ELSEVIER

Room temperature magnetic order in an organic magnet derived from polyaniline

Naveed A. Zaidi[a,*], S.R. Giblin[b], I. Terry[b], A.P. Monkman[a]

[a]Organic Electroactive Materials Research Group, Department of Physics, University of Durham, Rochester Building, South Road, Durham DH1 3LE, UK
[b]Department of Physics, University of Durham, South Road, Durham DH1 3LE, UK

Abstract

We report on the synthesis and characterisation of a new type of polymer, PANiCNQ produced from polyaniline (PANi) and an acceptor molecule, tetracyanoquinodimethane (TCNQ). PANiCNQ combines a fully conjugated nitrogen containing backbone with molecular charge transfer side groups and this combination gives rise to a stable polymer with a high density of localised spins which are expected to give rise to coupling. Magnetic measurements suggest that the polymer is ferri- or ferro-magnetic with a Curie temperature of over 350 K, and a maximum saturation magnetization of $0.1 \, JT^{-1} \, kg^{-1}$. Magnetic force microscopy images support this picture of room temperature magnetic order by providing evidence for domain wall formation and motion. The magnetic measurements reveal that the magnetically ordered state develops with time, taking several months to reach completion; X-ray diffraction data demonstrate that there is a concomitant evolution of the polymer chains from an amorphous state to a partially ordered form. Estimates of spin density from integrated electron spin resonance lines are larger than values obtained from the saturation magnetisation by a factor of 7 which leads us to tentatively conclude that PANiCNQ exhibits ferrimagnetic order.
© 2004 Elsevier Ltd. All rights reserved.

Keywords: Plastic magnet; Magnetic polyaniline; TCNQ

1. Introduction

For many years chemists and physicists have striven to synthesize ever more intricate molecules which would support higher and higher densities of radical, spin bearing states. The molecules being so designed that the interactions between each spin gave rise to ferromagnetic ordering. In almost all cases, this interaction has proved to be weak so that the ferromagnetic phase was only observed at very low temperatures [1–4], also as the radicals had to be generated by oxidation, great difficulties arose when trying to maintain a high packing density and degree of order, whilst permitting access of the oxidising agents into the structure to form the radicals [5]. Thus, the magnetic order measured in all these systems is very small and only observed at very low temperatures. Two recent reports have given encouragement though: a weakly ferromagnetic phase, at room temperature, of carbon was reported by Makarova et al. in

C_{60} [6], and Rajca et al. reported a ferromagnetic phase below 10 K in a polymeric form of a high spin state aromatic molecule [7]. Earlier, Torrance et al. synthesised poly(1,3,5-triaminobenzene) which when oxidised with iodine was reported to show a ferromagnetic phase up to 400 °C [8]. Unfortunately, this latter work has been difficult to reproduce. Crayston et al. [9] have recently reviewed other developments in the field of organic magnets.

To overcome many of the problems associated with the generation of spins via oxidation in the molecule of interest, and to produce a high spin-bearing polymer that is stable in air, our magnetic polymer has been designed with emeraldine base polyaniline (PANi) as the starting material. PANi has already attracted interest as an organic magnet because of the potentially strong exchange interactions occurring through the π-conjugated back-bone. Ito et al. [10] have already shown that there is evidence for a weak ferromagnetic exchange interaction between the spins of oxidised *meta*-polyaniline at low temperatures. Moreover, Wienk et al. [11] have specifically identified PANi with its *meta* and *para*-aniline oligomers as building blocks for

* Corresponding author. Tel.: +44-191-334-3558; fax: +44-191-334-3585.
E-mail address: n.a.zaidi@durham.ac.uk (N.A. Zaidi).

ferromagnetic exchange. Our polyaniline has been well characterized [12] and has been shown to form an air-stable electrical conductor with metallic properties, that is also highly processible [13]. We chose to form localised spin states which interact with this conjugated polymer by reacting it with a well known stable radical forming molecule, tetracyanoquinodimethane (TCNQ) [14], see Fig. 1, which readily produces charge transfer (CT) complexes with electron donors. TCNQ also tends to form stacked ordered structures [15] when in CT complexes and we believe this is an important property in the drive for an inter-polymer chain exchange interaction. The resulting polymer, which we denote as PANiCNQ shown in Fig. 1, is expected to have six interacting spins giving rise to a net spin of $S = 1$ per repeat unit. In the following report we describe the synthesis of PANiCNQ along with its characterization, and demonstrate that this organic magnet exhibits spontaneous magnetic order at room temperature.

