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HIGH PRESSURE CONDUCTIVITY AND MORPHOLOGY OF CONDUCTING POLYMER COLLOIDS

M. C. ARONSON[1], M. ALDISSI[2], S. P. ARMES[3] AND J. D. THOMPSON[4]
(1) The Harrison M. Randall Laboratory of Physics, University of Michigan, Ann Arbor, MI 48109, USA; (2) Champlain Cable Corporation, P. O. Box 7, Winooski, VT 05404, USA;(3) School of Chemistry and Molecular Sciences, University of Sussex, Brighton BN1 9QJ, UK; (4) Los Alamos National Laboratory, Los Alamos, NM 87545, USA.

INTRODUCTION

The development of conducting colloids stemmed from applications driven needs for processable conducting polymers. Because conducting polymers are aggregated in nature, due to their conjugated backbones, the preparation of colloidal systems of these aggregates is an attractive approach to by-passing the intractability problem. The reason for focussing on the two particular colloidal systems studied here, polypyrrole and polyaniline, is the fact that their air-stability is much better than other conducting polymers.

The preparation of colloidal polypyrrole in aqueous media using commercially available water-soluble polymers as steric stabilizers was reported earlier [1-4]. In all cases, the particle morphology was spherical and usually monodisperse (± 15% standard deviation). The actual particle diameter obtained depends on the nature of the stabilizer, its concentration and molecular weight and varies over a range of 50-450 nm. The conductivities of compressed pellets or thin films fabricated from aqueous dispersions of the polypyrrole particles were surprisingly high (0.1-2.0 $\Omega^{-1}.cm^{-1}$), despite the presence of up to 10-15 wt% of the insulating adsorbed steric stabilizer [3].

We have reported on our systems earlier in various publications [5-9] with the goal of widening the spectrum of steric stabilizers and the detailed study of various properties of the various systems to optimize the materials for colloidal stability, high conductivities and film-forming properties.

The main distinction between polypyrrole and polyaniline colloids is that the former is formed by physical adsorption ,via hydrogen bonding, of the steric stabilizer onto the polypyrrole particles, and the latter is formed by

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steric stabilizer onto the polypyrrole particles, and the latter is formed by chemical grafting of polyaniline onto the steric stabilizer chains. The efforts to produce colloidal polyaniline via physical adsorption failed. Polyaniline colloidal particles have a needle-like shape with a length in the range 100-200 nm and a width in the range 10-50 nm. Morphology of both polypyrrole and polyaniline samples was studied using electron microscopy (scanning-SEM, transmission-TEM and scanning tunneling microscopy-STM) [5-10].

The purpose of the present study is to understand the conduction process in these colloids by determining the pressure-dependent behavior of the conducting cores as well as the effect of pressure on the role of the insulating steric stabilizer component. The application of high pressure to conducting polymers in general increases their electrical conductivity because it increases interchain coupling, minimizing potential barriers and enhancing electron hopping between chains.

To our knowledge, the pressure-dependent study of polyaniline has never been carried out. However, study of bulk polypyrrole was performed [11,12] between ambient pressure and 10 kbar above room temperature with no phase transition observed.

EXPERIMENTAL

Colloidal polypyrrole and polyaniline particles were prepared in the presence of PVA as a steric stabilizer in similar conditions to those reported earlier [5,6,8]. Films were cast from the dispersions for conductivity measurements.

Platinum wires were attached to free standing films in a four probe configuration using aquadag. Hydrostatic pressures were achieved using a self-clamping Be-Cu cell [13] with a 1:1 mixture of isoamyl alcohol and pentane as a pressure transmitting medium. The pressure was determined using a superconducting Pb manometer.

RESULTS AND DISCUSSION

Scanning tunneling microscopy (STM) studies [10] have shown that the small scale morphologies of polyaniline and polypyrrole colloids are similar. Namely, for the purpose of resistivity measurements, each may be thought of as a network of conducting grains embedded in a background of insulating steric stabilizer. It is further found that the resistivity is essentially uniform within different grains and in the interface region between grains. Although the complex structure of the films make it difficult to compare the resistivities of the films to those of the bulk materials, the film morphology suggests

that the temperature dependence of the film resistivity should be similar to that of the bulk material.

