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Transport Phenomena of Poly(3-alkylthiophene)
at the Solid-Liquid Phase Transition

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We have tried to confirm the sign inversion of the photocarrier in regiorandom poly(3-octadecyl-thiophene), PAT18, by means of the time-of-flight (TOF) method. It was found that the hole mobility decreases with increasing temperature. At the temperature near the solid-liquid phase transition, the hole mobility decreases drastically, and eventually the melting temperature, it was impossible to evaluate the hole mobility from noisy transient photocurrent. On the other hand, transient photocurrents based on electron transport are observed above the melting point. The negative carrier mobility was evaluated in the range from 10^{-6} to 10^{-5} cm^2/Vs, which is comparably the hole mobility at the solid state. Moreover, the electrical conductivity changes drastically at the instant of the solid-liquid phase transition, and transport in the liquid state has been not influenced remarkably by applied hydrostatic pressure, which suggests electronic transport but not ionic transport. These facts suggests that the same mechanism, for example interchain hopping limits carrier transport, and the negative carrier is electron. This uniwue phenomenon is interpreted as modulation of electronic energy state caused by conformational change of the main chain,

We have already reported that the continuous-wave photocurrent measurements on PATns suggest the sign inversion of dominant photocarrier from positive to negative associated with the solid to liquid phase transition.[1],[2] However, the carrier type could not be identified whether electronic or ionic, because ionic carrier may also produce photocurrent upon continuous-wave photoirradiation. This fact lead us to confirm that the dominant photocarrier was changed from hole to electron at the solid to liquid phase transition by evaluating the mobility of photocarriers in PATns by the time-of-flight (TOF) method.

Figure 1 shows typical transient photocurrent and its Scher-Montroll plot, observed at 26°C upon anode (Al) irradiation, where the transporting carrier is the hole. There is a clear bend point in Scher-Montroll plot, from which the hole mobility is calculated as 2.6×10^{-6} cm^2/Vs. This value is the same order as in a previous report by another group.[3] Temperature dependence of transient photocurrents upon anode irradiation is shown in Fig. 2. Clear transient photocurrents were observed over the range of 37-84°C with gradual shift of the transit time to longer by increasing

temperature. The hole mobility were calculated to be 3.2×10^{-6} and $6.2 \times 10^{-6} \text{cm}^2/\text{Vs}$ from these transit times at 37 and 84°C, respectively. Above 84 °C, the transient photocurrents decease drastically and the transit time becomes much longer. The hole mobility at 95°C was found to be $1.2 \times 10^{-8} \text{cm}^2/\text{Vs}$. Eventually, only noisy transient photocurrents were observed above 107°C, and there were no clear bend point available for the mobility evaluation.
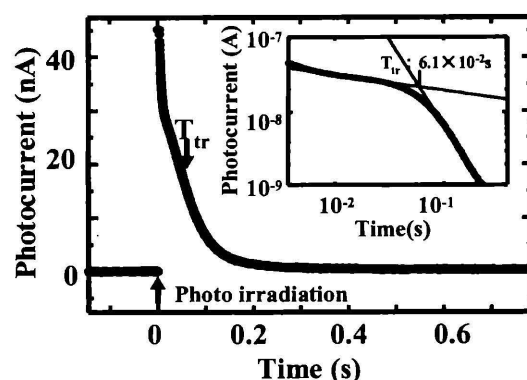

Figure 1. Transient photocurrent for anode irradiation at room temperature. Inset shows the Scher-Montroll plot of the photocurrent.
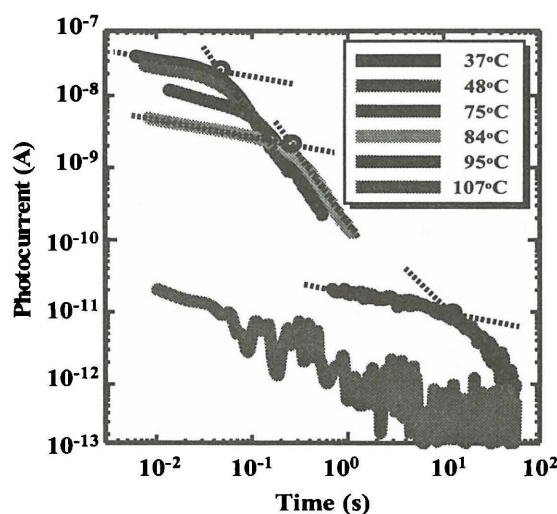

Figure 2. Transient photocurrent at various temperature upon anode irradiation.