2. Experimental

We synthesized PANiCNQ by taking the emeraldine base form of polyaniline (see Fig. 1), which is soluble in *N*-methly-2-pyrrolidinone (NMP), and adding TCNQ (2 equivalent). Upon heating at 150 °C over night, the formerly blue solution turns dark red/black. The solution was filtered and NMP was removed in vacuo. Both filtrate and the solid showed a strong absorption band at $\lambda_{max} = 492$ nm, see Fig. 2.

3. Results and discussion

Bespalov and co-workers observed a similar change in absorption when TCNQ was reacted with aniline type molecules in solution [16]. Dimitriev et al. [17] have also studied mixture of PANi, C_{15}TCNQ and dodecylbenzene-sulphonic acid in DMF, and also report the formation of a peak at 490 nm, among other peaks. After drying at a moderate temperature (40 °C) the polymer is still readily soluble in NMP and also in many other common solvents including acetone, behaviour very different from the parent polyaniline base used. Drying at 180 °C in a vacuum oven for two days yields a black solid that, on dissolving, gives intense blue/green solutions, an indication we initially took to imply that the polyaniline had become conductive. However, the optical absorption spectrum of this blue/green solution is not typical of protonated polyaniline, and it demonstrates that an intramolecular charge transfer has occurred between the TCNQ and the polyaniline, forming stable zwitterions along the chain, which we believe to be an intermediate state in the reaction. In fact, the solubility of PANiCNQ is very different to PANi which also demonstrates that TCNQ is covalently bonded to the polyaniline.

UV absorption spectra now show new absorption maxima at 625 and 661 nm with a weaker band at 492 nm (see Fig. 2).

Fast Fourier transform infrared spectroscopy was carried out on the polymer and follows our published work [18], most importantly there are new cyanides stretches at 2185 cm^{-1}. We ascribe the absorption at 2185 cm^{-1} to TCNQ having covalently bonded to the PANi at the phenyl sites, along the polyaniline backbone. A strong, broad absorption between 2600 and 3300 cm^{-1}, indicative of NH stretches, is observed and this protonation could occur during synthesis, as hydrogen cyanide is produced during the reaction and could readily protonate imine sites with CN^{-} counter ions. The gas permeation chromatography and the elemental analysis indicate that the polymer has reduced in molecular weight and CHN content compared to PANi. From the IR data and previous known reactions of TCNQ a tentative structure for PANiCNQ is given in Fig. 1. One important observation is that the addition of the TCNQ will not affect the quinoid ring as it is electron deficient. Simple calculations of the lowest energy state associated with the bonding of the TCNQ groups onto the backbone of PANi have shown that this repeat unit is more stable than those with other possible arrangements of the side chains. However, it is possible for the reaction not to have gone to completion and that there may be less than two TCNQ side groups per (four phenyl ring) repeat unit.

