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Side chain liquid crystalline polypyrrole
Part I: Synthesis and characterization

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A new class of side chain liquid crystalline polymers containing a polypyrrole main chain has been synthesized. These materials were shown to be promising because they combine orientational behaviour and useful electrical properties. Two chemical processes of polymerization were carried out using ferric chloride or iodine as oxidizing agent. All the polypyrroles obtained exhibited smectic A phases. Polymerization in solution was achieved by ferric chloride in an organic solution containing an additional naphthalenesulphonate dopant; the conditions of polymerization were adjusted in order to obtain melt processible and mesomorphic polymers. Polymerization with iodine was performed in bulk, allowing the reaction to be effected on the oriented mesophase of the monomer. Room temperature conductivities of the polypyrrole synthesized by either process reached about 10^{-2}–10^{-4} S cm^{-1}.

1. Introduction

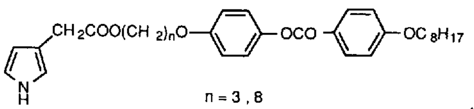
Introducing liquid crystalline behaviour into conducting polymers is of special interest because of the potential for combination of the electrical and orientational properties [1, 2]. For instance, in an electroactive chain, orientation of mesogenic substituents linked to the main chain could modify the conformation of the backbone and, consequently, induce specific electronic properties such as anisotropy of conductivity. Different mesomorphic polymers with conjugated backbones have already been investigated, such as polyacetylenic and polydiacetylenic derivatives [1–6], polynitriles [7] or polyheptadiyne [8]. However, in many cases, the transport conductivity of the main chain is drastically affected by the grafting of such large mesogenic moieties [2].

Polypyrrole or polythiophene are probably more promising candidates, since β-substituted derivatives can be appropriately functionalized while preserving a relatively high conductivity [9–11] and good thermal stability [12, 13]. Some mesogenic thiophene [14] and pyrrole [15, 16] monomers have been synthesized, but without, at the present time, conversion into liquid crystalline polymers. This paper reports the mesomorphic and electrical properties of the first side chain liquid crystalline polypyrroles. It also includes a description of the synthesis of the monomers and the conditions of their polymerization.

2. Materials and results

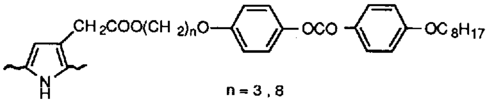
2.1. *Synthesis and polymorphism of monomers*

The mesogenic moiety is attached to the β-position of the pyrrole ring via a carboxyl function and a spacer of variable length (n = 3 and 8):



"$\mathrm{Py}_n\mathrm{C}_8$"

The polymerization will occur in the α-position:



"$\mathrm{PPy}_n\mathrm{C}_8$"

The monomers $\mathrm{Py}_n\mathrm{C}_8$ are synthesized as shown in the scheme. The β-regioselective sythesis requires the use of indirect method involving several steps [17]. Electrophilic attack on the pyrrole in the α-position is prevented by conversion to N-tosyl pyrrole, allowing the Friedel-Crafts acylation in the β-position. A methylene link is introduced between the carboxyl group and the pyrrole ring to avoid conjugation of electrons of the functional group with the