Transient photocurrents by the cathode (ITO) irradiation observed at various temperatures are shown in Fig. 3. In contrast to the case of anode irradiation, it is impossible to evaluate the negative carrier mobility below 85°C, because we observed the polarity reversal of photocurrents below 85°C. That is, the transient photocurrents are abnormal and are not understood as dispersive electronic transport. However, as shown in Fig. 3 above 90°C clear transient photocurrents, which can be analyzed by the Scher-Montroll model are observed. The negative carrier mobility was estimated as 4.9×10^{-6}-$8.4 \times 10^{-6} \text{cm}^2/\text{Vs}$ in the temperature range of 90-114°C.

Figure 4 summarizes the temperature dependence of the hole and negative carrier mobility of PAT18. It is clearly shown that the sign of the photocarrier in PAT18 inverts approximately at 90 °C. It is reported that the hole mobility of solid state regioregular PAT18 increases with increasing temperature.[4] However, it is found that the hole mobility in regiorandom PAT18 decreases with increasing temperature in this study. This difference in the temperature dependence of the hole mobility between regioregular PAT18 and regiorandom PAT18 is caused by the difference in their

temperature range. Regioregular PAT18 was measured below room temperature where the lattice structure is probably stable. Therefore, the hole mobility increases with increasing temperature by the thermal activation of hopping. On the other hand, the phenomenon in regiorandom PAT18 is interpreted in terms of the reduced interchain hole hopping probability originating from the thermal vibration of main and side chain vibration near the melting point.
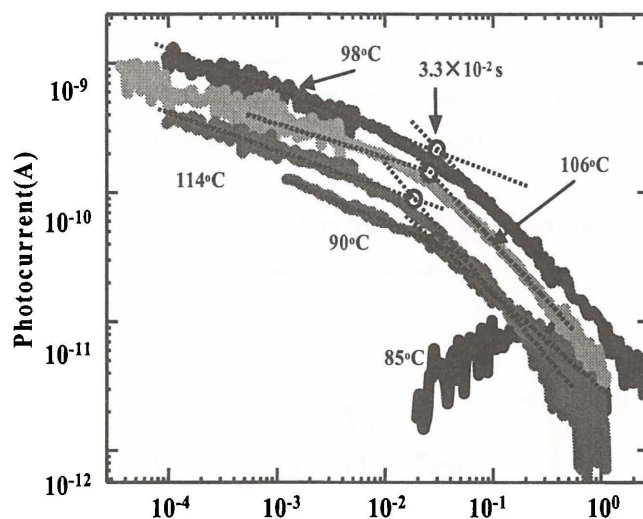

Figure 3. Transient photocurrent at various temperatures upon cathode irradiation.
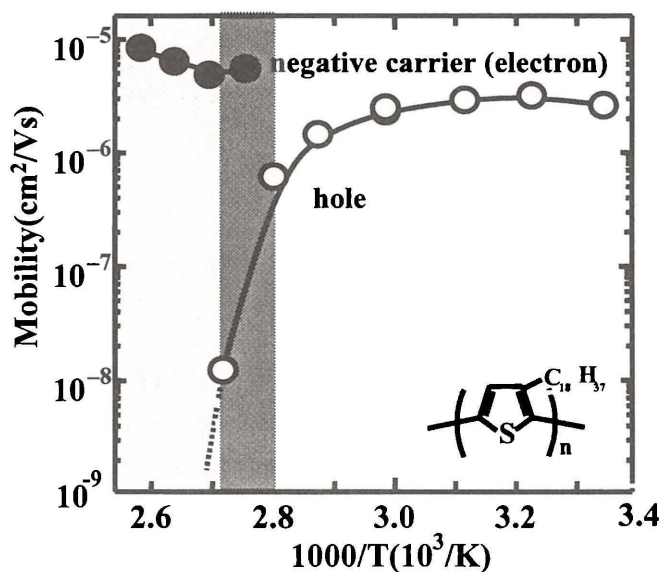

Figure 4. Temperature dependence of hole and negative carrier mobility in poly(3-octadecuyl- thiophene).