Magnetization measurements of the polymer were made with a vibrating sample magnetometer (VSM) at temperatures from 77 K to room temperature, and with a commercial Quantum Design dc SQUID magnetometer at temperatures down to 4 K. Initially, all materials were found to be diamagnetic as shown in the inset of Fig. 3 (curve a), with a magnetic susceptibility that was independent of temperature. The measured values of the magnetic susceptibility showed a great deal of variability from different samples prepared, with values varying from -4 to -8×10^{-9} m^3 kg^{-1}. Inductively coupled plasma mass spectroscopy (ICPMS) were performed by dissolving the samples completely in nitric acid and then the analysis were carried out, indicating metal impurities of 7 ppm of Ni and trace of Fe are present. Assuming this impurity content is homogeneous throughout the sample, we expect the transition metal ions to give a paramagnetic contribution to the magnetic properties of the samples, and, given Ni contamination of 10 ppm, we estimate a mass susceptibility at room temperature to be in the range 10^{-10} to 10^{-11} m^3 kg^{-1}. This figure is much smaller than the diamagnetic value obtained from the data shown in the inset of Fig. 3 (curve a), where we calculate a mass susceptibility of -5×10^{-9} m^3 kg^{-1}. In the extremely unlikely event that the trace impurity elements are present in bulk form we would expect the magnetic data to show evidence of saturation magnetisation. However, such features are not observed in Fig. 3 (curve a) clearly demonstrating that the contamination plays no role in the magnetic properties we observe in PANiCNQ. In
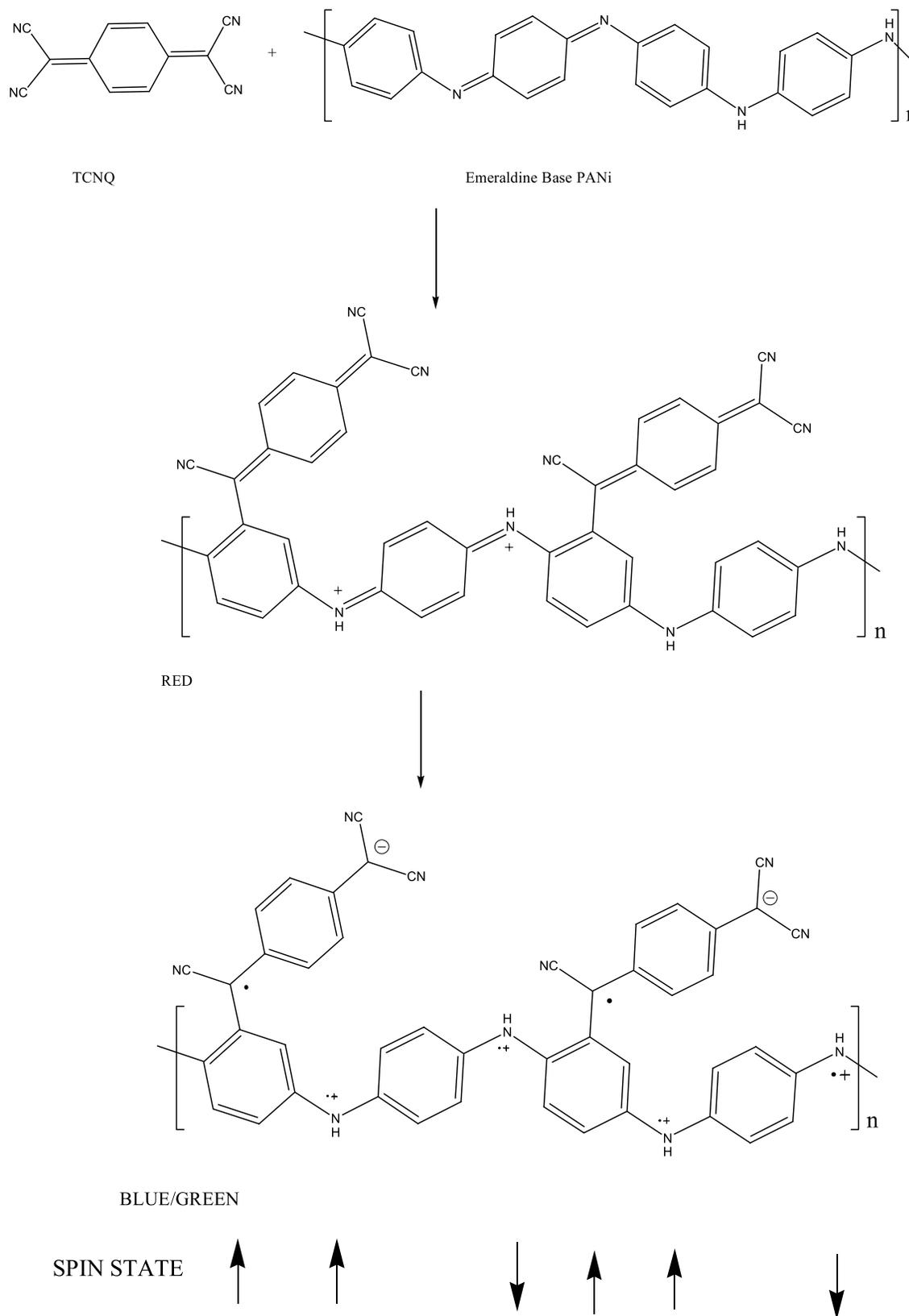
Fig. 1. Chemical structure of PANi and TCNQ along with the most plausible form for the magnetically ordered polymer PANiCNQ.
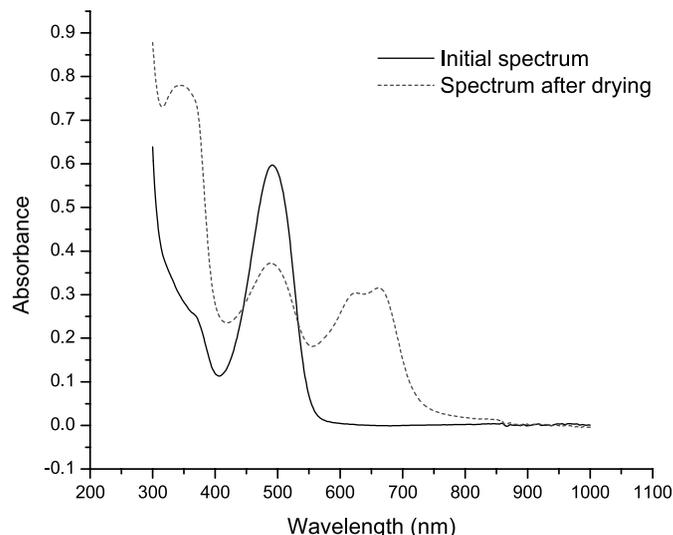
Fig. 2. Optical absorption spectrum of as-synthesised PANiCNQ showing the strong absorption maximum at 492 nm, and the spectrum of the material after the intramolecular charge transfer has occurred in solid state across the aromatic rings. Both spectra were measured with the polymer dissolved in NMP.

