BUTTERWORTH HEINEMANN

Polymer Vol. 36 No. 14, pp. 2733–2738, 1995

0032-3861/95/$10.00+0.00

Thermal doping of polyaniline with dodecylbenzene sulfonic acid without auxiliary solvents

K. Levon*, K.-H. Ho and W.-Y. Zheng
Department of Chemistry, Polytechnic University, 6 Metrotech Centre, Brooklyn, NY 11201, USA

and J. Laakso, T. Kärnä, T. Taka and J.-E. Österholm
Corporate R&D, Technology Centre, Neste Oy, PL 310, 06101 Kulloo, Finland
(Received 1 May 1994; revised 20 December 1994)

The doping of polyaniline has been achieved by introducing the dopant molecule into the solid, undoped polymer without the use of an auxiliary solvent. Complex formation in the solid phase occurs at elevated temperatures and results in the formation of a soluble and processable conducting complex. The complexation was followed by calorimetric studies during a heating scan and the exothermic heat complexation has been observed for the first time. The doping process is similar to the oxidation of an emeraldine base with traditional protonic acid doping, as observed by u.v. and i.r. spectroscopies. The improved processing conditions may be the result of the formation of a layered structure with strongly anisotropic characteristics, as determined by X-ray diffraction measurements.

(Keywords: thermal doping; polyaniline; layered structure)

INTRODUCTION

A major problem in applying electrically conducting polymers in practice has been the intractability and infusibility of the polymers, e.g. polythiophenes. The substitution of polythiophene with alkyl side chains provided essential processing properties for electroactive polymers[1]. Alkylation prevents packing of the chains and also increases the flexibility of the chains, thus resulting in a decrease of the isotropization temperature[2–4]. The important part in the substitution is the increase of entropy in these polymeric systems, which actually decreases the ordering from the three-dimensional orthorhombic unit cell to a two-dimensional layered structure with an increase in length of the side chain[5,6]. This anisotropy provides increased possibilities for processing and for the mixing of these polymers. Additionally, it has been shown that the alkyl substituents modify the interface between the polymeric components and make possible the mixing of these polymers with various matrix polymers, even on a molecular level[7]. Thus the improved mixing and the creation of multiple percolation pathways through a controlled phase separation have lowered the percolation threshold and optimized the amount of conducting polymer[8].

The remaining problems have been the doping and the stability of the doped system. Doping has usually been done with Lewis acids or iodine, or with small molecules either in the gas or liquid phases. Doping with small Lewis acids has been shown to be unstable owing to an additional oxidation process. Great progress towards stability has recently been achieved by a protonic acid doping method for polyaniline, resulting in a thermally stable doped complex[9,10]. Further, bulky protonic acids, such as *p*-toluene sulfonic acids, have been applied and, owing to the large substituents in the protonic acids, polyaniline has been found to be soluble in organic solvents in the doped state and the processing properties have greatly improved[11]. Similarly, Cao *et al.*[12] have introduced a method using dodecylbenzene sulfonic acid, resulting in a doped, conducting complex (*Scheme 1*) which is also soluble in organic solvents. In all of the above cases, the development has been limited by the use of an auxiliary solvent in the process.

