PII: S0032-3861(97)00187-0

Polymer Vol. 39 No. 2, pp. 475–483, 1998
© 1997 Elsevier Science Ltd
Printed in Great Britain. All rights reserved
0032-3861/97/$17.00 + 0.00

Structural and transport properties of thermally processable conducting polymer: polyaniline protonated with diphenyl phosphate

W. Łużny[a,]*, T. Kaniowski[a] and A. Proń[b]
[a]*Faculty of Physics and Nuclear Techniques, University of Mining and Metallurgy, Al. Mickiewicza 30, 30-059 Cracow, Poland*
[b]*Department of Materials Science and Ceramics, UMM, Cracow, and Department of Chemistry, Technical University, Warsaw, Poland*
(Received 29 March 1996; revised 20 November 1996)

Structural investigations of thermally processable, conductive polyaniline (PANI) are presented. Free standing, compact films of conductive polyaniline were prepared by hot pressing of polyemeraldine previously protonated with diphenyl hydrogen phosphate (DPHP) in chlorobenzene. The samples were then subjected to wide-angle X-ray diffraction (WAXD) and small angle synchrotron radiation scattering studies. Additionally, the temperature dependence of their conductivity was measured. Computer modelling was used in order to facilitate the interpretation of experimentally recorded diffractograms. These approaches have led us to an orthorhombic unit cell with a, b and c lattice constants of 4.4, 5.6 and 7.2 Å, respectively. Relative intensities of the diffraction peaks are strongly dependent on the temperature of pressing but show very little dependence on the time of pressing. This effect has been ascribed to the conformational changes in the polymer studied induced by external pressure at elevated temperatures, and more precisely, to the changes in the torsion angle between the phenylene rings and the zig-zag plane determined by nitrogen atoms. From two-dimensional SAXS patterns it can be concluded that the time of pressing has a strong impact on the average size of crystalline regions in the polymer whereas they do not change significantly with the temperature of pressing. It can be postulated that the decrease in the average crystallite size is associated with the cross-linking process occurring in the polymer upon extended pressing. © 1997 Elsevier Science Ltd.

(Keywords: conducting polymers; polyaniline; structure)

INTRODUCTION

Conductive macromolecular systems are usually obtained through appropriate modification of conjugated polymers. Unfortunately, conjugated polymers are extremely difficult to process. Due to strong interchain interactions these compounds are not soluble and do not melt, thus they can be neither solution nor thermally processed. For these reasons significant research effort has been directed, in the last decade, towards the synthesis of processable forms of electroactive polymers. Two approaches were used to achieve the solubility of conjugated polymers.

In the first approach conjugated polymers were solubilized by attaching long, flexible side chains to the stiff polymer backbone. This method turned out to be very successful in the case of polythiophene[1]. In the second approach the solubilizing group was introduced to the polymer matrix as an inherent part of the doping ion. This 'counter-ion induced processability' was first reported by Cao *et al.*[2] for functionalized sulfonic acids protonated polyaniline.

It has been shown recently[3–6] that phosphoric acid diesters can also serve as solubility inducing protonating agents. Moreover, two hydrophobic groups introduced to polyaniline with each dopant anion lead to its plastification. Therefore, the doped polymer can be thermally processed applying industrial methods typically used for processing of plasticized polymers.

The use of aromatic diesters instead of aliphatic ones leads to conducting systems thermally stable at temperatures exceeding 450 K. The main aim of this paper is to investigate the influence of thermal processing parameters on structural and transport properties of polyemeraldine protonated with diphenyl hydrogen phosphate (DPHP).

SAMPLE PREPARATION

Polyemeraldine base was prepared using standard procedures[7]. It was then protonated with DPHP in chlorobenzene. Typical content of PANI in chlorobenzene (calculated as polyemeraldine base) was 1 wt%. The protonation reaction was carried out at room temperature for 72 h. Two different $\mathrm{PANI_{mer}}$:DPHP molecule ratios were used: 1/1 and 1/0.5.

