All Polymer PTC Devices: Temperature-Conductivity Characteristics of Polyisothianaphthene and Poly(3-hexylthiophene) Blends

Chuanjun Liu, Kenji Oshima, Masato Shimomura, Shinnosuke Miyauchi

Department of Bioengineering, Nagaoka University of Technology, Kamitomioka-cho 1603–1, Nagaoka 940-2188, Japan

ABSTRACT: The present article is concerned with the temperature-conductivity characteristics of blends consisting of polyisothianaphthene (PITN) particles and a soluble poly(3-hexylthiophene) (P3HT). PITN was synthesized by direct conversion of 1,3-dihydroisothianaphthene (DHITN) monomer using *N*-chlorosuccinimide (NCS) as an oxidation/dehydrogenation reagent. The high conductivity and thermal stability of the doped and dedoped PITN were confirmed. Microscopic investigation by scanning electron microscopy (SEM) showed that the as-prepared PITN exhibited diversified shapes and sizes, with large rectangular particles having an average size of 2 ~ 5 μm and fine round particles ranging from 0.1 to 0.3 μm. The PITN particles were blended with the chemically synthesized P3HT as a high conductivity component to improve the conductivity and simultaneously maintain the positive temperature coefficient (PTC) effect of the original P3HT near its melting point. The temperature-conductivity characteristics for PITN-P3HT blends with various PITN contents showed that a blend having both a high conductivity (nearly 3 ~ 4 orders higher than that of the original P3HT) and a good PTC intensity could be obtained with a PITN content of 20 ~ 25%. The different temperature-conductivity behavior of P3HT blends filled with PITN as compared to other conducting particles, for example, carbon black, was explained by its unique dispersion structure due to a relatively higher adhesive interaction of PITN particles with the P3HT matrix during the precipitation process. The results from heating recycles revealed that the PTC effect of PITN-P3HT blends was not just related to the conductivity decrease of the P3HT matrix, arising from the conformational change of the conjugated backbone during the melting, but also to the dilution effect of the conducting percolation network due to the mobility of PITN particles induced by the viscosity decrease of the P3HT matrix. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 97: 1848–1854, 2005

Key words: poly(3-hexylthiophene); poly(isothianaphthene); conducting polymer; composite; positive temperature coefficient effect

INTRODUCTION

Materials with a positive temperature coefficient (PTC) have been extensively studied due to their great commercial potential. Generally, there are two categories of PTC materials, based on ceramics and polymers, respectively. Polymer-based PTC devices usually consist of composites made up of an insulating polymer matrix and conducting filler particles. Although the mechanism of the PTC effect for conducting polymer composites is still debated, it has been well accepted that the sharp change in resistance (or conductivity) depending on the temperature results from a disturbance in the continuity of the conducting percolation network formed by filled particles, owing to the volume expansion of the polymer matrix.

It has been reported that the electrical conductivity of long side-chain-substituted poly(3-alkylthiophene)s

decreases in a step-wise manner at the melting point, in terms of the shortening of the conjugation length, due to decreased coplanarity of the conjugation system (thiophene backbone) caused by the large conformational change during melting.[1–3] In their previous research works, the authors took a keen interest in this kind of temperature-dependence of conductivity in the case of soluble polythiophene derivatives with a view to fabricating PTC switching devices, because the PTC mechanism of this type of compound is widely different from that involved in conventional PTC materials.[4,5]

A significant PTC effect was observed near the melting point (~ 195°C) of a poly(3-hexylthiophene) film prepared by chemical oxidation with $FeCl_3$ at low temperature (−40°C).[6] However, low conductivity at ambient temperature (~ 10^{-8} S/cm) obviously limited its application. To improve the conductivity, different types of conducting particles (carbon black, ITO, and TiC) were introduced into the fractionated P3HT matrix, and the temperature-conductivity characteristics of the resulting mixtures were investigated.[7–10] The results demonstrated that composites of high molecu-

lar weight P3HT and relatively large conducting particles (e.g., TiC) exhibited a good PTC effect near the T_g temperature of P3HT. Yet the origination of the PTC effect in this case seemingly bore no relation to the conductivity decrease of the P3HT matrix caused by structural changes near the melting point. In addition, for CB and ITO particles with smaller sizes, no obvious PTC effect has been observed both at the T_g and T_m temperature, although the conductivity of composites has been improved by the introduction of filler particles.

