^{-1/4}$ dependence

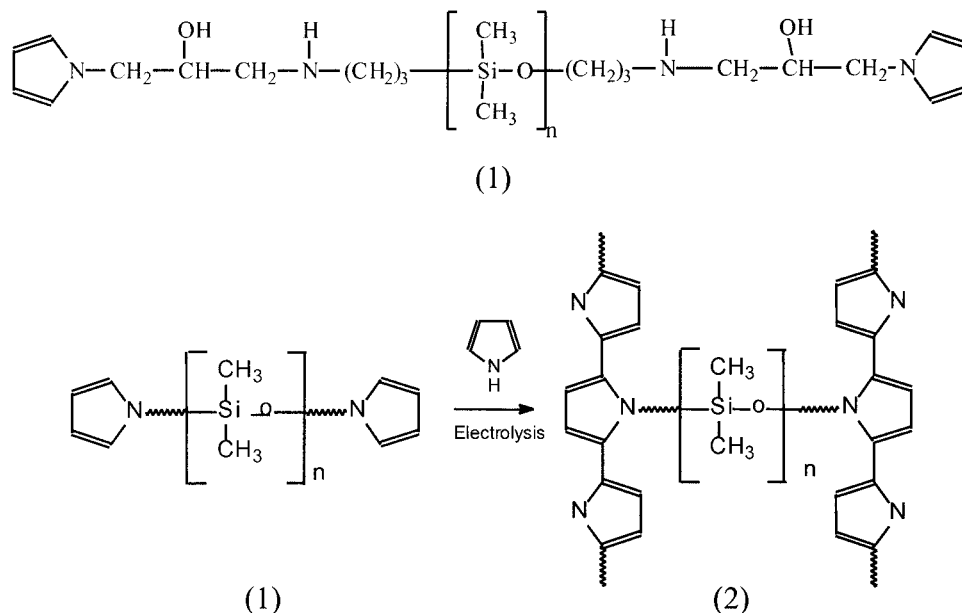
due to the hopping of carriers from localized states. Yet, the presence of blocks with no conjugation, that is, the insulating component of the block copolymer, may alter the conduction mechanism. If, however, the picture remains the same, this may as well be proof of a hopping process among the conductive blocks.

Pristine conducting polymers are insoluble and infusible materials and not quite suitable for device applications. Their processability has been improved by the synthesis of block and graft copolymers containing insulating and conducting sequences.^{6–10} Blending of conducting polymers with thermoplastic polymers is another attempt to modify their mechanical properties.^{11,12}

In this present work, we report on the temperature-dependent dc conductivity of paratoluene sulfonate-doped polysiloxane–PPy (**2**) copolymers (Scheme 1). Copolymerization was achieved by electropolymerization of the pyrrole monomer

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Scheme 1

through the pyrrole moieties present in the *N*-pyrrole-terminated polysiloxanes (1). Details of the synthetic part were explained in a previous article.⁶

EXPERIMENTAL

Pyrrole (Merck, Darmstadt, Germany) was distilled under nitrogen before use. Na-*p*-toluene sulfonate was used as received. The molecular weight ($M_n \sim 1200$) of the siloxane was found via both potentiometric titration and vapor-pressure osmometry.⁶ Block copolymer films of *N*-pyrrolyl-terminated polysiloxane and pyrrole were synthesized electrochemically at a constant potential of 1.1 V versus Ag^0/Ag^+ ($10^{-2} M$). A Wenking POS 73 potentiostat was used in the electrochemical polymerization. A three-compartment cell (50 mL) equipped with Pt foils (1.5 cm^2) as the working and counter electrodes and a capillary reference electrode (Ag^0/Ag^+) was used. The solvent-electrolyte couple was acetonitrile-Na-*p*-toluene sulfonate (PTSA).

A Pt electrode was coated with pyrrolyl-terminated polysiloxane which was previously dissolved in a CH_2Cl_2 (1% w/v) solution. Then, 0.03M pyrrole was introduced into the reaction medium and electrolysis was carried out at 1.1 V and room temperature under an inert atmosphere.

The supporting electrolyte concentration (PTSA) was adjusted to 0.125M in the electrolytic cell. After 2 h, the block copolymer films coated on

the Pt foils were peeled off as free-standing films. The films with different dopant concentrations were investigated by changing the concentration of the supporting electrolyte from 0.0625 to 0.0125M (from 1/2 to 1/10).