subsequent batches the contamination level was reduced consistently to lower values. The initial diamagnetic signal enabled a control experiment to be performed on each batch immediately after fabrication before the time induced phase transition.

The diamagnetic samples were left for three months in individually sealed containers. These samples were then measured again with the VSM and it was found that the magnetisation now displayed a saturating component superimposed upon a diamagnetic background, see Fig. 3 inset (curve b). The saturating component of the mass magnetisation was found to be $0.006 \, \mathrm{J \, T^{-1} \, kg^{-1}}$ and, although small, it indicated a significant change in the magnetic properties of the material with time. Such a time

dependence may be related to the synthesis of PANiCNQ being a kinetic reaction as is known to occur in many organic systems [19]. However, it was clear that the reaction was not 100% efficient as different parts of the same batch showed somewhat different mass magnetisations. We magnetically separated a sample from a batch with a 200 mT permanent magnet and the mass magnetisation subsequently increased by two orders of magnitude to $0.1 \, \mathrm{J \, T^{-1} \, kg^{-1}}$. ICPMS revealed that this magnetically separated sample had the same Ni concentration level as the non-separated specimens (demonstrating the homogeneous distribution of the metal impurities). The mass magnetisation increases by two orders of magnitude and the mass of the sample also decreased by two orders of magnitude, again
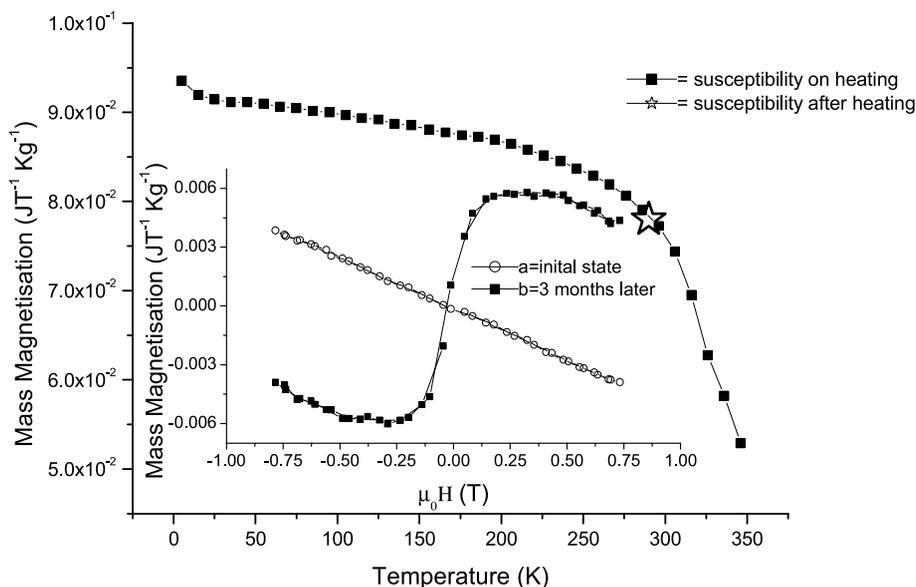