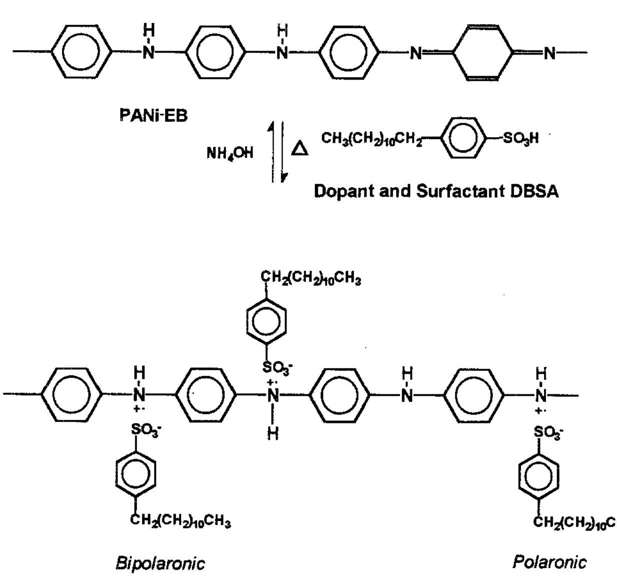
We have introduced alkyl substituents to the polymer backbone by complex formation with the use of an alkylated dopant and without the use of an auxiliary solvent. These alkyl substituents improve the processing of the doped complex. The complexation between polyaniline (PANi) and dodecylbenzene sulfonic acid (DBSA) has been followed by thermal analysis. The resulting complex is shown to form a layered structure in a stoichiometric ratio. Thus the order in the doped form differs essentially from the earlier forms of doped polyaniline.

EXPERIMENTAL

The *N*-methyl-2-pyrrolidone (NMP) and chloroform

---

* To whom correspondence should be addressed



Scheme 1

(CHCl$_3$) were of commercial grade, purchased from Aldrich, and were used without further purification. PANi ($M_w = 92\,200$, $M_w/M_n = 4.2$) was synthesized in sulfuric acid solution using ammonium peroxide as oxidant[13].

The influence of temperature on the complex formation was studied in three different ways. First, PANi and DBSA were weighed in a d.s.c. sample pan without any additional mixing for the calorimetric studies. A total weight of about 40 mg was measured and the pans were hermetically sealed. The second set of measurements was made in aluminium vessels with manual mixing before placing the samples in a preheated oven. The temperature of the oven was 80, 100 or 150°C and the time in the oven was either 30 min or 2 h. In the third set of measurements, the mechanically mixed samples were hot-pressed at four different temperatures under constant pressure and time.

U.v.-vis. spectroscopy was used to study the electronic structure of the polymers and the changes occurring in the electronic structure during the doping process. The undoped PANi was dissolved in NMP. The hot-pressed samples were dissolved in xylene and the oven-treated samples were dissolved in chloroform. The absorption spectra of doped and undoped PANi were studied for wavelengths between 300 and 900 nm. U.v. spectra were obtained with a Varian 100 u.v.-vis. spectrophotometer. I.r. spectra were recorded with a Perkin-Elmer 1600 *FT*i.r. spectrometer connected to a personal computer with a Spectrum Calculation program. The sample used for *FT*i.r. for the soluble fraction was a thin film and the insoluble fraction was pressed with KBr.

The exothermic complexation heats were determined by a Perkin-Elmer TAS7 DSC. The instrument was calibrated with indium (m.p. 156.6°C). A Phillips APD 3720 X-ray generator was used for the wide-angle X-ray diffraction (WAXD) experiments. The X-ray source was a XRG 3100 generator which utilized a CuK$_a$ target ($l_{Ka} = 1.5406$ Å) with settings of 40 kV and 20 mA.

RESULTS AND DISCUSSION

Calorimetric studies on the complexation

The heat of complexation between PANi and DBSA was observed during the initial thermal heating cycle. This heat of doping of complex formation was observed for the first time in the history of the doping of polymers, because in the past the doping process has been carried out either electrochemically or in gas or liquid phase at room temperature, and under these conditions calorimetric heat measurements have not been possible. The complexation occurs at elevated temperatures because at room temperature the self-association of the acid, DBSA, and PANi are strong and the diffusion is slow. The self- association becomes weaker and the diffusion process is accelerated with the increase of thermal energy, and the complexation can be observed as an exothermic heat in the heating cycle.

