

# Thermal Behavior of Polyaniline Films and Polyaniline–Polystyrene Blends

V. JOUSSEAUME, M. MORSLI, A. BONNET

Université de Nantes, Laboratoire de Physique des Solides pour l'Electronique, L.P.S.E., 2 rue de la Houssinière, BP 92208, 44322 Nantes Cedex 03, France

Received 21 February 2001; accepted 15 September 2001

**ABSTRACT:** In this article, a study of the thermal behavior of polyaniline films and polyaniline–polystyrene blends is presented. Transport measurements (electrical conductivity and thermoelectric power) at high temperature and thermogravimetric analysis show that an irreversible degradation is observed near 450 K for films doped with DiOHP and near 500 K for films doped with CSA. In both cases, the thermoelectric power is the most sensitive parameter to electrical degradation during the heating of conducting films. Electrical conductivity measurements during heating–cooling cycles show a diminution of the room temperature conductivity after evaporation of the solvent (water, *m*-cresol). A model of cluster with a variable diameter allows interpreting this phenomenon by assuming the existence of a sensitive frontier to the solvent at the periphery of conducting clusters. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 84: 1848–1855, 2002; DOI 10.1002/app.10468

**Key words:** conducting polymers; electrical conductivity; thermogravimetric analysis

## INTRODUCTION

Conducting polymers like polyaniline have shown possibilities for applications in optoelectronics and microelectronics devices.<sup>1–6</sup> But in any potential practical applications, knowledge of the stability and degradation mechanisms of this class of conducting polymer is of primary importance. Numerous studies are devoted to thermal studies of polyaniline, and they show that undoped polyaniline (polyemeraldine base form) does not show any significant decomposition below 700 K.<sup>7,8</sup> The lowered thermal stability of the conducting form is mainly attributable to the decomposition of the counterion.

Blends based on polyaniline have also attracted attention for potential use in a variety of

electrical and optical applications including for example organic light emitting diodes, EMI shielding, etc.<sup>9–12</sup>

In a recent article, transport properties in polyaniline doped with two different counterions and doped polyaniline–polystyrene blends have been described between 80 and 300 K by a model of conduction mainly limited by hopping or tunnelling between polaronic conducting clusters. Sometimes, a metallic behavior near room temperature is observed in rather ordered conducting polymers. It has been shown that the thermoelectric power reflects essentially the metallic behavior of the conducting clusters.

In this article, a thermal behavior study of these polyaniline films and polyaniline–polystyrene blends is presented. Electrical measurements (electrical conductivity, thermoelectric power) vs. temperature and thermogravimetric analyses (TGA) confirm the good appearance of PANI blends until temperatures up to 450 K.

Correspondence to: M. Morsli (mustapha.morsli@physique.univ-nantes.fr).

*Journal of Applied Polymer Science*, Vol. 84, 1848–1855 (2002)  
© 2002 Wiley Periodicals, Inc.

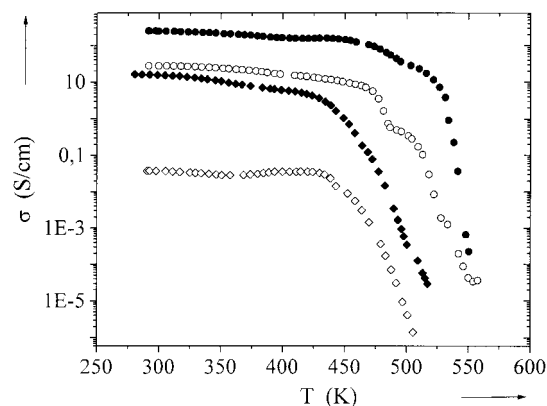
Electrical measurements during heating-cooling cycles have been undertaken in the aim to specify the role of solvent and water in conduction mechanisms. Results are interpreted in the framework of the same heterogeneous model, which has been proposed to explain conduction mechanisms in conducting polymers.<sup>13</sup>

## EXPERIMENT

Polyaniline films and polyaniline-polystyrene blends have been prepared as described previously.<sup>13</sup>

