

Temperature-Conductivity Characteristics of the Composites Consisting of Fractionated Poly(3-hexylthiophene) and Conducting Particles

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Received 29 September 1999; accepted 26 January 2000

ABSTRACT: Poly(3-hexylthiophene) (P3HT) synthesized by oxidative polymerization was fractionated by molecular weight by using organic solvents. The fraction of higher average molecular weight gave higher regioregularity and conductivity. Composites of the P3HT fraction having the highest molecular weight were prepared by use of the following conducting particles as fillers: titanium carbide (TiC), indium tin oxide (ITO), and carbon black (CB). Temperature-conductivity profiles of the composites showed that the resistance change with PTC (positive temperature coefficient) effect was strongly influenced by the content and size of conducting particles and the molecular weight of P3HT. Although no significant PTC effect for P3HT-CB composite and little effect for P3HT-ITO composite system were observed, the P3HT-TiC composite containing TiC of 70–80 wt % showed an obvious PTC effect that brought the conductivity change by about four orders of magnitude near the glass transition temperature of P3HT. However, such a remarkable PTC effect was not observed for the P3HT-TiC composite prepared with the P3HT fraction of low-molecular weight. It was shown that a good PTC effect could be achieved by the composite consisting of the P3HT of high-molecular weight and the conducting particles of relatively large size. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 77: 3069–3076, 2000

Key words: poly(3-hexylthiophene); fractionation; positive temperature coefficient effect; composite

INTRODUCTION

Poly(3-alkylthiophenes) have attracted much attention in recent years due to not only their conducting properties but their processibility based on their solubility in common organic solvents and fusibility.^{1,2} They are excellent candidates for various technological applications such as light-emitting diodes, nonlinear optical devices, field-effect transistors, and sensors.^{3–5}

We were interested in the electrical properties of P3HT, especially in PTC effect (i.e., the resis-

tance-switching with a PTC). The materials having PTC characteristics can be used to manufacture self-limiting heating cables and various switching devices (for example, overcurrent protectors or resettable fuses).^{6,7} In our previous studies, the PTC characteristics of cast films of P3HT, which was synthesized at a low temperature by chemically oxidative polymerization, were investigated.⁸ Although the P3HT cast film showed a significant PTC effect near the melting point, there still exists some difficulty in applying it to electric devices because of its low conductivity at room temperature.

The composites of P3HT and conductive particles, such as P3HT-TiC composite,⁹ are expected to have both PTC property and enhanced conduc-

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Journal of Applied Polymer Science, Vol. 77, 3069–3076 (2000)
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tivity. On the other hand, there still remains a possibility to improve the conductivity of P3HT itself. The anisotropy in electrical conductivity has been observed frequently for conjugated polymers. This observation suggests that electrical conduction occurs along polymer chains and that molecular weight and regioregularity of the polymers, which affect the conjugation length, are very important factors in electrical properties of the polymers. Thus, the conductivity of P3HT will be raised by the increase of its molecular weight and regioregularity.

In the present study, the P3HT prepared by chemically oxidative polymerization was fractionated by using organic solvents. The conjugation length and regioregularity of P3HT fractions were evaluated by UV-Vis and $^1\text{H-NMR}$ spectroscopy. The P3HT fraction having the highest average molecular weight, which was found to have the highest regioregularity and conductivity, was blended with conducting particles of different sizes (TiC, ITO, and CB). The temperature-conductivity characteristics of these three kinds of composites were investigated, and the conditions related to the resistance change with PTC were discussed.

EXPERIMENTAL

Materials

TiC was supplied by Furukawa Electric Co. (Tokyo, Japan), the particle size of which was 0.9–1.5 μm . ITO was supplied by Fujikura Chemical Industry Co. (Tokyo, Japan), the particle size of which was 0.5–1.0 μm . CB (Furnace black, Asahi AG 300) was obtained from Aasahi Carbon Co. (Niigata, Japan) and had an average particle size of 0.02 μm . 3-Hexylthiophene was supplied by Tokyo Chemical Industry Co. (Tokyo, Japan); it was purified by distillation under reduced pressure prior to use. Synthetic grade FeCl_3 from Merck (Darmstadt, Germany) was used without further purification. Other chemicals were guaranteed reagent grade or analytical grade commercial materials and used without further purification.

