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Solid State Ionics 145 (2001) 451–457

SOLID STATE IONICS

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Inelastic neutron scattering studies of polypyrroles and partially deuterated analogues

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Received 25 September 2000; received in revised form 30 November 2000; accepted 22 December 2000

Abstract

The inelastic neutron scattering (INS) spectra from 20 to 4000 cm^{-1} of various polypyrroles and their ring-deuterated analogues at 30 K shed light on the proton dynamics in these materials. The doped samples obtained by mild oxidation in the presence of $FeCl_3$ in acidic solution were either dedoped in alkaline solution or reduced with $TiCl_3$. The spectra give a continuum with constant intensity due to the recoil of free protons. Virtually all protons are free in the dedoped polymer. Additional protons in the doped and reduced polymers are bound. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Inelastic neutron scattering; Polypyrroles; Analogues

1. Introduction

Polypyrroles can be obtained by mild oxidation of pyrrole with various reagents (peroxides, chlorates, transition metals, halogens, etc.) [1,2]. These polymers and related compounds resulting from N-substitution or functionalisation or electrochemical oxidation in various solvents have been thoroughly investigated from both experimental [3–20] and theoretical viewpoints [21,22]. The various oxidation and protonated states are schematically illustrated through a ladder-like reaction scheme (Scheme 1). The neutral polymer **I** possesses a nondegenerate electronic ground state and the electronic band structure has a large gap of ~4 eV [21,23]. The neutral form can be protonated in acidic media and this chemical reaction is reversible. **II** (Scheme 1) corresponds to a protonation degree $p = 1/3$ (1/3 of the N-atom is protonated, see Section 2). The protonated form can be then oxidised into **III** or **IV** by removing electrons and protons in acidic media, and further deprotonation in alkaline media gives the neutral **V**. The reduction in alkaline media is irreversible and gives **VI**.

Because of the complex chemical reaction scheme, real samples are mixtures of various redox and ionic states and the electrical conductivity depends dramatically on the particular experimental conditions for sample preparation. For example, the conductivity can be as large as $\sim 10^{2}$ S cm^{-1} for a sample protonated at pH = 0 or as small as $\sim 10^{-10}$ S cm^{-1} after deprotonation by 1 M NaOH solution. The conductivity of the sample protonated at pH = 0 can be reduced by three orders of magnitude by

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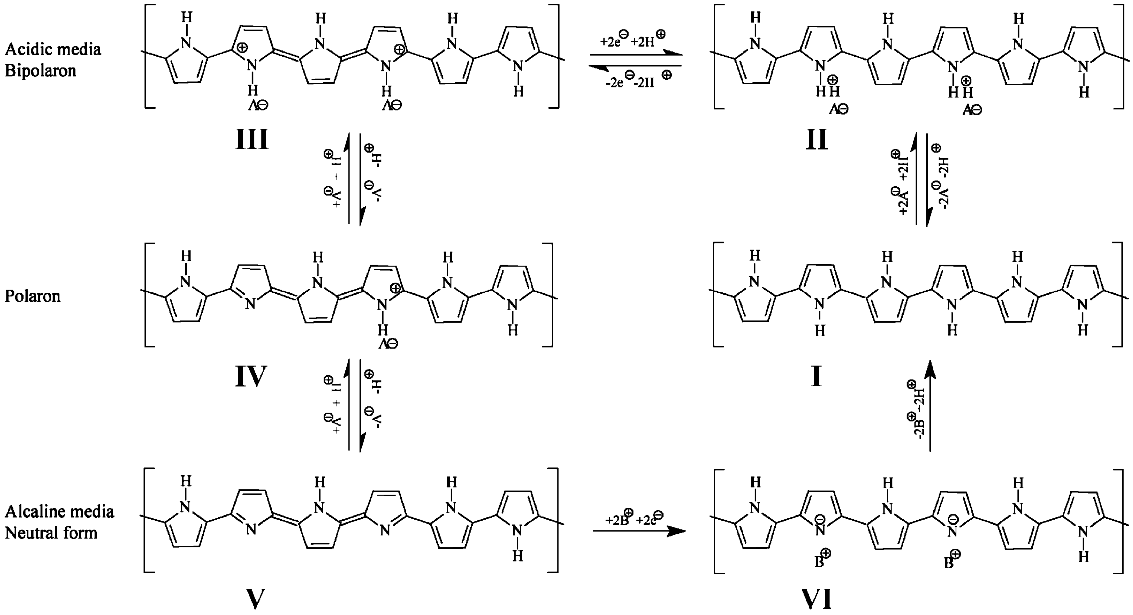
PII: S0167-2738(01)00943-2