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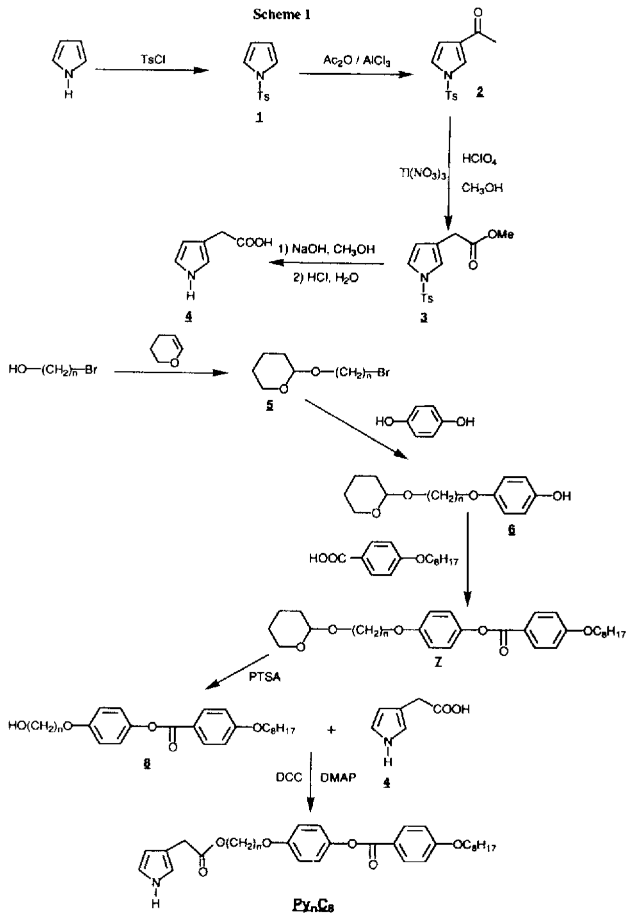

Scheme 1.

delocalized electronic system of the pyrrole backbone, which would reduce the conductivity [9, 10, 17].

Both monomer, with $n = 3$ and $n = 8$, exhibit a monotropic smectic A phase (see table 1) as established by polarizing optical microscopy. The S_A–I transition temperature increases with the length of the spacer, and the mesophase becomes more nearly enantiotropic in behaviour. The layer spacing, *d*, determined from the X-ray Bragg diffraction is equal to the length, *l*, of the molecule, assuming the most extended conformation, and corresponds to a single layer packing.

Table 1. Transition temperatures (°C), transition enthalpies ΔH (J g^{-1}) and layer spacings *d* in the smectic A phase for the Py$_n$C$_8$ monomers.

n	C_r		S_A		I	*d*/Å	*l*/Å†	ΔH_{I-S_A}
3	•	55	•	(44)	•	35	35·5	6
8	•	72	•	(68)	•	44	43	9

Parentheses denotes a monotropic transition. † *l* represents the length of the side group measured using all-*trans*-stereomodels, including the pyrrole ring.

2.2. *Polymerization of monomers*

The polypyrrole is obtained by oxidation of the monomer using either an electrochemical or a chemical method. In our case, the polymerization conditions have been adjusted in order to obtain fusible materials able to exhibit thermotropic mesomorphic character.

2.2.1. *Electrochemical polymerization*

Since electrochemical polymerization is known to provide films of substituted polypyrrole with high conductivity (up to 10 S cm^{-1}) [9–10], this was attempted with Py$_n$C$_8$. The reaction was carried out at constant current density, using a lithium perchlorate/propylene carbonate electrolyte (see experimental part). A homogeneous film was obtained. Unfortunately, however, this material is insoluble in all common solvents and infusible, and is without mesomorphic properties.

2.2.2. *Polymerization in solution with ferric chloride*

Polymerization of pyrrole in solution, using ferric chloride as oxidizing agent, has been widely studied [18–20]. A counter-ion is often added in order to enhance conductivity and stability [12, 13]. For this study, 1-naphthalenesulphonate has been chosen. The polymerization was performed using chloroform as solvent, with various molar ratios of ferric chloride (see example in table 2). The molar ratio of 1-naphthalenesulphonic acid with respect to monomer was kept constant at 0·3. A reaction time of 20 h was used, and purification was carried out by precipitation and washing with ethanol. Except for the polymers synthesized using the lowest amounts of $FeCl_3$, the GPC chromatograms showed no residual monomer, as confirmed by the ^{1}H NMR spectra in figure 2 (disappearance of protons of the pyrrole ring). Variations of the $FeCl_3$/monomer ratio (r_{FeCl_3}) have significant effects on the weight distribution of the polymers, since the molecular weight as well as the polydispersity increase with this ratio. $r_{FeCl_3} = 2·3$ corresponds to the stoichiometric ratio used for non-substituted polypyrroles. In our case, this ratio provides polymers exhibiting relatively large molecular weight distributions, with some high molecular weight macromolecules, leading to infusible materials. On the other hand, the polymer obtained with $r_{FeCl_3} = 0·7$

Table 2. Polymerization of Py$_8$C$_8$ in solution.

