Hindawi Publishing Corporation
International Journal of Polymer Science
Volume 2015, Article ID 280325, 5 pages
http://dx.doi.org/10.1155/2015/280325

Research Article

Structure and Electrical Study of New Chemically Modified Poly(vinyl chloride)

F. Ammari,[1] M. Dardouri,[1] M. Kahlaoui,[2] and F. Meganem[1]

[1]*Laboratory of Organic Synthesis, Faculty of Sciences of Bizerte, University of Carthage, Jarzouna, 7021 Bizerte, Tunisia*
[2]*Laboratory of Materials Physics, Faculty of Sciences of Bizerte, University of Carthage, Jarzouna, 7021 Bizerte, Tunisia*

Correspondence should be addressed to M. Kahlaoui; kahlaouimessaoud@yahoo.fr

Received 12 March 2015; Revised 20 May 2015; Accepted 26 May 2015

Academic Editor: Jose Ramon Leiza

The aim of this work was to study the structural and electrical properties of a new polymer obtained by functionalization of a commercial poly(vinyl chloride) (PVC) (Mw = 48000) by grafting aminoalkyl and aminoaryl groups. Modified poly(vinyl chloride) was prepared in two steps. The structural properties of the polymer were systematically investigated by varieties of techniques as differential scanning calorimetric (DSC), thermogravimetry analysis (TG), X-ray diffraction (XRD), and Fourier transform infrared (FTIR) spectroscopy. The electrical properties of the polymer were studied by electrochemical impedance spectroscopy (EIS).

1. Introduction

Taking into account its excellent miscibility, compatibility properties, good mechanical strength, low energy consumption, and its low cost [1–5], poly(vinyl chloride) (PVC) has been considered as a good candidate polymer for use in a great variety of electrochemical devices such as high energy density batteries, fuel cells, sensors, and electrochromic devices [6–8]. The development of PVC polymer with high ionic conductivity is one of the main objectives in polymer research. In fact, various approaches have been made to modify the structure of PVC polymer in order to improve their electrical, electrochemical, and mechanical properties. Among the modified PVC, we found those cited in many literatures [9–11]. In the present work, differential scanning calorimetric (DSC) studies, thermogravimetry analysis (TG), X-ray diffraction (XRD), Fourier transform infrared (FTIR), and temperature dependent conductivity were performed on a new polymer obtained by functionalization in two steps of a commercial poly(vinyl chloride) by grafting aminoalkyl and aminoaryl groups.

2. Experimental

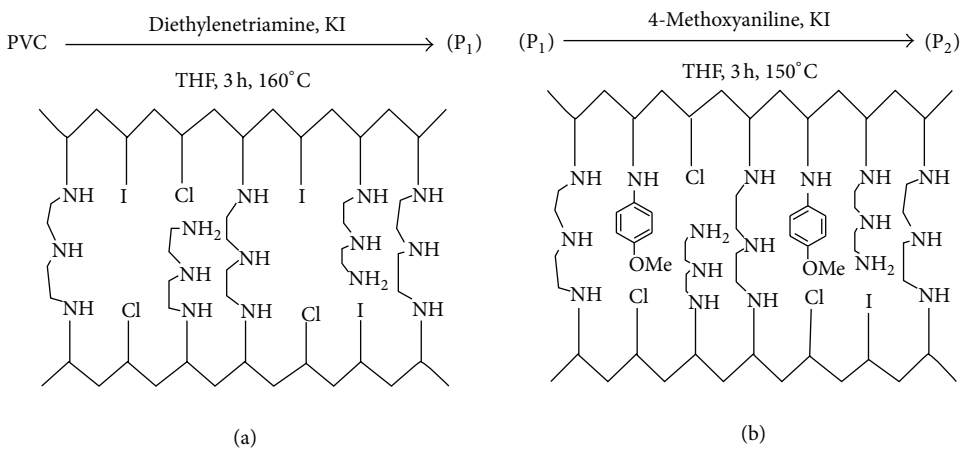
2.1. Chemicals. The commercial poly(vinyl chloride) Mw = 48000 (packed in Switzerland) was purchased from Fluka, diethylenetriamine and 4-methoxyaniline were purchased from Aldrich-Chemistry, 7924 Steinheim, Germany, and dioxane and THF were purchased from Prolabo (Groups Rône Poulenc).