Scheme 1.

electrochemical reduction at the potential ~ 0 V/NHE [24]. The main practical interest of these polymers stems from the excellent long-term stability of their conductive states and from the possibility of tailoring properties by synthesis [25–30].

Different approaches have been proposed to account for the electric conductivity of the doped polymers. Many of the properties that characterise heavily p-doped polypyrroles similar to **III** suggest that the electronic structure is that of a metal and the conductivity is determined by a disorder-induced metal-to-insulator (M–I) transition [19]. Structural defects like 2,4-linkages, hydrogen saturation, oxygen incorporation and disorder during the doping process limit the extended conjugation of the polymers. The rather low conductivity at room temperature (in the range from 10^{-10} to 10^{-11} S cm^{-1}) of polypyrroles prepared with acids or peroxides is attributed to the high degree of saturation of the pyrrole units caused by defects [31]. X-ray diffraction patterns of powdered polypyrroles produced through chemical oxidation reveal extremely disordered structures [32]. In order to avoid the disorder-induced M–I transition, ferric salts are commonly used as reagents for the synthesis of polypyrroles with high conductivity up to ~ 10^2 S cm^{-1} and great stability [33].

Alternatively, within the quantum chemistry framework, calculations performed on ‘quaterpyrrole’, a model chain containing four pyrrole rings [21,23], reveal that taking an electron out of the doped chain leads to the formation of a polaron such as in **IV**. The associated structural defect extends itself over a few rings and the binding energy is ~ 0.1 eV. When a second electron is taken out of the chain, the two unbound polarons spontaneously merge into a bipolaron (**III**) with a binding energy of ~ 0.7 eV. For higher degrees of oxidation, the overlap between the bipolaron states gives two rather wide (~ 0.4 eV) bipolaron bands in the gap. Polarons and bipolarons are supposed to be mobile charge carriers contributing to the electronic conductivity.

Polypyrroles have also enhanced ionic conductivity associated with the electronic conductivity [34] but this has been much less studied.

Though the key role of protonation in conducting properties of polypyrroles has been largely emphasised, the proton dynamics are rather poorly known. The infrared spectra of various doped polypyrroles are very similar and largely independent of the doping agent [17,35]. Bands due to the cyclic entities are observed between 1600 and 400 cm^{-1}. They are superimposed on a very broad plasma band and strong interaction with this continuum is likely to complicate the interpretation of the spectra [36].

Inelastic neutron scattering (INS) spectroscopy is the only technique that may provide clear information on the proton dynamics in polypyrroles. Because the scattering cross-section of hydrogen atoms (~ 81.7 b) is much greater than that for C (~ 5.6 b) and N (~ 11.5 b) atoms, the spectra are dominated by signals due to proton motions, and totally free of side effects encountered with optical techniques (namely, reflection or resonance). Interaction between neutrons and electrons is negligible. The proton selectivity can be further exploited because the deuterium atom has a much smaller cross-section (~ 7.6 b) than the proton. Specific deuteration of the rings provides a detailed view of the dynamics of protons involved in the conduction mechanisms. Therefore, INS is anticipated to give simple spectra that can be analysed with confidence.