Using the codissolution method, polyaniline (polyemeraldine base form) has been protonated in an *m*-cresol solution using one of two dopants: the camphor sulfonic acid (CSA) or the bis(2-ethyl-hexyl) hydrogen phosphate (DiOHP). 1/2 molar ratio of dopant molecule to PANI repeat unit have been used. Each solution cast film of polyaniline-polystyrene (PANI-PSt) blends has been prepared according the following process: a solution of 1% weight fraction of PANI-counterion in *m*-cresol was mixed with appropriate amounts of a solution of 10% weight fraction of polystyrene in *m*-cresol. This mixture was casted onto a glass substrate, and the solvents were slowly evaporated at a temperature of 333 K under neutral atmosphere for several hours. The weight fraction, *f*, of doped PANI in the blend varies from 1 to 20%. PANI-PSt blends are characterized by a very low percolation threshold ( $f < 1\%$ ). Above this percolation threshold, it has been shown that the polystyrene matrix has little influence on the electrical conduction, which occurs essentially along polyaniline fibrils.<sup>13</sup>

Electrical conductivity measurements versus temperature have been performed in the temperature range of 80–500 K following the standard four contacts method. The DC current has been provided by a Keithley 220 current source, and the voltage has been measured with a Keithley 182 voltmeter. Thermoelectric power has been measured as a function of temperature in the range of 80–500 K by using the four wires method described previously.<sup>14</sup> Electrical measurements (electrical conductivity and thermoelectric power) have been performed in a secondary vacuum for low temperature measurements (80–300 K) and in a purge nitrogen cell for high temperature measurements (300–500 K). Thermogravimetric analyses have been performed on a TGS-2 Perkin-Elmer system (Institut des Matériaux de Nantes).



**Figure 1** Variations of the electrical conductivity vs. temperature for conducting PANI films and PANI-PSt blends: ●, PANI-CSA; ○, PANI-CSA-PSt  $f = 20\%$ ; ◆, PANI-DiOHP; ◇, PANI-DiOHP-PSt  $f = 1\%$ .

Argon was used as the purge gas, and the heating rate was 5°C/mn. The temperature stability of the electrical conductivity has been evaluated by heating and cooling runs starting from 30°C up to 90, 120, or 150°C. The temperature was controlled using a BT300 controller (Air Liquide) and the heating and cooling rate was adjusted to 3°C/mn.

## RESULTS AND DISCUSSION

### Electrical Properties at High Temperature

Electrical conductivity measurements have been undertaken until temperatures up to 500 K. Results are presented in Figure 1 for doped polyaniline films and PANI-PSt blends. These measurements confirm the “metallic”-type behavior observed near room temperature for unblended PANI-DiOHP and for PANI-DiOHP-PSt blends above the percolation threshold.<sup>13</sup> Above 450 K, a large decrease of the electrical conductivity is observed, which correspond to an nonreversible degradation of the conducting polymer film. The critical temperature where the nonreversible degradation begins is in the range of 440–460 K for films doped with DiOHP. It can be noticed that even after dilution in the polystyrene matrix, this critical temperature remains practically the same.

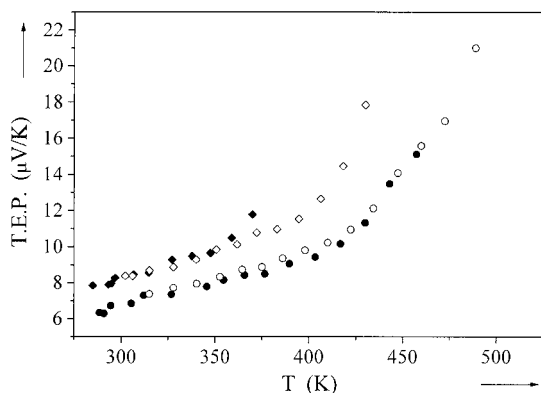
For films protonated with CSA, a similar behavior is observed (Fig. 1), with an increase of the resistivity when the temperature increases near room temperature, which confirms the “metallic”-

type behavior. Moreover, an irreversible degradation phenomenon appears above 500 K. As in the films doped with DiOHP, the degradation temperature is the same as well in unblended doped polymer as in the different blends studied. These results show that the interpenetrating fibrillar network of PANI present in PANI-PSt blends remains intact at temperatures above the glass transition temperature  $T_g$  of the polystyrene host matrix, indicating that the phase-separated network morphology is a thermodynamically stable phase.<sup>15</sup> Furthermore, thermal degradation effects seem basically independent of the weight fraction,  $f$ , of PANI in the blend.