Polymerization and Fractionation

P3HT was synthesized by a modified method of Sugimoto et al.¹⁰ 3-Hexylthiophene was polymerized by oxidation with FeCl_3 in chloroform: 200 μL of 3-hexylthiophene was mixed with 100 mL of

chloroform solution saturated with FeCl_3 , and the mixture was stirred at -40°C . After a polymerization of 2 h, the methanol was added to the reaction mixture to precipitate the polymer. The precipitate was collected by filtration and treated with 30% (v/v) solution of ammonia in ethanol for 1 h to remove surplus FeCl_3 . Finally, the product was rinsed with a large amount of ethanol and dried under reduced pressure at room temperature. This product was used as an original P3HT.

Prior to fractionation, the original P3HT was dissolved in hot toluene and kept at 8°C for 24 h. The solution was centrifuged at 10,000 rpm, 8°C for 1 h to remove the insoluble substances, and the supernatant was subjected to fractional precipitation. The fractional precipitation was carried out by adding methanol to the supernatant and by keeping it at 8°C for 24 h. First, 10% methanol was added to the supernatant. The precipitate was collected by centrifugation at 10,000 rpm, 8°C for 1 h and used as Fraction A. Succeedingly, further fractionations were carried out by incremental addition of methanol (5% to the supernatant) and six other fractions were precipitated. In this way, a total of seven P3HT fractions (A–G) of different molecular weights were obtained.

Preparation of P3HT Film

The films were prepared from 5% (w/v) solution of P3HT in toluene at room temperature. For different purposes, the P3HT solution was cast onto different substrates: Al_2O_3 substrates were used in electrical measurements, and quartz plates were used for measuring the UV-Vis spectra.

Preparation of P3HT Composites

The fractionated P3HT was dissolved in toluene. A known amount of conductive particles was added to the solution, and the mixture was stirred for more than 24 h to disperse the conductive particles homogeneously in polymer solution. Then, methanol was added to the mixture very slowly to precipitate the P3HT uniformly on the surfaces of conducting particles. The precipitate (i.e., P3HT composite) was filtered off and dried under reduced pressure. The pressed pellets of the composites that have a thickness of about 1.0 mm were prepared under 50 MPa for 1 min and cut into the samples of 4.0×8.0 mm.

Measurement of Conductivity

The samples were coated with gold and used to the determination of conductivity-temperature

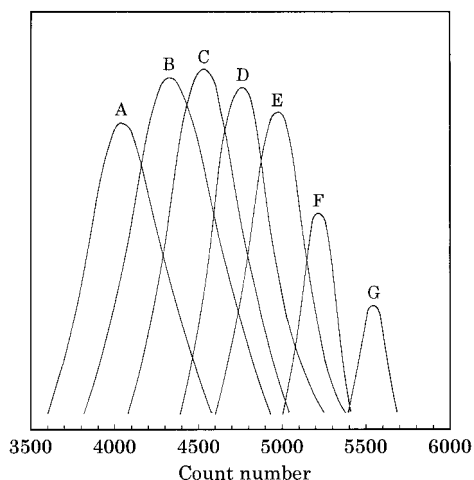


Figure 1 GPC pattern of P3HT fractions obtained by fractionation.

characteristics. Conductivity-temperature characteristics in the thickness direction were measured on a cryostat at a heating rate of 5°C/min *in vacuo*. Two-probe dc method was used and the ohmic contact was confirmed for each sample.

Instruments

The molecular weights and corresponding polydispersity indices of the P3HT fractions were determined by gel permeation chromatography (GPC) with Tosoh TSK-gel column by using chloroform as an eluant and polystyrene as a standard. UV-Vis spectra of toluene solution and cast film of each P3HT fraction were measured on a Shimadzu UV-3100PC spectrophotometer. ¹H-NMR spectra were recorded on a Jeol JNM-EX400 spectrometer by using CDCl₃ as a solvent and tetramethylsilan (TMS) as an internal standard.