2.2. Instrumentation. Electrochemical Impedance Spectra (EIS) were obtained using a Hewlett-Packard HP 4192 analyzer (99 Washington Street, Melrose, MA 02176-6024), IR: Thermo Scientific Nicolet IR 2000 (Verona Road, Madison, WI 53711-4495, USA), DSC: Setaram DSC 131 (7 L'Oratory Street, 69300 Caluire, France), TG: Setaram B.60 (7 L'Oratory Street, 69300 Caluire, France), and XR: X'Pert Pro. dar Panalytical min voltage 40 kV and current 30 mA (Oestliche Rheinbrückenstraße 49, 76187 Karlsruhe, Germany).

2.3. Structure of Amino-p-anisidine-PVC (P_2). Synthesis is described in our precedent work [11] as shown in Scheme 1.

3. Results and Discussion

3.1. DSC Analysis. The DSC diagram (Figure 1) of the commercial PVC shows a melting point at 279°C. The diagram of the material (P_2) shows an exothermic peak at 177°C and an endothermic transformation at 185°C.



Scheme 1: Structures of (a) amino-PVC (P_1) and (b) amino-p-anisidine-PVC (P_2).

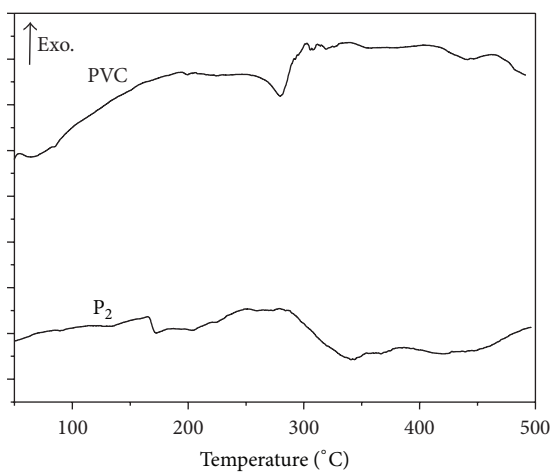


Figure 1: DSC diagrams of commercial PVC and polymer (P_2).

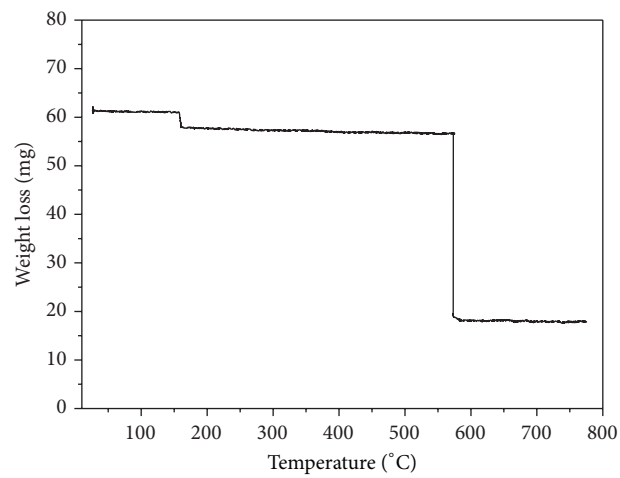


Figure 2: TG curves of polymer (P_2).

3.2. TG Analysis. In order to study the thermal stability of polymer (P_2), TG analysis has been done from room temperature to 800°C as shown in Figure 2. It can be seen that when (P_2) is heated at 156–169°C, the weight loss is about 3 mg and 38 mg while heated at 572–577°C. It is due to two factors including the elimination of HCl and HI groups and complete decomposition of the polymer.

3.3. Analysis by XRD. The X-ray diffraction pattern shows the amorphous nature of the commercial PVC and the studied polymer (P_2) (Figure 3).