$[FeCl_3]$/[monomer]	$\bar{M}_n$†	$\bar{M}_w/\bar{M}_n$
0·5	2000 + M‡	
0·7	6200	1·15
2·3	7500	1·90
5	insoluble	

†$\bar{M}_w/\bar{M}_n$: molecular weights (g mol^{-1}) determined by gel permeation chromatography relative to polystyrene standards.
‡ M: significant amount of residual monomer.

is perfectly melt processible, and could be used for the subsequent studies of orientation of the mesogenic groups.

Elemental analysis (see experimental section) was carried out on the polymer synthesized by ferric chloride oxidation, using two $FeCl_3$/monomer ratios. For $r_{FeCl_3} = 2{\cdot}3$, the data give the molar ratios of doping species to pyrrole ring as 0·10 for naphthalene sulphonate (NS^-), and 0·10 for Cl^- ion. For $r_{FeCl_3} = 0{\cdot}7$, these values are 0·11 for NS^-, and about 0·02 for Cl^-. In both cases, the Fe contents in the polymers must be interpreted by the presence of residual $FeCl_3$. These values, when compared with those obtained for polymerization of unsubstituted pyrrole [13], show that the doping is partial (0·20 for $r_{FeCl_3} = 2{\cdot}3$, instead of the value of 0·32 corresponding to total doping). Furthermore, when a ratio of 0·7 is used in order to achieve low molecular weights, this doping level falls to 0·13.

2.2.3. *Polymerization in bulk with iodine vapour*

Polymerizations of pyrrole with halogens have already been studied in solution [21]. Because of the potential interest of polymerization in an oriented mesophase, we have carried out this polymerization in bulk using iodine in the vapour phase. Furthermore, a study on Langmuir–Blodgett films Py_nC_8 proved the efficiency of iodine vapour in polymerizing these systems [22]. The monomer was polymerized at different temperatures, within its three phases (crystalline, smectic or isotropic). Gel permeation chromatography (GPC) experiments showed a total conversion of the monomer in all the cases (see figure 1), but an evolution of the molecular weight distribution with changing polymerization conditions. A detailed study was carried out on the monomer Py_3C_8. When the polymerization takes place in the crystalline or the smectic A phase of the monomer (respectively, at 25°C and 40°C), the molecular weights of the polymer are in the same range (6000–$8000\,g\,mol^{-1}$ relative to polystyrene standards), with a remarkably low polydispersity of 1·05–1·1 (see figure 1 (*a*)). The reaction time (4 h to 3 d) does not affect these characteristics. All polymers are soluble in the usual solvents such as tetrahydrofuran or chloroform. When the polymerization is performed in the isotropic state of the monomer (at 60°C), the polymerization leads quickly to high molecular weights. A fraction of the polymer becomes insoluble, and GPC measurements on the soluble fraction show a broad peak with some molecular weights up to $100\,000\,g\,mol^{-1}$ (see figure 1 (*b*)). A similar influence of mesogenic order on the kinetics of polymerization has been already reported [23]. The melt processiblity of these materials is intrinsically connected with their molecular weight. Unlike the high molecular weight polymers obtained from isotropic monomers, those synthesized within the mesophase of the monomer are perfectly fusible.