RESULTS AND DISCUSSION

Characterization of Fractionated P3HT

P3HT synthesized by oxidative polymerization was fractionated successfully by using organic solvents and seven fractions of different average molecular weight were obtained. The GPC patterns of the fractions of P3HT are shown in Figure 1. The molecular-weight parameters of P3HTs derived from the GPC measurements are presented in Table I. As expected, the GPC patterns of the fractions showed narrowed peaks. The polydispersity indexes of all the fractions are of small values. These results indicate that the organic solvent fractionation is very efficient for molecular-weight fractionation of P3HT.

To obtain some information about the regio-regularity of P3HT fractions, ¹H-NMR spectra of the fractions were measured. It has been known that the α-methylene and β-methylene proton of the alkyl group in P3HT can be resolved into two different diads: head-to-tail (HT) and head-to-head (HH).¹¹ The chemical shifts are HT = 2.80 ppm and HH = 2.58 ppm for α-methylene, and HT = 1.72 ppm and HH = 1.63 ppm for β-methylene. The ¹H-NMR spectra in Figure 2 shows the signals assigned to α-methylene protons of the P3HT fractions. It can be seen that the area ratio of HT signal to HH signal increases with an increase in the molecular weight of the fractions, although the chemical shifts of these signals do not vary. The HT coupling contents of the fraction A to G were calculated from the ¹H-NMR data in Figure 2 as follows: A, 86.9%; B, 83.8%; C, 80.6%; D, 77.2%; E, 73.7%; F, 69.3%; G, 63.0%. These results demonstrate that the higher the molecular weight of the P3HT fraction is, the higher regio-regularity the fraction has in its molecules. The regio-regularity and molecular weight of the P3HT fractions were reflected also in UV-Vis

Table I Molecular Weight Parameters of P3HT Fractions

Fractions	A	B	C	D	E	F	G
\overline{M}_w^a (10 ⁴)	8.37	5.99	4.07	1.81	1.20	1.06	0.88
\overline{M}_n^b (10 ⁴)	5.12	3.08	2.58	1.44	1.04	0.89	0.65
$\overline{M}_w/\overline{M}_n^c$	1.63	1.95	1.58	1.26	1.16	1.19	1.16
DP ^d	497	356	242	108	71	63	52

^a Weight-average molecular weight.

^b Number-average molecular weight.

^c Polydispersity index.

^d Degree of polymerization.

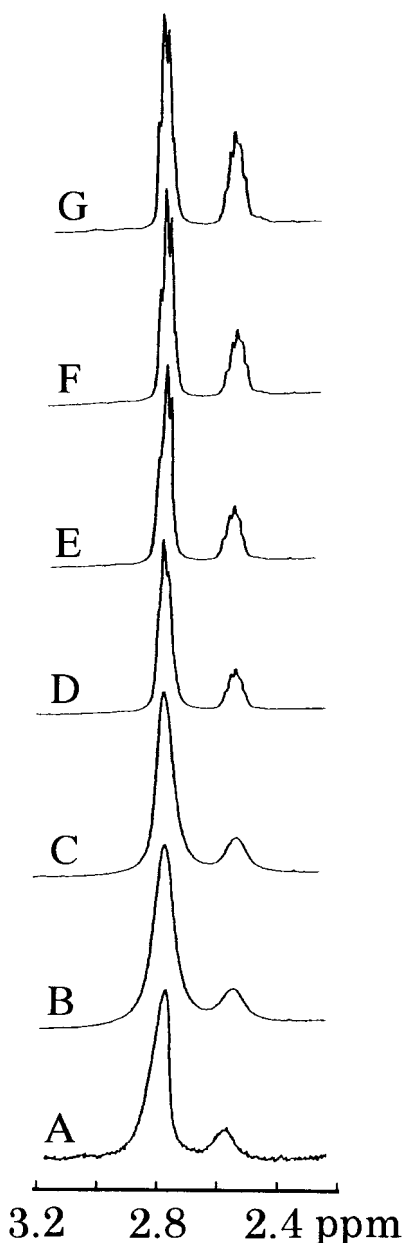


Figure 2 $^1\text{H-NMR}$ spectra of P3HT fractions in CDCl_3 .

