Preparation of a Poly(3-hexylthiophene)-Grafted Indium Tin Oxide/Poly(3-hexylthiopene) Composite and Its Conductivity–Temperature Characteristics

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ABSTRACT: The temperature–conductivity characteristics of poly(3-hexylthiophene) (P3HT) composites filled with P3HT-grafted indium tin oxide (ITO) particles were investigated in this work. The ITO particles were first treated with a silane coupling reagent of 3-aminopropyltriethoxysilane (APS), and then thiophene rings were introduced through a condensation reaction between the ending amino groups of APS and the carboxylic groups of thiophene-3-acetic acid. The composites were prepared by the polymerization filling of the 3-hexylthiophene (3HT) monomer with the thiophene-ring-introduced ITO particles. Elemental analysis, Fourier transform infrared, and X-ray photoelectron spectroscopy were used to confirm the grafting reaction on the ITO surface. The longer the polymerization time was or the higher the 3HT/ITO feeding ratio was, the more P3HT was grafted. The influence of the grafted amount on the electrical properties of ITO particles was attributed to the wrapping effect formed by the grafted P3HT on the surface of the ITO particles. The conductivity change of the P3HT-grafted ITO/P3HT composites was proved to be subject to the change in the average gap width of ITO interparticles, which was determined by the filling ratio of P3HT to ITO in the polymerization and the volume expansion effect of a P3HT thin film between neighboring ITO particles during the heating process. In comparison with the ungrafted ITO/P3HT composites, the grafting treatment enhanced the interaction between the particles and polymer matrix, and this was helpful for obtaining a more homogeneous dispersion structure for the composites and thus afforded a higher positive temperature coefficient intensity and better reproducibility. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 100: 1881–1888, 2006

Key words: composites; conducting polymers; fillers

INTRODUCTION

Poly(3-alkylthiophene)s have attracted wide research attention during the past years because of their novel electrical and optical properties and especially their processibility based on their solubility and fusibility resulting from the long side chain substituted on the conjugated backbone.[1] Dedoped poly(3-hexylthiophene) (P3HT) shows reproducible switching characteristic of conductivity due to a conjugation length change of the thiophene backbone caused by a dramatic disturbance of the hexyl chain during the melting and is promising for the fabrication of devices with a positive temperature coefficient (PTC) effect.[2] The conductivity–temperature characteristics of intrinsic P3HT and its composites mixed with various conducting particles have been reported in previous studies.[3–7] The results have demonstrated that the PTC effect of composites is greatly influenced by the dispersion state of filler particles in the P3HT matrix, which is actually determined by the mixing method and the properties of the filler particles.

To understand more electrical properties of composites based on P3HT, the conductivity–temperature characteristics of P3HT composites filled with P3HT-grafted indium tin oxide (ITO) particles were investigated in this study. The grafting reaction of P3HT on the ITO surface and the effect of the grafting treatment on the conductivity–temperature characteristics of the composites were mainly examined.

EXPERIMENTAL

Materials

ITO was supplied by Fujikura Chemical Industry Co. (Tokyo, Japan); its particle size was 0.5–1.0 μm. 3-Hexylthiophene (3HT), thiophene-3-acetic acid (T3A), 3-aminopropyltriethoxysilane (APS), and 1-ethyl-3-(3-dimethylaminopropyl)-carbodiimide hydrochloride (EDC) were supplied by Tokyo Chemical Industry Co. (Tokyo, Japan); synthetic-grade FeCl$_3$ from Merck (Darmstadt, Germany) was used directly. Other chemicals were reagent- or analytical-grade commercial materials and were used without further purification.

