The humidity dependence of the electrical conductivity of a soluble polyaniline–poly(vinyl alcohol) composite film

Kotaro Ogura,* Takayuki Saino, Masaharu Nakayama and Hiroshi Shiigi

Department of Applied Chemistry, Yamaguchi University, Ube 755, Japan

A humidity-sensitive composite film has been synthesized that consists of soluble polyaniline (PAn) and poly(vinyl alcohol) (PVA). PAn gave a percolation threshold where the electrical conductivity rose sharply at a volume fraction of 0.1%. This value is very small compared with that (about 5 vol%) reported in general for composite films consisting of conducting and non-conducting polymers, indicating that the two polymers used in this study were mixing completely. The conductivity of the PAn–PVA composite was proportional to the relative humidity, and the linearity was valid from 3×10^{-5} to 1.5×10^{-1} S cm^{-1}. The response time of the composite for the humidity change was 45 s and 9 min for moistening and desiccating steps, respectively. The conductivity of the composite film varied depending on the doping level of PAn, which was affected by the concentration of water molecules surrounding the conducting polymer. At high humidity, the PAn was in the form of an emeraldine salt, and transformed into a non-conducting base with decreasing environmental humidity.

Recently, the demand for humidity control has increased in fields such as air conditioning systems, electronics manufacture and drying processes for ceramics and foods.[1] However, commercial humidity sensors are far from satisfactory since a linear response to humidity is valid only in a limited range and hysteresis is often involved in the measurement of the response and humidity curves. Previously, we have reported that a composite film consisting of poly(*o*-phenylenediamine) (PoPD) and poly(vinyl alcohol) (PVA) has favorable characteristics for a humidity sensor, *i.e.* the electrical conductivity of the composite film is linearly related to the relative humidity and there is no hysteresis in the measurement. However, response times have not been determined, and the detailed sensing mechanism remains obscure. In order to clarify these questions and to develop a new humidity sensitive material we have prepared and studied a composite film consisting of soluble polyaniline (PAn) and PVA.

Although PAn has many useful functions, it is a green intractable powder and a non-processible material when prepared by ordinary procedures in hydrochloric or sulfuric acid solution. Ten years ago, however, PAn soluble in dimethyl sulfoxide (DMSO) and dimethylformamide (DMF) was prepared by chemical or electrochemical polymerization in a large protonic acid, such as toluene-*p*-sulfonic acid or sulfanilic acid;[3,4] such a soluble PAn may have various commercial applications.[5]

In measuring the conductivity of insulating polymers filled with conducting particles, conductivity is often observed to rise abruptly at a mass fraction of 10–20%.[6–8] This behavior (percolation) is attributed to the coagulation of particles to form conducting networks. As previously described, the composite film prepared from PoPD and PVA shows electrical conduction at a low volume fraction (about 0.2%) of conducting polymer and the conductivity of such composites varies in response to environmental humidity.[2] Soluble PAn is expected to have a lower percolation threshold in the formation of composite films with insulating polymers, and we have now applied such a composite film as a new sensing material for humidity.

Experimental

Soluble PAn was synthesized in aqueous solution as described by Li *et al.*[3] In the polymerization of aniline, toluene-*p*-sulfonic acid was used as a dopant. An aqueous solution (100 ml) of 0.15 M $(NH_4)_2S_2O_8$ was added slowly to a solution (100 ml) of 0.15 M aniline and 0.1 M toluene-*p*-sulfonic acid at room temp. After 8 h, a dark-green precipitate was separated by filtration, rinsed with the toluene-*p*-sulfonic acid solution, and dried under vacuum. The prepared PAn was submerged in DMSO and the insoluble residue removed by filtration. The PAn was recrystallized under vacuum, weighed, and again dissolved in DMSO to prepare a given concentration of PAn in DMSO. A homogeneous solution of a PAn–PVA composite was made by mixing the PAn–DMSO solution with a constant amount of PVA dissolved in DMSO. This solution was cast on a substrate, and the solvent was removed under vacuum to obtain the composite film.

To measure electrical conductivity, a comb-shaped microelectrode prepared by depositing a thin platinum film was used as the substrate.[2] The thickness of the applied composite film was 0.1 μm. The composite film-cast microelectrode was placed in a measuring cell connected to a vacuum line enabling us to introduce a controlled pressure of water vapor for the moistening process at 20 °C. Finally, the pressure was restored to 760 Torr by introducing nitrogen gas. The desiccation process involved pumping out the water vapor and admitting N_2 to 760 Torr.