spectra. Figures 3 and 4 show the UV-Vis spectra of toluene solution and cast film of each P3HT fraction, respectively. A red shift of λ_{max} was observed for both the solution and cast film corresponding to increasing molecular weight of the P3HT fraction. It is a point of interest that the red shift was more apparent for the cast film than for the solution. The high regioregularity and molecular weight are considered to be effective in maintaining the planarity of P3HT molecules. The pla-

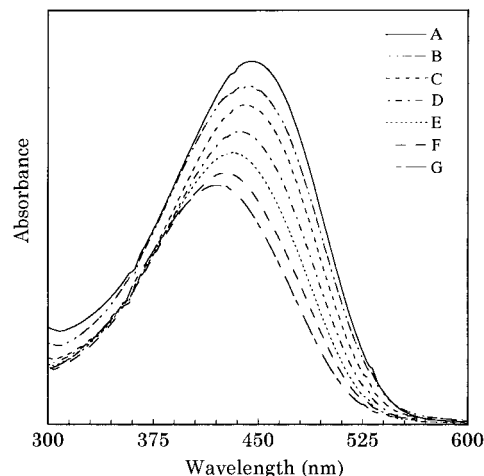


Figure 3 UV-Vis spectra of P3HT fractions in toluene solution.

narity of the molecules leads to a long conjugation structure and, as a result, gives a narrow-band gap to cause the red shift of λ_{max} .

Prior to preparation of P3HT composite, the conductivity of fractionated P3HT was investigated: the cast film of each P3HT fraction with a thickness of $10\ \mu\text{m}$ was prepared and the conductivity in thickness direction was measured at room temperature. As shown in Table II, the conductivity of the P3HT fraction varied remarkably with its average molecular weight. As the average molecular weight increased from 1.20×10^4 to 8.37×10^4 , the conductivity increased by a factor of about 200 from 8.01×10^{-8} to $1.55 \times 10^{-5}\ \text{S cm}^{-1}$. Thus, the conductivity of the P3HT fraction

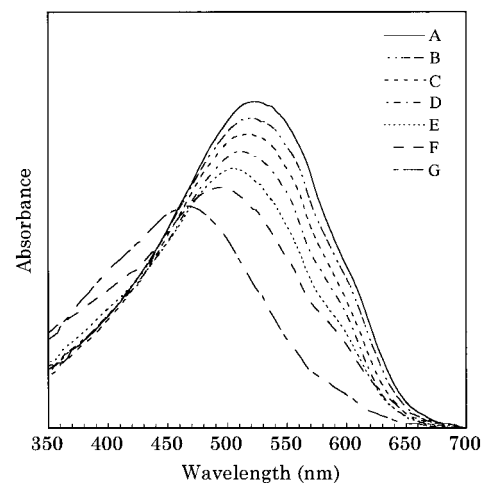


Figure 4 UV-Vis spectra of P3HT fractions of cast film.

Table II The Conductivity of P3HT Fractions (cast film) at Room Temperature

Fractions	A	B	C	D	E
Molecular weight (\overline{M}_w)	8.37×10^4	5.99×10^4	4.07×10^4	1.81×10^4	1.20×10^4
Conductivity ($S\text{ cm}^{-1}$)	1.55×10^{-5}	6.38×10^{-6}	3.19×10^{-6}	2.67×10^{-7}	8.01×10^{-8}

was found to depend on the molecular weight, which was related to the regioregularity of molecules. Namely, these results allow the consideration that the P3HT fraction of high-molecular weight, the molecular regioregularity of which is also high, has a long conjugation structure to show high conductivity.