Step.1 Silanization — Step.2 Condensation

Step.3 Grafting reaction and composite preparation
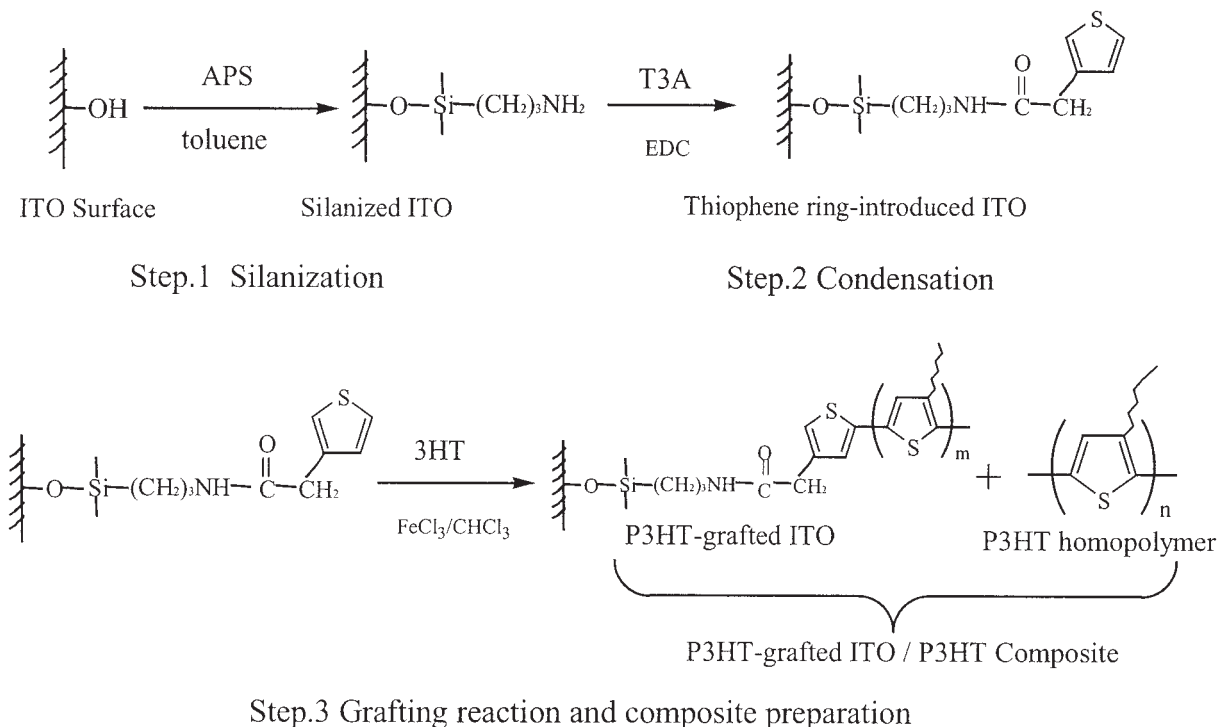
Scheme 1 Preparation procedure for P3HT-grafted ITO particles and P3HT-grafted ITO/P3HT composites.

Preparation of the P3HT-grafted ITO particles (Scheme 1)

Silanization

A 500-mL flask with 10 g of ITO particles after being dried in vacuo was exchanged with nitrogen fully at 110°C. Toluene (300 mL) and 10 mL of APS were added, and the mixture was refluxed for 2 h under a nitrogen atmosphere to react with the hydroxyl groups naked on the ITO surface. When the reaction was finished, the mixture was filtered with a 0.45-μm membrane under reduced pressure. The product was washed with methanol and dried *in vacuo* at 60°C for 24 h (step 1).

Condensation

The aforementioned silanized ITO particles (5 g) were suspended in 170 mL of the solvent acetone. Then, 0.696 g (4.9 mmol) of T3A and 1.41 g (7.35 mmol) of EDC as a condensation agent were added, and the mixture was stirred at room temperature for 24 h. The reacted mixture was filtered under reduced pressure with a 0.45-μm membrane. The ITO particles introduced with thiophene rings were washed with acetone and dried in vacuo at 60°C for 24 h (step 2).

Grafting

The aforementioned thiophene-ring-introduced ITO particles were stirred at −40°C in 200 mL of an FeCl$_3$-saturated chloroform solution. Then, the 3HT monomer was added, and the mixture was stirred for 24 h. The reaction product was precipitated with methanol and treated with a 30% (v/v) solution of ammonia in ethanol to remove surplus FeCl$_3$. The precipitate was rinsed with a large amount of ethanol and dried in vacuo at 60°C. The obtained product was Soxhlet-extracted with toluene for 24 h to separate the P3HT homopolymer, which finally afforded the P3HT-grafted ITO particles (step 3).

Preparation of the P3HT-grafted ITO/P3HT composites

The P3HT-grafted ITO/P3HT composites were prepared according to the polymerization filling process described in step 3 of Scheme 1 with the thiophene-ring-introduced ITO particles and 3HT monomer. The polymerization product, including both the P3HT-grafted ITO particles and the P3HT homopolymer, was not treated with Soxhlet extraction and was used directly to prepare the pellet sample for the following investigations on the conductivity–temperature characteristics. The component percentages of the composites were estimated from the weight ratio of thiophene-ring-introduced ITO particles to the final polymerization product.