In the case of polymerization in smectic monodomain, the monomer is first aligned by uniform magnetic field of 1 Tesla and held constant at a chosen temperature within the smectic domain (40°C for Py_3C_8), as previously described [2]. The polypyrrole obtained exhibits the same characteristics as the corresponding polymer realized in the non-oriented mesophase.

Since the polymers are free from monomer or oligomers, no purification is necessary, except for removing the excess of iodine under dynamic vacuum. On the final product, the UV spectrum exhibits only one

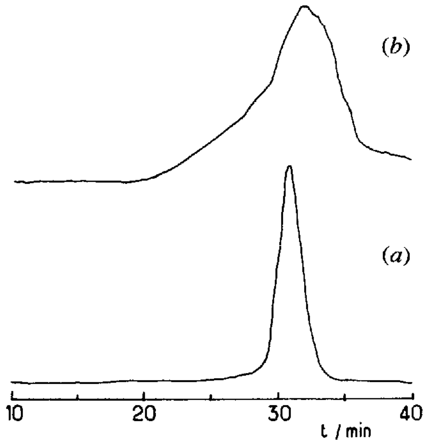

Figure 1. GPC traces of PPy_3C_8 polypyrrole obtained from polymerization in bulk with iodine vapour; (*a*) polymerization at 40°C. (*b*) polymerization at 60°C (elution time of the monomer: 39 min).

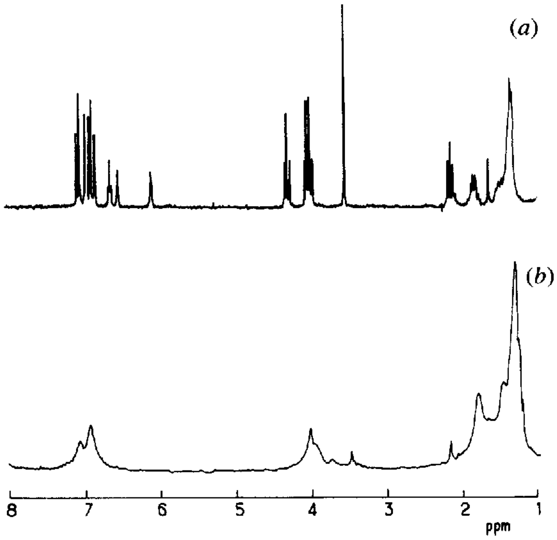

Figure 2. ^1H NMR spectra, sample in $CDCl_3$, of Py_3C_8 monomer (*a*) and the corresponding PPy_3C_8 polymer (*b*) obtained using the ferric chloride/naphthalenesulphonate system (see chemical shifts in the experimental part).

absorption peak from the doping species at 350 nm, assigned to the I_3^- species [2]. The amount of I_3^-, determined by weighing, is about 1 for every 3 monomer units, which corresponds to total doping .

2.3. *Polymorphism and electrical properties of polymers*

Polypyrroles obtained using $FeCl_3$ oxidation (with $r_{FeCl_3} = 0{\cdot}7$) exhibit two different smectic A phases. The layer spacing of these smectic phases have been determined by X-ray diffraction studies and are summarized in table 3. The spacing of the high temperature smectic A phase, $S_{A(HT)}$, is compatible with a single layer packing taking into account the length, l, of the side chain enlarged by the size of a napthalenesulphonate ion (5·5 Å as determined by X-ray diffraction). At low temperatures, the smectic phase, $S_{A(LT)}$, becomes partially bilayered, with an overlapping, x, of the mesogenic cores of about 16 Å in the two polymers ($d - 5{\cdot}5 = 2l - x$).

Polymers obtained by oxidation using iodine vapour from either an oriented or a non-oriented mesophase, exhibit, after elimination of excess of iodine, a smectic A mesophase. Although the precise determination of the clearing temperature is difficult because of the iodine evaporation and degradation, both polymers, with $n = 3$ or $n = 8$, are smectic until about 130–140°C (X-ray observations). In the polymer with the shorter spacer, the layer spacing ($d = 58$ Å) of the smectic phase, characterized by X-ray diffraction, is the same as that obtained at low temperatures in the polymer synthesized using a solution.