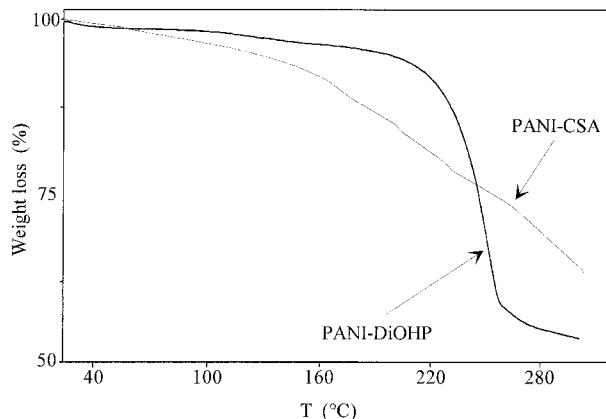
Finally, it can be pointed out that the degradation temperature obtained in the case of unblended and blended PANI-DiOHP films is below to that of PANI-CSA ones. Doping with CSA seems to conduct to a thermally more stable material than doping with DiOHP.

Thermoelectric power (TEP) measurements vs temperatures in the range of 270–450 K are shown in Figure 2 for PANI-PSt blends. They confirm the linear behavior of the thermoelectric power observed at low temperature, which can be associated to the quasi-metallic conduction of the conducting clusters.<sup>13,16</sup> No significant change in the slope of the TEP curves has been observed near room temperature. For temperatures higher than 400 K, the TEP increases very quickly and measurements become impossible.

These electrical measurements confirm for both studied families the existence of a metallic-type behavior already observed in the low-tem-



**Figure 2** Thermoelectric power variations vs. temperature for conducting PANI films and PANI-PSt blends: ●, PANI-CSA-PSt  $f = 2\%$ ; ○, PANI-CSA-PSt  $f = 10\%$ ; ◆, PANI-DiOHP-PSt  $f = 1\%$ ; ◇, PANI-DiOHP-PSt  $f = 10\%$ .

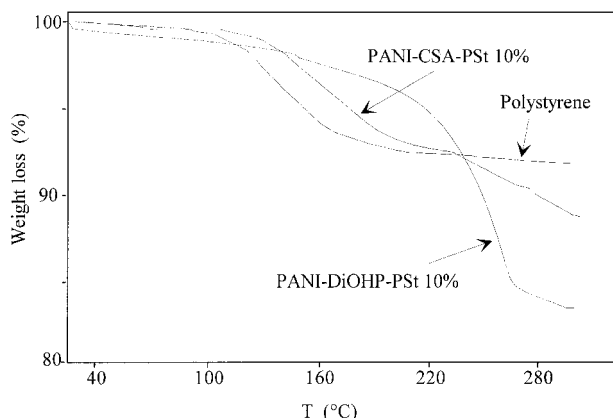


**Figure 3** TGA thermograms of doped polyanilines.

perature regime. This thermal behavior can be interpreted by confronting these electrical results with thermogravimetric analysis, which put in obviousness, the different phenomena occurring during the heating of conducting polyaniline films.

#### Thermogravimetric Analysis (TGA)

TGA measurements have been undertaken under neutral atmosphere (Argon) with at a heating rate of 5°C/min. Experimental results for polyaniline doped with DiOHP and polyaniline doped with CSA are represented in Figure 3. The PANI-DiOHP film presents a weight loss of 46% at 300°C with a large decrease near 210°C, while the PANI-CSA film reveals a less strong characteristic and a weight loss of 34% at 300°C. Below 100°C, the weak loss of mass observed can be associated with the evaporation of water for the both polyaniline families.<sup>7,17</sup> Between 100 and 220°C, the weight loss has mainly for origin the loss of solvent (*m*-cresol), which is especially present in the amorphous phases.<sup>17,18</sup> For the two families of doped polyaniline, a change in the slope of TGA curves is observed near 130°C. Abell et al.<sup>18</sup> have interpreted this behavior by assuming an increase of the amorphous zone volume in the material that allows an easier displacement of chains, favoring the solvent evaporation. Finally, in the case of polyaniline doped with DiOHP, a large weight loss is observed from 210°C, which corresponds to the degradation of dopant molecules.<sup>19</sup> In the case of films doped with CSA, the same phenomenon is not so clear even if the CSA degradation is commonly assumed beginning below 220°C.<sup>15</sup>



**Figure 4** TGA thermograms of PANI-PSt blends and polystyrene.

Similar results are obtained for PANI blends (Fig. 4) with a slight change in the temperature range of 100–160°C. This change can be attributed to a loss of mass observed in the polystyrene (Fig. 4) whose vitreous transition temperature  $T_g$  is near 100°C. The PANI-DiOHP-PSt 10% film presents a weight loss of 17% at 300°C while the PANI-CSA-PSt 10% film is characterized by a weight loss of 10% at the same temperature. These experimental results show that before 230°C, polyaniline-polystyrene blends have a better thermal stability than polystyrene, which shows a weight loss of 8% at 300°C.