Preparation of the ungrafted ITO/P3HT composites

ITO particles that were not treated with any processes were used directly to prepare the ungrafted ITO/
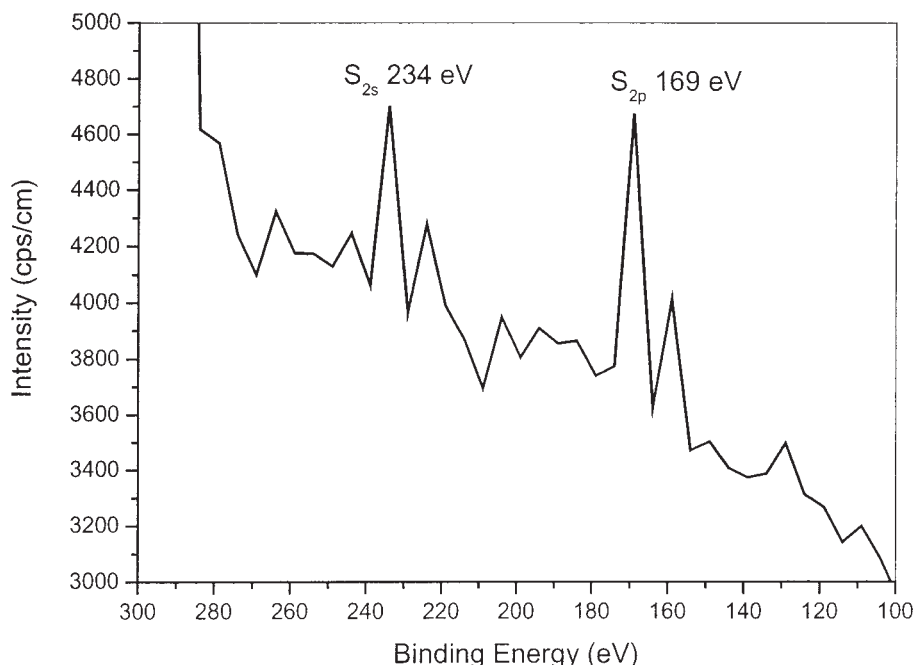
Figure 1 XPS of thiophene-ring-introduced ITO particles.

P3HT composites according to the same polymerization filling method used for the grafting-treated ITO particles. The component percentages of the composites were estimated from the weight ratio of the untreated ITO particles to the final polymerization product.

Sample preparation and measurement

The pellet samples for conductivity measurements were prepared according to ref. 6. The conductivity and scanning electron microscopy (SEM) were measured in the same way reported in ref. 7. Elemental analysis was carried out with a PerkinElmer series II CHNS/O analyzer (PerkinElmer Inc., Wellesley, MA). X-ray photoelectron spectroscopy (XPS) was carried out with an XP-HSIG (JEOL, Japan).

RESULTS AND DISCUSSION

Grafting reaction of P3HT onto the ITO surface

The hydroxyl groups naked on the ITO surface provided binding sites for the silanization coupling and the following grafting reactions. Elemental analysis was used to verify the coupling reaction between the ITO particles and silane coupling agent (APS). Elemental analysis results showed that the mass percentages of C, H, and N for silanized ITO particles were 0.34, 0.08, and 0.15%, respectively. The calculated molecular formula for the ending groups reacted on the ITO surface was $C_{2.8}H_{7.9}N$, which basically agreed with the formula of the aminopropyl group ($—C_3H_8N$).

Figure 1 presents XPS of thiophene-ring-introduced ITO particles after the condensation reaction between the amine groups of APS and the carboxyl groups of T3A. The peaks at 234 and 169 eV agree well with the binding energy of S_{2S} and S_{2P} of the sulfur atom,[8] and this corroborates that the thiophene ring was introduced onto the ITO surface. Fourier transform infrared (FTIR) spectra of thiophene-ring-introduced ITO particles before and after the grafting reaction with P3HT are compared in Figure 2. A marked difference in the wave-number range of 3000–2800 cm^{-1} is worth mentioning for the two samples, and it is amplified in the inset. No other peaks could be observed in this range for the ITO particles before the grafting reaction, but after that, three peaks were observed at wave numbers of 2956, 2928, and 2557 cm^{-1}, which could be attributed to the vibration peaks of ν_{as} (CH_3), ν_{as} (CH_2), and ν_s (CH_2), respectively. These results confirmed the existence of hexyl groups; that is, P3HT was successfully grafted onto the surface of ITO particles.