In order to evaluate quantitatively the stoichiometric ratio we performed a set of experiments in which we changed the composition in this PANi/DBSA binary mixture from 1 : 1 to 1 : 6 weight ratio. All the exotherms are shown in *Figure 1*. The first observation is that the peak temperature of the exotherm increases with increasing amount of DBSA. Although the temperature of the exotherm may not have equilibrium significance, the change of temperature and the heat value itself indicate that there may be an optimal ratio for the complexation. The change in temperature, as shown in *Figure 2*, reflects the fact that samples with ratios of 1 : 1 and 1 : 2 have an excess of unreacted PANi. As the ratio of the complexed material is unknown, we first divided the total amount of heat by the weight of PANi. This comparison does give an indication of the stoichiometric ratio, as shown in *Figure 3*; in samples with ratios of 1 : 1 and 1 : 2 the heat is smaller than in the sample with a 1 : 3 ratio, owing to the excess amount of PANi. In samples with ratios 1 : 5 and 1 : 6 the heat becomes smaller, presumably owing to the excess amount of strongly associating DBSA. We can conclude at this point that the optimal ratio is between 1 : 2 and 1 : 4.

In the next step, assuming that the above estimation is correct, we followed a procedure for finding the heat evolved for the complex in a stoichiometric ratio of the components. We analysed the complex formation by thermal analysis in the following manner. We assumed that in the sample with a 1 : 1 ratio there is an excess amount of PANi and we calculated new total weights

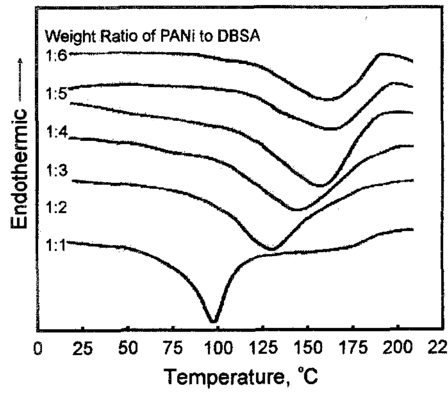


Figure 1 D.s.c. thermograms for polyaniline mixtures with different ratios of DBSA

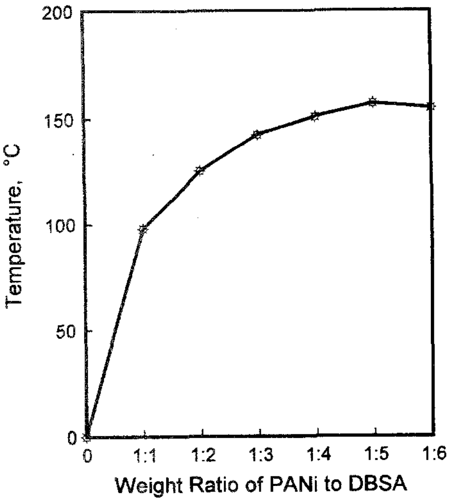


Figure 2 Peak temperatures of the exotherms for different sample ratios

using ratios of 1 : 1.25, 1 : 1.5, 1 : 2, 1 : 2.5, 1 : 3 and 1 : 3.6 by subtracting the excess amount of PANi. We used the same ratios for the sample with a 1 : 4 ratio but subtracted the assumed amount of excess DBSA. We calculated the new total weights for the samples with ratios of 1 : 2 and 1 : 3 in a similar way. Then we divided the heat values by these new total weights and plotted the values for the four experimental samples as shown in *Figure 4*, in which the x-axis presents the newly calculated weight ratios. If all the samples had the same stoichiometric ratio of the components there should be a common intercept for the lines. From the graphical presentation one can observe that the common solution gives $120 \pm 10\,\mathrm{J\,g^{-1}}$ as the heat value and a ratio of about 1 : 2.5 (1 : 0.7 molar ratio) for the components. Another way of presenting the results from these calculations is shown in *Figure 5*. In this case we calculated the total weights using ratios of either 1 : 2.5 or 1 : 3.0 for the four experimental samples which are now presented on the x-axis. The heat values obtained are quite constant between 120 and $130\,\mathrm{J\,g^{-1}}$. The weights and heat values using a ratio of 1 : 2.5 are also shown in *Table 1*. The total weight in the second column is the initial total weight used for the sample preparation. The initial unchanged weights and the new weights calculated for the 1 : 2.5 ratio for both PANi and DBSA are indicated.