---

* To whom correspondence should be addressed

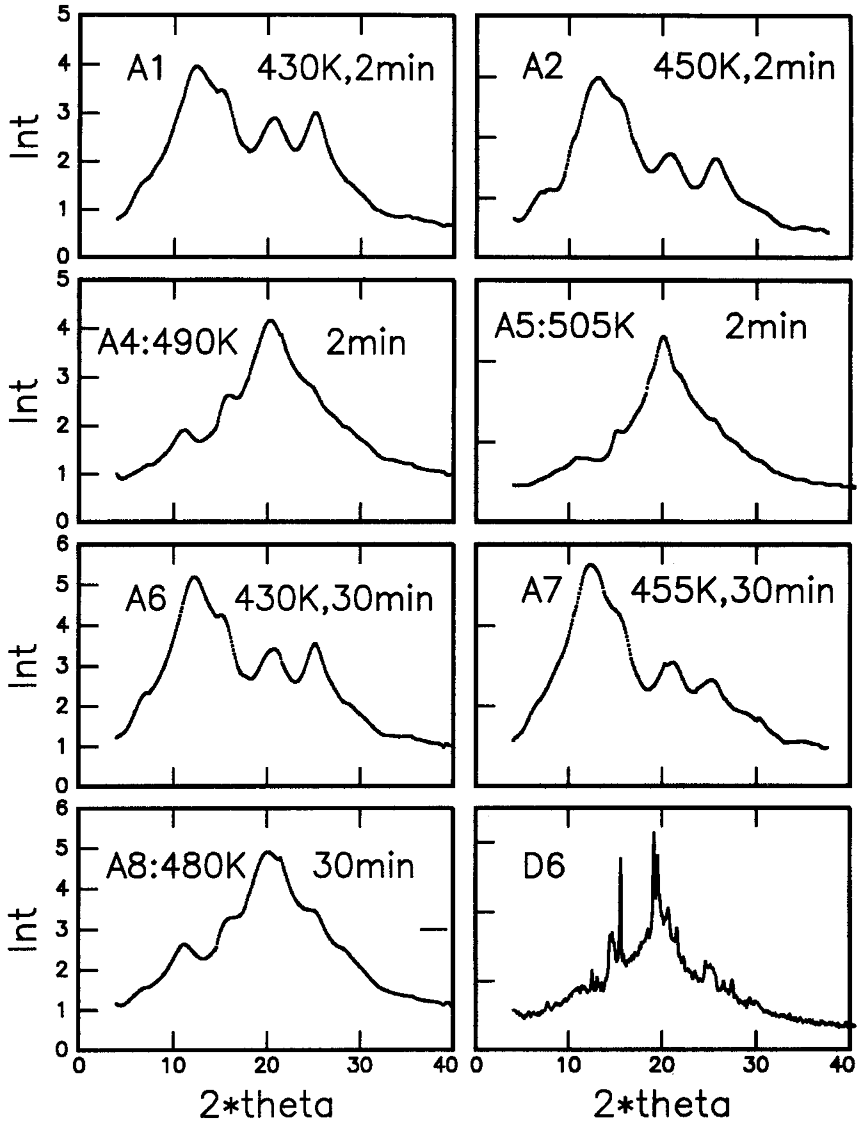

Figure 1 Experimental diffractograms obtained for the samples of the series A and for the sample D6 of DPHP protonated PANI. The result for the sample A3 has been neglected, because it gave evidence of almost complete, structural degradation of this sample. The temperature and the time of pressing are denoted for each sample

Upon protonation with DPHP part of polyemeraldine becomes soluble. The soluble and insoluble fractions can be separated by centrifugation. It should be stressed here that the soluble fraction is always enriched in the ester with respect to the PANI : DPHP ratio used for the protonation. Consequently the insoluble fraction contains less ester molecules per PANI mer than the initial mixture used for the protonation. As determined by elemental analysis the composition of the insoluble fraction is PANI(DPHP)$_{0.56}$ if PANI$_{\mathrm{mer}}$: DPHP ratio 1/1 is taken for the protonation reaction. In the case of PANI$_{\mathrm{mer}}$: DPHP ratio 1/0.5 in the protonating medium the insoluble fraction shows the composition of PANI(DPHP)$_{0.44}$.

Two different procedures of polymer processing were applied:

(a) In the first procedure chloroform washed insoluble fraction of DPHP protonated PANI was dried at 330 K until constant mass and then hot pressed between two aluminium sheets using the force of *ca.* 50 kN; samples PANI(DPHP)$_{0.44}$ (the series A), and PANI(DPHP)$_{0.56}$ (the series C) were prepared;

(b) In the second procedure the soluble and insoluble fractions were not separated. Therefore chemical compositions of the samples were identical to the compositions of the protonating media. After the evaporation of the solvent the polymer samples were pressed in identical conditions as described above; samples PANI(DPHP)$_{0.50}$ (the series B), and PANI(DPHP)$_{1.0}$ (the series D) were prepared.

By hot pressing, compact films or plates are prepared of a thickness typically between 0.1–0.4 mm. Such samples were used for the structural and electrical transport studies.

X-RAY DIFFRACTION MEASUREMENTS—RESULTS AND DISCUSSION

X-ray diffraction experiments were carried out on a HZG-4 wide-angle diffractometer. A Cu-anode tube with a Ni-filter was used. The measurements were performed in a typical Bragg geometry ($\theta, 2\theta$) in a reflection mode.