Grafted amount of P3HT on the ITO surface

The grafted amount was evaluated from the weight loss of P3HT-grafted ITO particles after the sintering treatment. The relationship between the grafted amount and polymerization conditions is shown in Table I. The longer the reaction time was or the higher the 3HT monomer/ITO particle ratio was, the more P3HT was grafted onto the ITO surface. Because the grafting reaction took place by means of the copoly-
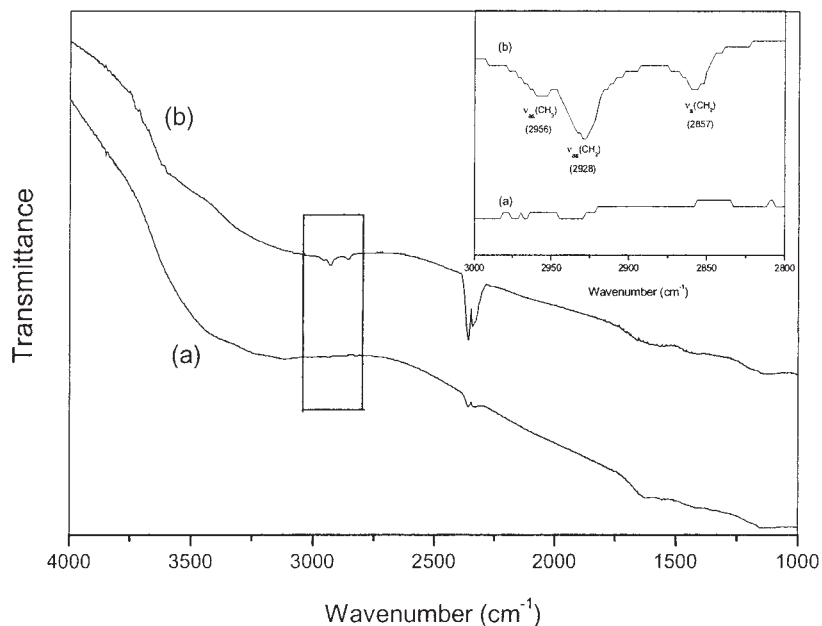
Figure 2 FTIR spectra of thiophene-ring-introduced ITO particles (a) before and (b) after a grafting reaction with P3HT. The inset shows a magnification of peaks in the range of 3000–2800 cm^{-1}.

merization of 3HT with the thiophene ring of T3A on the ITO surface, it is conceivable that the propagation of the P3HT chain on the grafted site of the ITO surface likely expelled the neighboring ITO particles from their aggregations and then formed a structure of ITO particles wrapped by P3HT molecules.[9] Assuming that the ITO particles were uniformly spherical with an average diameter of 0.75 μm and that the average molecular weight of P3HT was 83,700 (weight-average molecular weight),[6] we could estimate that there were approximately 10^4 P3HT molecules bound to each ITO particle when the grafted amount of P3HT was 1.6 wt % (the apparent densities of ITO and P3HT are 1.2 and 1.0991 g/cm^3, respectively, from our unreported data). This rough calculation seems to indicate that the P3HT molecules attached to the ITO particle surface were enough to form

the wrapping structure, although the grafted amounts of P3HT were low (1.6–2.8 wt % under these reaction conditions).

Conductivity–temperature characteristics of the P3HT-grafted ITO particles

Figure 3 shows the temperature dependence of the conductivity for both the P3HT-grafted ITO particles and the ungrafted ITO particles. The conductivity of the grafted particles at the ambient temperature decreased with an increase in the grafting ratio. The influence of the grafting treatment on the electrical properties of the fillers was attributed to two effects: the aforementioned wrapping effect and the uniform dispersion effect of particles in the polymer matrix.[10] In addition, the sample with 1.6% grafting showed a slight PTC effect; that is, its conductivity slightly decreased with an increase in the temperature. This result further confirmed the existence of the wrapping structure and its influence on the electrical properties of the ITO particles.