In this work, another attempt was made by introducing a conducting polyisothianaphthene (PITN) as the filler particle into the P3HT matrix. PITN was expected both to enhance the conductivity of the blends, as a high conductivity component, and to retain the PTC effect near the melting point of P3HT. PITN, due to its low band gap arising from the ring-fusing effect of benzene on the polythiophene backbone, shows high intrinsic conductivity without the doping process, thus leading to good environmental stability.[11] High conductivity and thermal stability are, no doubt, essential if one considers using PITN as a filling component.

In the present study, PITN was synthesized through direct conversion of 1,3-dihydroisothianaphthene with N-chlorosuccinimide as an oxidation/dehydrogenation reagent. Its conductivity and thermal stability were thoroughly investigated. PITN-P3HT blends were prepared by the dissolution/precipitation method because of the solubility of P3HT. The temperature-conductivity characteristics of blends with various PITN contents were studied. The microscopic structures of PITN, P3HT, and their blends were investigated via SEM. A heating recycle experiment was carried out to determine the effect of thermal treatment on the conducting percolation network and the PTC effect during the melting process of the P3HT matrix.

EXPERIMENTAL

Materials

3-hexylthiophene (Tokyo Kasei Kogyo, Japan), FeCl$_3$ (Merck-Schuchardt, Germany), sodium sulfide nonahydrate (Aldrich), $\alpha'\alpha$-dichloro-o-xylene (Aldrich), N-chlorosuccinimide (Nacalai Tesque, Japan), and tetraphenylphosphonium chloride (Nacalai Tesue, Japan) were used without further purification. Other chemicals were guaranteed reagent or analytical grade commercial materials and used directly.

Synthesis of P3HT

P3HT was synthesized through chemical oxidation of the 3HT monomer with FeCl$_3$ in chloroform at $-40°C$
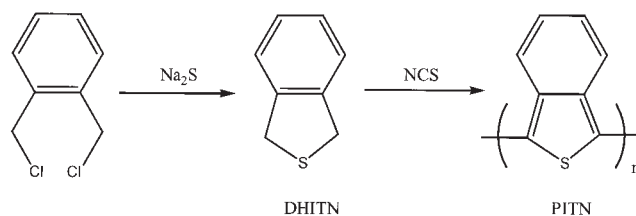
Scheme 1 Schematic diagram of the synthetic route to PITN.

as previously described.[6] P3HT dedoped with the ammonia/ethanol solution was used as the matrix polymer without further fractionation.

Synthesis of PITN

PITN was synthesized according to Scheme 1: sodium sulfide nonahydrate (Na$_2$S·9H$_2$O), partially dissolved in a mixture of ethyl alcohol and water, was refluxed with α,α'-dichloro-o-xylene in a Soxhlet extraction apparatus until the solvent became transparent. Then, the mixture was filtered to remove the solid residue and was extracted with diethyl ether. Evaporation of the solvent afforded a light yellow oil liquid, 1,3-dihydroisothianaphthene (DHITN), which solidified on cooling in the refrigerator.[12,13] The obtained DHITN monomer was then refluxed with N-chlorosuccinimide (NCS) in carbon tetrachloride. After evaporation of the solvent, the residue was Soxhlet extracted with ethanol, tetrahydrofuran, chloroform, and light petroleum in sequence, for 24 h, respectively, followed by drying under vacuum to afford the doped PITN. The dedoped sample was obtained by treatment with concentrated aqueous NH$_3$ for 24 h.[14,15]

Authentic PITN, used for a comparison, was prepared according to Wudl's method via electrochemical polymerization of ITN monomer in an acetonitrile solution containing $0.1M$ tetraphenylphosphonium chloride at 1.2 V versus SCE.[16]

Preparation of the PITN/P3HT blends by dissolution/precipitation

P3HT was first dissolved in toluene. A given amount of PITN powder was added to the solution, and the mixture was stirred at least for 2 h to disperse the insoluble particles homogeneously in the polymer solution. Then, methanol was added into the mixture very slowly to precipitate the P3HT. The precipitate was filtered off and dried at reduced pressure. The disc samples of blends with an average thickness of 0.7 ~ 1.0 mm were prepared with a pressure of 400 kgf/cm^2 for 5 min and then cut into pellets of 4.0 × 6.0 mm.