Table 3. Phase transition temperatures and layer spacings of the smectic A phases for polypyrroles obtained in solution ($[FeCl_3]/[monomer] = 0{\cdot}7$).

	Transition temperature/°C					Layer spacing/Å	
n	$S_{A(LT)}$		$S_{A(HT)}$		I	$d_{SA(LT)}$	$d_{SA(HT)}$
3	●	120	●	160	●	57	40
8	●	50	●	130	●	72	46

Table 4. Conductivity ($S\,cm^{-1}$) of PPy_8C_8 polypyrroles, obtained by ferric chloride/naphthalenesulphonate oxidation.

$[FeCl_3]/[monomer]$	Solvent	Sample	Conductivity
0·7	Chloroform	Pressed pellet†	10^{-7}
		Melt-processed films	10^{-8}–10^{-9}
2·3	Chloroform	Pressed pellet	10^{-3}
		Melt-processed films	10^{-7}–10^{-8}
2·3	Propanol	Pressed pellet	10^{-2}

† Pressed under 5 tons during 10 mins.

On the contrary, the polypyrrole with the long spacer exhibits a mono-layer structure ($d = 44$ Å).

The conductivity of the polypyrroles obtained by ferric chloride oxidation was measured on two types of sample, pressed pellets of films obtained by melting. Measurements were made by a two probe technique and the results are shown in table 4. The conductivity determined on pressed pellets increases with the ratio of ferric chloride, from $10^{-7}\,S\,cm^{-1}$ for $r_{FeCl_3} = 0{\cdot}7$ to $10^{-3}\,S\,cm^{-1}$ for $r_{FeCl} = 2{\cdot}3$. This difference can be easily explained by the doping level of each polymer. The conductivity increases when a more protic solvent, like propanol, is used instead of chloroform ($10^{-2}\,S\,cm^{-1}$). However, the yield from the polymerization in this solvent is very low due to the poor solubility of the monomer. Measurements on the samples obtained by melting exhibit low conductivities, when compared to the pressed samples. In this case, the ratio of ferric chloride has no influence on the conductivity. Moreover, those differences do not result from any thermal de-doping or degradation, since the conductivity of a sample, successively molten and then pressed, is the same as that of the unheated sample. By this process, it was shown that high conductivities could only be obtained with compacted samples.

The conductivity of polypyrrole obtained by oxidation with iodine vapour was measured by dielectric measurements that allowed us to determine the variation of conductivity with frequency [24]. Figure 3 shows that, as is usual for conducting polymers, the conductivity can be separated into a frequency-independent contribution, which is predominant in the low frequency region, and a frequency-dependent contribution, which becomes appreciable at high frequencies. The conductivity at low frequency was $10^{-4}\,S\,cm^{-1}$. The value obtained is the same for both polymer samples with $n = 3$ or $n = 8$. for comparison, the d.c. conductivity, measured by the Van der Pauw technique [25], was $10^{-3}\,S\,cm^{-1}$. These values are stable over a few days at ambient temperature.

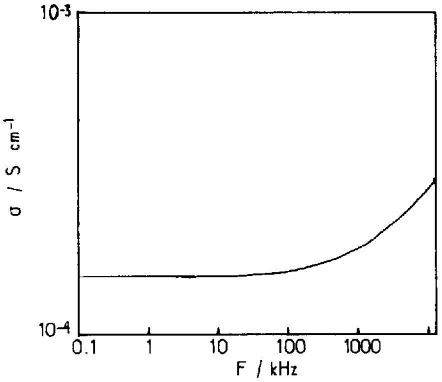

Figure 3. Conductivity versus frequency for I_3^- doped PPy_3C_8 polypyrrole.