Fourier transform infrared (FTIR) spectroscopic measurements were performed by both *ex situ* and *in situ* methods on a Shimadzu FTIR (Type 8100 M) spectrometer. *Ex situ* spectra of PAn, soluble PAn and PVA were obtained in the transmission mode as KBr tablets. The PAn–PVA composite film for the measurement of *ex situ* FTIR spectra was prepared by casting the mixed DMSO solution of PAn and PVA onto a silicon substrate, removing the solvent under vacuum, and finally peeling off the resulting film from the substrate to fix it to a sample holder. The *in situ* spectra of the composite film at various relative humidities were recorded by the reflection method. The composite film cast on stainless steel was held at 100% humidity for 10 h to moisten it, and the sample was transferred to a spectroscopic cell in a stream (2 dm^3 min^{-1}) of nitrogen gas at 12% humidity. The FTIR spectra of the film were measured every 2 min initially and every 30 min after 1 h, and the measurements were continued for 120 min at which the spectral features remained unchanged. Thus, the humidity in the composite film was assumed to vary from 100 to 12%.

Results and Discussion

The *ex situ* spectra of PAn in KBr are shown in Fig. 1 in which the sample was prepared with virgin (*a*) or recrystallized (*b*) PAn. The virgin PAn shows quinoid (Q) ring stretching at 1600 cm^{-1} and benzenoid (B) ring stretching at 1500 cm^{-1}, typical features of a semiquinoid structure of emeraldine type.[9] The peaks at 3450 and 2900 cm^{-1} correspond to N—H and C—H stretching, respectively. The bands at 1310 and 1250 cm^{-1} are attributed to the C–N stretching and deformation modes of the aromatic amine. The peak at 1145 cm^{-1} is due to the B—NH^{+}=Q vibration, indicating that PAn is conductive and is in the form of an emeraldine salt. The absorption peak at 815 cm^{-1} is due to the C—H bending of the aromatic ring. The absorption spectrum of the recrystallized PAn (curve *b*) has all bands of spectrum (*a*) and additionally bands at 1030, 1010, 744 and 690 cm^{-1}. The former two bands are considered to be a doublet due to the symmetric stretching vibration (1065–1050 cm^{-1})[10] of SO$_3$ of the toluene-*p*-sulfonic acid. The absorption peaks at 744 and 690 cm^{-1} are assignable to the C—H out-of-plane deformation of the aromatic ring and the C—S stretching vibration, respectively. It is therefore confirmed that toluene-*p*-sulfonic acid is incorporated into PAn. Such features were observed only for the soluble PAn, and the solubility is attributed to reduced interchain interactions, resulting in an increase of the interaction force between dopant and polar solvent.

The FTIR spectra of soluble PAn (*a*), PAn–PVA composites with volume ratios of 99.07:0.93 (*b*) and 99.84:0.16 (*c*), and PVA (*d*) are shown in Fig. 2. The volume of the composite film was determined from the calibration curve of the PAn or PVA *versus* its mass recorded beforehand. From Fig. 2, the composite film appears to be a simple mixture of PAn and PVA with no accompanying chemical interaction. The peaks at 3300, 1740, 1430 and 1250 cm^{-1} in curves (*b*), (*c*) and (*d*) are due to OH stretching, C=O stretching, C—H bending and C—H wagging vibrations, respectively, due to PVA.[11]

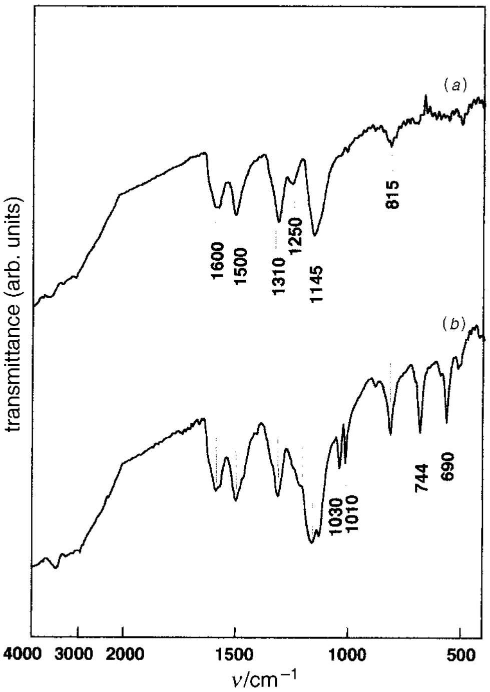


Fig. 1 *Ex situ* FTIR spectra of PAn in KBr. The sample was prepared with (*a*) virgin and (*b*) recrystallized PAn.