Table I summarizes the different critical temperatures corresponding to a strong variations of the physical parameter studied. The thermoelectric power is the most sensitive parameter to the degradation of polyaniline films at high temperature. For films doped with DiOHP, the degradation temperature deduced from electrical conductivity measurements occurs before the strong weight loss observed with TGA measurements. For films doped with CSA, TGA curves do not reveal a brutal phenomenon near to 230°C, temperature corresponding to the clear degradation observed with electrical conductivity measurements. In both cases, deprotonation seems to occur between 100 and 200°C, because of the degradation or migration of dopant. Indeed, some works have shown that a degradation of the  $\text{SO}_3^-$  bond in CSA is observed between 100 and 200°C.<sup>7</sup>

In polyaniline films and polyaniline-polystyrene blends, a heterogeneous picture can be used to explain the conduction mechanisms. In this case, the macroscopic electrical conductivity results of two conduction mechanisms that occur in

serial: a metallic-type behavior observed inside conducting clusters where conducting polyaniline chains are well ordered, in serial with a hopping mechanism between these clusters through insulating or less doped (and less ordered) regions. Previous works have shown that thermoelectric power is few influenced by barriers between conducting clusters.<sup>13</sup> Nevertheless, this electrical parameter is very sensitive to conducting clusters, which explain the sensitivity of the TEP during the heating of PANI films and PANI-PSt blends.

### Heating-Cooling Cycles

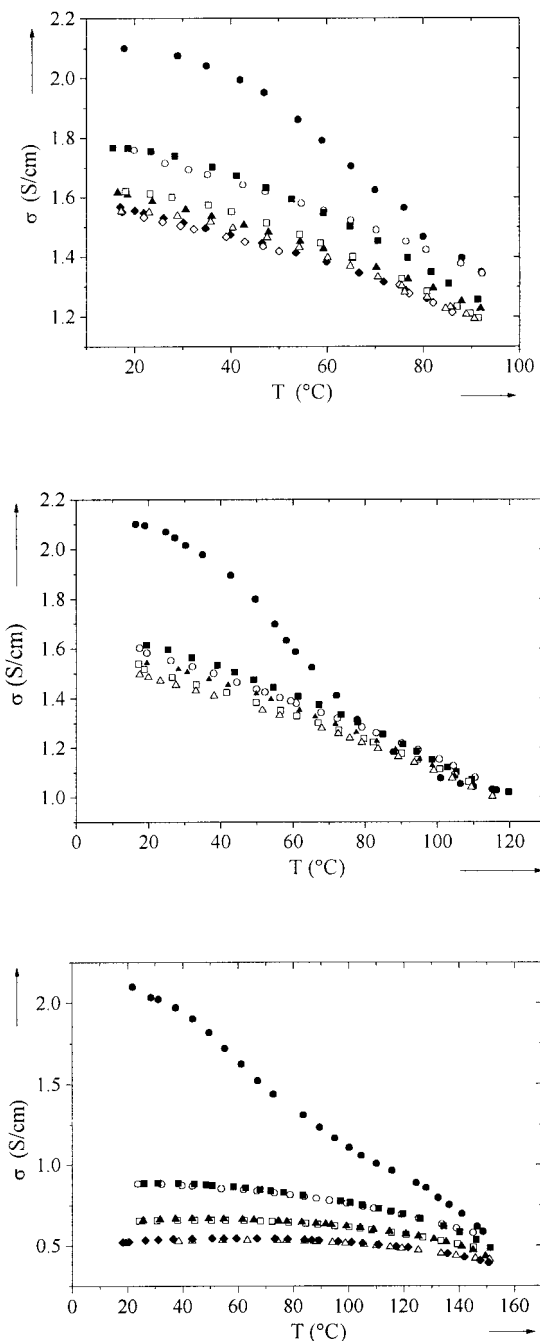
The loss of solvent put in obviousness by TGA measurements has some consequences on the electrical conductivity value. Indeed, conductivity measurements during heating-cooling cycles show a decrease of the electrical conductivity after evaporation of the solvent. Figure 5(b) presents variations of the electrical conductivity during three heating-cooling cycles for a PANI-DiOHP-PSt 10% film up to a maximal temperature of 120°C (the temperature increases or decreases by 3°C/min). After the first cycle, a decrease of the conductivity at room temperature of 25% is observed (2.1 to 1.6 S/cm). Next, cycles do not show additional information, and they follow the same curve as in the first heating-cooling cycle.