The experimental diffractograms obtained for the

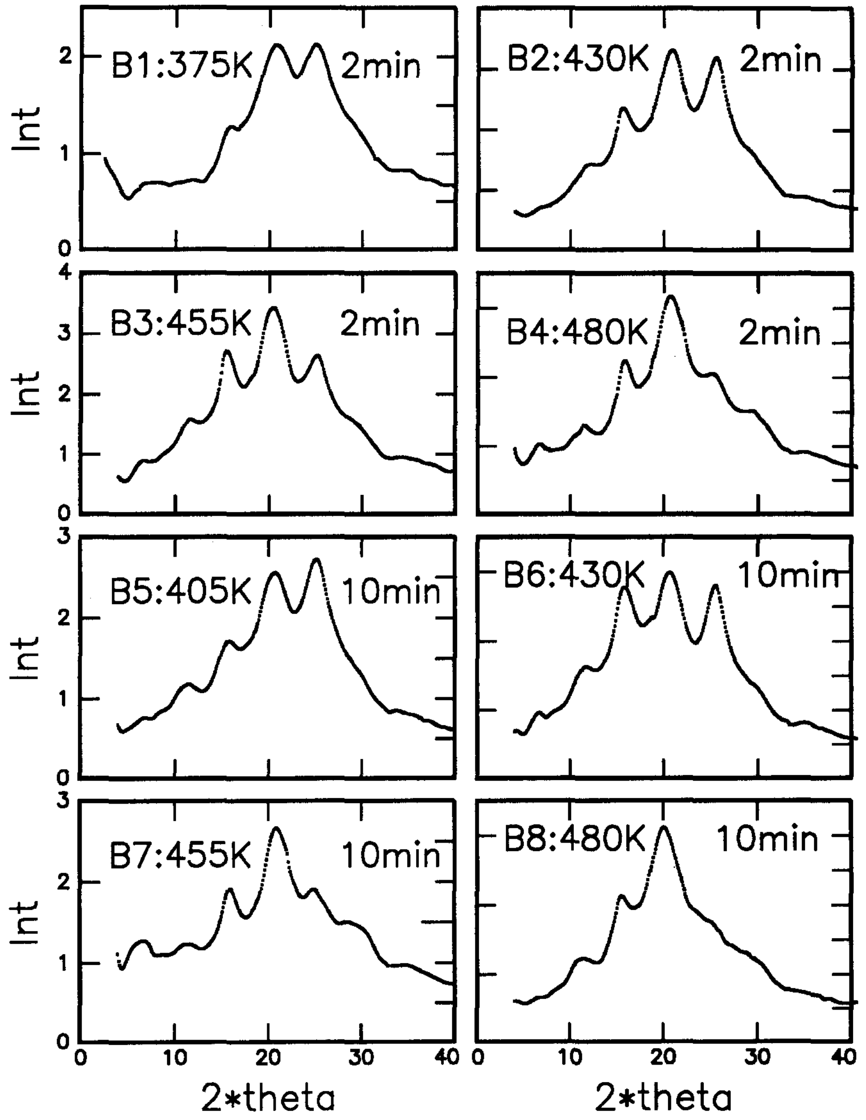

Figure 2 Experimental diffractograms obtained for the samples of the series B of DPHP protonated PANI. The temperature and the time of pressing are denoted for each sample

samples of series A, B and C are presented in *Figures 1–3*. The results obtained for the samples of series D have shown, that due to the excess of the protonating agent in the initial mixture, the samples acquired have formed the inhomogeneous two-phase systems with the precipitation of crystalline DPHP. A representative example of such diffractogram (for the sample D6) is presented in *Figure 1*. Therefore, the samples of series D were not subjected to further investigation.

The first evident conclusion from *Figures 1–3* is that the parameters of pressing have a strong impact on the experimental diffractograms of the samples studied. It should be underlined that within each series the chemical composition of each sample is identical but the differences between particular diffraction patterns may be very significant.

Secondly, it seems that the samples of series A, B and C are homogeneous and they form a one-phase system. There exists no evidence, by X-ray diffraction, of precipitation-like structures, or even a one-dimensional, long range order, as has been found for PANI protonated with heteropolyacids[8,9].

The next observations are as follows. The crystallinity of the samples studied may differ remarkably: some of the samples exhibit quite high crystallinity (for example: B6, C1), the others are almost completely amorphous (for example A5). The diffractograms of DPHP protonated polyemeraldine are rather different from those obtained for ES-I and ES-II forms of HCl protonated polyemeraldine[10]. In some cases, they also differ from the diffractogram of camphor sulfonic acid protonated PANI cast from *m*-cresol solution[11]. However, to the first approximation, some of the diffraction patterns obtained in this work can be considered as typical of polyemeraldine salt. This is not unexpected since the protonation levels in all samples studied are close to 0.5, i.e. the value expected for ideal polyemeraldine salt.

The diffraction pattern obtained for the sample B6, which exhibits remarkably high diffraction maxima, can be used as the 'key' for the interpretation of the remaining diffraction patterns. This diffractogram can be characterized by the set of three reflections with the higher relative intensity, for $2\theta \approx 15.6$, 20.4 and 25.3°, respectively. Additionally, three distinct reflections of lower intensity can be distinguished, for $2\theta \approx 6.7$, 11.5 and ~30°. The thorough analysis shows, that this set of reflections can be observed for all samples, but their relative intensity varies (and in some cases is very low).