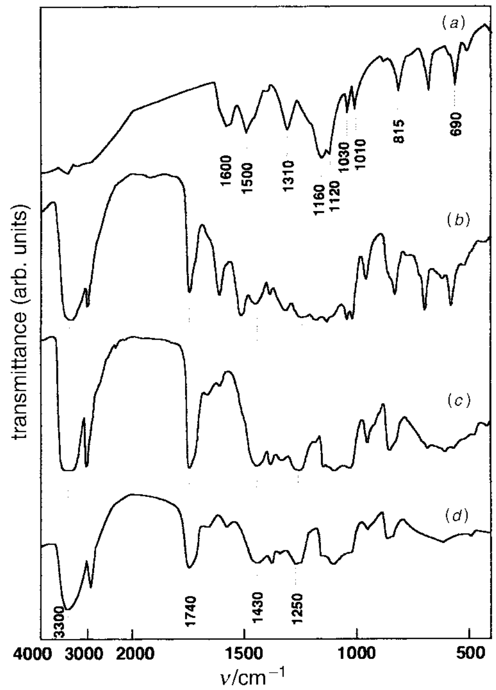


Fig. 2 FTIR spectra of (*a*) PAn soluble, PAn–PVA composites with volume ratios of (*b*) 99.07:0.93 and (*c*) 99.84:0.16 and (*d*) PVA

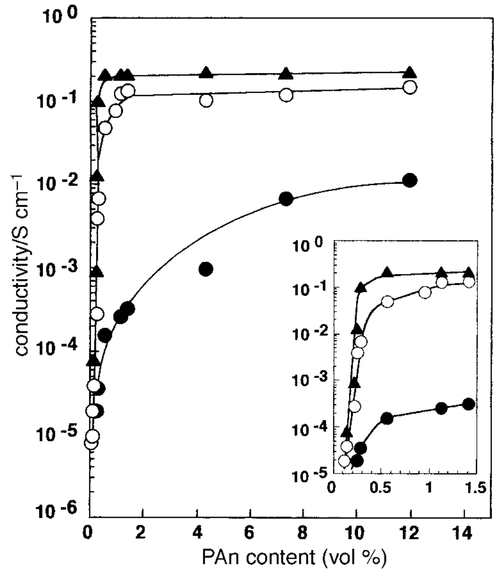


Fig. 3 Dependence of electrical conductivity of the PAn–PVA composite film on the PAn content at various relative humidities: (●) 0, (○) 55 and (▲) 100%

In Fig. 3, the electrical conductivity of the composite film is plotted *versus* the vol% of PAn in the PAn–PVA composite. The change in conductivity is conspicuous at about 0.1 vol% of PAn and approaches a constant value that depends on the relative atmospheric humidity. The change in conductivity is more than four orders of magnitude due to percolation behavior described above.[12,13] The percolation threshold obtained here is much lower than the value (about 5 vol%) cited for composites consisting of conducting particles and insulating polymers,[14] indicating that the composite prepared in the present study undergoes complete mixing. This property of the composite film is very important for constructing highly sensitive humidity-sensor as described below.

The electrical conductivity of the composite film is plotted *versus* the atmospheric humidity in Fig. 4. The conductivity is proportional to the relative humidity, and the linear portion extends from 3×10^{-5} to 1.5×10^{-1} S cm^{-1} for the change in humidity from 20 to 100%. Such high sensitivity has never been achieved with commercial humidity sensors. The value

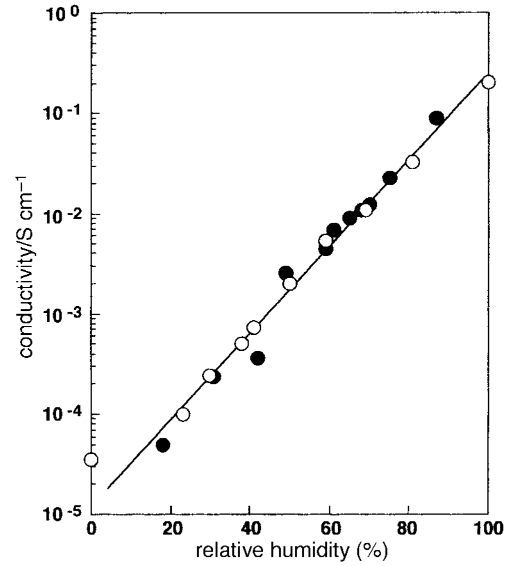


Fig. 4 Relationship between the conductivity and relative humidity in the (○) desiccating and (●) moistening processes. The composite film was prepared with 0.28 vol% PAn and 99.72 vol% PVA.

of the conductivity at 0% of humidity deviates from a straight line. This is probably caused by residual water molecules owing to inadequate vacuum. Measurements for the moistening and desiccating processes showed no hysteresis.