Similar results are obtained for PANI-CSA-PSt 10% films [Fig. 6(b)]. After the first cycle, a diminution of the conductivity at room temperature of 25% is observed (8 to 6 S/cm). As in PANI-DiOHP-PSt blends, the next cycles follow the same curve as in the first cycle. This behavior, also observed in polypyrrole films obtained from a solution of this polymer in *m*-cresol,<sup>19,20</sup> has been attributed to the evaporation of the solvent (espe-

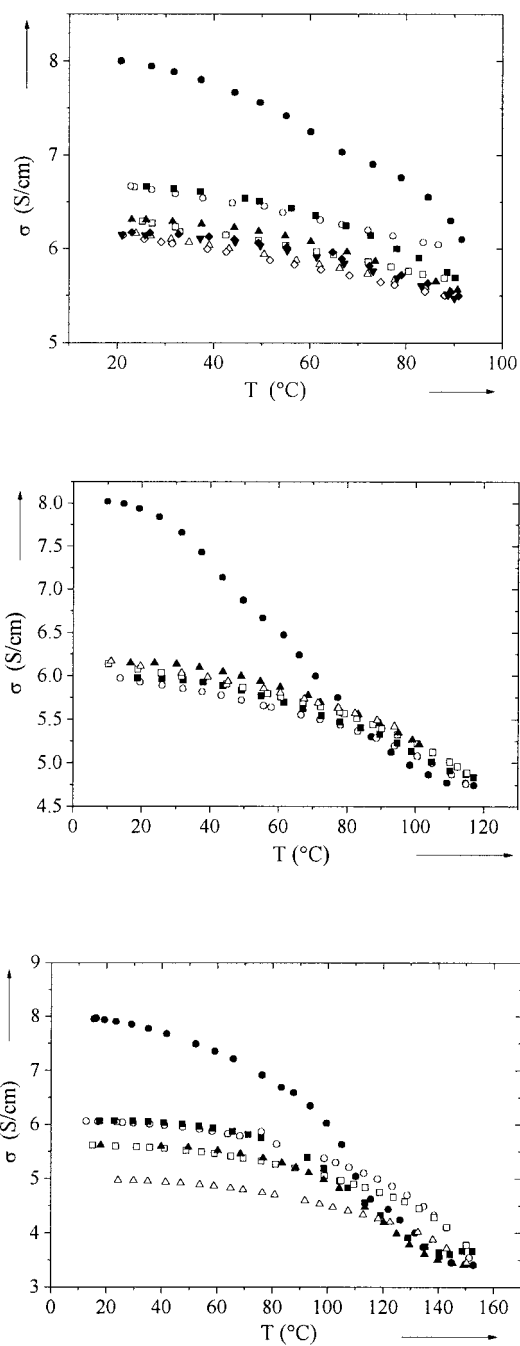
**Table I** Critical Temperature Corresponding to Strong Variations of the Physical Parameters Studied for PANI Films Doped With DiOHP or CSA

	Films Doped with DiOHP	Films Doped with CSA
Electrical conductivity measurements	450 K	500 K
T.E.P. measurements	400 K	425 K
Thermogravimetric analysis	480 K	

cially *m*-cresol) during the first heating. Others works have shown that the presence of the solvent (*m*-cresol) in polyaniline films can improve the value of the electrical conductivity.<sup>21</sup>



**Figure 5** Change in electrical conductivity of PANI-DiOHP-PSt 5% film in repeated heating-cooling cycles between room temperature and (a) 90°C; (b) 120°C; (c) 150°C (for each cycle, ●, first heating; ○, first cooling; ■, second heating; □, second cooling; ▲, third heating; △, third cooling; ◆, fourth heating; ◇, fourth cooling).



**Figure 6** Change in electrical conductivity of PANI-CSA-PSt 5% film in repeated heating-cooling cycles between room temperature and: (a) 90°C; (b) 120°C; (c) 150°C (for each cycle, ●, first heating; ○, first cooling; ■, second heating; □, second cooling; ▲, third heating; △, third cooling; ◆, fourth heating; ◇, fourth cooling).