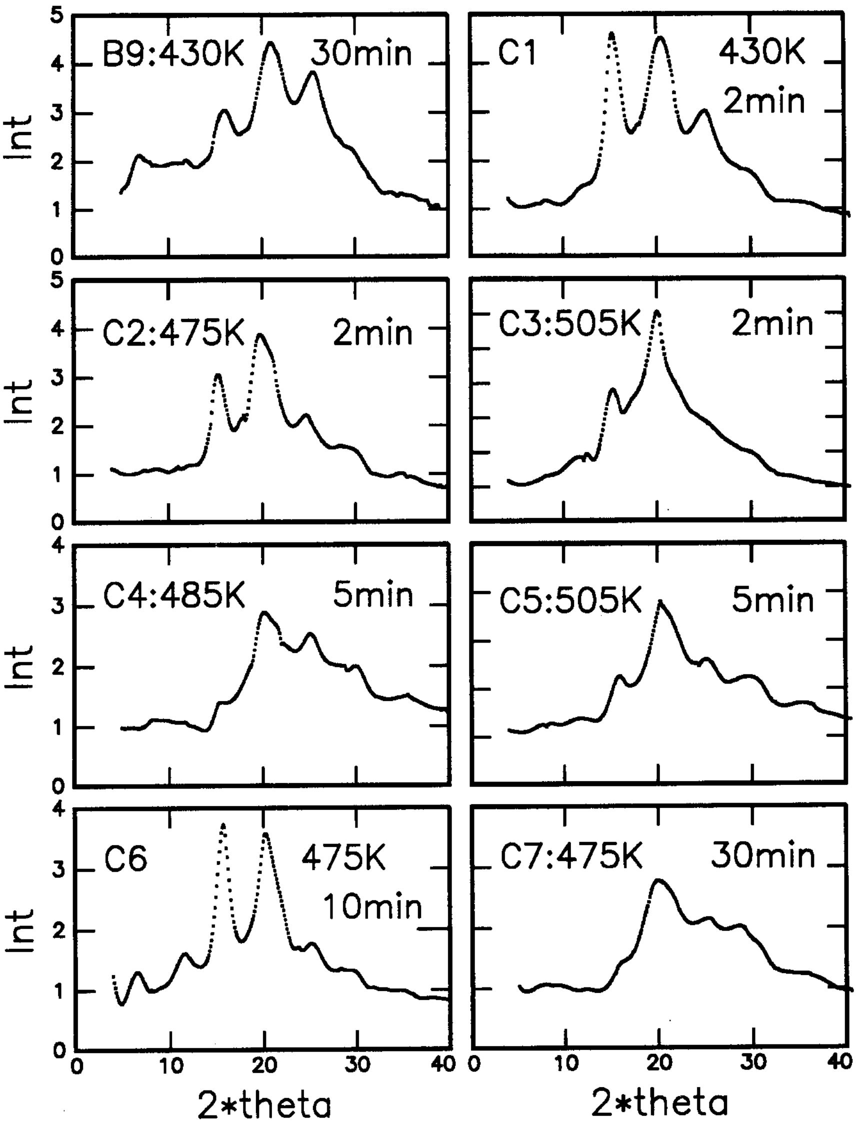

Figure 3 Experimental diffractograms obtained for the sample B9 and for the samples of the series C of DPHP protonated PANI. The temperature and the time of pressing are denoted for each sample

Two types of diffractograms can be distinguished in the A series: A1, A2, A6 and A7 exhibiting almost identical parameters form the first group whereas A4, A5 and A8 form the second group. The main difference between these two groups of diffractograms is the existence of a dominant double diffraction maximum for $2\theta \approx 12-15°$ in the first group. This maximum is absent in the second group where a maximum for $2\theta \approx 20°$ dominates. The samples of the second group were processed at higher temperatures.

The results obtained for series B show a higher variety. Taking into account, however, the processing parameters together with the resulting diffractograms, few classes in this series can be proposed. B2, B6 and B9 exhibit similar diffraction patterns, as well as the following pairs of samples: B1 and B5, B3 and B7, B4 and B8.

This observation can be helpful for the interpretation of the diffraction data recorded for the C series. To the first approximation these results resemble the ones obtained for the B series. However the relationship between the shape of the diffractogram and the parameters of thermal processing is not so evident.

To summarize, one can state that all diffractograms collected for all three series studied, can be characterized by a set of a few diffraction reflections at fixed positions, but showing different relative intensities. Also, the diffraction patterns are mainly determined by the crystallization temperature. The influence of the time of pressing is much less pronounced.

In view of the obtained experimental results one can suggest that all samples studied exhibit one crystalline structure, which is strongly modified during the hot pressing process. This implies the high differences in the relative intensities of the diffraction peaks for successive samples.

Since some of the diffraction patterns presented here are different than those reported earlier in the literature[10], we were tempted to propose a new model which would correctly describe the crystalline structure of the system studied. In all our samples protonation level was close to 0.5, i.e. the value expected for ideal polyemeraldine salt which implies one anion per two monomers. The presence of the anions had therefore to be taken into consideration in the modelling of the crystalline structure.

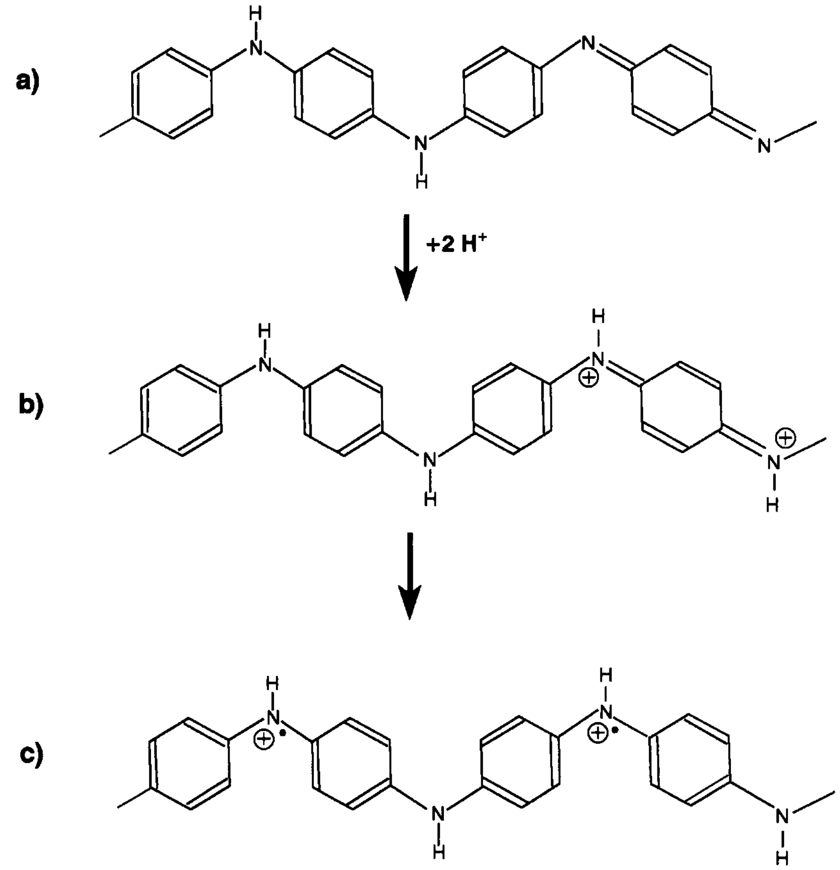

Figure 4 Scheme of the protonation process in PANI

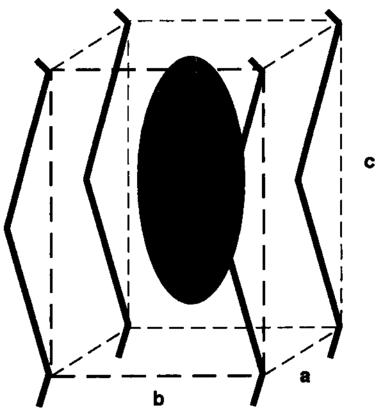

Figure 5 Schematic diagram of the orthorhombic unit cell used in the computer modelling of the crystalline structure of DPHP protonated PANI. The oval shape represents the position of the dopant anion