Previous INS work on polyanilines and ring-deuterated analogues [37] has revealed that most protons normally supposed to be bound to the N-atoms, behave as a gas of free particles in both emeraldine bases and salts. A new electronic band-scheme was proposed to account for the interplay of electronic and protonic conduction.

Because polypyrroles and polyanilines are quite similar, we have undertaken INS studies of polypyrroles and ring-deuterated analogues with various protonation and oxidation degrees.

2. Experimental

The fully deuterated pyrrole was obtained by exchanging the fully hydrogenated molecule in a heavy water solution of DCl at pH 1 [38]. The doped polymers were obtained with $FeCl_3$ in H_2O (or D_2O) solutions carefully degassed under controlled Ar atmosphere [39,40]. The elemental analysis is compatible with the chemical formula $C_4NCl_{1/3}$, corresponding to **III**. The amount of Fe is negligible (~ 0.5 wt.%). The polymers were dedoped under an N_2 atmosphere in carefully degassed NaOH 1 M. The products were washed under controlled atmosphere, then dried under vacuum and kept in sealed glass tubes. The doped polymers were reduced with $TiCl_3$ 1.9 M in chlorhydric acid 2 M. Three grams of polymer and 50 cc of the solution were stirred during 24 h under an Ar atmosphere and then filtered. The polymer was washed with HCl 1 M and then methanol. The samples were dried under vacuum and were kept in sealed tubes.

INS spectra were obtained with the TFXA-spectrometer at the ISIS pulsed neutron-source (Rutherford Appleton Laboratory, Chilton, UK). The resolution was $\Delta\omega/\omega \sim 2\%$. About 5 g of sample was wrapped in aluminium foils and then loaded in a closed-cycle refrigerator at ~ 30 K. Spectra were converted from time-of-flight to energy-transfer according to standard procedures. Intensities were renormalised according to the amount of sample in the beam.

3. INS spectra and proton dynamics

The INS spectrum of the fully hydrogenated dedoped polypyrrole **V** is presented in Fig. 1A. Band frequencies and tentative assignments are gathered in Table 1. Rather sharp bands are observed on the top of a continuum of intensity extending over the whole spectral range. The intense bands at 790, 880, 1050 cm^{-1} are the CH bending modes. The CH stretching modes are between 3100 and 3300 cm^{-1}. The weaker bands at 565, 635, 695 and 1255 cm^{-1} correspond to

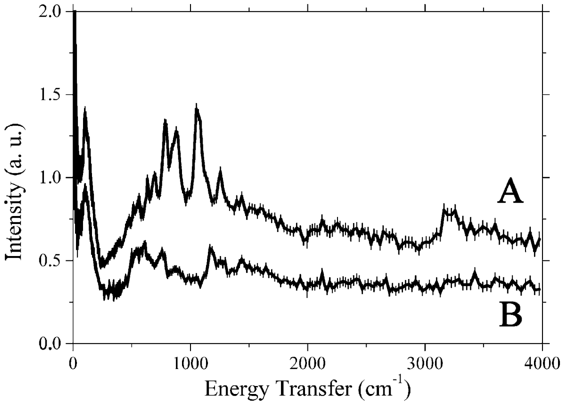


Fig. 1. INS spectra of dedoped neutral polypyrroles at 30 K (**V** in Scheme 1). A: totally hydrogenated, B: ring-deuterated.