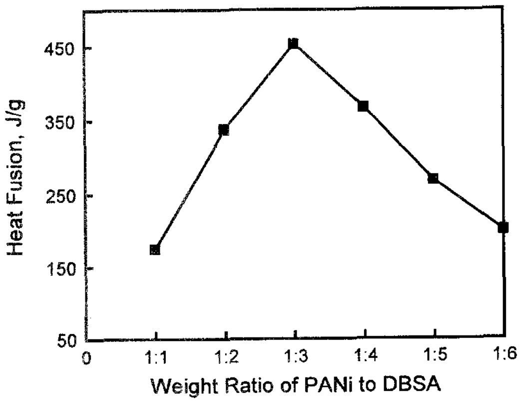


Figure 3 Heat of complexation when the measured heat value is divided by the weight of polyaniline

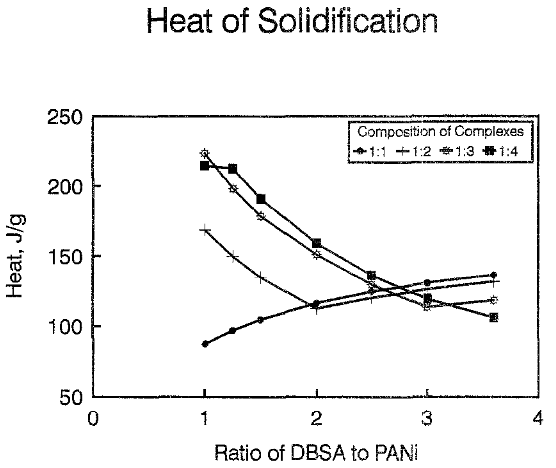


Figure 4 Heat values when the measured heat is divided by different polyaniline/DBSA ratios. The curves represent our four experimental samples while the x-axis presents the calculated new ratios

Another approach to investigate the stoichiometric ratio in the complex is to apply a water wash method to remove the excess DBSA, leaving only the DBSA with PANi which is complexed with the imine groups. We made four different complexes, without any additional mixing, at different temperatures and times with weight ratios of 1 : 3.6 and applied continuous extraction with water for 24 h. As the initial amount of PANi is known (and no PANi is removed during the extraction) we can subtract the amount of DBSA from the remaining total weight after the extraction. The result, as shown in *Table 2*, gave the same ratio (1 : 2.5 or 1 : 0.7 molar ratio) as in the calorimetric studies, indicating that the complex formation does occur in stoichiometric ratio.

Spectroscopic studies of the complex

The oven-treated and the hot-pressed samples were characterized by u.v.-vis. spectroscopy. The electronic transitions in the undoped PANi (emeraldine base, corresponding to pH 7, dissolved in NMP) appear for benzoid amine and quinoid imine at ranges 325 nm and 620 nm, respectively, as observed in *Figure 6a*. The oven-treated samples were dissolved in chloroform. Doping at 80°C and at 100°C results in the decrease of the intensities of the above-mentioned absorption peaks

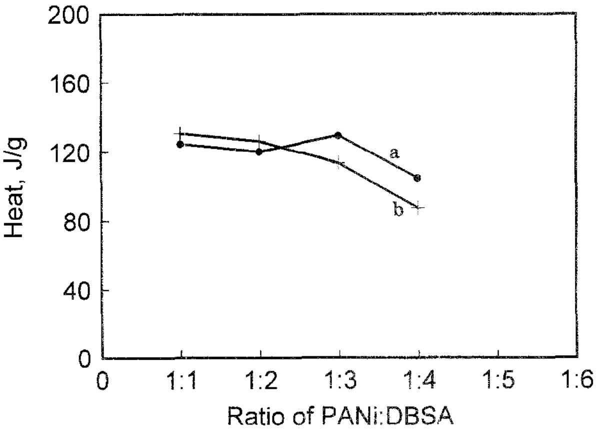


Figure 5 Heat values when ratios of 1 : 2.5 (a) and 1 : 3 (b) were used for the calculation. The x-axis represents the experimental values

