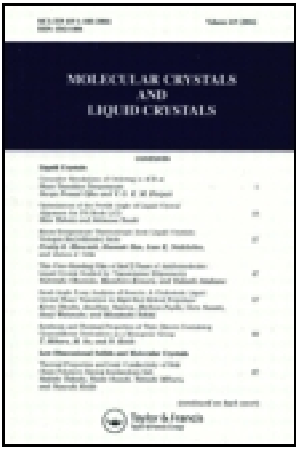

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The Soliton State of Heavily Doped Polyacetylene

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The Soliton State of Heavily Doped Polyacetylene

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We propose that the heavily doped polyacetylene is formed by the soliton-antisoliton pair condensation which is a mixed state of the delocalized charge carriers and the virtually bound states. With this proposal, the metallic conductivity and the temperature independent magnetic susceptibility as well as the infrared active vibrational modes (IRAV) observed in the heavily doped polyacetylene can be understood simultaneously. Furthermore, the persistence of the C=C and C—C vibrational modes appeared in Raman spectra for the heavily doped polyacetylene can also be understood with this soliton-antisoliton condensed state model. The highest conductivity estimated from this phenomenological model is $\sigma_{RT} \simeq 35{,}000$ S/cm, consistent with the observed (and confirmed) maximum conductivity of the heavily doped polyacetylene.

Keywords: polyacetylene, heavily-doped, soliton–antisoliton pair condensation

INTRODUCTION

Approximately twenty prototypes of conjugated polymers are known as conductive polymers. Each prototype polymers can have many substituents as its derivatives, so that hundreds of conductive polymers are currently under investigation. Among them, the heavily doped polyacetylene is unique, since it has the simplest backbone structure and it shows the highest conductivity. The confirmed maximum conductivity is $\sigma_{\max} = 30{,}000$ S/cm for the $FeCl_3$ doped stretch-oriented polyacetylene.[1] This conductivity value is about 100 times higher than those of other known conductive polymers. It is difficult to understand such a high conductivity value if one thinks about its complex morphology. Microscopically, the degeneracy of ground state of conducting polymers seems to be important for the excitations of solitons, polarons and bipolarons which can contribute to the high conductivity.[2,3] However,

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whether the charge transport mechanism in heavily doped polyacetylene is three-dimensional[4] or quasi-one dimensional[5] is not clarified yet.

We have measured the temperature dependence of d.c. conductivity and thermoelectric power for the transition metal halides doped polyacetylene films.[1,6,7] The data can be summarized as follows. (1) The metallic polyacetylene shows quasi-one–dimensional charge transport mechanism. To support this conclusion, we compared the temperature dependent anisotropy of conductivity for the non–degenerate ground state conducting polymers such as PPV derivatives.[5] (2) Thermoelectric power data indicate that there exists an interaction between the delocalized charge carriers in the polymer chain and the dopant ions located nearby the chain. Thermoelectric power (TEP) is a zero current transport coefficient, *i.e.*, it measures the voltage drop across the sample due to the thermal gradient rather than the electrical current. Therefore, it is insensitive to the complex morphological interruptions of the system and it can measure the intrinsic properties of the conductive polymers.[8]

RESULTS AND DISCUSSIONS

Figure 1 shows the soliton-antisoliton pair condensation model of the heavily doped polyacetylene. As shown in the figure, metallic polyacetylene chain is not a uniform bond length chain. Instead, there exists fully dimerized portions of the chain at the boundary of soliton–antisoliton pair even for the uniformly doped sample and the number of such boundary increases in proportion to the doping concentration. Within a strictly one-dimensional model, the soliton-antisoliton pair condensation occurs at 5 ~ 6% of doping concentration.[9] Above this concentration, the soliton wave function overlaps completely resulting that the electronic density of state forms an extended state. Since each soliton is pinned at its dopant site, the charges in the polymer chain tunnel to their neighbor solitonic states. This picture is quite similar with that of the macroscopic quantum tunneling theory[10] except that we are working on the amplitude solitons, *i.e.*, topological solitons rather than the phase solitons occurring in the charge density wave system. If the Fröhlich mass in macroscopic quantum tunneling theory is replaced with the soliton mass in

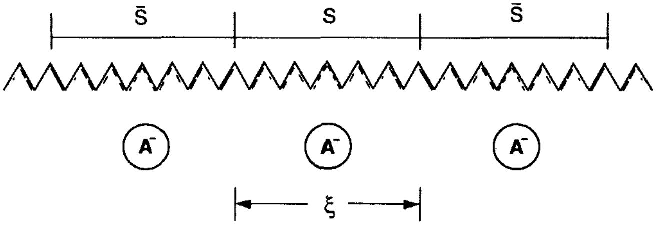

FIGURE 1 The soliton (S)-antisoliton ($\bar{S}$) pair condensation in heavily doped polyacetylene. ξ is the width of a single soliton which is about 15 carbon atoms distance. Note that only at the center of a soliton (or antisoliton), the bond alternation parameter is zero, *i.e.*, uniform bond length and there exist a net bond alternation around the center of a soliton (or antisoliton) becoming fully dimerized at the boundary of a soliton and antisoliton pair. (See figure 3 of reference 5.) A^- represents the acceptor dopant.