3.4. IR Spectroscopy. Figure 4 shows the IR spectra of the powder form of the studied polymer. The spectrum of the commercial PVC shows a high intensity band assigned to the stretching vibration ν_{C-Cl} at 690 cm^{-1}. The spectrum of P_2 shows two broad peaks around 3382.97 and 3309.42 cm^{-1} attributed to the stretching vibration of NH primary amines, some bands of stretching vibration $\nu_{C=C\,(arom)}$ at 1617, 1513, and 1437 cm^{-1}, ν_{C-O} at 1244, and bending vibration bands

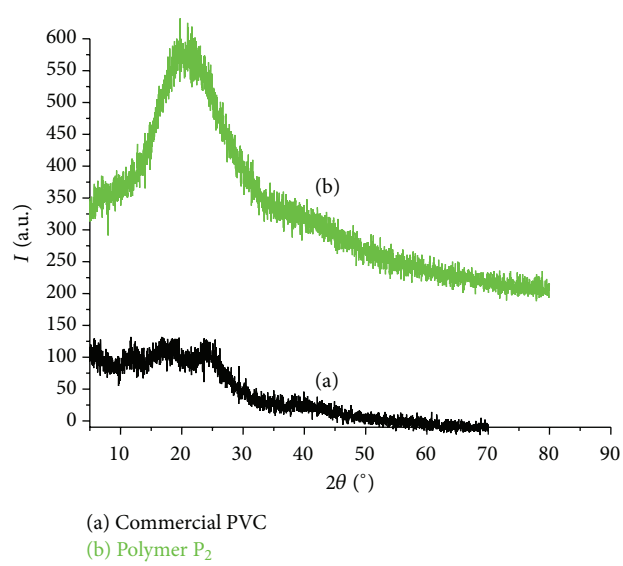


Figure 3: XRD of commercial PVC and polymer (P_2).

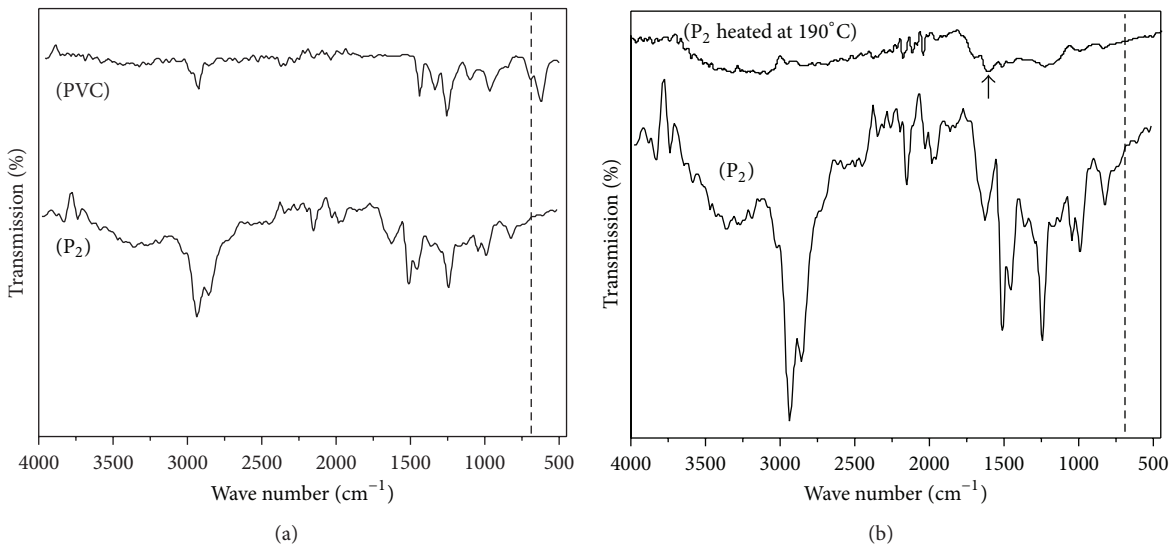


Figure 4: IR spectra of (a) PVC and (P_2) and (b) (P_2) and (P_2) heated at 190°C.

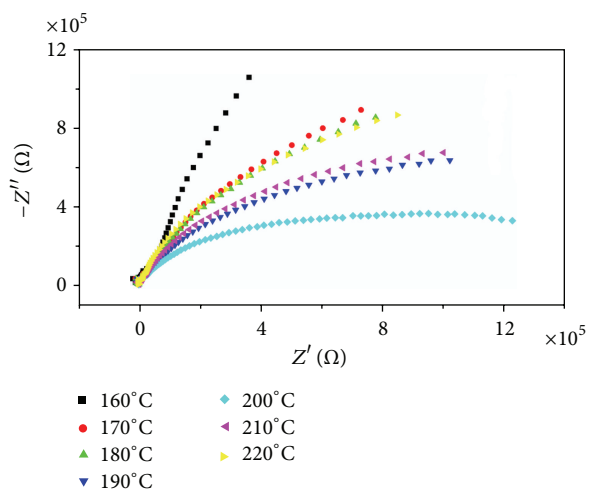


Figure 5: Complex plane impedance plots of polymer (P_2) at different temperatures.