Table 1 Complexation heat values calculated for 1 : 2.5 weight ratio

Initial weight ratio	Total weight (mg)	PANi (mg)	DBSA (mg)	Total weight used (mg)	Heat value (kJ)	Heat of complexation (J g^{-1})
1 : 1	38.8	7.8^{a}	19.4^{b}	27.2	3.39	124.7
1 : 2	44.5	11.8^{a}	29.6^{b}	41.4	5.00	120.7
1 : 3	43.6	10.9^{b}	27.3^{a}	38.2	4.86	127.5
1 : 4	44.0	8.8^{b}	22.0^{a}	30.8	3.25	105.0

[a] New weight for 1 : 2.5 weight ratio
[b] Unchanged weight

(*Figure 6*, samples 3 and 4) as complexation takes place. Additionally, an absorption appears at 460 nm which can be assigned to the oxidation of an aromatic ring in the dopant molecule or to the first polaronic level. The main feature is the appearance of a transition at more than 700 nm, typical for the formed polaron structure. Treatment at 150°C results in a strong transition at 460 nm with a small shoulder at 520 nm and the polaronic transition between 700 and 800 nm disappears. The formation of a transition responsible for the delocalized polarons at wavelengths above 850 nm is possible.

The hot-pressed samples and undoped PANi were dissolved in *p*-xylene. Doping in the hot-pressed samples, when pressed at 120 or 145°C, results in a similar phenomenon as for the sample treated in the oven at 150°C (*Figure 6*, samples 6 and 7). The typical absorptions for PANi have disappeared, no absorption for polaron formation between 700 and 800 nm can be observed and a moderately strong peak at 460 nm with a shoulder at 520 nm appears. Again, it is possible that an absorption for the delocalized polarons may exist at wavelengths above 900 nm. Doping in the hot-pressed samples at 175 and 195°C results in the appearance of a dominant absorption for the polaronic transition between 700 and 800 nm, as seen in *Figure 6* for samples 8 and 9. After a prolonged period of pressing at 195°C, the absorption above 700 nm decreases (*Figure 6*, sample 10), indicating that a degradation process has started at these elevated temperatures. It is also possible that the appearance of the polarons at 175 and 195°C is an indication of thermal degradation of the assumed delocalized structures.

Interesting features are observed in the u.v. spectra of the samples prepared at between 120 and 150°C by either preparation method. The absorption at 700 nm has disappeared and the absorption seems to increase when approaching the value of 900 nm. This occurs without a decrease in the conductivity. After the thermal doping, all of our samples have conductivities of between 1 and 5 S cm^{-1}. The change may be related to structural and conformational changes during the doping processes, as observed by MacDiarmid[14].

