



High Pressure Studies on the Transport Properties of TSO-Doped Polypyrrole Polymer

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Abstract The pressure dependence of the electrical resistivity of (TSO) doped-polypyrrole as a function of temperature was measured up to 6 GPa for the first time using cubic anvil high pressure cell. It is observed that the room temperature resistivity decreases with increasing the pressure up to 6 GPa and the increasing in resistivity found at low temperature is suppressed steadily with increasing the pressure. The value of residual resistivity and electron scattering factor decreases with the application of pressure, indicating that the pressure decreases the inter-chain distance and enhances the charge transfer of carriers of (TSO) doped- polypyrrole.

Keywords Electrical properties, Metallic conductor, Polymer, High pressure and Cubic cell

Introduction

The electrical transport properties in heavily doped conjugated polymers have been an intriguing subject in relation to a quasi one-dimensional structure and unavoidable disorders. In the first generation of conducting polymers, the room temperature high electrical conductivity turned to be nonmetallic on cooling [1]. However, the thermoelectric power showed quasi linear temperature dependence, and temperature dependence of magnetic susceptibility indicated the presence of paramagnetism [2-3]. The presence of metallic phase, which is characterized by finite electrical conductivity even at low temperature, has been established in heavily doped polymers such as polyacetylene, polypyrrole and polyaniline [4-9]. The room temperature high conductivity in doped conjugated polymers was also changed to nonmetallic on cooling in later [10-11]. This has been understood as the effect of disorders for a system made of quasi one-dimensional conductors with a paracrystalline structure [12-13]. However, through improvements in synthesis, the conductivities of doped polypyrrole have been raised steadily with remarkable residual conductance even at low temperature has been realized. Since doped polypyrrole has quasi one-dimensional electronic structure, the highly anisotropic transport properties are expected, however it would be different due to the random orientation of polymer chains. When it is uniaxially stretched, the aligned structure of polymer chains may better exhibit the one-dimensional characteristics of the sample.

Polypyrrole is characterized as quasi one-dimensional system, but polymer chains are randomly distributed and there must be sufficient inter-chain transfer of the quasi three-dimensional transport is involved. This fact can be observed from the enhancement of metallic conductance by pressure and the restriction to the dopant species in which the small anion of PF_6^- can bring about the metallic conductance [11]. Some polymers may have electrical properties which resemble those of conventional semiconductors, metals or even superconductors. The temperature dependence of resistivity under pressure for metallic (PF_6) doped-polypyrrole, nonmetallic (PF_6) doped-polypyrrole and p-toluenesulfonate (TSO) doped-polypyrrole has been reported [1]. The predominant rise in resistivity found in (TSO) doped-polypyrrole is suppressed steadily up to 10 Kbar. So, it is important to check the suppression of resistivity at higher pressure. The purpose of this paper is to study the temperature dependence of resistivity of (TSO) doped-polypyrrole under high pressure.



Materials and Methods

The preparation of (TSO) doped-polypyrrole by electrochemical method and their basic structural, physical properties were described by Yamaura et al. [10] and Gilani et al. [11]. For conventional four probe technique, the electrical contacts are made by Dupont 4922N silver paint and gold wire with a diameter of 10 μ m. The typical sample size used was 0.7 \times 0.3 \times 0.15mm³. Resistivity at ambient pressure was measured using home-made cryostat from room temperature down to liquid helium temperature. Whereas the temperature dependence of resistivity under pressure up to 6 GPa was measured using cubic anvil device [19]. The sample was immersed in a pressure medium of Daphne 7373 oil to maintain the hydrostatic pressure, and encapsulated in a Teflon cell, which is surrounded by pyrophyllite block. This block is compressed evenly from six directions with six tungsten carbide (WC) anvils. The six WC anvils crush the pyrophyllite gasket and compress the Teflon cell from six directions equally and the hydrostatic nature of the pressure is maintained beyond the solidification of the pressure medium. Furthermore, since the load from outside is controlled during cooling, pressure is kept constant in the course of the temperature cycle.

Results and Discussion

The temperature dependence of the electrical resistivity of (TSO) doped-polypyrrole under high pressures up to 6 GPa is shown in Figure 1. It shows that the room temperature electrical resistivity monotonically decreases at initially applied pressures and it increases with decreasing the temperature with applied pressure noted that a change of finite density of states at Fermi level. The increase in electrical resistivity found at low temperature is suppressed steadily with increasing the pressure up to 6 GPa. The occurrence of metallic conduction in metallic (PF₆) doped-polypyrrole is enhanced by the decrease in the interchain spacing of the polypyrrole units by the pressure [11]. Hence the suppression of resistivity at low temperature in (TSO) doped-polypyrrole with increasing the pressure is may be due to the pressure effect on the inter-chain spacing of the polypyrrole units with the frequent transfer of the charged carriers.