Table 1
Band frequencies (cm^{-1}) and tentative assignments for the fully hydrogenated and ring-deuterated polypyrroles at 30 K: neutral (PPNh$_2$) and (PPNd$_2$), doped (PPDh$_2$) and (PPDd$_2$), and protonated (PPHh$_2$)

PPNh$_2$	PPNd$_2$	PPDh$_2$	PPDd$_2$	PPHh$_2$	Assignments
100 s	100 s	110 s	100 m	100 vs	lattice
390 vw	–	–	280 w	–	chain + ring
470 vw	–	–	435 w	–	chain + ring
515 vw	530 m	–	–	–	chain + ring
565 w	–	570 vw	–	545 vw	chain + ring
635 m	–	625 w	–	625 w	chain + ring
695 m	–	695 m	–	685 m	chain + ring
–	605 m	–	570 m	–	γ CD
–	760 m	–	770 m	–	δ CD + γ NH
790 s	–	790 s	–	790 s	γ CH
880 s	–	895 s	–	880 s	γ CH
1050 s	–	1085 s	–	1050 s	δ CH
–	1165 m	–	1200 vw	–	chain + ring
1255 m	–	–	–	1240 m	chain + ring
–	1275 w	1275 w	–	–	chain + ring
		1375 w	–	1395 m	chain + ring
1430 vw	1440 vw	1415 w	1415 m	–	chain + ring
		1460 m	1480 m	1460 m	chain + ring δ NH
–	–	3130 m	–	3130 m	ν CH
3210 m	–	3225 m	–		ν CH

s: strong; m: medium; w: weak; v: very.

ring and chain vibrations slightly coupled with the proton modes. These bands disappear upon ring-deuteration while the intensity of the continuum is divided by a factor of ~2 (Fig. 1B). The remaining weak bands for the deuterated sample are due to ring modes centred at ~600 cm^{-1} and CD bending modes at ~605 and 760 cm^{-1}. The weak bands centred at 1165 and 1440 cm^{-1} are too weak to be the bending modes of the protons bound to N-atoms in **V**. The total intensity of these bands is much less than 25% of that of the CH bending modes estimated from spectrum A. Frequencies and intensities are more consistent with stretching modes of the rings and chains anticipated in this frequency range. The rather intense infrared bands reported in the same frequency range [17] provide further support to this assignment. Therefore, we conclude that most of the protons in the ring-deuterated dedoped polymer are not bound to N atoms. They are free to recoil and with the TFXA spectrometer, the continuum with constant intensity is the signature for free particles with mass 1 amu [41]. There is no evidence for any intensity cut-off at low frequency and so the protons are totally free. The binding energy is less than ~20 cm^{-1} and negligible at room temperature. The decrease of the continuum intensity upon deuteration of the bound protons is in accordance with the theory [37]. Finally, the band at ~100 cm^{-1} is virtually unaffected by deuteration. The apparent decrease of intensity at maximum upon ring-deuteration is largely due to the change of intensity of the underlying

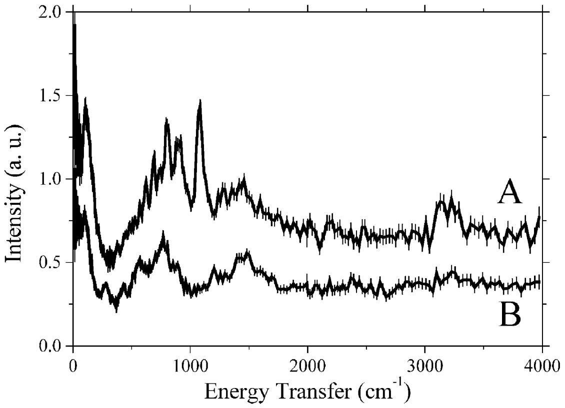


Fig. 2. INS spectra of doped polypyrroles at 30 K (**III** in Scheme 1). A: totally hydrogenated, B: ring-deuterated.