## Conductivity–temperature characteristics of the P3HT-grafted ITO/P3HT composites

After the first heating run with a thermal conditioning effect, the conductivity–temperature characteristics of the P3HT-grafted ITO/P3HT composites in the second heating run were recorded (Fig. 4). Apparently, the component variation of the composites not only influenced the conductivity at the ambient temperature but

TABLE I
Grafted Amount of P3HT on ITO Particles Under Various Polymerization Conditions

Feeding amount		Polymerization time (h)	Sintering loss (mg)[a]	Grafted amount (wt %)[b]
1TO (mg)	3HT (mg)			
600	374	1	0.6	1.2
600	374	24	0.8	1.6
400	374	24	1.4	2.8

[a] The sintering loss was evaluated by the weight decrease of a 50-mg P3HT-grafted 1TO sample after it was sintered at 500°C for 6 h.
[b] The grafted amount was defined as sintering loss (mg)/50 (mg).
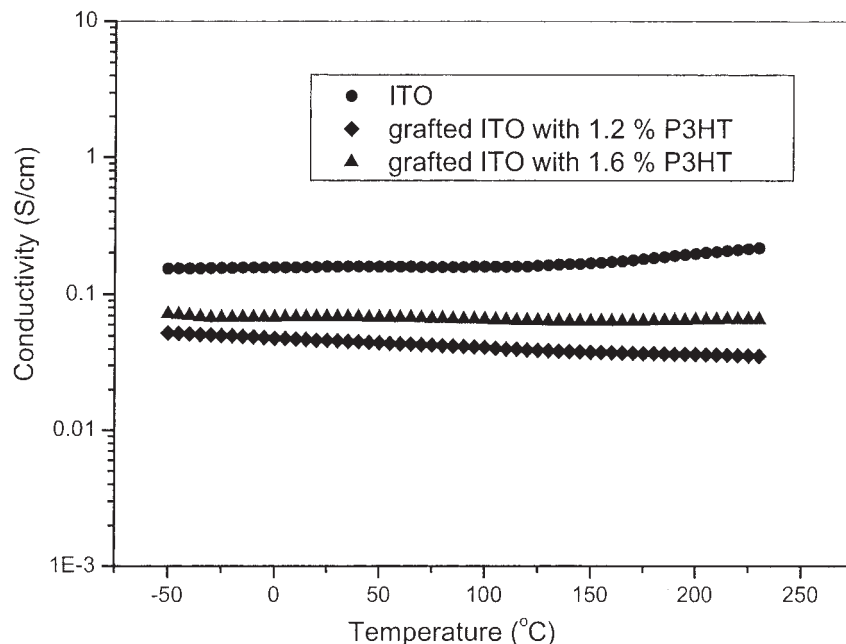
Figure 3 Conductivity change as a function of temperature for ITO and P3HT-grafted ITO particles.