Fig. 3. The temperature dependence of the mass magnetisation of the magnetically separated sample with a T_C of approximately 360 K. The inset shows a non-magnetically separated sample before and after the phase transition.

emphasising that contaminants play no part in the magnetic behaviour. The temperature dependence of the magnetisation of the magnetically separated sample was measured with a dc SQUID magnetometer at an applied field of 750 mT, and is shown in Fig. 3. Clearly, the Curie temperature, T_c, is above 350 K, the highest temperature achievable in our experiment. Importantly, the T_c of PANiCNQ is hundreds of Kelvin below those of the ferromagnetic transition metals found to be contaminating the material. The mass magnetisation at 750 mT is also shown after cooling the sample to room temperature and it is clear that heating the material has no effect upon the magnetic properties. This observation is supported by thermogravimetric analysis of a sample which demonstrated stability of the polymer up to 800 K.

The electron spin resonance (ESR) spectrum of a sample which showed ferromagnetic behaviour gave a line at $g = 2.0045$ and a peak-to-peak width of 0.54 mT. Such a line is characteristic of the presence of free radicals, and demonstrates that ferromagnetic or ferrimagnetic impurities are not the cause of the saturating magnetisation in our samples. By integrating the area under the ESR line we estimate that there are about 10^{21} spins kg^{-1}. Such a number is about a factor of 7 greater than that determined from the saturation value of the magnetisation data, and we tentatively conclude that the sample is ferrimagnetic. However, the TCNQ attachment to another site on the phenyl ring could lead to an antiferromagnetic coupling where $S = 0$ in a repeat unit. This conclusion supports the proposed spin structure shown in Fig. 1, where the intra-chain exchange is a combination of antiferromagnetic and ferromagnetic interactions, along the backbone of the polymer structure. We note, however, that the inhomogeneous nature of the doping, may also lead to paramagnetic and, perhaps, ferromagnetic areas within the material contributing to the magnetic properties of PANiCNQ.

The magnetic nature of PANiCNQ is dramatically demonstrated by Magnetic Force Microscopy (MFM) images obtained from a representative sample. Fig. 4(b), (d) and (f) show a sequence of phase contrast MFM images taken in succession while Fig. 4(a), (c) and (e) demonstrate atomic force microscopy (AFM) obtained in the same sequence (measured in tapping mode). We interpret these images as evidence for a domain wall in the material (dark/light striations in Fig. 4(b), (d) and (f)), which appears to be driven across the material with time. It is likely that domain wall moves in response to the driving force of the MFM tip used to image the sample, as has been observed in, for example, thin Permalloy films [20].

The time dependent change in the magnetism is accompanied by a change in the structure of PANiCNQ as shown in the X-ray diffraction data of Fig. 5. We initially observe a broad peak in the data with a maximum around 19° which is characteristic of amorphous emeraldine base form of PANi [21]. However, diffraction data obtained from the same sample three months later demonstrates that the

broad peak has moved by 5.6°, and there is also a sharp peak that appears at a d-spacing of 1.22 nm. We interpret these changes as an indication that the polymer chains become more aligned, and that the material is becoming more structurally ordered with time. It is noted that polyaniline is known to become partially crystalline when doped, with a correlation existing between the protonation of the –N= in the emeraldine base and the crystalline form [21]. With PANiCNQ, we believe that the structural transformation is assisted by the presence of residual NMP in the solid phase which is known to act as a plasticizer in films of PANi [22]. However, the changes we observe cannot be attributed to PANi plasticized by NMP alone [22], or indeed to protonated PANi (emeraldine salt) [21]. It is known that TCNQ acceptor molecules preferentially stack in charge transfer salts and we believe that such a preference may be the driving mechanism for the structural ordering of PANiCNQ with time.