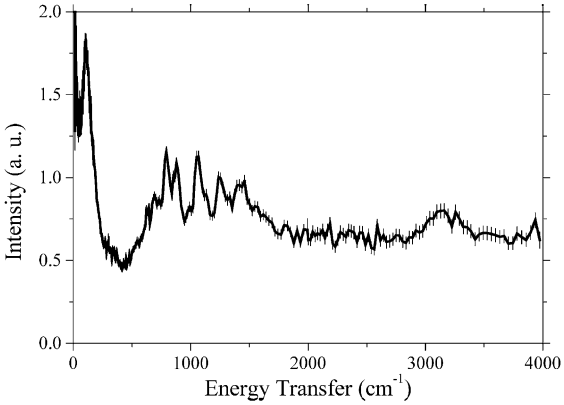


Fig. 3. INS spectrum of the reduced, protonated, totally hydrogenated polypyrrole at 30 K (**II** in Scheme 1).

continuum. This band is attributed to collective modes of the chain.

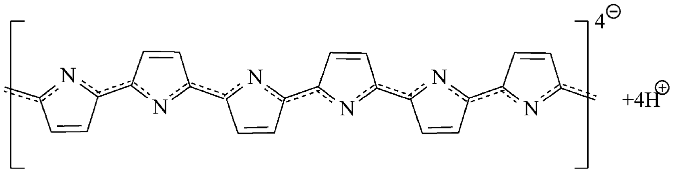
The spectra of the doped samples **III** (Fig. 2) can be interpreted along the same lines. The band frequencies are not significantly affected (Table 1). For the ring-deuterated sample (Fig. 2B) the main difference compared to Fig. 1B is the occurrence of two rather broad bands centred at 770 and 1480 cm^{-1}. These bands are logically attributed to bending modes of bound protons associated with the doping agent. Indeed, there is no significant change of the continuum intensity compared to the dedoped polymer (Fig. 1) and simple examination of Figs. 1 and 2 confirms that there is virtually no bound proton in the neutral polymer.

For the reduced doped sample (Fig. 3) there is still no significant change of the continuum intensity. The main consequence of protonation is an increase of the band intensity at 1460 cm^{-1}, presumably due to a greater amount of bound protons. Unfortunately, in the absence of the partially deuterated sample, it is not possible to observe the intensity at ~ 770 cm^{-1}. On the other hand, band frequencies and intensities for the CH bending modes are not strongly changed upon reduction. Broadening of the band at 1050 cm^{-1} counterbalances the apparent decrease of the intensity at maximum.

4. Conclusion

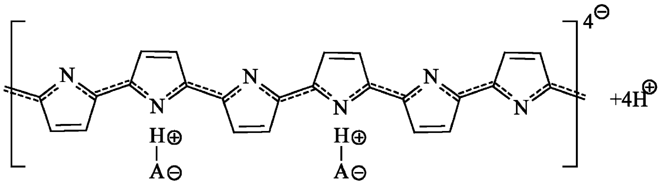
With the INS technique, we can distinguish different types of protons in polypyrroles. The most significant result is the existence of free particles with mass 1 amu. The amount of recoiling particles is apparently unaffected by doping, reduction and protonation. Unfortunately, as neutrons do not probe the electric charge of the free particles, H^+, H^0 or, much less probably, H^- entities cannot be distinguished.

In the neutral dedoped polymer, all hydrogen atoms normally supposed to be bound to the N atoms, as shown in **V**, do behave as free-recoiling particles. As previously proposed for polyanilines [37], the existence of free particles can be regarded as a consequence of electron and charge delocalisation. The tentative structure, **VII**, corresponds to a fully occupied electronic band and maximum charge delocalisation.



VII

Upon doping, the additional protons in **III** are essentially bound, presumably to the doping agent, for the vibrational modes of the polymer frame are changed very little. We suppose that the real structure is between the polaron structure **III** and the totally conjugated extended structure **VIII**.



VIII

Partial charge transfer between the polymer and the doping agent may withdraw electrons from the electronic band of **VIII** and yield electric conductivity with metallic character.

The amount of bound protons increases further upon reduction and protonation in accordance with **II**. The additional protons are bound to N-atoms and destroy electron delocalisation along the polymer. The electronic conductivity is thus dramatically depressed.

