

STUDIES ON ENHANCED CONDUCTIVITY OF STRETCHED CONDUCTING POLYMERS*

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ABSTRACT

A physical model of series of the conductivity on chain and the interchain conductivity between chains is proposed to explain enhanced conductivity of stretched conducting polymers. This model suggests that the enhanced conductivity for stretched conducting polymers might be due to increasing of the interchain conductivity between chains along the elongation direction after drawing processes if the conductivity on chain is assumed much larger than that of the interchain conductivity between chains. According to this model, it is expected that the temperature dependence of conductivity measured by four-probe method for stretched conducting polymers is controlled by a variation of the interchain conductivity between chains with temperature, which can be used to explain that a metallic temperature dependence of conductivity for stretched conducting polymers is not observed although the conductivity along the elongation direction is enhanced by two or three orders of magnitude.

INTRODUCTION

It has been known that the conductivity of stretched conducting polymers at room temperature exhibits a strong anisotropy. This means that the conductivity parallel to the elongation direction ($\sigma_{\parallel}$) is enhanced by two or three orders of magnitude depending on the elongation ratio. On the other hand, the conductivity perpendicular to the stretching direction ($\sigma_{\perp}$) is independent of the elongation ratio. In general, this anisotropy in conductivity for stretched conducting polymers could be achieved up to $100^{[1]}$, depending on the polymeric structure, polymerization and doping conditions. However, the point of view in the explanations of enhanced conductivity for stretched conducting polymers are quite different. Those points of view could be summarized into three types as follows: those of

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increasing of conductivity on chains^[2](i. e. increasing chain length and higher conjugation); (2) those of increasing of the interchain conductivity between chains^[3]; and (3) others, such as increasing degree of crystallinity^[4]. Recently, author^[3] reported that the conductivity of the oriented polyaniline (PANI) films at room temperature could be able to achieve up to 500 S/Cm with conductivity anisotropy as high as 20 : 1. Moreover, the orientation parking of the intergranular or interchain along the elongation direction for stretched PANI films has been demonstrated by means of polarized IR spectra, SEM and X-ray diffraction. Based on these experimental results, it is reasonable to believe that the enhanced conductivity by stretching processes for conducting polymers might mainly be due to increasing interchain coupling, minimizing potential barriers and increasing charge carriers hopping between chains. In order to support this conclusion, thus, it is necessary to design a physical model for explaining the reason of enhanced conductivity for stretched conducting polymers.

In this paper, a physical model of series of the conductivity on chain and the interchain conductivity between chains is proposed. This model suggests that the main reason of enhanced conductivity for stretched conducting polymers might be due to increasing of the interchain conductivity between chains. The expected behaviors suggested by this model are consistent with the experimental observations from oriented PANI films^[3].

EXPERIMENTAL EVIDENCES FOR PROPOSED PHYSICAL MODEL

As known, the conductivity is expressed as

$$\sigma = ne\mu \quad (1)$$

where n is density of charge carriers, e is the electron charge, and μ is the mobility of charge carriers. In general, the conductivity of conducting polymers depends on the polymeric structure, doping level, properties of dopants, polymerization conditions and so on. However, a change in conductivity at room temperature for stretched conducting polymers is measured as a function of the elongation ratio without the change of other conditions. Thus, a variation of conductivity measured by four probe method for stretched conducting polymers mainly depends on changing of the mobility of charge carriers because of unaffection of stretching on the density of charge carriers. Moreover, the morphology of conducting polymers exhibits a fibrillar or granular morphology. It has been demonstrated that the fibrillar or granular itself is metal-like, which is around by insulator materials, called as "conducting island". Ginder et al.^[5] reported that the

conductivity of "conducting island" of PANI itself could be achieved up to 10^3 S/Cm . This suggests that the microscopic localized state or across interfibrillar or intergranular barriers is exited. This is supported by the fact that the temperature dependence of conductivity measured by four probe method for conducting polymers shows a semiconducting behavior obeyed Variable Range Hopping (VRH) Model^[6]. This is attributed to the contact resistance in the interfibrillar or intergranular regions of conducting polymers. It has been demonstrated that the temperature dependence of conductivity measured by Voltage Shorted Compaction (VSC) method^[7-8] for conducting polymers could show a metallic behavior^[9-12], which indicates an interfibrillar or intergranular resistance in conducting polymers is present. Therefore, the interchain conductivity should be considered for the conducting polymers. In other words, both conductivity on chain and across interchain conductivity between chains are contributed to the conductivity measured by four probe method.