COMPUTER MODELLING—PRELIMINARY RESULTS

It is well known, that, during the protonation of polyemeraldine, base imine nitrogens are preferentially protonated as schematically depicted in *Figure 4*. The protonation involves, in addition, an internal redox reaction which transforms the protonated chains (*Figure 4b*) into the chains exhibiting poly(semiquinone radical) type of structure (*Figure 4c*). Therefore, the stoichiometry of all structural units of the polymer chain is identical, and one dopant anion is associated with every two phenylene rings of the PANI backbone. This allows us to assume that the unit cell contains two phenylene rings of the PANI main chain and one dopant anion originating from DPHP.

The model calculations have been carried out assuming that DPHP protonated PANI forms an orthorhombic, primitive unit cell analogous to that proposed in ref. 10 for ES-I. Such structure is schematically sketched in *Figure 5*. At the lattice constants *a*, *b* and *c* the following values have been fitted: 4.4, 5.6 and 7.2 Å, respectively.

Representative results of the calculated intensities, positions and indexation of the Bragg reflections for such model structures are presented in *Figure 6*, together with experimentally recorded diffraction patterns of three differently processed samples (B5, B6 and B7).

It seems that the origin of the three main diffraction peaks in *Figure 6* is rather obvious, as well as the origin of the weak maximum in the vicinity of 30°. Relative intensities of the three principal reflections, i.e. (0 1 0), (1 0 0) and (1 1 0) strongly depend on the conformation of polyemeraldine chain, and more precisely, on the torsion angle γ between two adjacent phenylene rings. The results of calculations show that a rather good agreement between the calculated and experimentally observed intensities of Bragg reflections can be obtained for $\gamma \sim 25–45°$. In general, with decreasing γ the intensity of (0 1 0) reflection grows whereas the intensity of (1 1 0) decreases. The comparison of these model results with the experimental diffractograms presented in *Figure 10* suggests that the hot pressing at higher temperatures leads to the better planarity of the PANI chain. This is manifested by a remarkable increase of the (0 1 0) reflection at the expense of the (1 1 0) reflection. This is

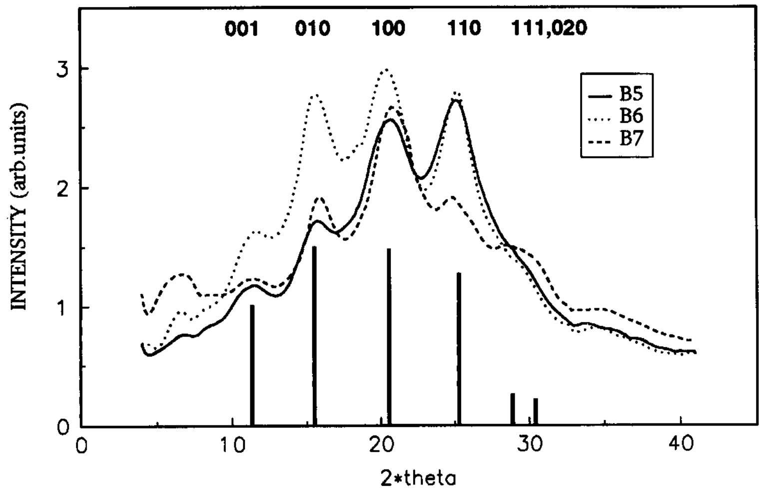

Figure 6 Comparison of experimental diffraction patterns obtained for three selected samples of the series B of DPHP protonated PANI with the results of the model calculations

not unexpected since intuitively pressing at elevated temperature should lead to more crystalline samples with better chain planarity.

The problem of the (0 0 1) reflection should be discussed in greater detail. The results of the model calculations obtained hitherto show an intermediate value of its intensity. However, the experimentally determined intensity is lower for both the B and C series and higher for the A series. One can suggest that the solution of this problem may be found in the explanation of the role of the DPHP originating anion localization in the unit cell. The results presented above have been obtained for the exact definition of its position, which is related to the ideal order of the dopant anions along the polymer chain and for ideal stoichiometry of $\mathrm{PANI(DPHP)_{0.5}}$. In reality, the position of the DPHP originating anions are widespread. In addition in the A and C series the samples do not exhibit ideal stoichiometry of $\mathrm{PANI(DPHP)_{0.5}}$, the former exhibiting slight deficit of the dopant ($\mathrm{PANI(DPHP)_{0.44}}$) whereas the latter slight excess ($\mathrm{PANI(DPHP)_{0.56}}$). It should be stressed here that the lowest discrepancy between the calculated and observed intensity of the (0 0 1) reflection is found for sample B6 which shows the best stoichiometry ($\mathrm{PANI(DPHP)_{0.5}}$) and the highest crystallinity. Thus, it can be postulated that the spread in the three coordinates describing the position of the doping anions has a great impact on the intensity of the (0 0 1) reflection. In a real situation, the position of the DPHP anion has a wide spread. This suggestion is related to all three coordinations describing the position of this anion in the unit cell. Especially, the *z* coordination should be considered, due to the fact the dopant anions are less densely packed in this direction. Higher disorder in this direction leads to a remarkable decrease of the (0 0 1) reflection intensity.