To deduce the electrical behavior of the films with respect to the supporting electrolyte concentration (SEC), temperature-dependent conductivity measurements were carried out on the copolymer films under a vacuum in the temperature range of 100–320 K using a Cryogenics closed-cycle helium cryostat. The temperature of the samples was controlled by a DRC-91C Lake Shore temperature controller. The electrical contacts were obtained using conductive silver paint and copper wires. Strip contacts were applied to both ends of the samples. For dc conductivity measurements, a Keithley 220 constant current source and a Keithley 619 electrometer were used. The thickness of all the samples was around 60 μm .

RESULTS AND DISCUSSION

Block copolymers (doped with PTSA) were washed in dichloromethane (which is the solvent for *N*-terminated pyrrolyl polysiloxane) to remove the unreacted polymer. The surface morphologies of the washed electrolytic films were investigated by scanning electron microscopy (SEM). The results of the electrode and electrolyte sites of the materials with low supporting electrolyte concen-

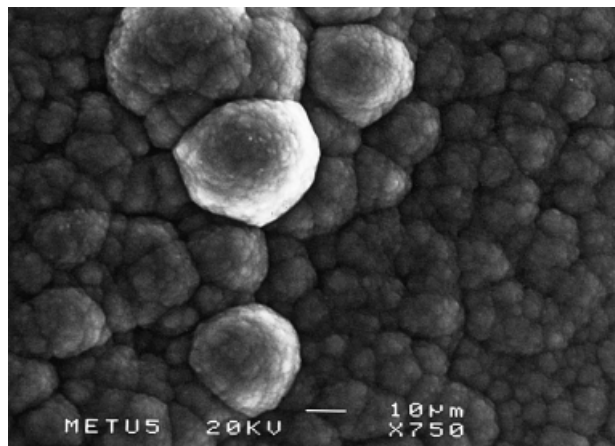


Figure 1 SEM pattern of the electrode and electrolyte sites of a typical sample.

trations are shown in Figure 1. The irregular granules at the solution side were crowded when the electrolyte concentration was decreased. The surface of the electrode side was very smooth in all cases.

To investigate the charge-transport mechanism in the obtained films, the temperature dependence of the electrical conductivity was studied in the range of 100–320 K for all samples. The room-temperature conductivity of the films listed in Table I decreased from 1.9 to 4.4×10^{-4} ($\Omega \text{ cm}$) $^{-1}$ as the SEC was decreased from $1/2$ to $1/10$. The variation of the room-temperature resistivity (ρ) with the SEC is illustrated in Figure 2. Resistivity is observed to increase with decreasing SEC according to the relation $\rho = Cx^{-b}$, where x stands for the SEC and b is the power factor. From the slope of $\text{Log } \rho - \text{Log } x$ variation (inset of Fig. 2), b was found to be around 5.

The polymer films investigated in this study are of an amorphous structure. In amorphous

Table I Room-temperature Values of Conductivity, Resistivity, and Activation Energy

Sample	SEC ^a	ρ ($\Omega \text{ cm}$)	σ ($\Omega \text{ cm}$) $^{-1}$	E_a (meV) (above 280 K)
A	1/2	0.52	1.90	15.4
B	1/4	61.0	1.6×10^{-2}	15.8
C	1/6	200.2	1.2×10^{-3}	30.6
D	1/8	903.3	1.1×10^{-3}	34.8
E	1/10	2288.0	4.4×10^{-4}	62.5

^a 1 refers to a 0.125M supporting electrolyte concentration.

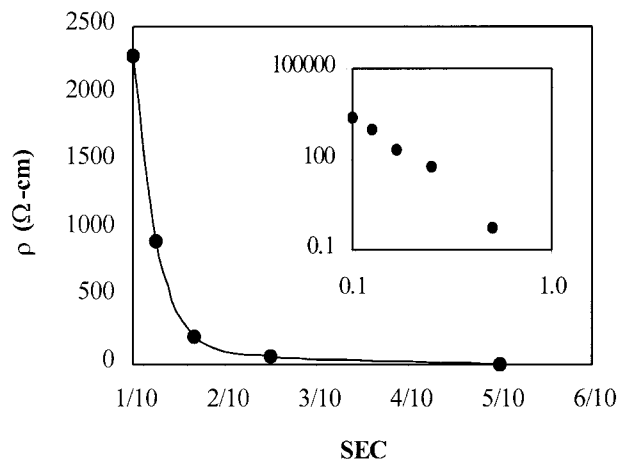


Figure 2 Variation of the room-temperature resistivity with respect to the SEC of the films. The inset shows logarithmic variation of the ρ -SEC dependence.