$\delta_{\text{Ctét–H (Me)}}$ at 1332 and $\delta_{\text{Ctét–H (aromp-sub)}}$ at 828 cm^{-1}; we also note that the band $\nu_{\text{C–Cl}}$ at 690 cm^{-1} becomes very low compared to that corresponding to the PVC as a consequence to the increase of the number of chlorine atoms substituted by diethylenetriamine groups. The IR spectrum of the polymer (P_2) heated at 190°C shows the appearance of a band of vibration $\nu_{\text{C=C}} = 1605\ cm^{-1}$ and the disappearance of the band $\nu_{\text{C–Cl}}$ at 690 cm^{-1} which indicates the removal of HCl and HI groups giving rise to a conjugated system having an alternate of single and double bonds.

3.5. Electrical Study

3.5.1. Electrical Measurements. The powders were ground in an agate mortar and then pressed at 4 tons into cylindrical pellets with 11.8 mm in diameter and 2.7 mm in thickness. Electrochemical Impedance Spectra (EIS) were obtained using a Hewlett-Packard HP 4192 analyzer. The impedance measurements were taken in an open circuit using two electrode configurations with signal amplitude of 50 mV and a frequency band ranging from 5 Hz to 13 MHz. Both pellet surfaces were coated with silver pastes electrodes while the platinum wires attached to the electrodes were used as current collectors. All these measurements were performed at equilibrium potential at a temperature ranging between 160°C and 220°C.

3.5.2. Electrochemical Characterization. Figure 5 shows the Nyquist diagram obtained from pellet of amino-p-anisidine-PVC (P_2) between 160°C and 220°C which appears as a semi-circle and the amplitude of this arc is thermally dependent. The impedance spectra plotted in Figure 5 were analyzed by fitting the data with the equivalent circuit shown in Figure 6. In this figure, L corresponds to an inductance which is usually

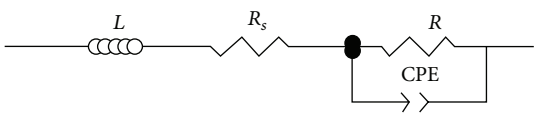


FIGURE 6: Equivalent circuit used for fitting the impedance data.

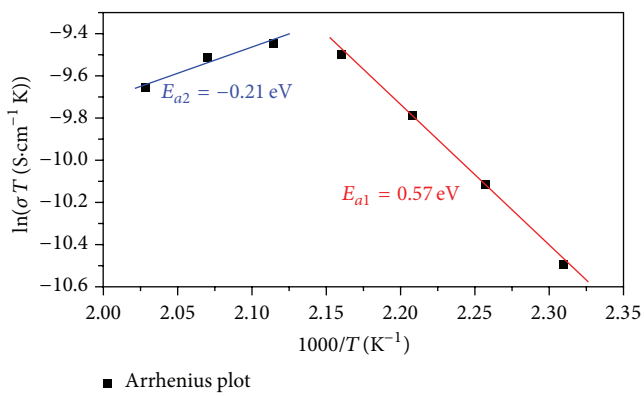


FIGURE 7: Arrhenius plots of the conductivity of polymer (P_2) solid solutions.

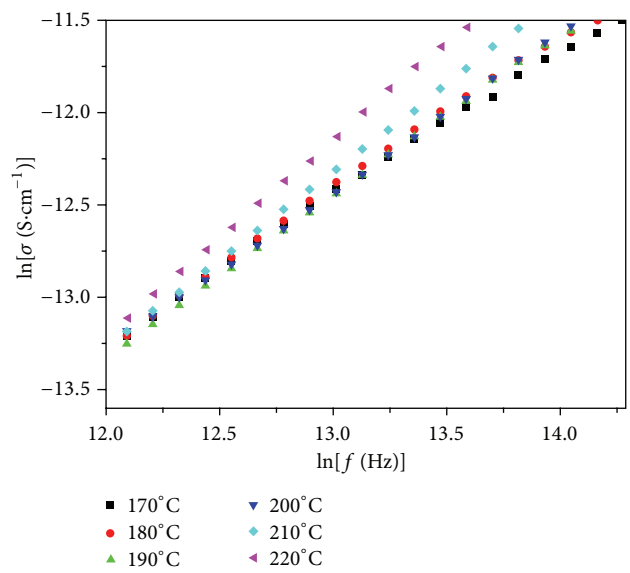


FIGURE 8: ln(σ) versus ln(f) for amino-p-anisidine-PVC (P_2).

associated with the platinum current-voltage probes; R_s is the ohmic resistance of the amino-p-anisidine-PVC (P_2); R is resistance and CPE is a constant phase element representing time-dependent capacitive elements.