The position of this reflection should also be discussed. As has been mentioned above, it is related to the lattice constant *c* equal to *ca.* 7 Å. This value leads to the pitch of the zig-zag slightly greater that in the case of PANI protonated by HCl[10]. This effect can be related to the presence of a rather big anion between two adjacent macromolecules: the anion induced stretching of the polymer zig-zag should, in the same time, lead to the decrease of its width. The angle of the zig-zag (i.e. the angle between two nitrogen atom–phenylene ring bonds) corresponding to this value of the lattice constant *c* is *ca.* 150°, and this value is acceptable.

The origin of a small diffraction maximum in the vicinity of 6° is so far unclear, because it does not appear in the results of the model calculations. Perhaps, in some samples the ordering along the *z* axis leads to the doubled period in this direction. Then, this reflection would have the indices (0 0 1), and the maximum for $2\theta \approx 12°$ would have the indices (0 0 2)—similarly, as in the case of PANI protonated with heteropolyanions[9].

At the end of this discussion, it is worth comparing these results with the ones obtained for PANI protonated with camphorsulfonic acid[11]. The diffractogram presented there exhibits only three distinct maxima, related to the distances: 5.6, 4.6 and 3.5 Å. From the conclusions drawn in this discussion it is reasonable to assume that these reflections have the indices (0 1 0), (1 0 0) and (1 1 0) respectively, which can be treated as a good confirmation of our results. The lack of the reflection (0 0 1) is very characteristic for this class of polymer systems, as well as the almost identical values of the lattice constants *a* and *b*, despite the remarkably higher diameter of the protonating anion. This conclusion gives evidence for a certain universality of the PANI crystalline structure model proposed in this work.

SMALL-ANGLE SCATTERING OF SYNCHROTRON RADIATION—EXPERIMENTAL RESULTS AND DISCUSSION

SAXS measurements were performed using synchrotron radiation as HASYLAB, DESY (Hamburg). The aim of this work was to obtain some information concerning the influence of the parameters of processing of the samples PANI + DPHP on their supramolecular structure, by detecting their SAXS patterns. These investigations were performed on the instrument POLYP installed in HASYLAB, using transmission mode of the experiment. The two-dimensional (2D) SAXS patterns have been obtained, and the Guinier plots for the samples investigated have been calculated.

As has been mentioned in the previous section,

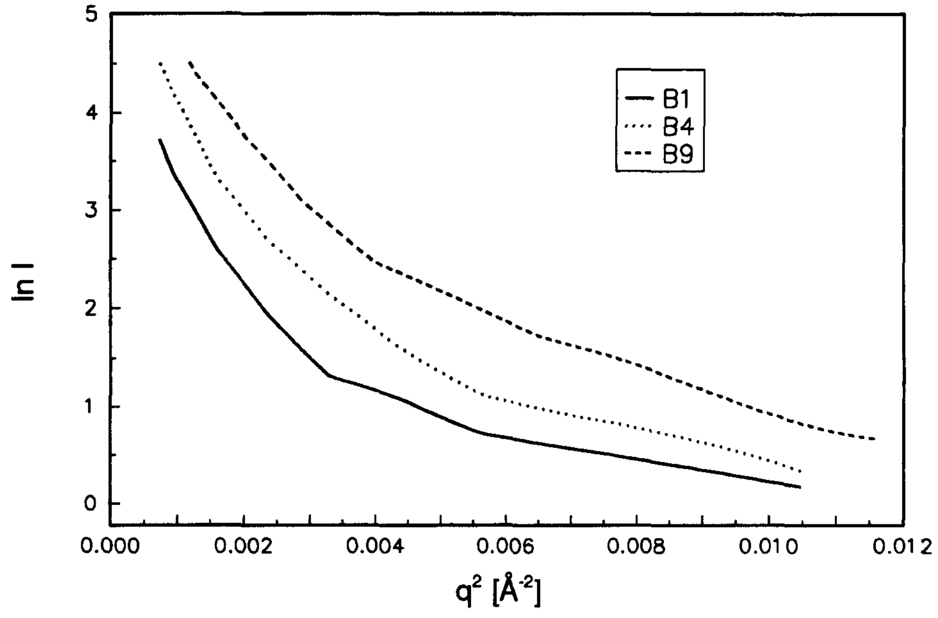

Figure 7 Guinier plots obtained for three selected samples of the series B of DPHP protonated PANI

particularly interesting results from the WAXD experiments have been obtained for the samples of series B. Therefore, this series was subjected to the SAXS measurements. For each sample of this series the 2D SAXS pattern has been recorded and two Guinier plots have been calculated.

The first conclusion of this work is as follows: the 2D SAXS patterns are completely isotropic for all samples investigated. This gives the evidence that the process of hot pressing does not influence any special, distinguished direction in the sample. The cross-sections of the scattering patterns have not demonstrated any long period effects, and this suggests that the well defined lamellae do not exist in the polymer system studied.

Because all Guinier plots calculated in this work have been very similar to each other, only three example diagrams, for samples B1, B4 and B9 are shown in *Figure 7*.

One can see from this figure that the rectilinear segment in the beginning of the Guinier curve is visible for all samples. This suggests that there are rather well defined boundaries of the crystalline regions of the polymer studied, and that these regions can be estimated by the spherical shape. It allows us to approximate the radius of gyration for the samples, which can describe the average diameter of the crystalline regions. The results of these calculations are collected in *Table 1*.