Temperature-Conductivity Characteristics of the P3HT Composites

Taking the above results and discussion into account, the P3HT fraction of the highest molecular weight (Fraction A) was selected as the matrix material of the composites. Three kinds of P3HT composites, P3HT-TiC, P3HT-ITO, and P3HT-CB, were prepared and the conductivity of each composite was measured at room temperature as a function of the filler content. Figure 5 shows the conductivity data for these composites. It is generally considered that the electrical properties of such composite materials reflect a mechanism of percolation.¹² According to this mechanism, a particular transition occurs at a critical concentration of conducting particle, and above the critical concentration, the charge carriers are formed by a

continuous infinite network of the conducting particles which are in physical contact or in tunnel mechanism.¹³ The data in Figure 5 show that the percolation thresholds (critical concentration) are 68 wt % TiC for P3HT-TiC composite, 40 wt % ITO for P3HT-ITO composite, and 18 wt % CB for P3HT-CB composite. Furthermore, the percolation thresholds were found to increase with an increase in the size of conductive particles. It is considered that the conducting particles of a small size have large accumulation energy to form a network of aggregates, and thus, conducting pathways are formed in the polymer matrix more easily than the composite filled with conducting particles of a large size and same content.¹⁴ Therefore, the size of the conducting particles is an important factor in the electrical properties of the composites.

Figures 6, 7, and 8 show the temperature dependence of the conductivity of P3HT-TiC, P3HT-ITO, and P3HT-CB, respectively. No significant PTC effect for P3HT-CB composite (Fig. 6) and a slight PTC effect for P3HT-ITO composite (Fig. 7)

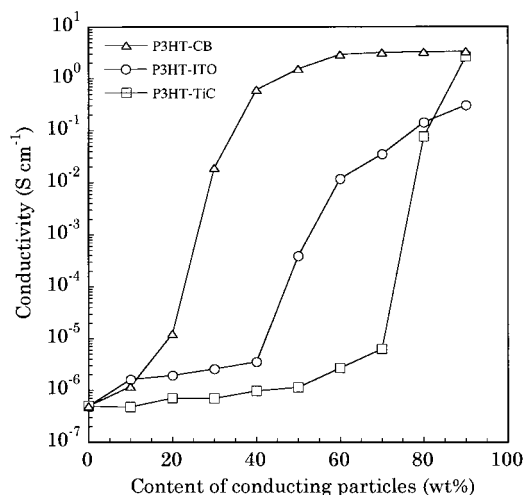


Figure 5 Dependence of conductivity of P3HT (Fraction A) composites on the content of conducting particle at room temperature.

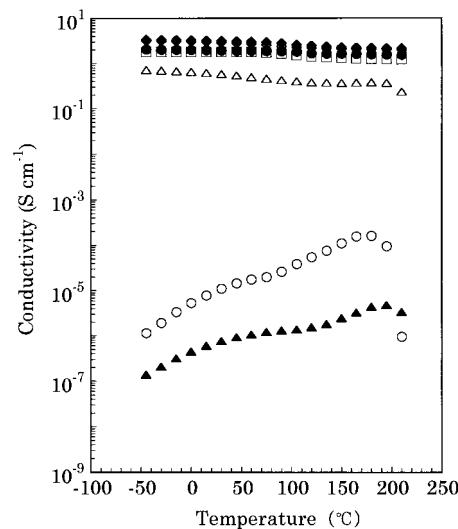


Figure 6 Temperature dependence of conductivity of P3HT (Fraction A)-CB on the content of CB: ▲, 0 wt %; ○, 20 wt %; △, 40 wt %; ◇, 60 wt %; ◆, 70 wt %; ●, 80 wt %; □, 90 wt %.

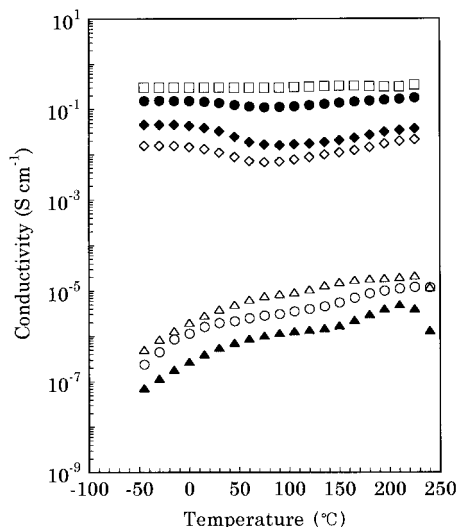


Figure 7 Temperature dependence of conductivity of P3HT (Fraction A)-ITO on the content of ITO: \blacktriangle , 0 wt %; \circ , 20 wt %; \triangle , 40 wt %; \diamond , 60 wt %; \blacklozenge , 70 wt %; \bullet , 80 wt %; \square , 90 wt %.