also changed the manner of conductivity with increasing temperature. For conducting polymer composites, the conducting filler particles in the percolation network are either contacted directly or separated by a very narrow interparticle gap, across which electrons can transfer by tunneling or hopping.[11,12] The electron hopping or tunneling probability between neighboring filler particles is dominated by the effective tunneling distance (usually <100 Å), and the tunneling current generally decreases exponentially with an increase in the interparticle gap width.[13] In the case of the P3HT-grafted ITO/P3HT composite, because of the homogeneous dispersion state caused by the grafting treatment, the results in Figure 4 actually show that the conductivity of the composites changed with the average gap width of the interparticles, which was
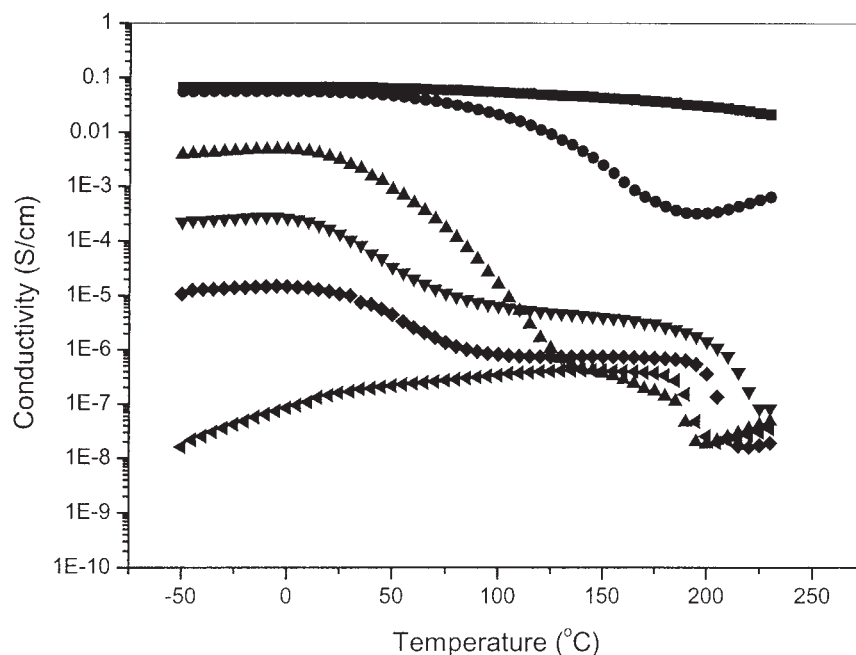
Figure 4 Conductivity change as a function of temperature for P3HT-grafted ITO/P3HT composites with various P3HT contents (second heating run): (■) 15, (●) 25, (▲) 29, (▼) 42, (◆) 49%, and (◄) 58%.
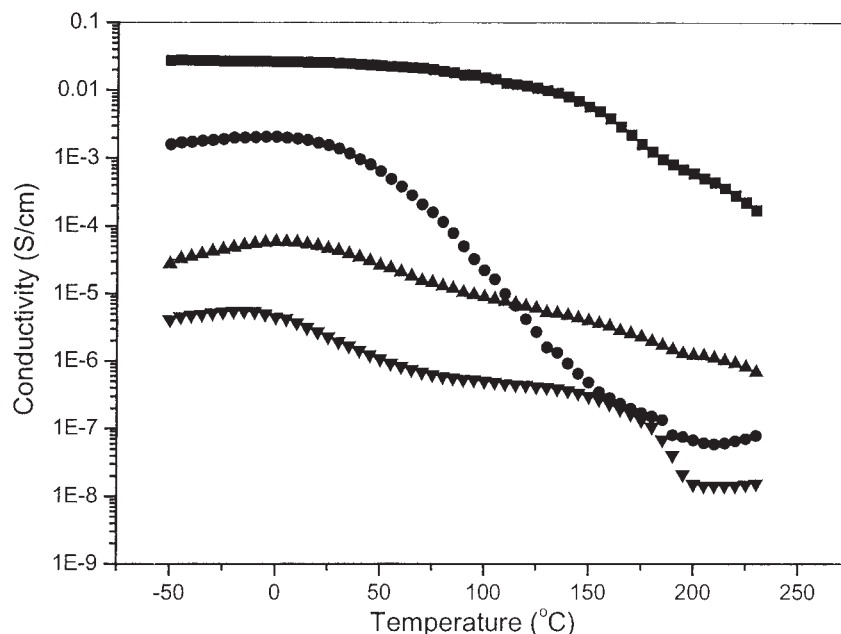
Figure 5 Conductivity change as a function of temperature for ungrafted ITO/P3HT composites with various P3HT contents (second heating run): (■) 22, (●) 30, (▲) 40, and (▼) 51%.

determined by the filling ratio in the polymerization and the volume expansion effect of P3HT during the heating process.

When the P3HT content was low (e.g., <25%), the direct contact of aggregated particles resulted in higher conductivity at room temperature (σ_{RT}) and weaker PTC intensity. With an increase in P3HT, the ITO particles in aggregations were separated gradually by the enhanced grafting effect and increased filling amount of P3HT, and then the electron tunneling through the thin P3HT film began to dominate the percolation current, leading to a decrease in σ_{RT}. At the same time, the volume expansion effect of the P3HT thin film with heating became apparent and produced an increase in the average interparticle gap and a dramatic change in the tunneling current with increasing temperature. Thus, the composites showed a significant PTC effect, as observed in the composite with 29% P3HT. When the content of P3HT increased further, the gap width of interparticles was enlarged over the effective tunneling distance, the conducting paths between neighboring particles were broken, and the volume expansion exerted no influence on the electron transport. Thus, the PTC effect was weakened gradually, and the composites showed conductivity–temperature characteristics similar to those of the original P3HT (as shown by the 58% composite).