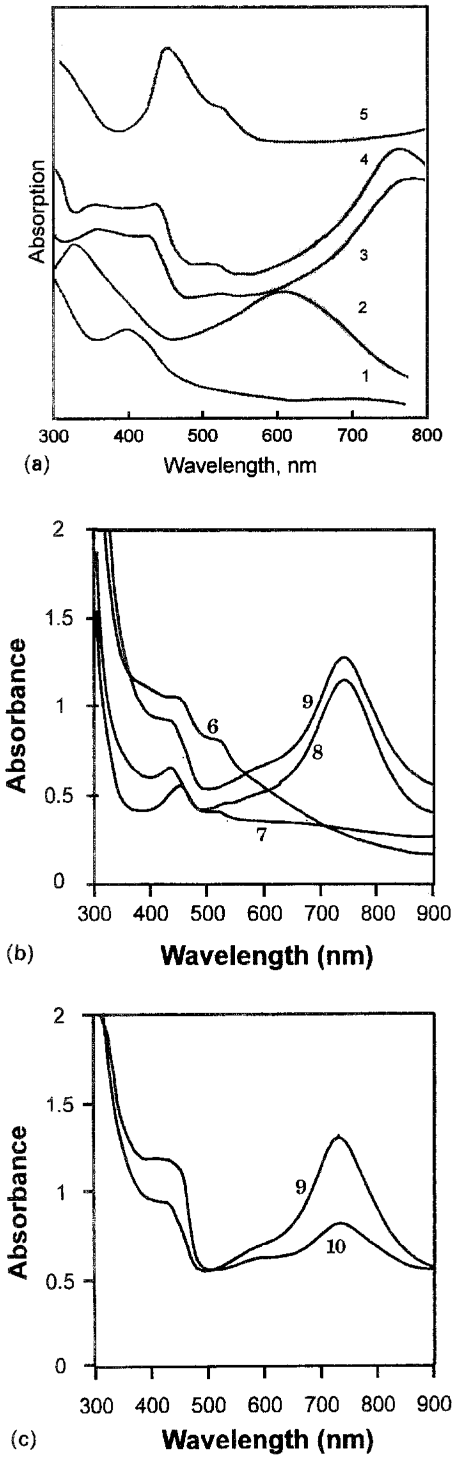


Figure 6 U.v.-vis. spectra of DBSA (1), polyaniline (2), the oven-treated samples at 80°C (3), at 100°C (4), at 150°C (5) and the hot-pressed samples at 120°C (6), 145°C (7), 175°C (8) and at 195°C (9). Sample (10) is a sample kept at 195°C for a prolonged period

Table 2 Results from water extraction

Sample no.	Temp (°C)	Time (min)	PANi (g)	DBSA (g)	Total weight (g)	Weight ratio	Weight removed by H_2O (g)	DBSA left (g)	Final weight ratio
1	100	30	2.34	7.88	10.22	1 : 3.37	2.24	5.64	1 : 2.41
2	100	120	3.08	10.38	13.47	1 : 3.37	2.85	7.53	1 : 2.44
3	80	120	2.78	10.14	12.92	1 : 3.65	2.88	7.26	1 : 2.62
4	150	120	2.78	9.63	12.41	1 : 3.46	3.25	6.39	1 : 2.44