semiconductors, if the main conduction mechanism is due to the carriers excited beyond the mobility edge into nonlocalized or extended states (which tends to occur at high temperatures), the conductivity is expressed as¹³

$$\sigma = \sigma_0 \exp(-E_a/kT) \quad (1)$$

Here, σ_0 is the preexponential factor, and E_a , the activation energy of carriers and given by $E_F - E_V$ for this case. If the conduction is due to the excitation (hopping) of carriers into the localized states at band edges, the conductivity expression is then given by

$$\sigma = \sigma_1 \exp\{[-(E_F - E_1 + \Delta E)/kT]\} \quad (2)$$

where ΔE is the hopping activation energy, and E_1 , the band-edge energy. For the above two modes of conduction, the variation of $\text{Ln}(\sigma)$ against T^{-1} is expected to be a straight line. The conduction may also be due to carriers hopping between localized states near the Fermi level. Hopping can take place between nearest neighbors or to more distant sites (variable range hopping) which gives rise to the $T^{-1/4}$ dependence of the conductivity in three dimensions. The plots of the $\text{Ln}(\sigma)$ against T^{-1} for different samples are illustrated in Figure 3. The conductivity increased with the temperature for all samples, but the increase in conductivity is more pronounced for the films with a low doping concentration.

In general, the $\text{Ln}(\sigma) - T^{-1}$ variations are not linear in the whole temperature range, indicating

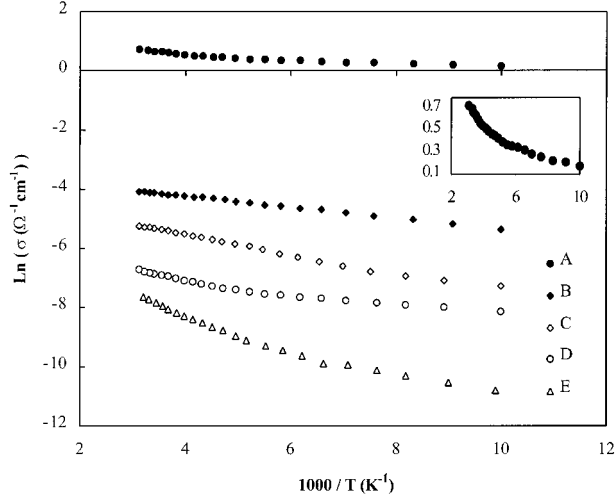


Figure 3 Conductivity–temperature variation of polysiloxane–PPy conducting copolymers with different SECs between 100 and 320 K.

the validity of the temperature-dependent activation energy as shown for a typical sample in the inset of Figure 3. The activation energy values calculated from the slopes of straight regions above 280 K are listed in Table I and were found to increase with decreasing SEC values. The non-linear behavior of the $\text{Ln}(\sigma) - T^{-1}$ variation, the presence of temperature-dependent activation energy with low values around room temperature, implies that the conduction due to the excitation of carriers into the mobility edge and/or to the localized states at the band edges is not adequate to explain the conductivity of H-type polysiloxane–PPy block copolymers.

The temperature-dependent conductivity data were thus analyzed according to Mott’s hopping mechanism.¹³ Since PPy is a polymer having non-degenerate ground states and charge transport occurs by polarons and, predominantly, bipolarons,^{5,14,15} such a mechanism is consistent with the existence of a high density of states in the band gap. Localization of the charge carriers may give rise to the formation of polarons and the charge transport may be considered due to the variable range hopping, for which the conductivity is expressed as

$$\sigma = \sigma_0 \exp[-(T_0/T)^{1/4}] \quad (3)$$

The preexponential factor σ^0 and the degree of disorder T_0 are related to the density of localized states $N(E_F)$ and wave-function decay constant α by the following relations^{16–18}:

$$\sigma_0 = e^2 a^2 \nu_{\text{ph}} N(E_F) \quad (4)$$

$$T_0 = [\lambda \alpha^3 / k N(E_F)] \quad (5)$$

where λ is a dimensionless constant (~ 18.1), ν_{ph} represents the phonon frequency ($\sim 10^{13}$ Hz),¹⁶ a is the hopping distance, and e and k have their conventional meanings. The other two hopping parameters, hopping distance R and the average hopping energy W , are expressed as