Conductivity measurements

Gold was evaporated onto the surface of the pellets, and silver paste was used to glue the leads with the
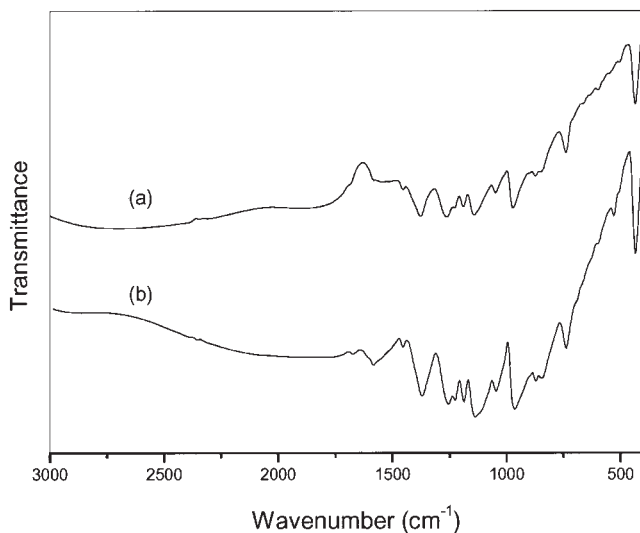
Figure 1 FTIR spectra of (a) PITN prepared by chemical oxidation with NCS from DHITN, and (b) reference PITN obtained by electropolymerization from ITN.

electrodes. Ohmic contact was confirmed for each sample. The conductivity was measured with a two-probe DC method in the direction of the thickness. The temperature-dependence of the conductivity was recorded with a digital multimeter (Hewlett–Packard, maximum range $120 M\Omega$) in vacuum with a heating rate of 5°C/min.[9]

Scanning electron microscopy (SEM)

SEM observations were carried out with a JSM-6310F scanning microscope (JEOL, Japan).

RESULTS AND DISCUSSION

Synthesis and conductivity of PITN

Although PITN has many novel electronic and optical properties, due to its very low band gap, investigation into its properties was often hampered by the lengthy synthetic procedures. That is why a large amount of research during the past 20 years mainly focused on its chemical and electrochemical syntheses. In the present research, the PITN was prepared through direct conversion of 1,3-dihydroisothianaphthene (DHITN) with *N*-chlorosuccinimide (NCS) as an oxidation/dehydrogenation reagent. Compared to other methods of PITN synthesis, the advantage of this approach is that the reaction gives PITN in one step with good yield.

The infrared spectra of the as-prepared PITN and the authentic PITN are identical, as shown in Figure 1. All of the major peaks of PITN were observed in both infrared spectra.[16] It is apparent, from the temperature-dependence of conductivity in Figure 2, that the
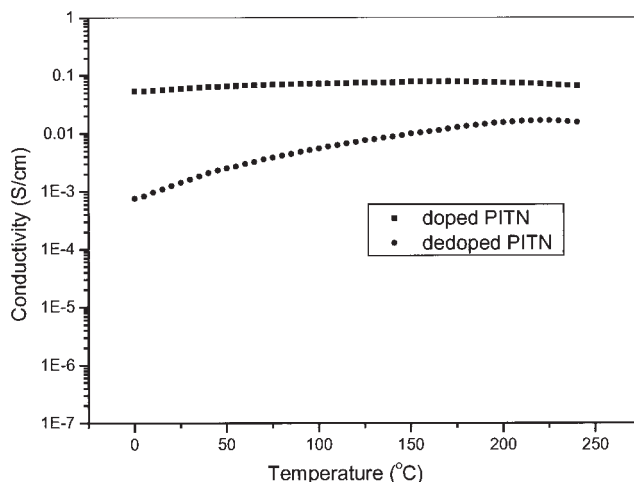

Figure 2 Temperature dependence of conductivity for the doped and dedoped PITN.

room temperature conductivity of doped PITN is in the order of 10^{-2} S/cm, that is, one order higher than that of dedoped PITN (10^{-3} S/cm). This result confirms that PITN has a high intrinsic conductivity with a relatively low doping amount, which is exactly the characteristic of PITN with a small band gap.