polyacetylene, the conductivity can be enhanced to the corresponding ratio. By this analogy, we can understand the high conductivity of the heavily doped polyacetylene at least within the first handed phenomenological model. Incidentally, the effective mass of the $NbSe_3$ is about $m^* = 120$ m_e and the soliton mass in polyacetylene is known to be $m_s = 7$ m_e. Taking the conductivity of $NbSe_3$ as 2,000 S/cm, the conductivity of the heavily doped polyacetylene is estimated to be ~35,000 S/cm consistent with the observed (and confirmed) maximum conductivity of the $FeCl_3$ doped polyacetylene.[1] However, since the heavily doped polyacetylene is a completely different system, one has to work out theoretically as an independent problem to fit all the experimental data. The calculation having a soliton band merging with the conduction or valence band in polyacetylene[3] could interpret some of the experimental data unambiguously. With our model of the soliton state of heavily doped polyacetylene, the new intense Raman modes at ~1270 cm^{-1}, ~1200 cm^{-1} and ~1600 cm^{-1} appeared in the alkali metal doped polyacetylene at doping level of $y > 5 \sim 6\%$[11] could also be understood as following. At $y \simeq 5 \sim 6\%$ of doping level, the soliton wave functions are overlapped completely and for the higher doping concentrations such as in the case of the alkali metal doping, the boundary of the soliton–antisoliton pair tends to be disturbed due to the presence of alkali metal dopant in its neighbor. Then, because of the extra charge transfer to the boundary of the soliton–antisoliton pair, the unperturbed dimerized portion of the polyacetylene chain begins to disappear and one can argue that this is the origin of the new Raman modes appearing for $y > 5 \sim 6\%$ doping concentration.

With a simple minded picture of the morphology of the system, it is tempting to conclude that the heavily doped polyacetylene is an assembly of the simple metallic strands of finite length.[12] In this case, the three-dimensional interchain hopping is essential to avoid the localization effect within a single chain and hence to be highly conducting. On the other hand, the infrared active vibrational (IRAV) mode with the appearance of a pseudo gap as well as the persistence of the C=C and C—C stretching modes in Raman spectra for the heavily doped polyacetylene cannot be understood consistently within the simple metallic strand picture. One has to assume an inhomogeneous doping to interpret the Raman spectra of doped polyacetylene. Then, the contradiction comes in immediately, since the strength of the IRAV modes increases with doping concentration indicating that the inhomogeneously doped region increases upon doping. Furthermore, in the three-dimensional picture, there is only one semiconductor-metal transition concentration at which it becomes metallic. However, it is well established that there exist two transition concentrations in doped polyacetylene. Therefore, to understand the non-simple metallic properties of the heavily doped polyacetylene, there has to be some more than the simple metallic strand picture.[13]

For other conductive polymers whose conductivity is not so high compared to the conductivity of the heavily doped polyacetylene, one can think about the three-dimensional delocalization model where the complex morphological effect comes in importantly.[4] Microscopically, one should remember that the polyacetylene is the only polymer which has the degenerate ground state and all the other conductive polymers have the non-degenerate ground state. Therefore, the intrachain motion is energetically more favorable than the interchain hopping in polyacetylene. Another point one should remember is the role of the interfibrillar contact resistances. By stretching the pristine polymers, the better aligned fibrillar morphology polymer films have been obtained and the magnitude of the parallel direction conductivity ($\sigma_{\|}$) as well as the conductivity anisoptropy ($\sigma_{\|}/\sigma_{\perp}$) increase as the stretching ratio increases. Upon doping, the ($\sigma_{\|}$) and ($\sigma_{\|}/\sigma_{\perp}$) also increase as the doping concentration increases.[14] Therefore, the resistor network model[15] which ignores the interfibrillar contact resistances must be re-examined.

SUMMARY

Some complicated interpretations for the metallic nature of heavily doped polyacetylene were discussed. A series of experimental results reflect one-dimensional and soliton related electronic structure. Our proposal of the soliton-antisoliton condensed stated can explain the observed metallic conductivity, temperature independent magnetic susceptibility, IRAV modes with weak pinning of π electrons as well as the persistence of C—C and C═C vibrational modes in Raman spectra, consistently. Further experiments such as the direct observation of the soliton-antisoliton pair are expected to prove the soliton state of heavily doped polyacetylene.

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