The temperature dependent study of the electrical resistivity between ambient pressure and 15 kbar for both materials showed that the resistivity rises quickly with decreasing temperature, increasing more than three orders of magnitude from the room temperature values of 1.5 and 5.95 Ω.cm for polypyrrole and polyaniline colloids respectively. In both cases, as the applied pressure increases, the resistivity at all temperatures decreases markedly.

Highly conducting bulk polypyrrole samples were found [14] to have a temperature dependent conductivity $\sigma(T)$ characteristic of three dimensional variable range hopping: $\sigma(T) = \sigma_1 \exp(-A_1/T^{1/4})$, where σ_1 and A_1 are both dependent on sample doping level. A qualitatively different behavior was found for bulk polyaniline [15], where the temperature dependence of the conductivity was found to obey $\sigma(T) = \sigma_2 \exp(-A_2/T^{1/2})$. This result was explained by postulating the presence of isolated regions with high doping levels and correspondingly high conductivities. Electrical conduction occurs when carriers hop from metallic island to metallic island, with a frequency which is highly dependent on the electric field strength.

In order to compare the conduction process in both the colloids and the bulk materials, we have plotted the logarithm of the conductivity of colloidal polypyrrole as a function of $1/T^{1/4}$ in Fig. 1, for pressures ranging from ambient pressure to 15 kbar. Below approximately 100 K, the temperature dependence of the resistivity agrees very well with that of variable range hopping found in the bulk material. We tentatively associate the departure of the data from linearity at the highest temperatures with a small temperature dependence of the pressure known to occur in our pressure cell over this temperature interval (T> 100 K). As the pressure is increased, σ_1 increases from its 1 bar value of 0.2 $(\Omega.cm)^{-1}$ to 0.6 $(\Omega.cm)^{-1}$ at 10 kbar. Over the same pressure range, A_1 decreases monotonically from -10.35 to 6.21 $K^{1/4}$. σ_1 and A_1 can be expressed [16] in terms of the density of states at the Fermi level $N(E_f)$, the mean hopping distance R, and the wave function fall-off $1/\alpha$:

$$\sigma_1 \sim e^2 N(E_f) R^2, \qquad A_1 \sim 2[3/2\pi]^{1/4}\, \alpha^2/\kappa_B N(E_f)$$

where e is the electronic charge and κ_B is the Boltzmann constant.

Although an independent determination of the pressure dependences of $N(E_f)$, R or α is lacking, a qualitative description is still possible. The conduction in polypyrrole involves the limited overlap of almost localized defect states near the Fermi level. The decrease in $1/\sigma_1$ and A_1 can be consistently explained by assuming that these states become less localized under pressure. That is, localized energy levels which are sharp at 1 bar are smeared out at

high pressures, decreasing the overlap factor α. Whether $N(E_f)$ increases or decreases with delocalization depends critically on whether the localized states lie near or exactly at the Fermi level. Assuming that an enhanced hopping distance R results from pressure-induced delocalization, the decrease in σ_1 for increased R suggests that the carriers correspond to defect states very close to the Fermi level, consistent with a pressure-induced decrease in $N(E_f)$. In conclusion, apart from geometrical considerations related to the film morphology, we find that the measured resistance of polypyrrole latex films agrees quite well with that of bulk polypyrrole. The defect states associated with variable range hopping appear to become more delocalized under pressure, and the density of states reduced. It would be most interesting to investigate these findings further by performing similar high pressure experiments on bulk polypyrrole.

We find no such close correspondence to the bulk properties in the polyaniline latex films. To demonstrate this, we have plotted the natural logarithm of the conductivity as a function of $T^{-1/2}$ at 1 bar, 6.5 kbar and 15 kbar in Fig. 2. It is clear that the temperature dependence of the conductivity at ambient and high pressures cannot be adequately described by the extended hopping expression applicable to bulk polyaniline, except perhaps over a meaninglessly limited temperature range. We have also tried to fit the measured resistance to other physically relevant expressions, but with a similar lack of success.