Figure 2 also reveals that the conductivity of dedoped PITN gradually increases with increasing temperature, while the conductivity of doped PITN submitted to the thermal treatment is fairly stable. This high thermal stability for the doped PITN is very different from common conducting polymers, because the conductivity of these polymers will generally suffer a sharp decrease due to thermal dedoping during the heating process. In addition, the conductivity of both doped and dedoped PITN remains nearly unchanged even when treated at 240°C for 5 h (Fig. 3).
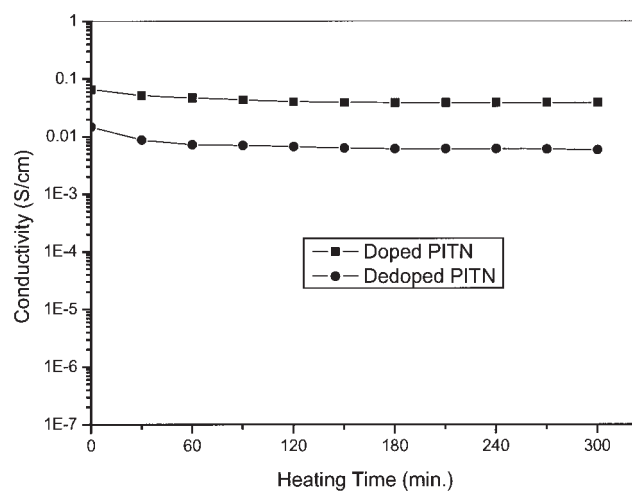

Figure 3 Dependence of conductivity on time of thermal treatment at 240°C.
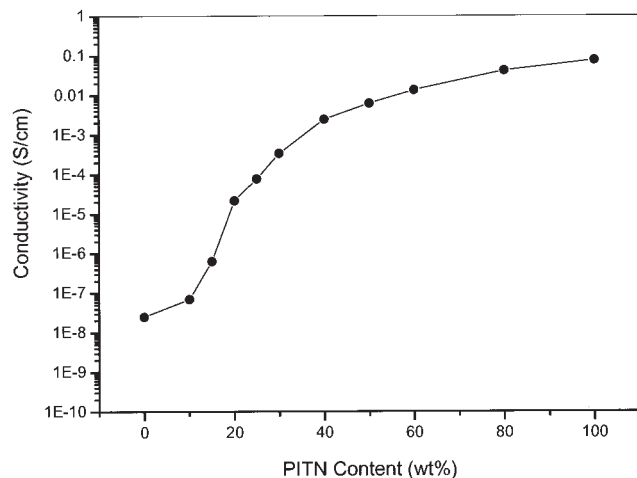
Figure 4 Conductivity of PITN-P3HT blends as a function of PITN content at room temperature (20°C).

This thermal stability and high conductivity for both doped and dedoped PITN may make them more suitable as a polymer-type filler than previously studied conducting polymers, such as polyaniline or polypyrrole, for which the composites can only be processed in the undoped state and generally require a postdoping process for filler particles to obtain conductivity.[17–19] For example, the preparation of polyaniline/epoxy resin composites usually involves a complicated processing approach because the influence of dopant on the conductivity and the performance of the final composite cannot but be considered.[20–22]

Temperature-conductivity characteristics of PITN/P3HT blends

The conductivity of PITN/P3HT blends at the ambient temperature is plotted in Figure 4. Generally, the enhancement effect of filler particles on the conductivity of conducting polymer composites can be explained by the percolation theory. The main notion of this theory is the concept of percolation threshold—a minimal filler concentration, C_p, at which a continuous conducting chain of microscopic length appears in the system.[23] A low percolation threshold C_p (~ 10 wt %) was observed for the PITN-P3HT composite, as shown in Figure 4, which means that only a small amount of PITN can form the conducting network, and thus, make a contribution to the conductivity of composites. The low C_p is similar to the results observed in P3HT composites filled with small size CB and ITO particles in our previous study.[9] The results shown in Figure 4 seem to indicate that the as-prepared PITN particles are of small size, too. The microscopic aspects, visible from the accompanying SEM photographs, support this point.