(1) dc Conductivity Study. For a pellet with thickness d and section area S, the dc conductivity was calculated using the following relation:

$$\sigma = \frac{1}{R} \times \frac{d}{S}. \quad (1)$$

Activation energies (E_a) were obtained by fitting the conductivity data to the Arrhenius relation for thermally activated conduction which is calculated using the following equation:

$$\sigma = \frac{A_0}{T} \exp\left(-\frac{E_a}{kT}\right), \quad (2)$$

where σ, A_0, E_a, k, and T are, respectively, the conductivity, preexponential factor, activation energy, Boltzmann constant, and absolute temperature.

Figure 7 shows the Arrhenius plot of the dc electrical conductivity for the sample named amino-p-anisidine-PVC (P_2) in the temperature range 160–220°C. As can be seen in Figure 7, the Arrhenius plot shows a significant curve which may be interpreted as a transition behavior of the polymer. This curvature is observed at around 190–200°C and arises from the differences in the conduction mechanism due to the changes in the behaviors of the polymer at 160–190°C and 200–220°C temperatures. On the other hand, most likely the transport of ions must occur via indirect motion along a convoluted path restricted to the plasticizer-phase, which is responsible for low conductivity at PVC polymer [4].

The increase in conductivity may be explained by the formation of a conjugate system with the elimination of HCl and HI groups as shown in the TG analysis described previously.

The observed conductivity of this polymer was equal to 2.16 10^{-7} S/cm at 190°C, which was higher than 10^{-8} S/cm found for the polyacene quinone radical (PAQR) [12] and also higher than that reported in literature [13] for the polymer poly-2-[(4-mercaptophenyl) imino methyl] phenol (P-4-MPIMP) and polymer-metal complex compounds which is between 10^{-11} and 10^{-10} S/cm.

(2) Frequency Dependence of ac Conductivity. The dependence of σ_{ac} with frequency at different temperature is shown in Figure 8. Its value is related to frequency by the following relation [14]:

$$\sigma_{ac} = A \cdot \omega^s, \quad (3)$$

where A is a temperature dependent constant and s is the power exponent. The evolution of s with temperature is tributary to the conduction mechanism.

The estimated power exponent s values are shown in Table 1 in terms of temperature. This power exponent fluctuates with temperature between 0.84 and 0.95 in 170°C–220°C domain.

Variations of the power exponent s with the temperature do not meet any of the known models, such as the quantum mechanical tunneling (QMT) model [15–17], the overlapping-large-polaron tunneling (OLPT) model [16–18], and correlated barrier hopping (CBH) model, developed by Elliott [19, 20].

4. Conclusion

This work allowed for studying the new material amino-p-anisidine-PVC (P_2) obtained by functionalization of a PVC (Mw = 48000). XRD result shows amorphous nature of P_2. The endothermic transformations were confirmed by

Table 1: Power exponent of the polymer (P_2) for different temperatures.

Temperature (°C)	Power exponent s
170	0.88
180	0.91
190	0.89
200	0.84
210	0.95
220	0.94

electrical properties. These results show that the polymer (P_2) may be useful in a great variety of electrochemical devices such as rechargeable batteries, super-capacitors, and gas sensors.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgments

The authors wish to thank the officials of Organic Synthesis Laboratory and Materials Physics Laboratory.

References

[1] Z. Ahmad, N. A. Al-Awadi, and F. Al-Sagheer, "Morphology, thermal stability and visco-elastic properties of polystyrene-poly(vinyl chloride) blends," *Polymer Degradation and Stability*, vol. 92, no. 6, pp. 1025–1033, 2007.