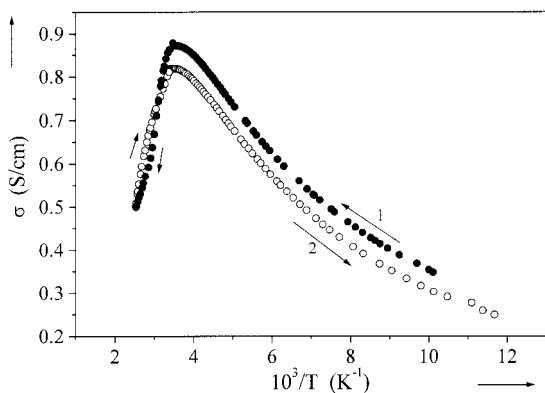
In the case of polyaniline, water can also play a role in this process because it has been shown that it can influence strongly electrical properties of doped polyaniline.<sup>22-24</sup> For example, Matve-



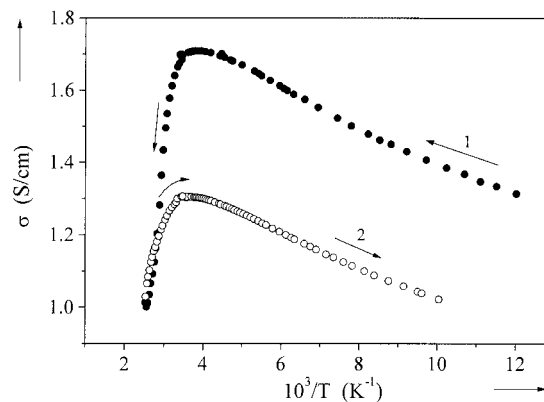
eva<sup>23</sup> has presented a model describing the reversible water molecule absorption at the aniline units (protonation by water) involving hydrogen bonds between water molecules and polyaniline chains. During the polymer heating, the evaporation of water leads to a deprotonation of the polymer chain. According to these authors, this model can also be extended in the case of polar solvent like *m*-cresol.

To complete this study, heating-cooling cycles up to different temperatures (90, 120, 150°C) have been undertaken. Figure 5(a) presents variations of the electrical conductivity vs. the temperature for PANI-DiOHP-PSt blends for cycles up to 90°C and Figure 5(c) presents these same variations for cycles up to 150°C. In the first experience (up to 90°C), the second cycle does not follow the same curve as in the first cooling. After several cycles, the electrical conductivity reaches gradually a limit value. In this case, the solvent is not totally evaporated after the first cycle and several rises-descents in temperature are necessary before to reach a stable state. After three cycles up to 90°C, a 1.6 S/cm conductivity at room temperatures is observed like for cycles up to 120°C.

When the upper limit of the heating cycles was raised to 150°C, this value of 1.6 S/cm is exceeded after the first cycle and the electrical conductivity at room temperature in the second heating and the subsequent cooling and heating cycles became lower and lower as the heating-cooling cycles were repeated. Nevertheless, each heating curve superimposes to the preceding descent until 130°C and then diverges a little. This behavior seems indicate that an electrical degradation oc-



**Figure 7** Change in electrical conductivity of PANI-DiOHP-PSt 5% films in a heating-cooling cycle between 80 and 393 K.



**Figure 8** Change in electrical conductivity of PANI-CSA-PSt 5% films in a heating-cooling cycle between 80 and 393 K.

urs near 130°C. Indeed, the amount of solvent, which can modify the electrical conductivity, is evaporated after a heating up to 120°C, and no changes are observed between the first cooling and the second heating until 130°C. Then, a degradation of the film occurs and at the following cooling, the conductivity curve does not follow the last cycle curve. At the following heating, the same behavior is observed up to 130°C and then the film is damaged a little more. The same process occurs during each cycle.

Similar results are obtained for PANI-CSA-PSt films (Fig. 6). These measurements confirm the important role of the solvents (*m*-cresol, water) on the electrical conductivity. Furthermore, a degradation of the electrical conductivity is observed from 130°C for the two studied families.

In the aim to complete these results, a heating-cooling cycle between 80 and 393 K has been undertaken. Results are presented on Figure 7 for a PANI-DiOHP-PSt 5% film and on Figure 8 for a PANI-CSA-PSt 5% film. These curves show that the low temperature behavior seems to be few affected by the partial evaporation of solvent. Nevertheless, a meticulous examination of these curves reveals a slight increase of their slope at low temperature. In the case of the film doped with DiOHP, the model of tunnel effect limited by the charging energy of conducting clusters (CELT model)<sup>13,25</sup> allows to account for the variations of the electrical conductivity at low temperature as well before as after the partial evaporation of the solvent

$$\left( \sigma = \sigma_0 \exp \left[ - \left( \frac{T_0}{T} \right)^{1/2} \right] \right).$$