The conductivity *versus* humidity curves for PAn and PAn–PVA composites of various volume ratios are shown in Fig. 5. The composite films having PAn of 0.23 and 0.28 vol% exhibit a linear relationship covering three orders of magnitude, but there is no linear dependency for pure PAn and the composites containing PAn higher than 4.3 vol%. It is therefore considered that the PAn in the composite film plays an important part in detecting water molecules in the atmosphere. Nechtschein *et al.* have also reported that the presence of water favors the electrical conductivity of pure PAn.[15] The increase in conductivity is limited to one order upon a change of water pressure from 0 to 15 Torr, which is comparable with our result for pure PAn shown in Fig. 5. They interpret such humidity dependency on the basis of a proton exchange between the polymer solid phase and the water mobile phase. In the present case, however, such interpretation does not seem to be valid since the change in conductivity of the composite film ranges over three orders of magnitude.

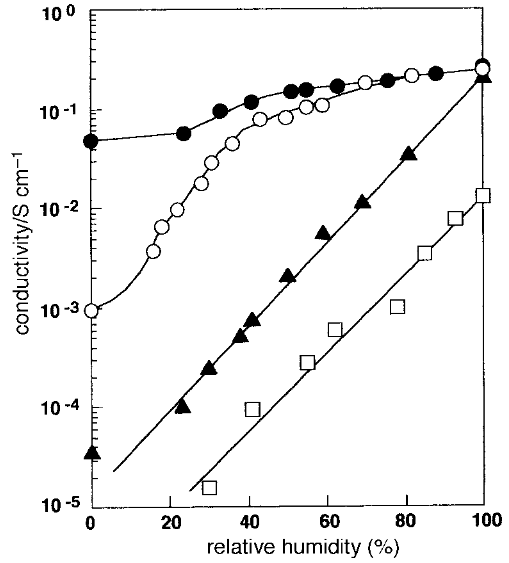


Fig. 5 Dependence of electrical conductivity of PAn and PAn–PVA composites on the relative humidity at 20 °C. The films were (●) 100 vol% PAn, (○) 4.3 vol% PAn–95.7 vol% PVA, (▲) 0.28 vol% PAn–99.72 vol% PVA and (□) 0.23 vol% PAn–99.77 vol% PVA. The thickness of the film cast on the microelectrode was always 0.1 μm.

In order to determine the response time, the conductivity of the composite film was monitored in a measuring cell in which the humidity was increased and decreased repeatedly. Typical results are shown in Fig. 6 where the humidity was changed between 53 and 28%. The response time was about 45 s and 9 min for the moistening and desiccating steps, respectively. It is noteworthy that the composite film responds more rapidly to moisture than drying conditions. Such a difference in the sensing rate is probably attributable to the strong affinity of

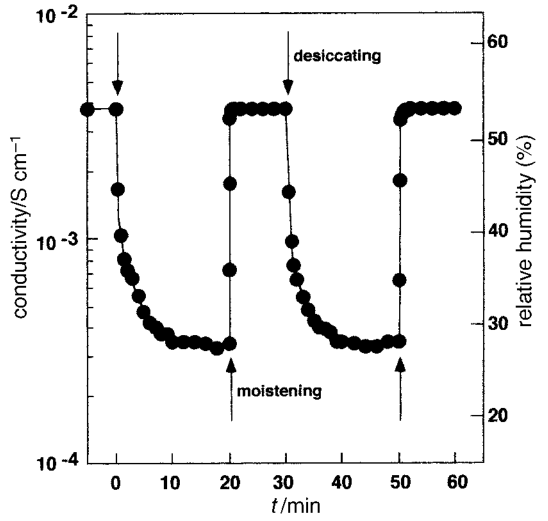


Fig. 6 Conductivity and relative humidity as a function of time. Desiccating and moistening processes were begun at the point indicated by the arrow.