The magnetic behaviour we observe with PANiCNQ may be understood by considering earlier investigations on conjugated systems. The initial work carried out by Longuet–Higgins [23] predicted a triplet ground state in trimethylenemethane and this was later proved by experiment [24]. This topological model relies upon connectivity in the structure to determine the nature of spin coupling in aromatic molecules, with the *ortho-* and *para-*states forming an antiferromagnetic coupling unit and only those with a *meta-*orientation forming a ferromagnetic coupling unit, with a triplet ground state formed. This idea has been adapted by many to investigate fully conjugated π systems as reviewed by Docherty [25] and Crayston [9]. Applying the theory to PANiCNQ, we see that each repeat unit has a net spin of 1. Every time a repeat unit is added to the polymer chain the net spin will increase. The molecule has a natural pathway for connectivity along the conjugated backbone of the system and we have utilised this property in the design of the molecule giving rise to the ferrimagnetic behaviour seen in all three batches that we have synthesized to date. As well as the intra-chain exchange interaction we believe that there may be an inter-chain exchange mechanism. For example, the structural ordering seen in PANiCNQ may meet the requirements for inter-chain interactions, as proposed by McConnell [26] where a staggered π stacking fulfils the criteria for positive and negative spin densities to ensure a ferromagnetic exchange interaction between the chains. Thus, the growth of the magnetisation is likely to be concomitant with the increased structural ordering in PANiCNQ.

4. Conclusion

In conclusion, we have demonstrated that the new organic polymer PANiCNQ exhibits magnetic order at room temperature. Radical formation is by an intrinsic charge transfer mechanism. Magnetisation data and the
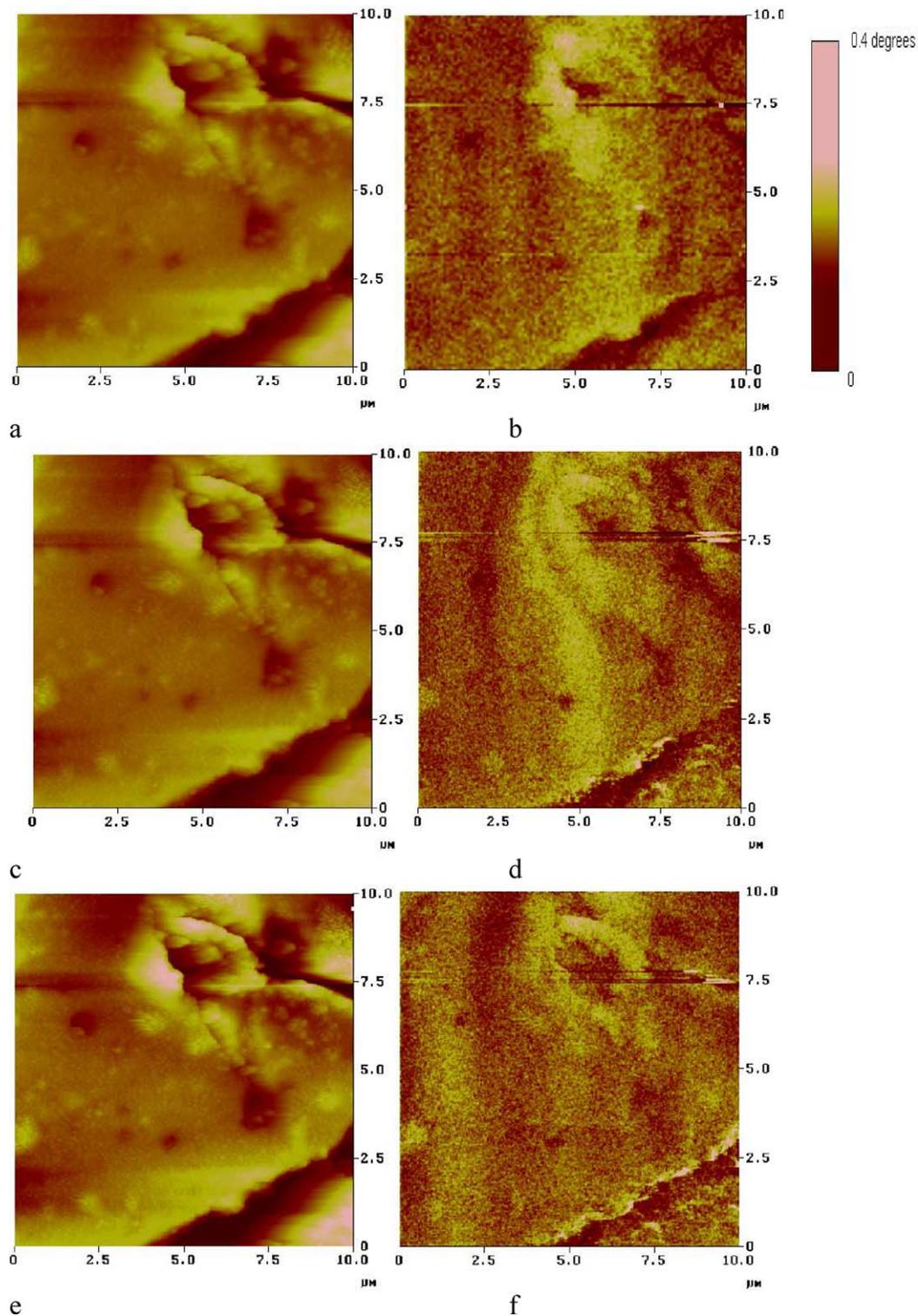
Fig. 4. AFM images (a, c, e) and MFM images (b, d, f) of sample of PANiCNQ taken after the magnetic transition. The AFM images were taken in tapping mode and MFM images were recorded in phase mode with a VEECO MESP tip scanning from left to right. A magnetic domain wall can be seen being driven through the material.