**Table II** Electrical Values Deduced by the Fit of the Electrical Conductivity Data for Conducting PANI-PSt Blends before and after a Heating–Cooling Cycle between 80 and 393 K

	Before Heating		After a Heating–Cooling Cycle	
Films Doped with DiOHP	$\sigma$ (300 K) (S/cm)	$T_0$ (K)	$\sigma$ (300 K) (S/cm)	$T_0$ (K)
	2.1	659	1.6	724
Films doped with CSA	$\sigma$ (300 K) (S/cm)	$T_1/T'_0$	$\sigma$ (300 K) (S/cm)	$T_1/T'_0$
	8	1.4	6	1.5

The characteristic temperature  $T_0$  of this model, which is directly related to characteristic dimension of the conducting clusters,<sup>26</sup> increases slightly after a heating–cooling cycle (Table II).

For films doped with CSA, previous works have shown that the CELT model is no longer relevant because the charging energy is very weak and a mechanism of fluctuation induced tunnelling (FIT model) occurs at low temperature.<sup>13</sup>

$$\left( \sigma = \sigma_0 \exp \left[ - \left( \frac{T_1}{T'_0 + T} \right) \right] \right)$$

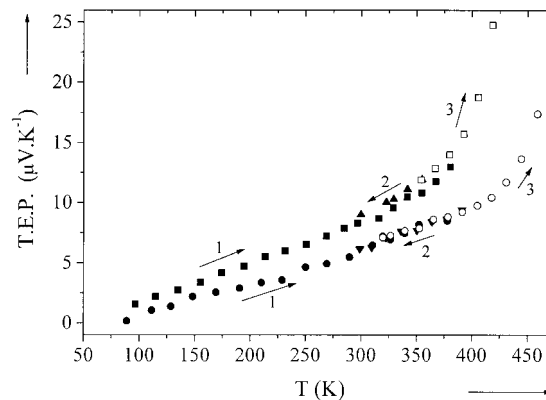
According to Schimmel,<sup>27</sup> the ratio of the characteristic temperatures  $T_1/T'_0$  is directly connected to the width,  $s$ , of the barrier between clusters. Results of the fit for these films are presented in Table II. In the case of films doped with DiOHP, an increase of  $T_0$  can be related to the diminution of the average cluster size,  $d$ , and the increase of the distance  $s$  between these conducting clusters. For films doped with CSA, use of Schimmel relationships shows that an increase of  $T_1/T'_0$  can equally be connected to the increase of the barrier width between clusters. But in this case, this hypothesis remains difficult to confirm because the increase of the  $T_1/T'_0$  ratio is very weak.

Thermoelectric power measurements have been undertaken during a heating–cooling cycle between 80 and 393 K in the aim to confirm the preceding hypothesis. Results are presented in the Figure 9. Variations of the TEP are not too affected by the evaporation of solvent. This result is in agreement with the hypothesis of the weak diminution of the cluster size after a heating–cooling cycle. Indeed, the TEP reflects essentially the intrinsic nature of conducting clusters, and it is little influenced by the fine barrier (insulator or less doped barrier) between these conducting clusters. A weak variation of the cluster size and, therefore, of the width of the zone between clusters, does not induce important changes in variations of this electrical parameter.

A model of conducting cluster with a variable diameter has been presented by Kahol et al.<sup>28</sup> to interpret humidity effects on electronic properties of polyaniline. They propose that conducting clusters are constituted of well-ordered chains (zone of high cristallinity). Fine strongly disordered zones separate these clusters. In their “variable-size metallic island” model, the boundary separating the ordered and disordered region is not sharp, but has a fairly large width, which depends on the amount of moisture present in the sample. This frontier would be constituted of rather delocalized polarons for “wet” samples and more localized for “dried” samples. This picture seems in good agreement with our results, and it allows explanation of the increase of the distance between clusters observed after partial evaporation of the solvent. However, it is difficult to specify the exact nature of solvent that induces this change of clusters size (water or *m*-cresol). Furthermore, this model is in agreement with works that have shown that the solvent is especially present in amorphous phases.

## CONCLUSION

In this article, a study of the thermal behavior of polyaniline films and polyaniline–polystyrene



**Figure 9** Thermoelectric power variations in a heating–cooling cycle between 80 and 500 K.

blends has been presented. Transport measurements (electrical conductivity and thermoelectric power) at high temperature and thermogravimetric analysis show that an irreversible degradation is observed near 450 K for films doped with DiOHP and near 500 K for films doped with CSA. In both cases, the thermoelectric power is the most sensitive parameter to electrical degradation during the heating of conducting films.