Apparently, the homogeneous dispersion state of ITO particles caused by the grafting treatment is a key factor making the conductivity–temperature behavior of composites subject to delicate changes of the average interparticle gap width with increasing tempera-

ture. Assuming that all the ITO particles had an identical spherical size with a diameter of 1 μm and were wrapped by a thin layer of P3HT with the same thickness and that the wrapped ITO particles were arranged regularly in the composite in terms of the so-called cubic closest packed structure model, we estimated the weight ratio of ITO to P3HT needed to generate a critical contact to be about 76:24. Undoubtedly, this assumption is just a rough model because the interparticle gap and its distribution are generally affected by many practical parameters.[12] However, the experimental results seem to roughly coincide with this model. For example, the composites began to show a PTC effect with 25% P3HT, whereas the most significant PTC effect was observed for the sample with about 30% P3HT; this might be attributed to the fact that the change in the average gap width with increasing temperature at this content was exactly over the effective tunneling distance of electrons.

Comparison of the grafted composite with the ungrafted composite

To determine to what degree the grafting treatment affected the dispersion state and the PTC effect of the composites, the conductivity–temperature characteristics of the grafted ITO/P3HT composites were compared with those of the untreated ITO/P3HT composites prepared by the same polymerization-filling method. The temperature dependence of the conductivity of the untreated ITO/P3HT composites in the same second heating run is shown in Figure 5. The
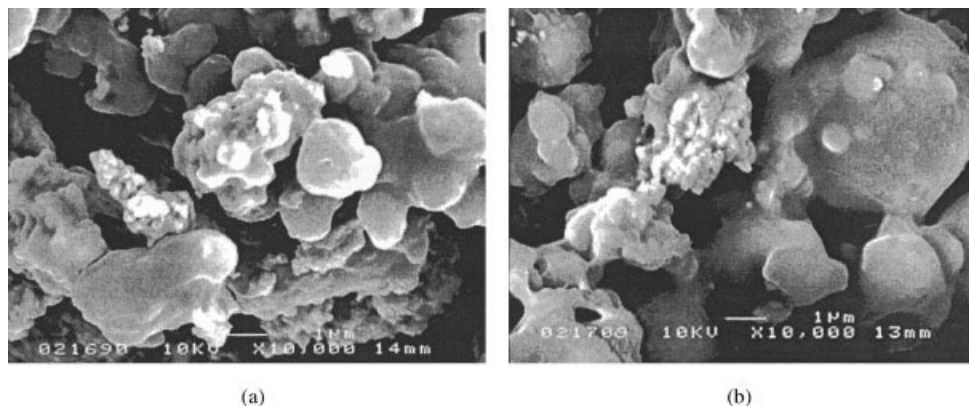
Figure 6 SEM images for composites of 30% P3HT with (a) grafted ITO and (b) ungrafted ITO.
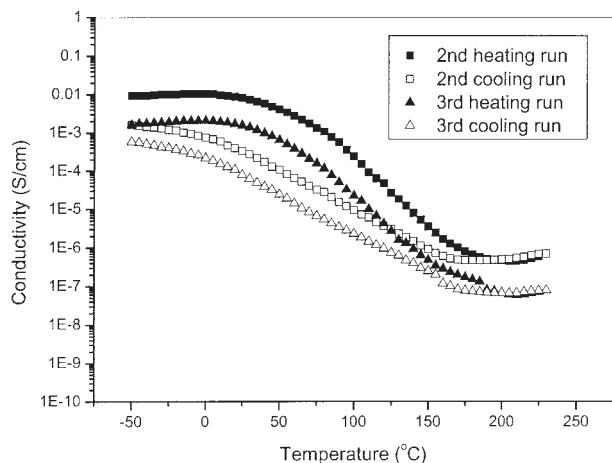
ungrafted composites showed lower conductivities at the ambient temperature than grafted composites with almost the same P3HT content; this is contrary to common sense about the influence of the grafting treatment on conductivity.[10,14] In addition, the ungrafted composites showed a weaker PTC intensity than the grafting-treated composites, although an obvious PTC effect was also observed for the composite with 30% P3HT. These results could be attributed to the fact that the dispersion state of ITO particles in the ungrafted composites was poorer than that in the grafted composites. The SEM photographs in Figure 6 for two kinds of composites with a close P3HT content prove the wrapping structure of P3HT on the ITO surface in both cases. However, the particle aggrega-

tion in the untreated composites seemed to be more obvious than that in the grafted composites. This kind of inhomogeneous structure of bigger particle aggregations wrapped by P3HT actually resulted in an increase in the gap width for the electron tunneling when the ungrafted composite was compared with the grafted one with the same P3HT filling content. Therefore, a lower σ_{RT} value and weaker PTC intensity were observed for the ungrafted composites.