3. Conclusions

Some mesogenic pyrrole derivatives were synthesized and polymerized to provide smectic A side chain polypyrroles. Oxidation of the monomers by an iodine or ferric chloride/naphthalenesulphonate system led to auto-doped polymers, the conductivity of which was found to be about 10^{-2}–10^{-4} S cm^{-1}. Obtaining melt processible and orientable materials with the ferric chloride/naphthalenesulphonate system, was shown to be incompatible with a maximum doping. On the other hand, the study of bulk oxidation, using iodine vapour, led to polymers with a reasonable conductivity which is stable over a few days at ambient temperature. This process allowed us to consider polymerization in the oriented mesophase of the monomer. In this way, the orientation of the mesogenic groups could be preserved for polymers. Orientation has to be achieved in the final polymer from polymerizations in solution. In this last case, the conductivity will be lower. The effects of this orientation on the backbone conformation and on conducting properties will be described in the part II of this series.

4. Experimental

4.1. *Synthesis of monomers*

A typical procedure, for the case where $n = 3$, is given below. Pyrrole-3-acetic acid was synthesized according to a literature procedure [26].

4.1.1. *Synthesis of 3-bromo-1-tetrahydropyranyloxypropane* (**5**)

10 g (0·072 mol) of 3-bromopropan-1-ol were dissolved in 100 ml of CH_2Cl_2, and the mixture was cooled to 0°C. 7·4 g (0·088 mol) of dihydropyran were added dropwise, and the reaction was started by addition of some crystals of *p*-toluenesulphonic acid (PTSA) The mixture was stirred during 15 min. The reaction was stopped by the addition of 0·5 g of $NaHCO_3$. After evaporation of the CH_2Cl_2 and dissolution of the residue in ethyl acetate, the product was purified by filtration through silica gel. Yield 15·4 g (96 per cent). ^{1}H NMR ($CDCl_3$, δ): 1·65–2·15 (8 H, C–CH_2–C), 3·5–4 (2 H, CH_2–Br; 4 H, OCH_2), 4·6 (1 H, O–CH_{pyran}–O).

4.1.2. *Synthesis of 4-(1-tetrahydropyranyloxypropanoxy) phenol* (**6**)

5·76 g (0·1 mol) of KOH were dissolved in 50 ml of ethanol. 19·2 g (0·17 mol) of hydroquinone were added, and the mixture was heated under reflux while a solution of 15·4 g (0·07 mol) of (**5**) in 150 ml of ethanol was added dropwise. The reaction mixture was boiled for 20 h, the solvent was then evaporated off and the residue added to 100 ml of water/ice. The product was extracted into ether, washed with water, and dried over Na_2SO_4. Purification was effected on a silica gel column, with a 1 : 1 heptane/ether mixture as eluent. Yield 10·6 g (60 per cent). ^{1}H NMR (CD_3COCD_3, δ): 1·55–1·95 (8 H, C–CH_2–C), 3·5–4 (6 H, OCH_2), 4·6 (1 H, O–CH_{pyran}–O), 6·8 (4 H arom.), 7·8 (1 H, phenol OH).

4.1.3. *Synthesis of 4-(3-hydroxypropyloxy) 4-octyloxyphenylbenzoate* (**8**)

5·8 g (23 mmol) of (**6**), 6·25 g (25 mmol) of 4-octyloxybenzoic acid [2], 5·15 g (25 mmol) of dicyclohexylcarbodiimide (DCC) and 0·31 g (2·5 mmol) of 4*N*,*N*-dimethylaminopyridine (DMAP) were dissolved in 100 ml of CH_2Cl_2, and the resulting solution was stirred overnight at room temperature. The solution was filtered, evaporated, and the compound was recrystallized from ethanol. Yield 9·7 g (87 per cent). This intermediate compound (**7**) was dissolved in a CH_2Cl_2 (70 ml)/CH_3OH (120 ml) mixture. 0·3 g of PTSA were then added and the solution was stirred for 1 h at room temperature. The solvents were evaporated, and (**8**) was obtained by recrystallization of the residue from methanol. Yield 7·4 g (92 per cent) ^{1}H NMR ($CDCl_3$, δ): 0·9 (3 H, CH_3), 1·35–2·1 (14 H, C–CH_2–C), 4 (6 H, OCH_2), 7 (6 H arom. *ortho* to OCO and *ortho* to OCH_2–), 8·1 (2 H arom. *ortho* to COO).