were observed in a particular range of the filler concentration. It can be considered for these composites that the expansion of P3HT at an elevated temperature is not enough to break conducting pathways in the network of the conducting particles. In the case of P3HT-TiC composite (Fig. 8), remarkable features were observed in its electrical behavior. The conductivity of the composite

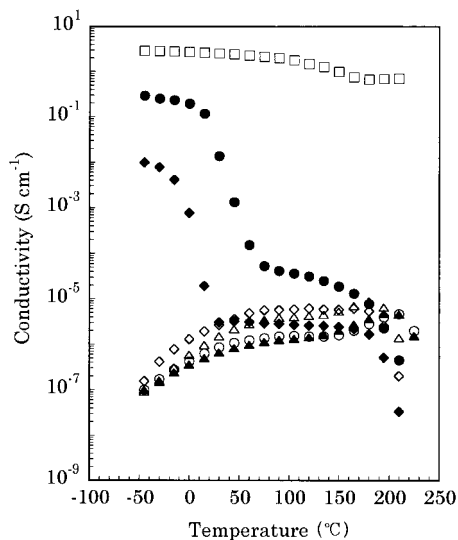


Figure 8 Temperature dependence of conductivity of P3HT (Fraction A)-TiC on the content of TiC: \blacktriangle , 0 wt %; \circ , 20 wt %; \triangle , 40 wt %; \diamond , 60 wt %; \blacklozenge , 70 wt %; \bullet , 80 wt %; \square , 90 wt %.

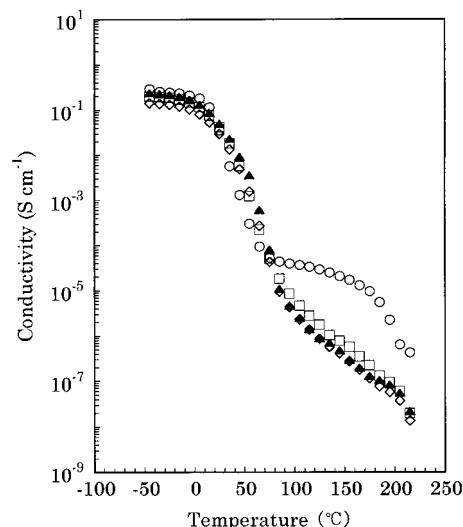


Figure 9 Reproducibility of temperature dependence of conductivity of P3HT (20 wt %)-TiC (80 wt %) composite: \circ , 1st run; \square , 2nd run; \blacktriangle , 3rd run; \diamond , 4th run.

containing TiC of 90 wt %, which was similar to that of TiC, almost did not change over the range of temperatures from -50 to 220°C . On the other hand, the conductivity of the composites with the TiC content < 60 wt %, which was similar to that of P3HT, presented a PTC effect near the melting point of P3HT (200°C).^{8,15} However, in the case of the composite with the TiC content of 70–80 wt %, which was slightly higher than the percolation threshold, the conductivity changed drastically by about four orders of magnitude between 10^{-1} and 10^{-5} S cm^{-1} in the vicinity of room temperature. This remarkable PTC effect is essentially quite different from that observed near the melting point of P3HT. Namely, the TiC particles in the composite can be considered to play an important role in the PTC effect in the vicinity of room temperature. This PTC effect may be attributed to the size of the TiC particles, which is larger than those of the ITO and CB. As shown in Figure 9, the PTC effect of the P3HT-TiC composite was reproducible, although the conductivity profile in the first run was slightly different from others.