[2] M. Tang and W.-R. Liau, "Solvent effect on the miscibility of poly(4-hydroxystyrene)-poly(ethylene oxide) blends," *European Polymer Journal*, vol. 36, no. 12, pp. 2597–2603, 2000.

[3] K. Pielichowski and I. Hamerton, "Compatible poly(vinyl chloride)/chlorinated polyurethane blends: thermal characteristics," *European Polymer Journal*, vol. 36, no. 1, pp. 171–181, 2000.

[4] A. M. Stephan, T. P. Kumar, N. G. Renganathan, S. Pitchumani, R. Thirunakaran, and N. Muniyandi, "Ionic conductivity and FT-IR studies on plasticized PVC/PMMA blend polymer electrolytes," *Journal of Power Sources*, vol. 89, no. 1, pp. 80–87, 2000.

[5] M. Alamgir and K. M. Abraham, "Li ion conductive electrolytes based on poly(vinyl chloride)," *Journal of the Electrochemical Society*, vol. 140, no. 6, pp. L96–L97, 1993.

[6] T. Uma, T. Mahalingam, and U. Stimming, "Solid polymer electrolytes based on poly(vinylchloride)-lithium sulfate," *Materials Chemistry and Physics*, vol. 90, no. 2-3, pp. 239–244, 2005.

[7] S. Ramesh and M. F. Chai, "Conductivity, dielectric behavior and FTIR studies of high molecular weight poly(vinylchloride)-lithium triflate polymer electrolytes," *Materials Science and Engineering B: Solid-State Materials for Advanced Technology*, vol. 139, no. 2-3, pp. 240–245, 2007.

[8] S. Ramesh, A. H. Yahaya, and A. K. Arof, "Dielectric behaviour of PVC-based polymer electrolytes," *Solid State Ionics*, vol. 152-153, pp. 291–294, 2002.

[9] R. Vinodh, A. Ilakkiya, S. Elamathi, and D. Sangeetha, "A novel anion exchange membrane from polystyrene (ethylene butylene) polystyrene: Synthesis and characterization," *Materials Science and Engineering B: Solid-State Materials for Advanced Technology*, vol. 167, no. 1, pp. 43–50, 2010.

[10] S. Moulay, "Chemical modification of poly (vinyl chloride)-Still on the run," *Progress in Polymer Science*, vol. 35, no. 3, pp. 303–331, 2010.

[11] F. Ammari and F. Meganem, "Poly(vinyl chloride) functionalization by aliphatic and aromatic amines: application to the extraction of some metal cations," *Turkish Journal of Chemistry*, vol. 38, pp. 638–649, 2014.

[12] B. Wang, L. Ma, C. Hao, and Q. Lei, "Synthesis of polyacene quinone radical polymers with controllable conductivity and their smart electrorheological behavior," *Synthetic Metals*, vol. 182, pp. 28–32, 2013.

[13] I. Kaya and F. Baycan, "Synthesis, characterization, conductivity, band gap and thermal analysis of poly-2-[(4-mercaptophenyl) imino methyl] phenol and some of its polymer–metal complexes," *Synthetic Metals*, vol. 157, no. 16-17, pp. 659–669, 2007.

[14] A. K. Jonscher, "The 'universal' dielectric response," *Nature*, vol. 267, no. 5613, pp. 673–679, 1977.

[15] I. G. Austin and N. F. Mott, "Polarons in crystalline and non-crystalline materials," *Advances in Physics*, vol. 18, no. 71, pp. 41–102, 1969.

[16] A. R. Long, "Frequency-dependent loss in amorphous semiconductors," *Advances in Physics*, vol. 31, no. 5, pp. 553–637, 1982.

[17] A. Ghosh and D. Chakravorty, "AC conduction in semiconducting CuO-Bi_2O_3-P_2O_5 glasses," *Journal of Physics: Condensed Matter*, vol. 2, no. 24, pp. 5365–5372, 1990.

[18] M. Pollak, "Temperature dependence of ac hopping conductivity," *Physical Review*, vol. 138, no. 6, pp. 1822–1826, 1965.

[19] S. R. Elliott, "A.c. conduction in amorphous chalcogenide and pnictide semiconductors," *Advances in Physics*, vol. 36, no. 2, pp. 135–217, 1987.

[20] S. R. Elliott, "A theory of a.c. conduction in chalcogenide glasses," *Philosophical Magazine*, vol. 36, no. 6, pp. 1291–1304, 1977.