4.1.4. *Synthesis of* Py_3C_8

6 g (15 mmol) of (**8**), 2 g (16 mmol) of pyrrole-3-acetic acid 3·3 g (16 mmol) of DCC and 0·2 g (1·6 mmol) of DMAP were dissolved in 70 ml of CH_2Cl_2, and the resulting solution was stirred overnight at room temperature. The solution was filtered, evaporated, and the pure Py_3C_8 was obtained by chromatography on silica gel using 1 : 1 heptane/ether as eluent. Yield 6·1 g (80 per cent). ^{1}H NMR (see figure 2 (*a*); $CDCl_3$, δ): 0·9 (3 H, CH_3), 1·35–2·1 (14 H, C–CH_2–C), 3·5 (2 H, pyran–CH_2–COO), 4–4·3 (6 H, OCH_2), 6·1 (1 H, pyran β-position), 6·6 (2 H, pyran α-position), 7 (6 H arom. *ortho* to OCO and *ortho* to OCH_2), 8·1 (2 H arom. *ortho* to COO), 8·3 (NH). All monomers gave satisfactory elemental analysis: calculated for Py_3C_8: C, 71·00; H, 7·29; O, 18·93; N, 2·76. Found: C, 71·06; H, 7·15; O, 18·34; N, 2·79 per cent.

4.2. *Polymerization*

4.2.1. *Electropolymerization*

Electropolymerization was carried out using platinum electrodes, with an anode surface of 78 mm^2. The reaction medium (monomer 0·1 M, $LiClO_4$ 1 M in propylene carbonate) was degassed by argon bubbling. Polymerization was galvanostatically controlled; the current was set to 50 μA until deposition charges of 2 C cm^{-2} were reached. Films were rinsed with acetone and dried in vacuum.

4.2.2. *Polymerization using ferric chloride*

A solution of anhydrous $FeCl_3$ 0·1 M, 1-naphthalenesulphonic acid 0·04 M and Py_nC_8 0·14 M ($r_{FeCl_3} = 0{\cdot}7$) in chloroform was stirred at room temperature during 20 h. The polymer in solution was then precipitated in an excess of ethanol, and repeatedly washed with ethanol. The powder was vacuum dried at room temperature. The ^1H NMR spectrum is given in figure 2 (*b*). Elemental analysis: for $r_{FeCl_3} = 0{\cdot}7$; C, 71·73; H, 7·99; N, 2·10, O, 13·59; S, 0·53; Cl, 2·74; Fe, 1·40; for $r_{FeCl_3} = 2{\cdot}3$: C, 68·83; H, 7·65; N, 2·22; O, 16·62; S, 0·41; Cl, 3·08; Fe, 1·33 per cent.

4.2.3. *Polymerization using iodine vapour*

The monomer was spread by spin coating on a glass plate and exposed during several hours to saturated iodine vapour at a controlled temperature. The monomer conversion was monitored by GPC. The excess of iodine was removed under a dynamic vacuum (0·5 mmHg) at 25°C during two hours.

4.3. *Materials and instrumentation*

Pyrrole and propylene carbonate were distilled before use. All other reagents and solvents were used as received. Pyrrole compounds and polymers were stored under nitrogen at 0°C.

GPC measurements were performed using THF solutions and a Varian apparatus fitted with five TSK columns calibrated with polystyrene standards. DSC analysis was carried out using a DSC7 Perkin–Elmer apparatus at 10°C min^{-1}, with open cups. NMR spectra were recorded using a Bruker 300 MHz.