These results unequivocally show that the average diameter of the crystalline regions decreases with the time of pressing whereas the temperature of pressing has a negligible effect on this parameter. One can suggest that this effect is related to the secondary processes occurring in the already crystallized polymer. As has been shown[12], pressing of PANI samples protonated by diesters of phosphoric acid leads to the enhancement of their Young's modulus, as well as to the enhancement of their tensile strength. Both effects can be attributed to the cross-linking of the polymer. The cross-linking of the polymer with the products of the degradation of diesters, as well as with the macromolecules themselves is also well established on the basis of d.s.c. curves[12]. One can state now, that the decrease of crystalline regions diameter forced by the enhancement of the time of hot pressing is caused mainly by the process of cross-linking.

The agreement between the radii of gyration obtained here, with the average diameters of the crystalline regions estimated from the width of the diffraction peaks, should be underlined. Both methods give values in the vicinity of 100 Å.

At the end of this discussion the following effect should be underlined. As it has been mentioned in the previous section, for the samples of series B the strong impact of the pressing temperature on their diffraction patterns has been observed, whereas the time of pressing has a negligible influence on them. Quite opposite behaviour is demonstrated by the SAXS results, where the pressing time has a great impact, and the temperature of pressing is almost not important for the SAXS patterns.

CONDUCTIVITY MEASUREMENTS—RESULTS AND DISCUSSION

Conductivity measurements have been performed using the standard four-electrode method of van der Pauw[13]. The digital multimeter Hewlett-Packard 34401 has been used for voltage and current measurements. The thickness of samples were measured with accuracy at least 0.01 mm.

For all samples of the series A, B and C the conductivity in room temperature has been measured. The results are collected in *Table 1*.

The results of the conductivity measurements seem to indicate that for identical processing parameters, the samples of the C series show the highest conductivities (compare, for example, the following sets of samples: A1, B2, C1 or A3, B4 and C2). As expected, the room temperature conductivities are strongly dependent on the processing parameters, decreasing with the increase of the time and/or the temperature of hot pressing. It is highly probable that this effect is related to the dopant-assisted cross-linking induced by hot pressing (*vide supra*).

Table 1 Characteristics of DPHP protonated PANI samples investigated: radii of gyration obtained for the samples of the series B, conductivity at room temperature, parameters of fitting of the temperature dependencies of the conductivity for the selected samples, according to equation (1)

No. of sample	Radius of gyration (Å)	Conductivity (S cm^{-1})	Parameter σ_0 (S cm^{-1})	Parameter T_0 (K)
A1	—	6.9	51.6	1174
A2	—	12.5	—	—
A3	—	0.07	—	—
A4	—	0.3	—	—
A5	—	0.1	—	—
A6	—	4.5	—	—
A7	—	1.0	—	—
A8	—	1.4	32.3	2891
B1	65	15.1	38.2	1559
B2	66	4.3	—	—
B3	64	4.9	—	—
B4	63	1.5	28.9	2545
B5	60	9.5	—	—
B6	58	4.6	—	—
B7	59	1.7	—	—
B8	57	1.2	—	—
B9	45	0.2	2.2	1595
C1	—	40.6	111.5	205
C2	—	8.2	—	—
C3	—	0.2	—	—
C4	—	12.2	—	—
C5	—	4.5	—	—
C6	—	8.1	—	—
C7	—	0.5	2.1	675

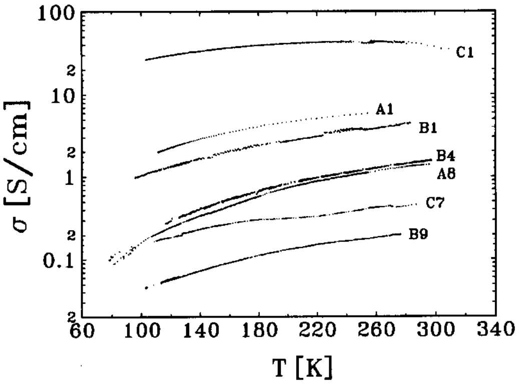

Figure 8 Temperature dependencies of the conductivity for selected samples of DPHP protonated PANI

The sample A3 whose diffractogram shows features characteristic of structural degradation, shows one order of magnitude lower room temperature conductivity than other samples.

Particularly high conductivity has been measured for the C1 sample. This effect correlates well with the high crystallinity of this sample (see *Figure 3*). In view of the discussion of the effect of chain conformation on the shape of the diffractogram it can be stated that in the case of this sample the chain is more planar than in other samples since the ratio of the intensities of (0 1 0) to (1 1 0) reflections is the highest. Evidently more planar conformation facilitates the delocalization of polarons and leads to better conductivities.

The temperature dependencies of the conductivity, measured for selected samples of the series A, B and C, are presented in Fig. 8. For all samples studied, these relations show the activation type: the conductivity increases with the temperature. Only for the sample exhibiting the highest conductivity at room temperature (C1) the change in its temperature dependence is observed above 250 K. The decrease of the conductivity with increasing temperature is typical of well-conducting systems (as metals), influenced by the enhancement of the thermal excitations concentrations (i.e. phonons), which scatter the charge carriers. In the case of quasi-one-dimensional metals, high energy phonons, which participate in scattering of electrons, can be excited only in elevated temperatures[14].