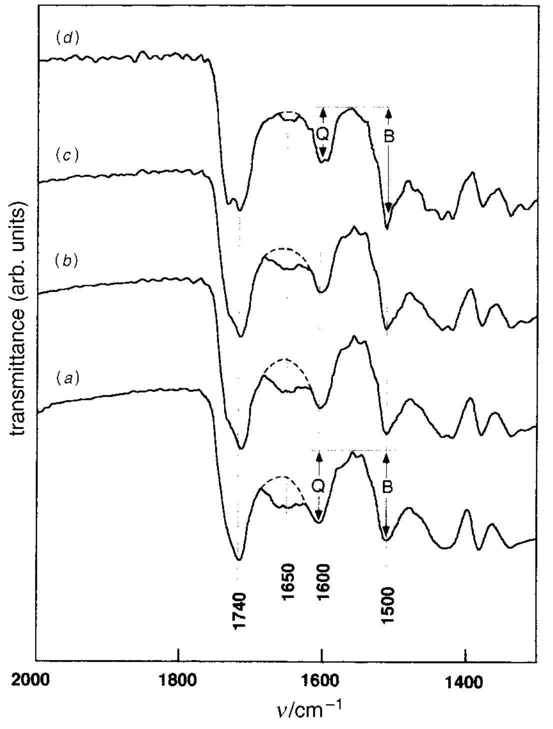
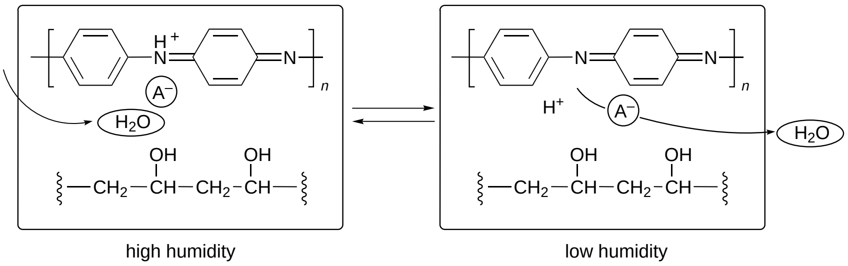


Fig. 7 *In situ* FTIR spectra of a PAn–PVA composite film subjected to various humidities. The measurement of curve (*a*) was performed on a sample that had previously stood for 10 h in an atmosphere of 100% humidity. Curves (*b*), (*c*) and (*d*) were taken after the sample used in (*a*) had been flushed with nitrogen gas containing 12% humidity for 20, 30 and 90 min, respectively.



Scheme 1

PVA for water, which results in the rapid incorporation of water into the composite but a slow diffusion out again. In fact, the conductivity response time from dry to wet state and from wet to dry was shorter and longer, respectively, when the volume ratio of PVA in the composite was decreased.

Fig. 7 shows the *in situ* spectra of the PAn–PVA composite at various humidities. Curve (*a*) was recorded just after the composite film kept for 10 h at 100% humidity was transferred to the spectroscopic cell. The composite film was then subjected to a stream of N_2 at 12% humidity, and curves (*b*) and (*c*) were taken after 20 and 30 min, respectively. Curve (*d*) was measured after 90 min, and as the spectral features remained constant after this time, the humidity within the composite film can be assumed to have equilibrated with the N_2 atmosphere. The broad band around 1650 cm^{-1} [between 1740 (PVA) and 1600 cm^{-1} (PAn)] is assignable to the OH bending vibration of H_2O. The intensity of this band decreases with decreasing humidity, indicating that some moisture was removed from the composite film. As described above, the absorption peaks at 1600 and 1500 cm^{-1} are assignable to the quinoid (Q) and benzenoid (B) ring stretching of the emeraldine form of PAn, respectively. At high humidity (curve *a*), the spectral intensities of the Q and B bands are comparable, a feature typical of an emeraldine salt.[16] However, the intensity of the B band was higher than that of the Q band with decreasing humidity (curve *c*, *d*). This indicates that benzenoid units occupy a greater volume than quinoid units[17] and that the emeraldine base gains an advantage over the salt in the dry state. Hence, the desiccating process in the composite film results in the transformation of the PAn from the emeraldine salt to the base.

On the other hand, a large tilt is observed in the spectrum above 1800 cm^{-1} for the composite film with higher humidity (Fig. 7, curve *a*, *b*), but the tilt becomes small with decreasing the humidity (curve *d*). This is probably related to electron excitation in the polaron-energy band that is peculiar to a conducting polymer.[18] This result is consistent with the above-mentioned view that the PAn in the composite is conducting at higher humidity but is insulating at low humidity.