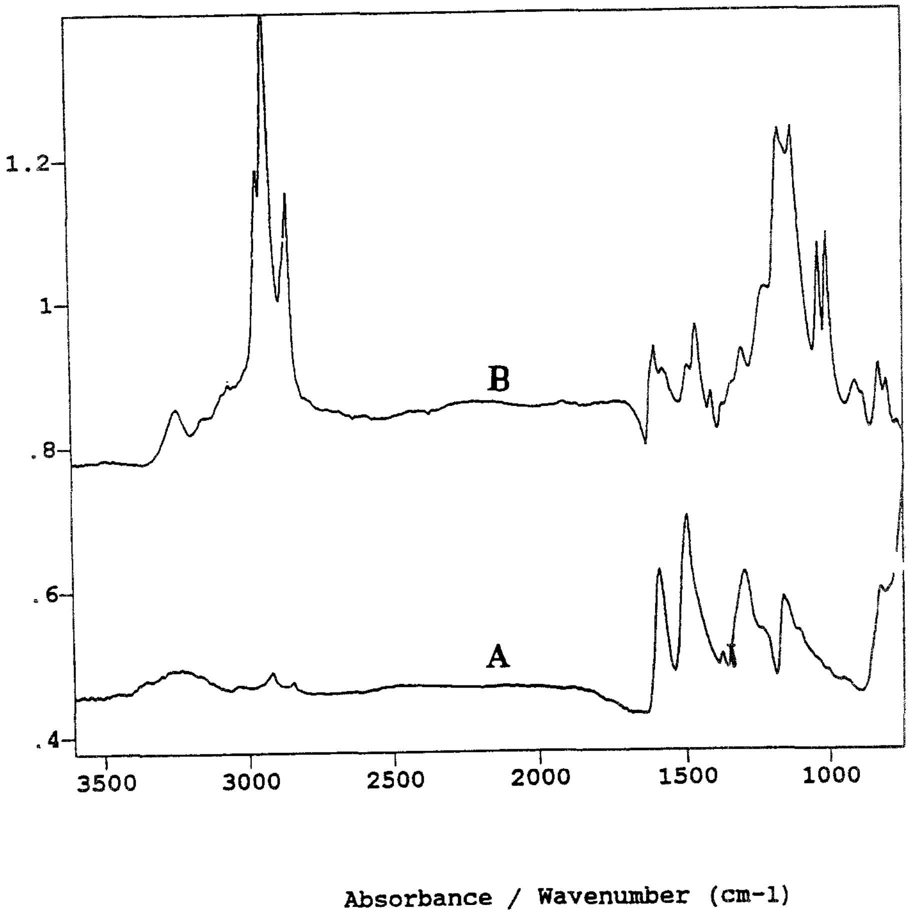


Figure 7 *FT* i.r.-spectra of polyaniline (A) and polyaniline–DBSA complex (B)

The doping process was also characterized by i.r. spectroscopy. *Figure 7A* presents the *FT* i.r. spectrum for PANi–emeraldine base (EB) and *Figure 7B* shows that for the soluble complex which was oven-treated at 80°C. EB is well characterized by the N–H stretching at 3247.3 cm^{-1}, which disappears after doping. Furthermore, the C–C stretching modes of the aromatic ring are typical for quinoid imine (Q) structure at 1583.0 cm^{-1} and for benzonoiddiamine (B) at 1491.6 cm^{-1}. The change in the intensity ratio of the two stretching modes and the appearance of multiple peaks are evidence for the protonation process. The weak C–N stretching mode in QBQ units at 1375 cm^{-1} also disappears after protonation on doping. The increase in planarity through changes in the conformation after doping can be observed in the shifts of C–N–H wagging mode (from 1214.3 to 1296.2 cm^{-1}) and C–N stretching through C–N–C angle (from 1214.3 to 1236.8 cm^{-1}). As the doping process with DBSA can be characterized with *FT* i.r., as explained above, the attachment of DBSA in PANi can also be observed, for instance at 2922 cm^{-1}, the region for aliphatic C–H stretching, and also the vibration band of sulfates at 1117.8 cm^{-1}. The resonant structure effect on the out-of-plane bending of the *para*-substituted aromatic ring (from 828 to 796 cm^{-1}) is also enhanced owing to the existence of this bending mode in both components.

Structural studies

Interestingly, the formation of a layered structure can be observed by X-ray diffraction. The diffraction peak in *Figure 8* at the low angle ($2\theta \approx 27$ Å) indicates the presence of layered structures as 27 Å accounts for the separation of the polymer backbones by the alkyl side chains with some degree of interdigitation. Such a structure is well known for alkylated stiff polymers and has also beenobserved in polypyrrole–dodecylbenzene sulfonate salt by Wernet *et al.*[15], who showed that the presence of the alkyl groups prevents the close packing of the polymer chains increasing the entropy and at the same anisotropy. As shown in *Figure 7*, the layered structure has been formed at 80°C for the oven treatment.

The complex is soluble in several organic solvents, such as tetrahydrofuran and chloroform, in the doped state. Additionally, the complex is processable by