results of ESR suggest the polymer is ferrimagnetic with a Curie temperature above 350 K. This magnetically ordered state develops with time and is accompanied by a structural ordering of the polymer. Whilst the majority of samples we have synthesized show no evidence of magnetic hysterisis, we have recently discovered a method of producing PANiCNQ with coercive fields of up to 25 mT, and we will report on this work in a subsequent paper. We believe
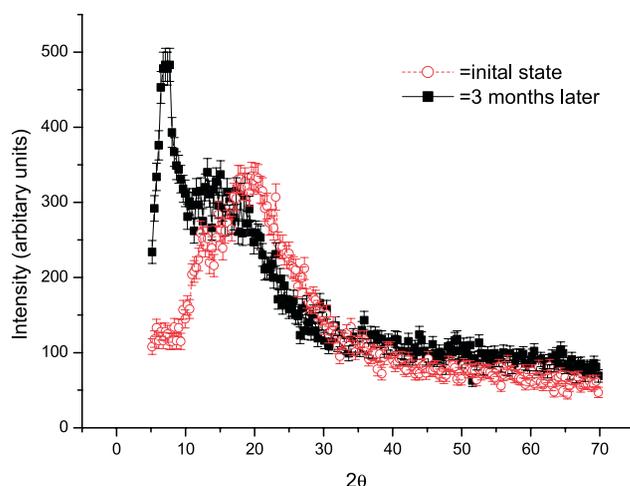
Fig. 5. X-ray powder diffraction before and after the phase transition.

PANiCNQ represents a new way to generate organic magnets; circumventing many of the previous problems encountered, and from this initial polymer much better systems can be synthesised in the future.

Acknowledgements

References

[1] Miller JS, et al. Ferromagnetic behavior of [FE(C5ME5)2]$^+$[TCNE]$^-$ structural and magnetic characterization of decamethylferrocenium tetracyanoethenide, [FE(C5ME5)2]$^+$[TCNE]$^-$MeCN, and deca-methylferrocenium pentacyanopropenide, [FE(C5ME5)2]$^+$ [C3(CN)5]$^-$. J Am Chem Soc 1987;109:769–81.