The mechanism by which the composite film senses water molecules is shown in Scheme 1 where A represents the toluene-*p*-sulfonate ion.

Water molecules are sensed through the PVA in the composite, and the conductivity of the composite film changes depending on the doping level of PAn, which is affected by the concentration of water molecules surrounding the conducting polymer. At high humidity, water molecules are trapped by PVA since this polymer has a rather high affinity for water. In this situation, the doping level of PAn stays high, and the polymer conducts. On the other hand, some water molecules are removed from PVA at low humidity, and simultaneously the dopant anions are de-doped in the acid form (HA) from the conducting polymer, resulting in a decrease in conductivity. This process is reversible, and the conductivity changes between the conducting ($\sim 10^{-1}$ S cm^{-1}) and insulating ($\sim 10^{-5}$ S cm^{-1}) levels in response to the variation between dry and wet states. The excellent linear dependency of conductivity on humidity, reflecting the reversible incorporation and ejection of water molecules occurring in the composite film, is favorable to the construction of a humidity sensor.

Conclusions

1. Percolation behavior was observed in measuring the electrical conductivity of a PAn/PVA composite film; the percolation threshold was about 0.1 vol% PAn in the composite.

2. The conductivity of the PAn–PVA composite film was proportional to the relative humidity, and the linear portion extended from 3×10^{-5} to 1.5×10^{-1} S cm^{-1} on changing in humidity from 20 to 100%. The linear range was affected considerably by the volume ratio of PAn to PVA in the composite film. The response time of the composite at 28 to 53% and 53 to 28% humidity was about 45 s and 9 min, respectively.

3. Water molecules were sensed through the PVA in the composite, and the conductivity of the composite film changed depending on the doping level of PAn, which was affected by the concentration of water molecules surrounding the conducting polymer. At high humidity, the PAn was in the form of the conducting emeraldine salt. Desiccating the composite transforms the conducting PAn salt to the non-conducting base.

References

1 H. Arai, *Denki Kagaku (J. Electrochem. Soc. Jpn)*, 1982, **50**, 38.
2 K. Ogura, H. Shiigi and M. Nakayama, *J. Electrochem. Soc.*, 1996, **143**, 2925.
3 S. Li, Y. Cao and Z. Xue, *Synth. Met.*, 1987, **20**, 141.
4 Y. Cao, G. M. Treacy, P. Smith and A. J. Heeger, *Appl. Phys. Lett.*, 1992, **60**, 2711.
5 Y. Cao, P. Smith and A. J. Heeger, *Synth. Met.*, 1993, **55**, 3514.
6 E. C. Cooper and B. Vincent, *J. Phys. D: App. Phys.*, 1989, **22**, 1580.
7 H. L. Wag, L. Toppare and J. E. Fernandez, *Macromolecules*, 1990, **23**, 1053.
8 E. Ruckenstein and S. Yang, *Polymer*, 1993, **34**, 4655.
9 Z. Ping, *J. Chem. Soc., Faraday Trans.*, 1996, **92**, 3063 and references cited therein.
10 L. J. Bellamy, in *The Infra-red Spectra of Complex Molecules*, 3rd edn., Chapman and Hall, London, 1975, p. 394.
11 C. A. Finch, in *Polyvinyl Alcohol*, ed. C. A. Finch, Wiley, London, 1973, p. 214.
12 J. Garland, *Trans. Metall. Soc., AIME*, 1966, **236**, 642.
13 A. Malliaris and D. T. Turner, *J. Appl. Phys.*, 1972, **42**, 614.
14 K. Miyasaka, K. Watenabe, E. Jojima, H. Aida, M. Suita and K. Ishikawa, *J. Mater. Sci.*, 1982, **17**, 1610.
15 M. Nechtschein, C. Santier, J. P. Travers, J. Chroboczek, A. Alixa and M. Ripert, *Synth. Met.*, 1987, **18**, 311.
16 I. Harada, Y. Furukawa and F. Ueda, *Synth. Met.*, 1989, **29**, E303.
17 L. W. Shacklette, J. F. Wolf, S. Gould and R. H. Baughman, *J. Chem. Phys.*, 1988, **88**, 3955.
18 N. S. Sariciftci, H. Kuzmany, H. Neugebauer and A. Neckel, *J. Chem. Phys.*, 1990, **92**, 4530.

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