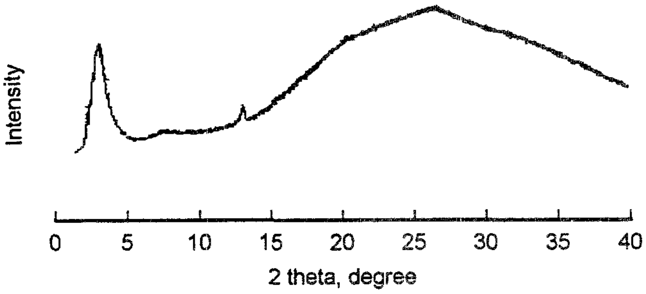
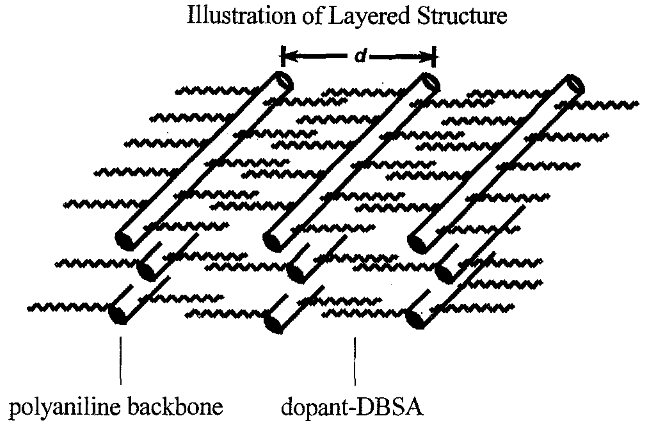


Figure 8 X-ray diffraction pattern of the oven-treated samples at 80°C



Scheme 2

extrusion methods, partly because the glass transition of PANi has decreased from about 150°C to temperatures close to room temperature owing to the lubricating effect of the highly substituted dopant. It is also probable that the layered structure, as presented in *Scheme 2*, is important in the improved processing conditions. The possible anisotropy, especially at elevated temperatures, may increase the flow properties of the doped complex. A third essential feature of the use of DBSA is the possibility of modifying the interfacial energy when blended with the matrix polymers. We have shown in the past that this effect can be obtained with the alkylated conducting polymers in the undoped state[7], and in the near future we will present our results on the blending of the PANi/DBSA complex with selected matrix polymers, with control of the percolation threshold.

REFERENCES

1 Elsembauer, R. L., Miller, G. G., Khanna, Y. P., McCarthy, E. and Baughman, R. H. *Electrochem. Soc., Ext. Abstr.* 1985, **85**(1), 1

2 Ho, K.-S., Bartus, J., Levon, K., Mao, J., Zheng, W.-Y., Laakso, J. and Taka, T. *Synth. Met.* 1993, **55–57,** 384

3 Chen, S. A. and Ni, J. M. *Macromolecules* 1992, **25,** 6081

4 Bolognesi, A., Porzio, W., Provasoli, F. and Ezquera, T. *Makromol. Chem.* 1993, **194,** 817

5 Tashiro, K., Ono, K., Minagawa, Y., Kobayashi, M., Kawai, T. and Yoshino, K. *J. Polym. Sci., Polym. Phys.* 1991, **29,** 1223

6 Ballauff, M. *Angew. Chem.* 1984, **28,** 253

7 Ho, K.-S., Levon, K., Mao, J., Zheng, W.-Y. and Laakso, J. *Synth. Met.* 1993, **55–57,** 3591

8 Levon, K., Margolina, A. and Patashinsky, A. Z. *Macromolecules* 1993, **26,** 4061

9 Chiang, J. C. and MacDiarmid, A.G. *Synth. Met.* 1986, **13,** 193

10 Travers, J. P., Chroboczek, J., Devreus, F., Genoud, F., Nechteschein, M., Syed, A., Geneis, E. M. and Tsintavis, C. *Mol. Cryst. Liq. Cryst.* 1985, **121,** 193

11 Schaklette, L.W., Han, C.C. and Luly, M.H. *Synth. Met.* 1993, **55–57,** 3532

12 Cao, Y., Smith, P. and Heeger, A. J. *Synth. Met.* 1992, **48,** 91

13 Cao, Y., Andreatta, A., Smith, P. and Heeger, A. J. *Polymer* 1989, **30,** 2305

14 MacDiarmid, A. G. Materials Research Society Meeting, November 1993, Boston, MA

15 Wernet, W., Monkenbusch, M. and Wegner, G. *Makromol. Chem., Rapid Commun.* 1984, **1,** 165