PHYSICAL MODEL

In fact, a complex series-parallel model of conductivity on chain and the interchain between chains to describe conductivity of conducting polymers at room temperature is not possible. Based on the above described, however, it is expected that the conductivity of conducting polymers measured by four probe method is controlled by both conductivity on chain and interchain between chains. Thus, it is reasonable to assume that the measured resistance (R_m) for conducting polymers might be considered as a series of resistance on chain (R_c) and the interchain between chains (R_i), which can be expressed as

$$R_m = R_c + R_i \quad (2)$$

and

$$\rho = 1/\sigma \quad (2-a)$$

$$R = \rho \cdot L/S \quad (2-b)$$

where ρ and σ are resistivity and conductivity, respectively, whereas L and S are length and surface of across section of sample, respectively. If the equation (2-a) and (2-b) are used instead of equation (2), so that

$$\left(\frac{1}{\sigma} \cdot \frac{L}{S}\right)_m = \frac{1}{\sigma_c} \left(\frac{L}{S}\right)_c + \frac{1}{\sigma_i} \left(\frac{L}{S}\right)_i \quad (3)$$

or

$$\left(\frac{1}{\sigma}\right)_m = \frac{1}{\sigma_c} \left(\frac{S}{L}\right)_m \cdot \left(\frac{L}{S}\right)_c + \frac{1}{\sigma_i} \left(\frac{S}{L}\right)_m \left(\frac{L}{S}\right)_i \quad (4)$$

let

$$\left(\frac{S}{L}\right)_m \cdot \left(\frac{L}{S}\right)_c = a \quad (4-a)$$

and

$$\left(\frac{S}{L}\right)_m \cdot \left(\frac{L}{S}\right)_i = b \quad (4-b)$$

Thus

$$\sigma_m = \frac{\sigma_c \sigma_i}{a\sigma_i + b\sigma_c} \quad (5)$$

where σ_c is the conductivity on the chains, while σ_i is the interchain conductivity between chains, a and b are assumed as a constant, which is independent on temperature and related to chain coupling between chains. The equation (5) is a mathematical expression for physical model proposed in this paper. As shown in equation (5), one can see that the measured conductivity for conducting polymers not only depends upon the conductivity on chains, but also on the interchain conductivity between chains. This suggests that the interchain coupling plays an important role to determine the electrical properties of conducting polymers, especially the temperature dependence of conductivity. In general, the energies required for transport of charge carriers along the chains are less than that of across interchain. So, it is expected that the condition of $\sigma_i \ll \sigma_c$ is satisfied. If this condition is assumed, the equation (5) could be reduced as

$$\sigma_m \doteq \sigma_i / b \quad (6)$$

The equation (6) suggests that the conductivity of conducting polymers at room temperature is controlled by the interchain conductivity between chains when the $\sigma_i \ll \sigma_c$ condition is satisfied. At this condition, the temperature dependence of conductivity for conducting polymers is expressed as

$$\frac{\partial \sigma_m}{\partial T} \doteq \frac{1}{b} \frac{\partial \sigma_i}{\partial T} \quad (7)$$

According to the equation (7), it indicates that the temperature dependence of conductivity for conducting polymers only depends on the variation of the interchain conductivity between chains with temperature, which is in agreement with experimental observations obtained by four-probe method^[9-12]. That is why a metallic temperature dependence of the conductivity for highly doped conducting polymers is never observed instead of a semiconducting behavior obeyed VRH model^[6].