For the results presented, the best fitting has been obtained for the theoretical model assuming the tunnelling between small metallic islands[15] described by the formula:

$$\sigma = \sigma_0 \exp[-(T_0/T)^{1/2}] \qquad (1)$$

where σ_0 and T_0 are fitted constants. This formula can be considered as the interpolation between the Mott's model of variable range hopping (VRH) between localized states in low temperatures (with the exponent equal to 0.25) and the model of high temperature, activation type of conductivity with an exponent higher than 0.5. This dependence explains well the changes of conductivity in the wide temperature range. The fitting parameters: σ_0 and T_0 for all samples studied are collected in *Table 1*. The differences between the parameters σ_0 for various samples can be related to the changes of the conductivity characteristics of metallic islands, whereas the parameter T_0 describes the insulating barriers between these islands (this parameter is proportional to the height of these barriers). For all series of samples investigated, the enhancement of the temperature and the time of pressing leads to the decrease of the parameter σ_0 and to the increase of the parameter T_0. This is in good agreement with the results of the room temperature conductivity measurements: the samples with shorter times of pressing, and/or with lower temperatures of pressing exhibit higher conductivity.

By comparison of the experimental results for the series A and C (which differ in the protonation level), with the respective parameters of fitting, a very remarkable decrease of the parameter T_0 can be observed. This effect is related to the enhancement of the conductivity about one order of magnitude for the higher concentration of DPHP anions, which can be attributed to the lowering of sizes of the insulating areas between the metallic islands.

The comparison between the results obtained for the series A and B shows the higher conductivity of the insoluble fraction than the soluble one. The presence of the soluble fraction in the polymer sample leads to the decrease of its conductivity, particularly for the samples with longer times and higher temperatures of hot pressing. This decrease of conductivity can be well understood taking into account the results of the u.v.-vis.-n.i.r. measurements[16]. It has been shown there, that the existence of the free charge carriers (i.e. delocalized polarons) is mainly associated with the insoluble fraction, whereas the soluble fraction is characterized by the dominant share of the localized states of the charge carriers. This behaviour is well explained by differences between the conformations of both fractions[11]; the coil-like conformation of PANI chains is typical of the soluble fraction, whereas the insoluble fraction can be characterized by the expanded coil conformation.

To summarize, one can state that the conductivity of the samples of the DPHP protonated PANI strongly depends on the method of their processing. The high temperature and/or the long time of hot pressing leads to a strong decrease of the conductivity of the metallic-like areas in the sample, which implies the enhancement of the total resistance of the sample about two orders of magnitude. The increase in the protonation level results rather in the increase of the conducting islands dimensions than in the increase of the conductivity within these islands. As a result of the decrease of the average distances between these conducting areas, the energy of activation related to the parameter T_0 decreases. The differences between the conductivity shown by the insoluble and soluble fractions of the polymer system can be related to the differences between their conformations.

CONCLUSIONS

To summarize, we have carried out structural and electrical transport studies of thermally processed polyaniline protonated with diphenyl hydrogen phosphate. The obtained results allow for the formulation of the following conclusions:

(i) The use of lower pressing temperatures (up to 450 K) and short pressing times (2 min) leads to samples of better crystallinity and higher conductivity.

(ii) Although the diffractograms for particular samples differ, they can be characterized by the same set of a few Bragg reflections at fixed positions but showing different relative intensities. This means that all samples exhibit one crystalline structure which is strongly modified during thermal processing.

(iii) Preliminary results of computer modelling enabled us to propose the model structure of DPHP protonated polyemeraldine and explain to some extent the origin of the differences in the relative intensities of the Bragg reflections. These differences can be ascribed to the changes in the polymer chain planarity induced by hot pressing.

ACKNOWLEDGEMENTS

This work was financially supported by KBN Grant No. 3 P405 057 07. W.Ł. is very grateful to Professor H. G. Zachmann (deceased) and Dr G. von Krosigk from the University of Hamburg for making it possible to perform the investigations in HASYLAB. The fruitful discussions with Professor S. Nizioł are greatly acknowledged.

REFERENCES

1. Yen, K. Y., Miller, G. G. and Elsenbaumer, R. L., *J.C.S. Chem. Commun.*, 1986, 1346.
2. Cao, Y., Smith, P. and Heeger, A. J., *Synth. Met.*, 1992, **48**, 91.
3. Proń, A., Laska, J., Österholm, J.-E. and Smith, P., *Polymer*, 1993, **34**, 4235.
4. Laska, J., Proń, A. and Lefrant, S., *J. Polym. Sci.: Part A: Polym. Chem.*, 1995, **33**, 1437.
5. Laska, J., Proń, A., Zagórska, M., Łapkowski, S. and Lefrant, S., *Synth. Met.*, 1995, **69**, 113.
6. Laska, J., Girault, R., Quillard, S., Louarn, G., Proń, A. and Lefrant, S., *Synth. Met.*, 1995, **75**, 69.
7. Cao, Y., Andreatta, A., Heeger, A. J. and Smith, P., *Polymer*, 1989, **30**, 2305.
8. Hasik, M., Proń, A., Raynor, J. B. and Łużny, W., *New J. Chem.*, 1995, **19**, 1155.
9. Łużny, W. and Hasik, M., *Solid State Commun.*, 1996, **99**, 685.
10. Pouget, J. P., Jozefowicz, M., Epstein, A. J., Tang, X. and MacDiarmid, A. G., *Macromolecules*, 1991, **24**, 779.
11. Xia, Y., Wiesinger, J. M., MacDiarmid, A. G. and Epstein, A. J., *Chem. Mater.*, 1995, **7**, 443.
12. Laska, J., Ph.D. thesis, Warsaw Technical University, 1994 (in Polish).
13. van der Pauw, L. J., *Philips Res. Reports*, 1958, **13**, 1.
14. Kivelson, S. and Heeger, A. J., *Synth. Met.*, 1990, **22**, 371.
15. Sheng, P. and Klafter, J., *Phys. Rev. B*, 1983, **27**, 2583.
16. Proń, A., Łużny, W. and Laska, J., *Synth. Met.*, 1996, **80**, 191.