[2] Wudl F, Thompson JD. Buckminsterfullerene C-60 and organic ferromagnetism. J Phys Chem Solids 1992;53:1449–55.

[3] Yoshizawa K, Tanaka K, Yamabe T, Yamauchi J. Ferromagnetic interaction in poly(*meta*-aniline)-electron-spin-resonance and mag-netic-susceptibility. J Chem Phys 1992;96:5516–22.

[4] Rajca A, Wongsriratanakul J, Rajca S, Cerny R. A dendritic macrocyclic organic polyradical with a very high spin of $S = 10$. Angew Chem, Int Ed 1998;37:1229–32.

[5] Bushby RJ, Gooding D, Vale ME. High-spin polymeric arylamines. Philos Trans R Soc A 1999;357:2939–57.

[6] Makarova TL, et al. Magnetic carbon. Nature 2001;413:716–8.

[7] Rajca A, Wongsriratanakul J, Rajca S. Magnetic ordering in an organic polymer. Science 2001;1503–6.

[8] Torrance JB, et al. Ferromagnetic interactions in organic-solids—an overview of theory and experiment. J Appl Phys 1988;63:2962–5.

[9] Crayston JA, et al. Conceptual and synthetic strategies for the preparation of organic magnets. Tetrahedron 2000;56:7829–57.

[10] Ito A, et al. *N*-Alkyl group-substituted poly(*m*-aniline)S—syntheses and magnetic-properties. Macromolecules 1995;28:5618–25.

[11] Wienk MM, Jansen RAJ. High-spin cation radicals of *meta–para* aniline oligomers. J Chem Phys 1997;119:4492–501.

[12] Adams PN, Laughlin PJ, Monkman AP, Kenwright AM. Low temperature synthesis of high molecular weight polyaniline of enhanced conductivity. Polymer 1996;37:3411–7.

[13] Pomfret SJ, Adams PN, Comfort NP, Monkman AP. Inherently electrically conductive fibres wet spun from sulphonic acid doped polyaniline solution. Adv Mat 1998;10:1351.

[14] Melby LR, et al. Substituted quinidomethans II. Anion radical derivatives and complexes of 7,7,8,8, tetracyanoquinodimethane. J Am Chem Soc 1962;84:3374–87.

[15] Becker JY, Bernstein J, Bittner S, Levi N, Shaik SS. Stategic design of organic conductors. Structure of a prototypical molecule. J Am Chem Soc 1983;105:4468–9.

[16] Bespalov BP, et al. Photochemical reaction of TCNQ with aromatic rings. Zhurnal Org Khimii 1972;8:1662.

[17] Dimitriev OP, Lavrik NV. Protonation and charge transfer in poly-aniline: an optical absorption study of the mixed solutions. Synth Met 1997;90:1–4.

[18] Zaidi NA, Bryce MR, Cross GH. Synthesis and optical properties of new tricyano-*p*-quinodimethane dyes: molecular and polymeric systems. Tetrahedron Lett 2000;41:4645–9.

[19] March J. Advanced organic chemistry, 3rd ed. New York: Wiley; 1985. p. 183–194.

[20] Mamin HJ, Ruger D, Stern JE, Fontana RR, Kasiraj P. Magnetic force microscopy of thin permalloy films. Appl Phys Lett 1989;55:318–20.

[21] Pouget JP, et al. X-ray structure of polyaniline. Macromolecules 1991; 24:779–89.

[22] Chen C, Lee H. Polyaniline plasticised with 1-methyl-2-pyrrolidone: structure and doping behaviour. Macromolecules 1993;26:3254–61.

[23] Longuet-Higgins HC. Some studies in molecular orbital theory I. Resonance structures and molecular orbitals in unsaturated hydrocarbons. J Chem Phys 1950;18(3):265–74.

[24] Dowd PA. J Chem Phys 1966;88:2587.

[25] Docherty DA. Spin control in organic molecules. Acc Chem Res 1991;24:88–94.

[26] McConnell HM. Ferromagnetism in solid free radicals. J Chem Phys 1963;39:1910.