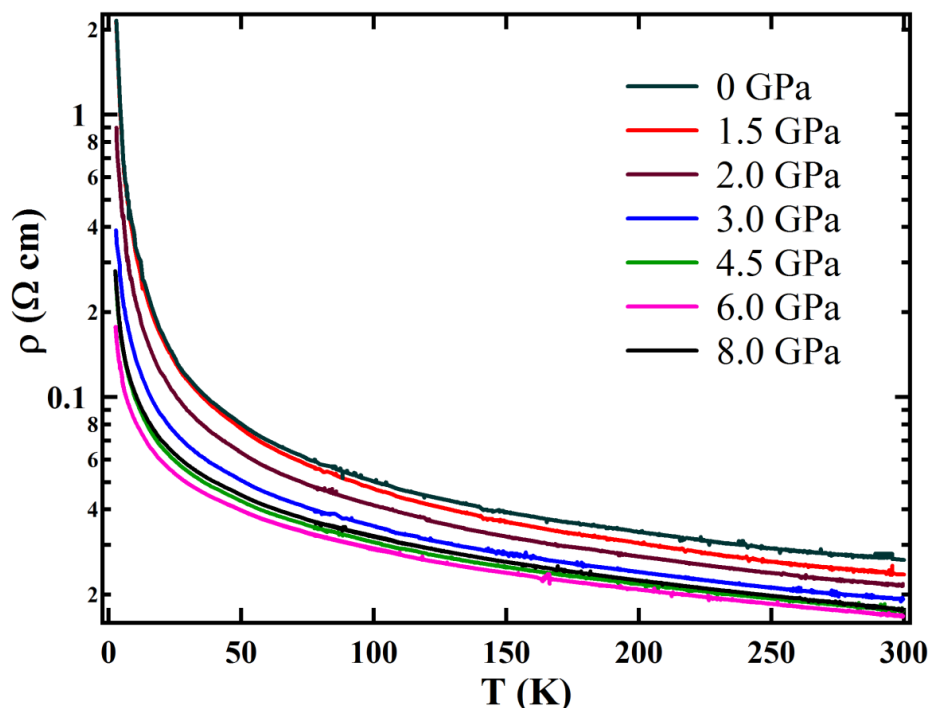


Figure 1: Temperature dependence of electrical resistivity in logarithmic scale of (TSO) doped-polypyrrole at ambient pressure and at different pressures up to 6 GPa.

Based on the quantum chemical viewpoints it has been pointed out that the bipolaron rather than polaron can be the charged carrier in the doped polypyrrole [14-15]. This contrasts with charged soliton model, proposed for polyacetylene with degeneracy in the topological order in the alternate bond and in the case of polypyrrole without topological degeneracy the polarons generated by doping can be stabilized by pairing [16]. However, due to the extent of bipolaron covering several pyrrole units, the interaction between the adjacent bipolarons is considerable for heavily doped case and the basis to stand the bipolaron model is violated. The studies based on infrared and spectroscopies assert the presence of the polaron rather than bipolaron [17].



The plot of electrical resistivity of TSO-doped polypyrrole polymer as a function of the square of temperature (ρ vs T^2) is shown in Figure 2. The relation between electrical resistivity (ρ), residual resistance and electron – electron scattering factor of materials at temperature (T) is given by $\rho = \rho_0 + (A \times T^2)$. Here ρ_0 is the residual resistivity (ohm cm) and A is the quadratic co-efficient of the electrical resistivity (ohm cm K^{-2}) or electron-electron scattering factor.

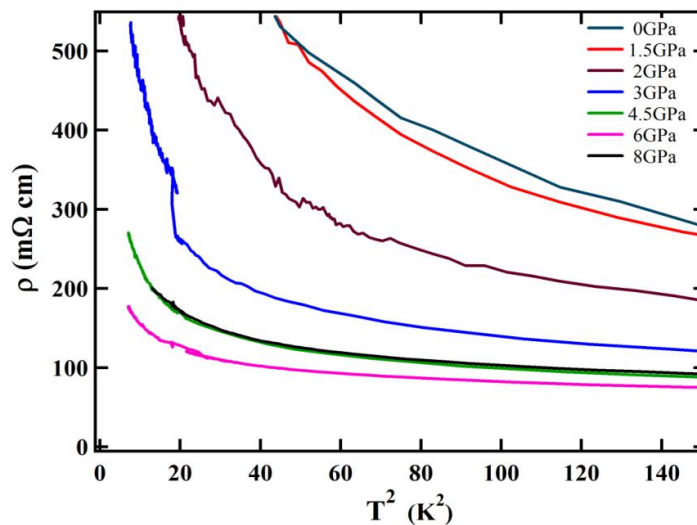


Figure 2: T^2 dependence of electric resistivity of (TSO) doped-polypyrrole at ambient and at high pressure up to 8 GPa.