Electrical conductivity measurements during heating-cooling cycles show a diminution of the room temperature conductivity after evaporation of the solvent (water, *m*-cresol). A model of cluster with a variable diameter allows interpreting this phenomenon by assuming the existence of a sensitive frontier to the solvent at the periphery of conducting clusters.

## REFERENCES

- Liess, M.; Chinn, D.; Petelenz, D.; Janata, J. *Thin Solid Films* 1996, 286, 252.
- Karg, S.; Scott, J. C.; Salem, J. R.; Angelopoulos, M. *Synth Met* 1996, 80, 111.
- Angelopoulos, M.; Patel, N.; Shaw, J. M.; Labianca, N. C.; Rishton, S. A. *J Vac Sci Technol B* 1993, 11, 2794.
- Yoshino, K.; Kaneto, K.; Takeda, S. *Synth Met* 1987, 18, 741.
- Yang, Y.; Heeger, A. J. *Nature* 1994, 372, 344.
- Mastragostino, M.; Marinangeli, A. M.; Corradini, A.; Giacobbe, S. *Synth Met* 1989, 28, C501.
- Yue, J.; Epstein, A. J.; Zhong, Z.; Gallagher, P. K.; MacDiarmid, A. G. *Synth Met* 1991, 41-43, 765.
- Kulkarni, V. G.; Campbell, L. D.; Mathew, W. R. *Synth Met* 1989, 30, 321.
- Colaneri, N. F.; Shacklette, L. W. *IEEE Transact Instrument Measure* 1992, 41, 291.
- Mäkelä, T.; Pienimaa, S.; Taka, T.; Jussila, S.; Isotala, H. *Synth Met* 1997, 85, 1335.
- De Lima, J. R.; Schreiner, C.; Hummelgen, I. A.; Fornari, C. C. M.; Ferreira, C. A.; Nart, F. C. *J Appl Phys* 1998, 84, 1445.
- Gustafsson, G.; Cao, Y.; Treacy, G. M.; Klavetter, F.; Colaneri, N.; Heeger, A. J. *Nature* 1992, 357, 477.
- Jousseaume, V.; Bonnet, A.; Morsli, M.; Cattin, L. *Eur Phys J AP* 1999, 6, 7.
- Bonnet, A.; Said, P.; Conan, A. *Rev Phys Appl* 1982, 17, 701.
- Yang, C. Y.; Reghu, M.; Heeger, A. J.; Cao, Y. *Synth Met* 1996, 79, 27.
- Kaiser, A. B. *Phys Rev B* 1989, 40, 2806.
- Amano, K.; Ishikawa, H.; Kobayashi, A.; Satoh, M.; Hasegawa, E. *Synth Met* 1994, 62, 229.
- Abell, L.; Pomfret, S. J.; Adams, P. N.; Monkman, A. P. *Synth Met* 1997, 84, 127.
- Kim, I. W.; Lee, J. Y.; Lee, H. *Synth Met* 1996, 78, 177.
- Omastova, M.; Kosina, S.; Pontieck, J.; Janke, A.; Pavlinec, J. *Synth Met* 1996, 81, 49.
- Avlyanov, J. K.; Min, Y.; MacDiarmid, A. G.; Epstein, A. J. *Synth Met* 1995, 72, 65.
- Pinto, N. J.; Shah, P. D.; Kahol, P. K.; McCormick, B. J. *Phys Rev B* 1996, 53, 10690.
- Matveeva, E. S. *Synth Met* 1996, 79, 127.
- Nechtschein, M.; Santier, C.; Travers, J. P.; Chroboczek, J.; Alix, A.; Ripert, M. *Synth Met* 1987, 18, 311.
- Jousseaume, V.; Morsli, M.; Bonnet, A.; Tesson, O.; Lefrant, S. *J Appl Polym Sci* 1998, 67, 1205.
- Zuppiroli, L.; Bussac, M. N.; Paschen, S.; Chauvet, O.; Forro, L. *Phys Rev B* 1994, 50, 5196.
- Schimmel, T.; Denninger, G.; Riess, W.; Voit, J.; Schwoerer, M.; Schoepe, W.; Naarmann, H. *Synth Met* 1989, 28, D11.
- Kahol, P. K.; Dyakonov, A. J.; McCormick, B. J. *Synth Met* 1997, 89, 17.