Since the STM measurements show that the inter- and intra grain resistivities are similar, the observation that the temperature dependence of the film resistance differs from that of the bulk polymer strongly suggests that the electronic structure of the conducting grains has been modified during preparation of the film.

One possibility is that the doping level is rather high in the grain, and the density of metallic islands is close to the percolation limit. In this case, the lack of a simple temperature dependence for the measured film resistance results from the near equivalence of contributions from inter-island hopping and metallic conduction along the percolating backbone. It is also possible that the electronic structure of the grains is modified at the intergrain interface possibly resulting from imperfect expulsion of the residual steric stabilizer. To distinguish between these two possibilities, more detailed temperature dependent STM investigations are required.

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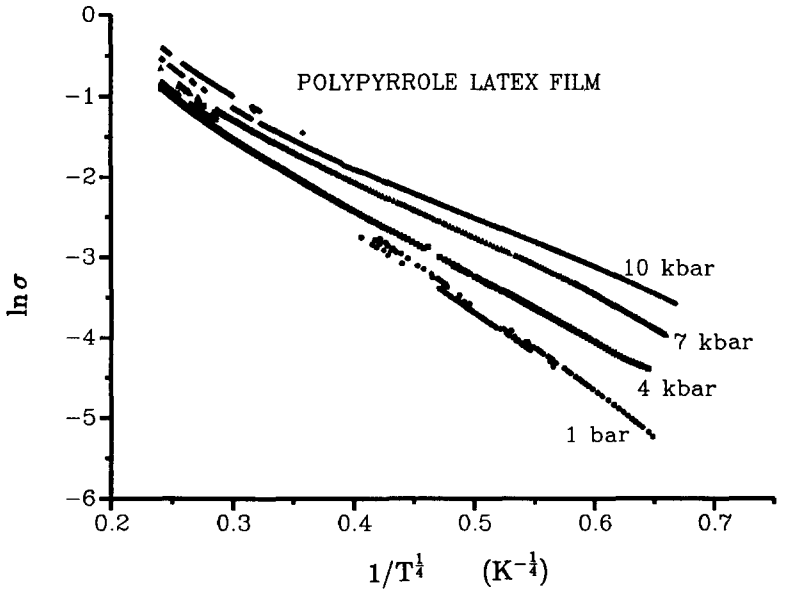

Fig. 1. Pressure and temperature dependence of the conductivity of polypyrrole/PVA colloids.

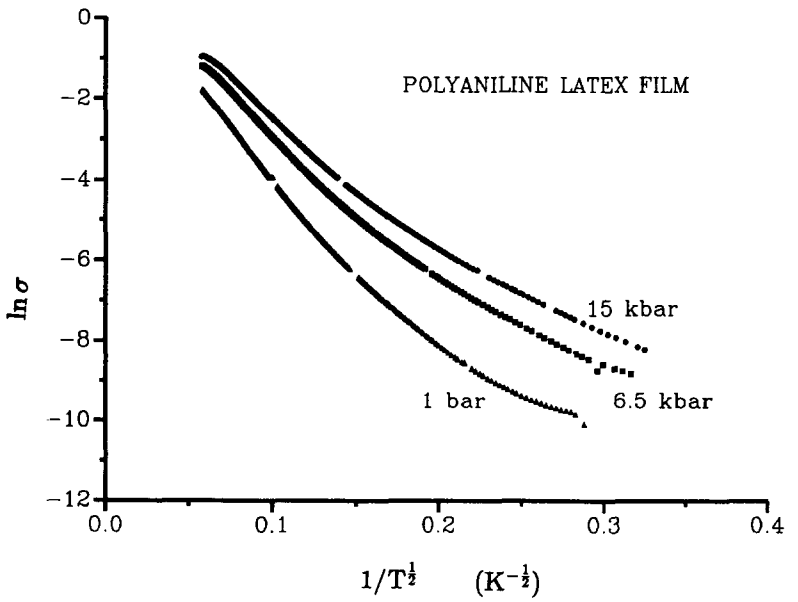

Fig. 2. Pressure and temperature dependence of conductivity of polyaniline/PVA colloids.

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