The conductivity-temperature characteristics of PITN-P3HT blends with various PITN contents are shown in Figure 5. The conductivity of the original P3HT pellet sample at room temperature lies in the order of 10^{-8} S/cm, which gradually increases with increasing PITN content. At the same time, the PTC effect of samples decreases when the percentage of PITN is over 30% and seemingly vanishes for higher contents. However, in the 20 $\sim$ 25% range, a blend exhibiting both a good PTC effect and improved conductivity, nearly 3 $\sim$ 4 orders higher than the original P3HT, was obtained. This result is very different from our previous results for composites prepared by blending P3HT (fraction A) with conducting CB and ITO particles having the same small sizes (0.02 and 0.5–1.0 μm, respectively).[9] For CB and ITO particles, the composites show a temperature-dependence of conductivity close to the original P3HT when the introduced amount of particles is lower than the percolation threshold C_p. However, once the content is higher than C_p, the conductivity increases sharply and the PTC effect disappears immediately. To sum up, these facts seem to imply the existence of a delicate balance between the enhancement effect of PITN on the conductivity of composites and the conductivity change of P3HT attributed to the deformation of the conjugated structure during the thermal process. Excessive enhancement of conductivity will offset the PTC effect, produced by the conductivity change of P3HT subjected to heating, thus leading to the disappearance of the PTC effect in blends. Comparison with the dependence of conductivity on filler content for various composites shows that the conductivity of PITN-P3HT blends is enhanced in a relatively smooth manner; but for P3HT-CB or ITO blends, the trend is rather uneven when the filler content is higher than C_p, so that it is easier for the PITN-P3HT blend to reach a trade-off between an improved conductivity
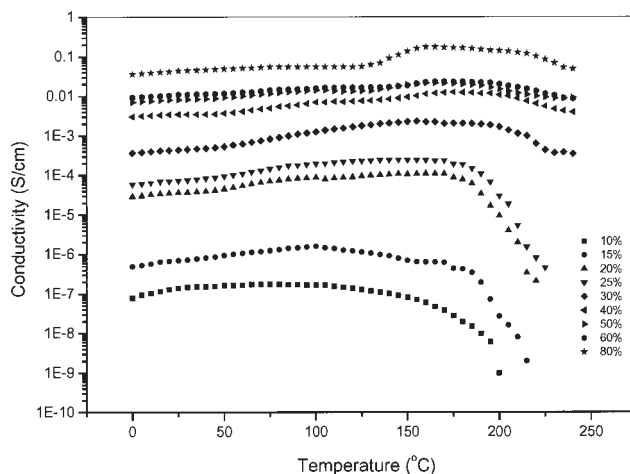

Figure 5 Conductivity-temperature characteristics of PITN-P3HT blends with various PITN contents.
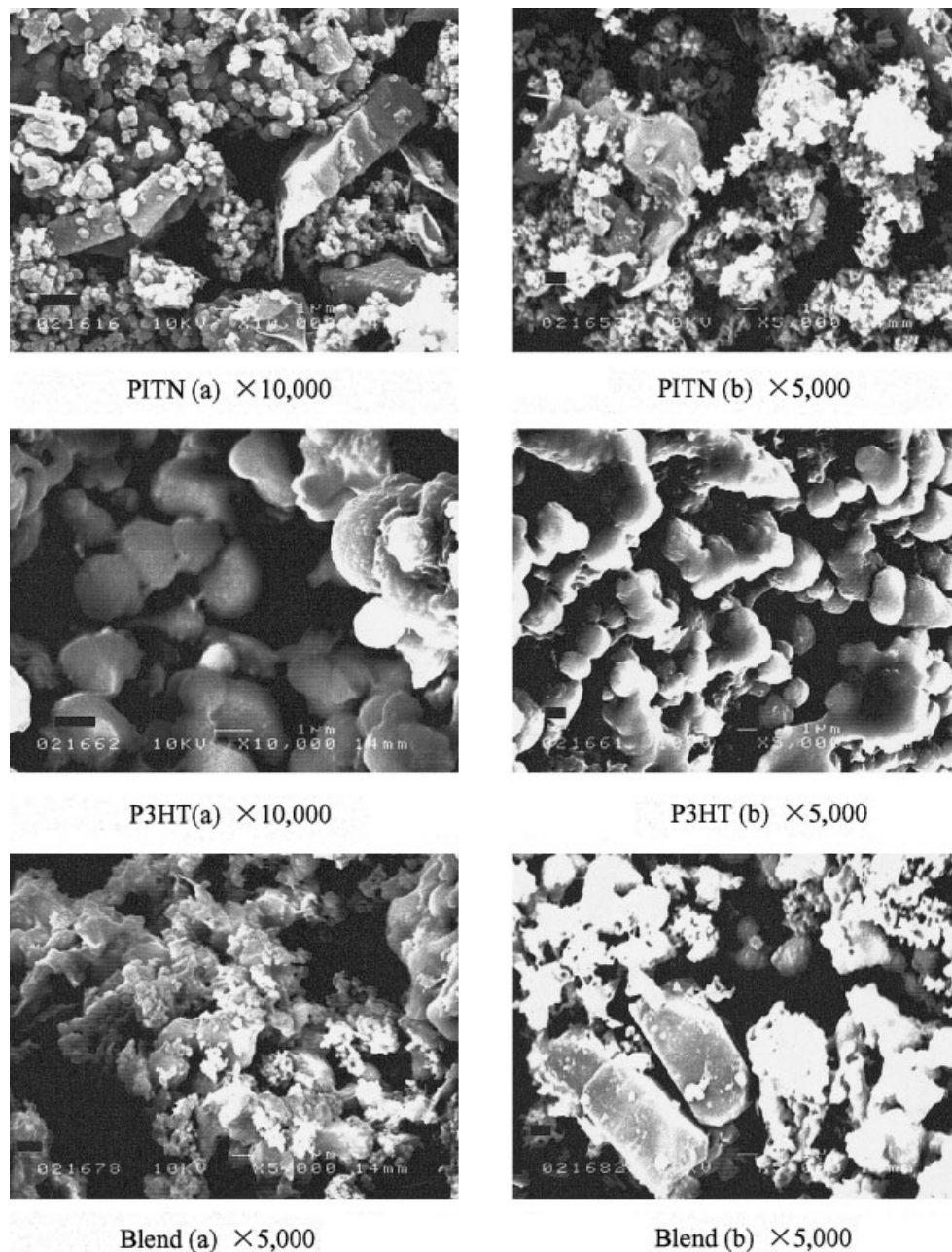
Figure 6 SEM photographs of PITN, P3HT, and a blend containing 20% PITN. Scale bars = 1 μm.