$$R = [9/8 \pi \alpha k T N(E_F)]^{1/4} \quad (6)$$

and

$$W = [3/4 \pi R^3 N(E_F)] \quad (7)$$

respectively. Using eqs. (6) and (4), then eq. (2) takes the form¹⁶

$$\sigma = \sigma_0 T^{-1/2} \exp[-(T_0/T)^{1/4}] \quad (8)$$

with $\sigma_0 = A[N(E_F)/\alpha]^{1/2}$ and $A = 3e^2 \nu_{\text{ph}} (8\pi k)^{1/2}$. To normalize the temperature dependence of the effective density of states, $\text{Ln}(\sigma T^{1/2})$ was plotted against $T^{-1/4}$. The plots are all linear in the whole temperature region and a typical plot is given in Figure 4. However, a good fit of the conductivity temperature data is a necessary but not sufficient criterion for the applicability of the Mott variable range hopping theory, that is, the hopping parameters should satisfy the Mott requirements. The Mott parameters T_0 and σ_0 are obtained from the slope and the intercept values of $\text{Ln}(\sigma T^{1/2}) - T^{-1/4}$ plots, respectively; then, $N(E_F)$, α , R , and W were successively determined using the appropriate relations.

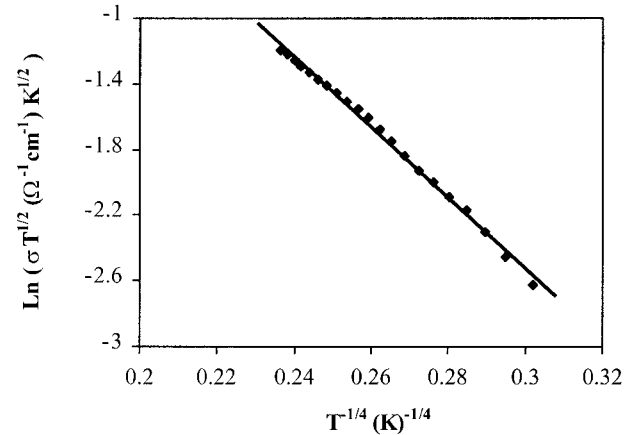


Figure 4 Plot of $\text{Ln}(\sigma T^{1/2})$ versus $T^{-1/4}$ for sample B.

Table II Calculated Mott Parameters

Sample	T_0 (K)	α (m^{-1})	$N(E_F)$ ($\text{eV}^{-1} \text{cm}^{-3}$)	R (m)	W (meV)	αR
A	9.63×10^4	4.32×10^8	3.76×10^{20}	3.04×10^{-9}	22.8	1.30
B	2.15×10^5	5.36×10^7	1.33×10^{17}	3.73×10^{-8}	34.7	1.99
C	1.35×10^6	8.50×10^8	8.50×10^{19}	3.72×10^{-9}	54.8	3.16
D	4.30×10^5	1.20×10^7	7.80×10^{14}	1.96×10^{-7}	40.8	2.35
E	4.72×10^6	2.27×10^9	4.58×10^{20}	1.91×10^{-9}	75.0	4.34

The calculated Mott parameters are given in Table II. The computed values of $N(E_F)$, the density of states at the Fermi level, are in the range of 10^{14} to $10^{20} \text{eV}^{-1} \text{cm}^{-3}$. The hopping parameters do not follow any systematic change with the supporting electrolyte concentration; however, they are found to satisfy the Mott requirements of $\alpha R \gg 1$ and $W \gg kT$ for the variable range hopping mechanism. When compared to the electrical conduction studies in amorphous materials^{16,19,20} and pristine PPy and its derivatives,^{21–23} we observed that the values of the Mott parameters for H-type polysiloxane PPy block copolymers are consistent with the hopping theory and the hopping parameters in the literature. Therefore, we conclude that in the studied temperature range conduction was predominantly provided by the Mott variable range hopping mechanism.

CONCLUSIONS

A novel conducting copolymer of PPy (conductive part) and polysiloxane (insulating regime) was synthesized. The films have structural amorphous semiconductor characteristics. The conductivity of the samples decreased with a decreasing supporting electrolyte concentration. The temperature-dependent conductivity data of the films measured between 100 and 320 K were analyzed with the Mott hopping theory and the dominant conduction mechanism in the studied temperature range was observed to be dominated by the Mott variable range hopping. Also, the reproducibility of the data indicated the homogeneity of the copolymer films.

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