The PTC effect of conducting polymer composites seems to result from a compromise between the structure of conducting particle network and the thermal expansion of polymer matrix.^{16,17} The PTC effect is often observed near the glass transition temperature (T_g) of the matrix at which the matrix becomes flexible and expands.^{18,19} As seen from Figure 8, in the case of the P3HT composite with the TiC content of 70–80 wt %, a drastic

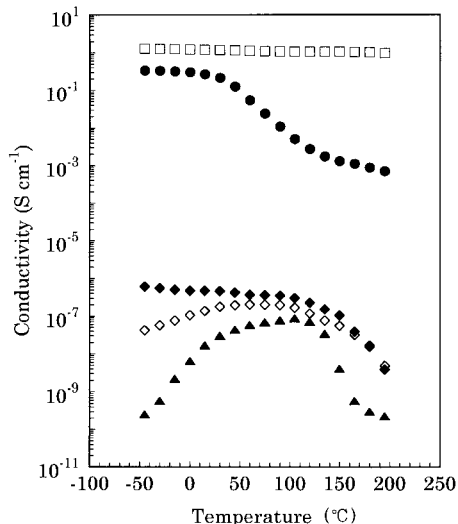


Figure 10 Temperature dependence of conductivity of P3HT (Fraction E)-TiC on the content of TiC: ▲, 0 wt %; ◇, 60 wt %; ◆, 70 wt %; ●, 80 wt %; □, 90 wt %.

change in conductivity was observed to start at around 10°C (i.e., T_g of P3HT).²⁰ This result suggests that an abrupt expansion of P3HT at the T_g loosens the aggregates of TiC particles to break conducting pathways and, consequently, an abrupt decrease in conductivity occurs. Although several studies have confirmed a correlation between material expansion and conductivity change, the mechanism of the PTC effect associated with the T_g of polymer matrix is not fully understood at present.²¹⁻²³

For a comparison, the conductivity of the composite consisting of the P3HT fraction of lowest average molecular weight (Fraction E) and TiC particle was measured. The percolation threshold for the P3HT (Fraction E)-TiC was 68 wt % TiC, which was the same value as that for the P3HT (Fraction A)-TiC. It is likely that the percolation threshold is not dependent on the molecular weight of P3HT. The temperature dependence of the conductivity of P3HT (Fraction E)-TiC is shown in Figure 10, which is quite different from the result shown in Figure 8. This composite with the TiC content of 80 wt % showed a change in conductivity only by about two orders of magnitude over a wide temperature range (50–130°C). As to the composite with the TiC content of 70 wt % or less, the conductivity was close to that of P3HT. It can be seen by comparing the results in Figures 8 and 10 that the sharp PTC effect of the P3HT-TiC composite shown in Figure 8 is associated with the high-molecular weight of the P3HT fraction (Fraction A) in the composite.

CONCLUSION

P3HT prepared by oxidative polymerization was fractionated by using organic solvents. The P3HT fraction of the highest average molecular weight, which had the highest regioregularity and conductivity, was selected and used to prepare the three kinds of the composites: P3HT-TiC, P3HT-ITO, and P3HT-CB. The temperature-conductivity characteristics of these composites containing various amounts of the conductive fillers were investigated, and attention was paid to the resistance changes with PTC.

No significant PTC effect for P3HT-CB composite and a slight effect for P3HT-ITO composite were observed in a particular range of the filler concentrations. However, P3HT-TiC composites with the TiC content of 70–80 wt % showed a remarkable PTC effect that was found as the conductivity change by about four orders of magnitude near T_g of P3HT. It was considered that an abrupt expansion of P3HT at the T_g broke conducting pathways by the aggregates of TiC particles and hence the drastic decrease in conductivity was observed. On the other hand, the P3HT-TiC composite prepared with the P3HT of low average molecular weight showed the conductivity change only by about two orders of magnitude.

The present study demonstrated that a good PTC effect can be achieved by the composite consisting of the P3HT of high-molecular weight and the conducting particles of relatively large size (TiC). Although the problem of whether the effects of material difference of conducting filler particles can be neglected or not is a matter for argument, it is likely that the size of filler particles plays an important role in the PTC effect of the composite. Concerning this consideration, electrical properties of the composites containing TiC particles of different sizes are being investigated in detail.

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