We have already reported that temperature dependence of conductivity in PATn under hydrostatic pressure.[5] For example, As evident in Fig 5, under hydrostatic pressure, similar temperature dependences of conductivity in solid and liquid states and a step-wise change at the solid-liquid phase transition were observed. In this case, the sample is poly(3-dodecylthiophene), PAT12 with alkyl side chain $-C_nH_{2n+1}$ of n=12.It is clear from this figure that the phase transition temperature increases with hydrostatic pressure. The step-wise change of conductivity at the phase transition can be explained by the increase of the bandgap and/or increase of carrier scattering. The

electrical conductivity in the solid phase increased with increasing pressure. This increase of conductivity by pressure can be tentatively explained in terms of the decrease of carrier scattering under pressure. On the other hand, in liquid phase, electrical conductivity and its activation energy are not influenced remarkably. If the conduction in liquid phase was originated in ionic transport, the conductivity should be much suppressed due to the decreased free volume under hydrostatic pressure. The observed small pressure dependence of conductivity seems to support the interpretation of electronic transport even in liquid phase.

And then, the fact that the negative carrier mobility in PAT18 is comparable to the hole mobility suggests the same mechanism, i.e. interchain hopping of carrier, dominantly governs the transport of both carrirs.

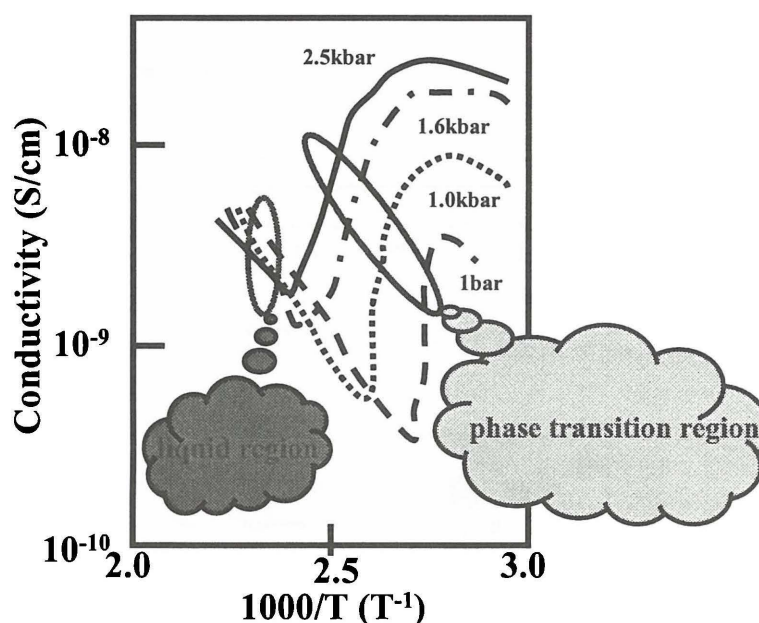Thus we have concluded that the negative carrier is not negative ion but electron.

Figure 5. Temperature dependence of electrical conductivity in poly(3-dodecylthiophene) under hydrostatic pressure.

The photocarrier mobility in poly(3-octadecylthiophene, PAT18 were studied by means of the TOF method. The hole mobility obtained at room temperature was the same order as in a previous report by another group. However, the hole mobility decreased from 2.6×10^{-6} to $1.2 \times 10^{-8} cm^2/Vs$ with increasing temperature from 26 to 95°C. It could not be evaluated above 107°C. However, the electron mobility is obtained above the pre-melt region. It is comparable to the hole mobility at room temperature. This unique phenomenon is due to the variation of electronic energy states in PAT18 caused by a twist of the main chain induced by thermal vibration of side chain.[6]

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