MECHANISM OF ENHANCED CONDUCTIVITY

For stretched conducting polymers, similarly, when the condition $\sigma_i' \ll \sigma_c'$ is satisfied, the conductivity of stretched conducting polymers at room temperature can also be given by

$$\sigma_m' \doteq \sigma_i' / b' \quad (8)$$

The definition of σ_i' , σ_c' and b' are the same as that given in equation (4a) and (4b). Thus, the ratio of the conductivity of stretched conducting polymers to that of unstretched polymers can be given by

$$\left(\frac{\sigma_m'}{\sigma_m}\right)_{\text{theor}} = \frac{b}{b'} \frac{\sigma_i'}{\sigma_i} \quad (9)$$

The physical meaning of the equation (9) suggests that the enhanced conductivity for stretched conducting polymers is mainly controlled by the ratio of the stretched interchain conductivity between chains to that of unstretched films if $\sigma_i \ll \sigma_c$ and $\sigma_i' \ll \sigma_c'$ are assumed. The results obtained from X-ray diffraction and SEM of stretched PANI films^[3] showed that an oriented arrangement of interchain packing was observed after drawing processes. This indicates that the interchain conductivity between chains is enhanced by drawing processes, which is consistent with the suggestions given by equation(9).

In experimental, moreover, the enhanced conductivity for stretched conducting polymers could be expressed by an experimental formula as

$$\left(\frac{\sigma_m'}{\sigma_m}\right)_{\text{expt}} = \sigma_0 + \alpha \frac{\Delta l}{l_0} \quad (10)$$

and
$$\Delta l = l - l_0 \quad (10\text{-a})$$

where σ_0 is the conductivity of unstretched samples, l and l_0 are length of sample before and after stretching, respectively, α is a constant related to slope of the linear of (σ_m'/σ_m) plotted to l/l_0 . By comparison of the equation (10) with equation(9), the equation(11) can be obtained as

$$\frac{\sigma_i'}{\sigma_i} = \frac{b'}{b} \left(\sigma_0 + \alpha \frac{\Delta l}{l_0}\right) \quad (11)$$

The equation (11) shows that the ratio of conductivity of stretched conducting polymers to that of unstretched sample not only depends on the drawing ratio, but also on the conductivity of unstretched sample. This means that the higher conductivity at room temperature for unstretched sample will show higher enhanced conductivity after drawing when the elongation ratio is a constant. This is in agreement with the fact that the enhanced conductivity of highly protonated PANI films is significant than that lower protonated samples^[3].

As shown in equation (11), moreover, it is noted that the enhanced conductivity along the elongation direction for stretched conducting polymers is mainly due to increasing of the interchain conductivity between chains with the increase of the drawing degree.

When the condition $\sigma_i' \ll \sigma_c'$ for stretched conducting polymers is satisfied, the temperature dependence of conductivity can be expressed as

$$\frac{\partial}{\partial T}(\sigma_m') = \frac{l}{b'} \frac{\partial \sigma_c'}{\partial T} \quad (12)$$

This equation indicates that the temperature dependence of conductivity for

stretched conducting polymers is mainly controlled by a variation of the interchain conductivity between chains with temperature. This is consistent with the fact that the temperature dependence of conductivity for stretched PANI films is exhibited a typical semiconducting behavior although its conductivity at room temperature increases two or three orders of magnitude after drawing^[3].

CONCLUSIONS

A model of series of conductivity on chain and the interchain conductivity between chains for conducting polymers is proposed to explain enhanced conductivity of stretched conducting polymers. When the condition $\sigma_i \ll \sigma_c$ is satisfied, this model suggests that: (1) The temperature dependence of conductivity for conducting polymers is mainly controlled by a variation of the interchain conductivity between chains with temperature. This is consistent with the fact that the temperature dependence of conductivity for conducting polymers never exhibited metallic temperature dependence of conductivity instead of a semiconducting behavior^[8-12]; (2) The enhanced conductivity of stretched conducting polymers might be due to an increasing of the interchain conductivity between chains after drawing processes; (3) The temperature dependence of conductivity for stretched conducting polymers is also controlled by a changing in the interchain conductivity between chains with temperature. This is in agreement with the fact that a semiconducting temperature dependence of conductivity for stretched PANI films^[3] has been observed although its conductivity at room temperature is enhanced by two or three orders of magnitude after drawing processes.

Keywords:

Stretched conducting film; Polyaniline; Conducting polymers

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