and a good PTC effect. This kind of diversity probably results from a unique dispersion state of PITN in the P3HT matrix, which is unlike that of other filler particles.

Morphological study of PITN-P3HT blends

To determine the dispersion effect of PITN particles in the P3HT matrix by this kind of dissolution/precipitation method, the microscopic aspects revealed by SEM for PITN, P3HT, and a blend with a 20% PITN content before pellet pressing, are shown in Figure 6.

No detailed information on the morphology and microscopic structure of chemically polymerized PITN is available in the literature. A relatively large average particle size of 12 $\sim$ 13 μm has been mentioned by Asselt and coworkers when they discussed the effect of morphology on the transparency for doped and dedoped PITN powder chemically synthesized from phthalic anhydride and phthalide.[24] The PITN particles obtained by DHITN with NCS showed very diverse shapes and sizes, that is, both large rectangular 2 $\sim$ 5 μm particles and 0.1 $\sim$ 0.3 μm fine particles were observed in the PITN powder. The di-

verse shapes and sizes of the resulting PITN powder are probably related to the synthetic approach. *N*-chlorosuccinimide (NCS) was primarily used as a dehydrogenation reagent to transfer poly(dihydroisothianaphthene) (PDHITN) into PITN. In the direct conversion from DHITN monomer to PITN, NCS acts both as an oxidation and a dehydrogenation reagent. Although this reaction has been widely adopted by many researchers, for its simplicity and effectiveness, its detailed reaction mechanism is not understood as yet. Since oxidation and dehydrogenation reactions happen simultaneously, one may assume that the existence of some structure defects during the polymerization process leads to the diversity of particle sizes and shapes.

P3HT particles have the shape of beads with an average size of $1 \sim 2$ μm after the precipitation. From the microscopic structure of the composite, it was found that the small size PITN particles are homogeneously attached on the surface of large-size P3HT beads, although some particle clusters may exist. Large PITN particles were also observed in the composite sample, but their dispersion was very random and isolated in the P3HT matrix. Consequently, the conducting network consists mainly of small PITN particles or particle clusters, although the existence of large rectangular particles may, to some extent, affect the conductivity of the blends.