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References

[1] Le Moigne, J., Soldera, A., Guillon, D., and Skoulios, A., 1989, *Liq. Crystals*, **6**, 627.

[2] Vicentini, F., Mauzac, M., Laversanne, R., Pochat, P., and Parneix, J. P., 1994, *Liq. Crystals*, **16**, 721.

[3] Tsibouklis, J., Werninck, A. R., Shand, A. I., and Milburn, G. H. W., 1988, *Liq. Crystals*, **3**, 1393.

[4] Le Moigne, J., and Hilberer, A., 1991, *Makromolek. Chem.*, **192**, 515.

[5] Garito, A. F., Teng, C. C., Wong, K. Y., and Zammani' Khamiri, O., 1984, *Molec. Crystals liq. Crystals*, **106**, 219.

[6] Zhang, X., Ozcayir, Y., Feng, C., and Blumstein, A., 1990, *Polym. Preprints*, **31**, 597.

[7] Barbarin, F., Dugay, M., and Fauxpoint, D., 1989, *Molec. Crystals. liq. Crystals*, **167**, 61.

[8] Jin, S. H., Choi, S. J., Ahn, W., Cho, H. N., and Choi, S. K., 1993, *Macromolecules*, 26, 1487.

[9] Delabouglise, D., Roncali, J., Lemaire, M., and Garnier, F., 1989, *J. chem. Soc., chem. Commun.*, 475.

[10] Delabouglise, D., 1992, *Synth. Met.*, **51**, 321.

[11] Rühe, J., Ezquerra, T. A., and Wegner, G., 1989, *Synth. Met.*, **28**, 177.

[12] Wang, Y., Rubner, M. F., and Buckley, L. J., 1991, *Synth. Met.*, **41**, 1103.

[13] Thieblemont, J. C., Planche, M. F., Petrescu, C., Bouvier, J. M., and Bidan, G., 1993, *Synth. Met.*, **59**, 81.

[14] Brice, M. R., Chissel, A. D., Gopal, J., Kathirgamanathan, P., and Parker, D., 1991, *Synth. Met.*, **39**, 397.

[15] Suzuki, H., Kaneko, T., Matsui, N., Hamamoto, I., Satoh, T., Nagosaki, F., and Katoh, T., 1991, PCT Int. Appl. WO9105, 769.

[16] Langley, P. J., Davis, F. J., and Mitchell, G. R., 1993, *Molec. Crystals liq. Crystals*, **236**, 225.

[17] Ho-Hoang, A., Fache, F., Boiteux, G., and Lemaire, M., 1994, *Synth. Met.*, **62**, 277.

[18] Walker, J. A., Warren, L. F., and Witucki, E. F., 1988, *J. polym. Sci., polym. Chem.*, **26**, 1285.

[19] Chao, T. H., and March, J., 1988, *J. polym. Sci., Polym. Chem.*, **26**, 743.

[20] Machida, S., Miyata, S., and Techagumpuch, A., 1989, *Synth. Met.*, **31**, 311.

[21] Kang, E. T., Tan, T. C., Neoh, K. G., and Ong, Y. K., 1986, *Polymer*, **27**, 1958.

[22] Jego, C., Agricole, B., Vicentini, F., Barrouillet, J., Mauzac, M., and Mingotaud, C., 1994, *J. phys. Chem.*, **98**, 13408.

[23] He, L., Zhang, S., Jin, S., and Qi, Z., 1994, *International Conference on Liquid Crystal Polymers, Beijing, China.*

[24] Legrand, C., and Parneix, J. P., 1990, *J. Phys., France*, **51**, 787.

[25] Van der Pauw, L. J., 1958, *Philips Res. Rep.*, **13**, 1.

[26] Kakushima, M., Hamel, P., Frenette, R., and Rokach, J., 1983, *J. org. Chem.*, **48**, 3214.