Figures 7 and 8 show the conductive characteristics as functions of temperature for two composites in several heating/cooling cycles. After the second heating run, the temperature–conductivity curves of the grafted composite showed good reproducibility, and the cooling curves were close to the heating curves,
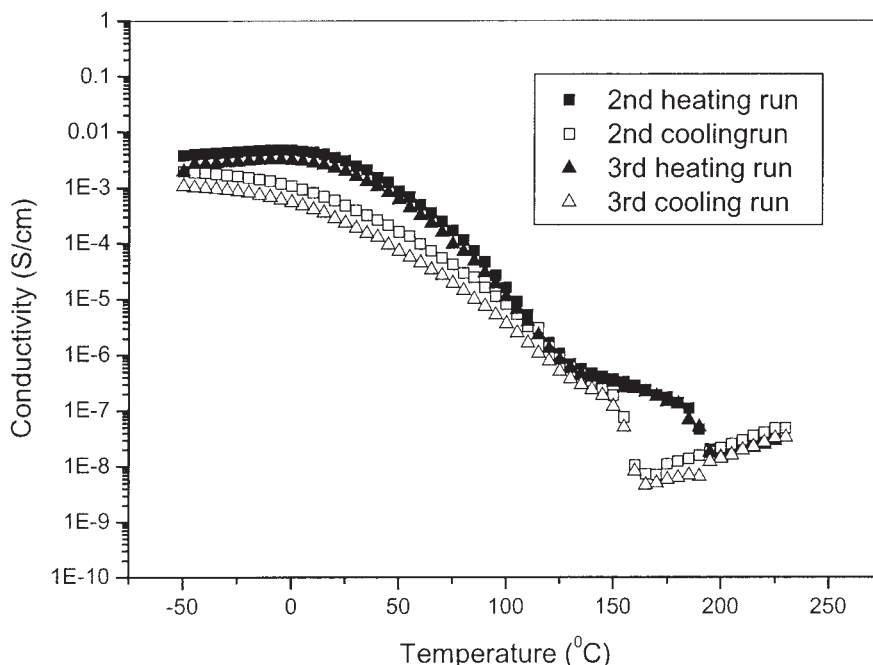
Figure 7 Temperature–conductivity behavior of P3HT-grafted ITO/P3HT composites with 29% P3HT under different heating/cooling cycles.

Figure 8 Temperature–conductivity behavior of ungrafted ITO/P3HT composites with 30% P3HT under different heating/cooling cycles.

whereas for the ungrafted composite, its conductivity deteriorated continuously with the heating cycles, and the PTC intensity tended to be weakened. Apparently, the grafting treatment enhanced the interaction between the ITO particles and P3HT matrix. This enhanced interaction caused the gap width of ITO particles sensitive to the temperature change during the heating process, simultaneously permitted the ITO particles to go back to the original position when the samples were cooled,[15] and thus afforded the improved PTC intensity and reproducibility, in comparison with those of the ungrafted composites.

Unlike the low percolation concentration generally shown in carbon black-filled conducting polymer composites, the most significant PTC effect for the P3HT-grafted ITO/P3HT composites was observed at a fairly high filler concentration (ca. 70 wt % ITO). The difference in the size of the filler particle is one of the possible reasons. For conducting polymer composites filled with small CB particles, some researchers have accepted that the change in the distribution factor of the gap distance (σ) has much greater influence on the PTC effect than the change in the average gap distance according to calculated results for the tunneling current.[16–18] However, the influence of σ on the generation of the PTC effect was probably weakened in this case because of the homogeneous dispersion state caused by the bigger particle size and the grafting treatment especially. Therefore, the PTC effect of the composites showed greater dependence on the change in the average gap width instead of σ. This could explain why the PTC transfer of the 30% composite occurred in the manner of a continuous conductivity decrease within a wide temperature range.

CONCLUSIONS

The P3HT-grafted ITO/P3HT composites were prepared, and their conductivity–temperature characteristics were investigated. The conductivity change of the composites was proved to be subject to the change in the average gap width of the ITO interparticles, which was determined from the filling ratio of P3HT to ITO in the polymerization and the volume expansion effect of a P3HT thin film between neighboring ITO particles during the heating process. In comparison with the ungrafted ITO/P3HT composites, the grafting treatment enhanced the interaction between the particles and polymer matrix, and this was helpful for obtaining a more homogeneous dispersion structure of the ITO particles in the P3HT matrix and thus afforded a higher PTC intensity and better reproducibility.

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