The dispersion state of PITN in the P3HT matrices agrees with the so-called structural system model, that is, the conducting network consists of small PITN particles sticking around the surface of large P3HT granules.[25,26] According to this model, the conducting properties of the composites are affected by the radii ratio of matrix particles (R_m) and filler particles (R_f). PITN, as a derivative of polythiophene, should have a stronger affinity with P3HT and shows better adhesive interaction between the filler and the matrix particles compared with other conducting fillers. This better adhesive interaction can make PITN more uniformly attached at the surface of P3HT particles during the precipitation process, thus forming a relatively homogeneous conducting network, which improves the conductivity of the blends in a smooth manner. On the contrary, although primary CB particles have much smaller size, they readily aggregate into particle clusters having larger secondary particle size due to the strong CB-CB interparticle interaction, which results in a more obvious jumping effect on the enhancement of conductivity. In brief, the introduction of conducting PITN, due to its stronger adhesive interaction with the P3HT matrix granules than other filling particles of the same small size, can more readily realize a trade-off between the improved conductivity and the retained PTC effect.
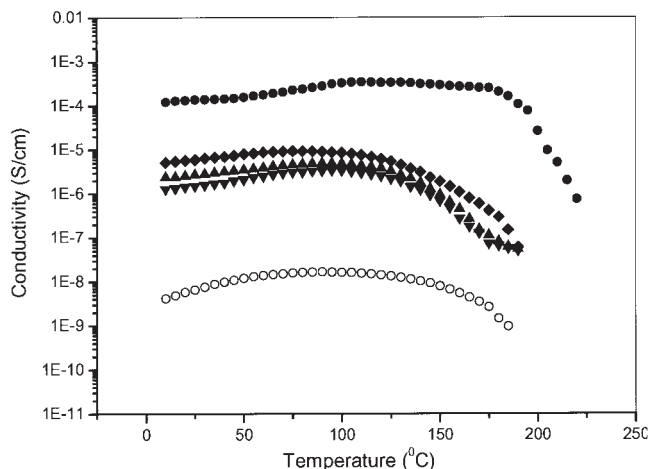

Figure 7 Conductivity-temperature characteristics of a PITN-P3HT blend containing 25% PITN under different heating cycles: ● 1st run; ◆ 2nd run; ▲ 3rd run; ▼ 4th run; and ○ the original P3HT in the 2nd run.

Results of the heating recycle

In the above discussion, we assumed that the conductivity change of the P3HT matrix, arising from the conformational deformation near its melting temperature, dominated the PTC origination of blends. As a matter of fact, it is not sure whether the conducting percolation network, formed by PITN particles in the P3HT matrix, is affected by the melting process and, then, makes a contribution to the PTC effect of blends. Therefore, we investigated the effect of heating recycles on the electrical properties of a blend with 25% PITN. Its temperature-conductivity behavior over four heating cycles is shown in Figure 7. The conductivity-temperature curve in the first heating cycle is significantly different from the curves in the later cycles. The decrease in conductivity between the first and the second heating run is more obvious than that of the following cycles, and the PTC transfer temperature of the initial blend is greatly shifted, too. Apart from the difference in conductivity, the conductivity-temperature curves from the second heating run are almost similar to those of the original P3HT pellets. These results seem to imply that the melting process of the P3HT matrix really affects the conducting percolation network formed by PITN particles with a unique dispersion structure.

According to the structural system model mentioned above, the small PITN particles, which occur in the conducting percolation network, are mainly located in the interface between the big P3HT granules. When the temperature reaches the melting point of P3HT, the viscosity decrease of the P3HT matrix inevitably increases the mobility of PITN. Therefore, the localized PITN tends to form a relatively homogeneous dispersion structure in the whole P3HT matrix

during the melting process, which may dilute the concentration of the conducting percolation network, thus leading to the conductivity decrease of the blends. As a result of the above analyses, one can conclude that the PTC effect of blends with percolation filler content (such as the case of 25%) is probably not only related to the conductivity decrease of the P3HT matrix, arising from the conformational change during the melting, but also to the dilution effect of the conducting percolation network, due to the mobility of PITN particles induced by the viscosity decrease of the P3HT matrix.

Although the dilution effect of the conducting network plays a part in the PTC origination, it will also deteriorate the electrical properties of the blends. These facts lead us to practical problems: how to stabilize the unique dispersion structure of PITN particles in the P3HT matrix, and how to obtain a blend having good reproducibility in the PTC effect. They will be dealt with in our next article.

CONCLUSIONS

The temperature-conductivity characteristics of blends consisting of two kinds of conducting polymers, polyisothianaphthene and poly(3-hexylthiophene), were investigated in this article, and attention was paid to the conductivity change with the PTC effect. The chemically synthesized PITN particles showed outstanding conductivity and thermal stability, which made them suitable as fillers. The blends were prepared through a dissolution/precipitation method based on the solubility of P3HT. Results on the temperature-conductivity characteristic of the blends confirmed that the introduction of PITN was an effective approach to improve the conductivity of blends and simultaneously to keep the PTC effect of the P3HT matrix, due to a unique dispersion structure caused by a relatively higher adhesive interaction between PITN particles and P3HT matrix granules during the precipitation process. The PTC effect of blends with the percolation content was probably not just related to the conductivity decrease of the P3HT matrix, arising from the deformation of the conjugated structure during the melting, but also to the dilution effect of the conducting percolation network, due to the mobility of PITN particles induced by the viscosity decrease of the P3HT matrix.