These conclusions emphasise the interplay of protonation, reduction and conductivity. The mechanism based on the existence of free protons and extended electronic band structure is quite similar in nature to that proposed for polyanilines [37]. For both kinds of polymers, the picture that emerges from INS studies is quite at variance from those based on long-lived localised excitations such as polarons or solitons [21,23]. However, there are noticeable differences regarding protonation. Whereas all protons are free in the emeraldine base, as in the neutral dedoped polypyrrole, additional protons in the emeraldine salt are trapped in shallow potential wells with a dissociation threshold of $\sim 300\ \mathrm{cm}^{-1}$. These protons are largely delocalised at room temperature and may contribute to the protonic conduction. In contrast to that, there is no visible increase of the amount of free species in the doped polypyrroles (Figs. 2 and 3). Presumably, potential wells for protons are deeper in polypyrroles than in polyanilines.

The existence of free protons is a strong support to the disorder-induced M–I transition mechanism in polypyrroles, while the quantum chemistry view appears less realistic. However, the conduction mechanism may depend on many parameters like doping and protonation degrees, polymer weight, structural and chemical disordering, etc. Different mechanisms may occur for different samples. For example, it can be suspected that the real structure of the dedoped neutral polymer could be close to **V** for small deprotonation degrees and close to **VII** for high deprotonation degrees. Consequently, the polaron mechanism could be more important at low doping degrees and the metal-like conductivity could be dominant for highly doped polypyrroles. As a first step, the preliminary studies presented above emphasise that the metal-like conduction is an important mechanism for doped polypyrroles.

Acknowledgements

We would like to thank M.-F. Lautié from LADIR for preparing the samples. The Rutherford Appleton Laboratory is thanked for access to neutron beam facilities.

References

[1] S. Rapi, V. Bochi, G.P. Gardin, Synth. Met. 24 (1988) 217.
[2] S. Machida, S. Miyata, T. Techagumpuch, Synth. Met. 31 (1989) 311.
[3] A.F. Diaz, A. Martinez, K.K. Kanazawa, J. Electroanal. Chem. 130 (1981) 181.
[4] A.F. Diaz, T. Bergon, Handbook of Conducting Polymers. Marcel Dekker, 1986.
[5] S. Kuwabata, H. Yoneyama, H. Takumara, Bull. Chem. Soc. Jpn. 57 (1984) 2247.
[6] C.K. Baker, Y.J. Qiu, R.J. Reynolds, J. Phys. Chem. 95 (1991) 4446.
[7] T. Hirai, S. Kuwabata, H. Yoneyama, J. Electrochem. Soc. 135 (1989) 1132.
[8] Y.J. Qiu, R.J. Reynolds, J. Polym. Sci., Part A: Polym. Chem. 30 (1992) 1315.
[9] J. Tanguy, N. Mermilliod, M. Hoclet, Synth. Met. 21 (1987) 97.
[10] Y.-F. Li, R.-Y. Qian, J. Electroanal. Chem. 362 (1993) 267.
[11] Y.-F. Li, C.R.-Y. Qian, Synth. Met. 28 (1989) C127.
[12] R.-Y. Qian, Q. J-J, D.-Y. Shen, Synth. Met. 61 (1993) 275.
[13] Q.-J. Xie, S. Kuwabata, H. Yoneyama, J. Electroanal. Chem. 420 (1997).
[14] Y.F. Li, Z.G. Li, Synth. Met. 94 (1998) 131–133.
[15] G.B. Street, T.C. Clarke, M. Krounbi, K. Kanazawa, V. Lee, P. Pfluger, J.C. Scottt, G. Weiser, Mol. Cryst. Liq. Cryst. 118 (1995) 178.
[16] F. Devreux, G. Bidan, A.A. Syed, C. Tsintavis, J. Phys. 46 (1985) 1595.
[17] H. Hyodo, A.G. Macdiarmid, Synth. Met. 11 (1985) 167.
[18] P. Pfluger, G.B. Street, J. Chem. Phys. 80 (1984) 544.
[19] C.O. Yoon, M. Reghu, D. Moses, A.J. Heeger, Phys. Rev. [Sect.] B 49 (1994) 10851–10863.
[20] S. Chakrabarti, B. Das, P. Banerji, D. Banerjee, R. Battacharya, Phys. Rev. [Sect.] B 60 (1999) 7691–7694.
[21] J.-L. Brédas, Electronic Structure of Highly Conducting Polymers, 1986 New York.
[22] W.R. Salaneck, O. Inganas, B. Themans, J.O. Nilsson, B. Sjogen, J.E. Osterholm, J.L. Bredas, J.L. Svenson, J. Chem. Phys. 89 (1988) 4613.
[23] J.L. Brédas, G.B. Street, Acc. Chem. Res. 18 (1985) 309.
[24] F. Hautiere-Cristofini, D. Kuffer, L.T. Yu, C. R. Acad. Sci. Paris, Ser. C 277 (1973) 1323.
[25] D. Marsitzky, K. Müllen, in: P. Bernier, S. Lefrant, G. Bidan (Eds.), Advances in Synthetic Metals. Twenty Years of Progress in Science and Technology. Elsevier, Amsterdam, 1999, p. 49.