The pressure dependence of the residual resistivity (ρ_0) and electron scattering factor (A) is shown in Figure 3 (a) and (b). At ambient pressure, the values of residual resistivity (ρ_0) and electron scattering factor (A) are 120 (m Ω cm) and 1.8 (m Ω cm K^{-2}). It is noted that, ρ_0 and A decreases drastically while increasing of pressure up to 8 GPa shows a strong electron correlation effect present in this compound. Also, this implies that the applied pressure decreases the inter-chain spacing and therefore, an enhancement of conductivity occurred at low temperature. (TSO) doped-polypyrrole has finite density of states at Fermi level and exhibits the metallic feature for thermoelectric power, heat capacity and spin resonance [18-19].

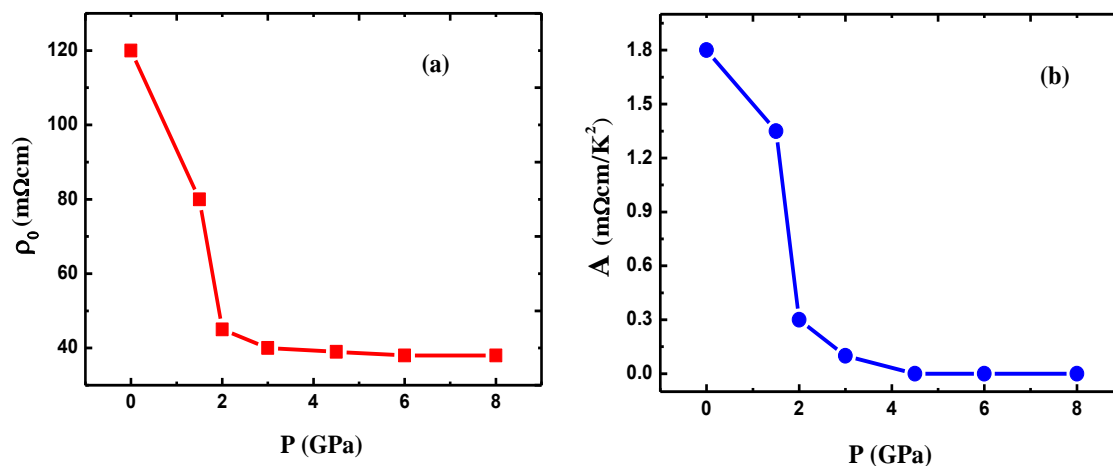


Figure 3: (a) The residual resistivity (ρ_0) and (b) electron–electron scattering factor (A) with respect to different applied pressure (up to 8 GPa from 0 GPa) of (TSO) doped-polypyrrole.

The degree of local order varies for (TSO) doped-polypyrrole depending on preparation method with the degree of crystallinity. In crystalline regions, the overlapping of orbitals could result in anisotropic delocalized state, whereas in the amorphous regions the polymer chains are weakly interacting and the electronic states are subject to one-dimensional localization. While the size and volume fraction of the crystalline region increases against an amorphous behavior, then the system is expected to undergo a transition from insulator to metal. The detection of metal-like characteristics in (TSO) doped-polypyrrole implies that the difference between non metallic and metallic phase in doped polypyrrole with dopant concentration of ~ 0.3 per pyrrole unit is ascribed to the degree of disorder related to interchain transfer of the carriers. Hence, increased fraction of metallic region is required



to understand the suppression of resistivity at low temperature with increasing the pressure in (TSO) doped-polypyrrole.

Conclusion

To summarize, pressure dependence of the electrical resistivity of (TSO) doped-polypyrrole as a function of temperature up to 6 GPa was carried out using cubic anvil cell for the first time. The room temperature electrical resistivity decreases with increasing the pressure and the resistivity increases at low temperature. The increasing in resistivity at low temperature is suppressed steadily due to the pressure. The applied pressure decreases the inter-chain distance of the polypyrrole units with the frequent transfer of the charged carriers which is similar to the effects observed in metallic (PF₆) doped-polypyrrole. The decrease in residual resistivity and electron scattering factor with respect to pressure has been observed. A suitable high pressure experiments such as neutron scattering analysis and theoretical investigations at high pressure is also highly desirable for further understanding of (TSO) doped-polypyrrole.

Acknowledgment

This work was supported by the Japanese Ministry of Education, Sport and Culture (MEXT).

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