References

1. Yoshino, K.; Park, D. H.; Park, B. K.; Onoda, M.; Sugimoto, R. Jpn J Appl Phys 1988, 27, L1612.
2. Yoshino, K.; Nakajima, A.; Onda, M.; Sugimoto, R. Synth Met 1989, 28, C349.
3. Yoshino, K.; Nakajima, A.; Onda, M.; Sugimoto, R. Solid State Commun 1988, 68, 513.
4. Shimomura, M.; Kaga, M.; Nakayama, N.; Miyauchi, S. Synth Met 1995, 69, 313.
5. Yamauchi, T.; Najib, H. M.; Liu, Y. W.; Shimomura, M.; Miyauchi, S. Synth Met 1997, 84, 581.
6. Liu, Y. W.; Oshima, K.; Yamauchi, K.; Shimomura, M.; Miyauchi, S. Synth Met 1999, 101, 451.
7. Liu, Y. W.; Oshima, K.; Yamauchi, K.; Shimomura, M.; Miyauchi, S. J Technol Edu 1999, 8, 35.
8. Liu, Y. W.; Hino, S.; Oshima, K; Yamauchi. T.; Shimomura. M.; Miyauchi, S. Kobunshi Ronbunshu 1999, 56, 440.
9. Liu, Y. W.; Oshima, K.; Yamauchi, T.; Shimomura, M.; Miyauchi, S. J Appl Polym Sci 2000, 77, 3069.
10. Miyauchi, S.; Kondo, T.; Oshima, K.; Yamauchi, K.; Shimomura, M.; Mitomo, H. J Appl Polym Sci 2002, 85, 1429.
11. Kobayashi, M.; Colaneri, N.; Boysel, M.; Wudl, F.; Heeger, A. J. J Chem Phys 1985, 82, 5717.
12. Onoda, M.; Morita, S.; Nakayama, H.; Yoshino, K. Jpn J Appl Phys 1993, 32, 3534.
13. Chen, W. T.; Bowmaker, G. A.; Seakins, J. M.; Cooney, R. P. Synth Met 2002, 128, 215.
14. Hoogmartens, I.; Vanderzande, D.; Martens, H.; Gelan, J. Synth Met 1992, 47, 367.
15. Hoogmartens, I.; Adriaensens, D.; Vanderzande, D.; Gelan, J.; Quattrocchi, C.; Lazzaroni, R.; Brédas, J. L. Macromolecules 1992, 25, 7347.
16. Wudl, F.; Kobayashi, M.; Heeger, A. J. J Org Chem 1984, 49, 3382.
17. Pron, A.; Österrholm, J. E.; Smith, P.; Heeger, A. J.; Laska, J.; Zagaorska, M. Synth Met 1993, 3520.
18. Shacklette, L. W.; Han, C. C.; Luly, M. H. Synth Met 1993, 55–57, 3532.
19. Fournier, J.; Boiteux, G.; Seytre, G.; Marichy, G. J Chim Phys 1998, 95, 1510.
20. Narkis, M.; Zilberman, M.; Siegmann, A. Polym Adv Technol 1997, 8, 525.
21. Haba, Y.; Segal, E.; Narkis, M.; Titelman, G. I.; Siegmann, A. Synth Met 2000, 110, 189.
22. Jia, W.; Tchoudakov, R.; Segal, E.; Joseph, R.; Narkis, M.; Siegmann, A. Synth Met 2003, 132, 269.
23. Kirkpatrick, S. Rev Mod Phys 1973, 45, 4, 574.
24. Asselt, R. V.; Hoogmartens, I.; Vanderzande, D.; Gelan, J.; Froehling, P. E.; Aussems, M.; Aagaard, O.; Schellekens, R. Synth Met 1995, 74, 65.
25. Malliaris, A.; Turner, D. T. J Appl Phys 1971, 42, 614.
26. Ponomarenko, A. T.; Shevchenko, V. G.; Enikolopyan, N. S. Adv Polym Sci 1990, 96, 125.