[26] J. Rodriguez, H.-J. Grande, T.F. Otero, in: H.S. Nalwa (Ed.), Organic Conductive Molecules and Polymers, vol. 2, Wiley, New York, 1997, p. 415.

[27] D. Stanke, M.L. Hallensleben, L. Toppare, Synth. Met. 55–57 (1993) 1108.

[28] R.V. Gregory, W.C. Kimbrell, H.H. Kuhn, Synth. Met. 28 (1989) 823.

[29] L.S. Hwang, J.M. Ko, H.W. Rhee, C.Y. Kim, Synth. Met. 55–57 (1993) 3671.

[30] R.H. Baughman, L.W. Shacklette, N.S. Nurthy, G.G. Miller, R.L. Elsenbaumer, Mol. Cryst. Liq. Cryst. 118 (1985) 253.

[31] G.P. Gardini, Adv. Heterocycl. Chem. 15 (1973) 67.

[32] W. Wernet, M. Monkenbusch, G. Wegner, Makromol. Chem., Rapid Commun. 5 (1984) 157.

[33] A. Pron, Z. Kucharski, C. Budrowski, M. Zagorska, S. Kirchene, J. Suwalski, G. Dehe, S. Lefrant, J. Chem. Phys. 83 (1985) 5923.

[34] I. Mamadou, L.T. Yu, R. Buvet, C. R. Acad. Sci. Paris, Ser. C 279 (1974) 931.

[35] G.B. Street, S.E. Lindsey, A.I. Nazzal, K.J. Wynne, Mol. Cryst. Liq. Cryst. 118 (1985) 137.

[36] M.D. McGehee, E.K. Miller, D. Moses, A.J. Heeger, in: P. Bernier, S. Lefrant, G. Bidan (Eds.), Advances in Synthetic Metals. Twenty Years of Progress in Science and Technology. Elsevier, Amsterdam, 1999, p. 49.

[37] F. Fillaux, N. Leygue, R. Baddour-Hadjean, S. Parker, P. Colomban, A. Gruger, A. Régis, L.T. Yu, Chem. Phys. 216 (1997) 281.

[38] F.A. Miller, J. Am. Chem. Soc. 64 (1942) 1543.

[39] S. Rapi, V. Bocchi, G.P. Gardini, Synth. Met. 24 (1988) 217.

[40] S.P. Armes, Synth. Met. 20 (1987) 365.

[41] F. Fillaux, S.M. Bennington, J. Tomkinson, L.T. Yu, Chem. Phys. 209 (1996) 111–125.