Some insights into the microstructure of polypyrrole

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Estimation of the molecular weight between crosslinks and determination of the average conjugation length in polypyrrole are reported. By applying the Flory equation to dimethylsulphoxide-swollen dedoped polymer, it was found that the molecular weight between crosslinks is larger than previously thought and lies in the range of 25–65 pyrrole units. U.v. and resonance Raman spectroscopy indicate that the average conjugation length is short. The upper limit is about 6 pyrrole units.

(Keywords: polypyrrole; molecular weight; conjugation length)

INTRODUCTION

The insoluble nature of polypyrrole precludes the application of standard characterization techniques for determining the molecular weight and conjugation length. These are variables that play an important role in controlling the physical, mechanical and electrical properties of polymers. Some indication of the magnitude of molecular weight was provided by polymerizing ^{3}H labelled 2,2′-dimethylpolypyrrole[1].

In 2,2′-dimethylpolypyrrole crosslinks occurring via the β positions cannot be formed and the resultant polymer is therefore linear, with only terminal pyrrole moieties retaining the tritium label. This approach enables determination of the molecular weight, which was found to be in the range 50 000–100 000, for the polymer doped with perchlorate and tetrafluoborate counter ions. However, in pyrrole itself, where the β positions are free, crosslinking can be expected. This results in a giant polymer network. Nazzal and Street[1] concluded that excess hydrogens found from elemental analysis are due to hydrogen present at the chain ends only, and that the chain length in polypyrrole may be as short as 6–8 pyrrole units. It was also concluded by Yakushi *et al.*[2] that polypyrrole may contain a wide range of chain lengths including some very short oligomers.

Little is known about the conjugation length in polypyrrole, but it may be quite different to that of 2,2′-dimethylpolypyrrole which has been shown to be quite long[1]. We have attempted to arrive at an estimate of the molecular weight between crosslinks and the conjugation length by using two approaches: swelling experiments by application of the Flory–Huggins theory of polymer solutions[3–5] and spectroscopic methods, including u.v. and resonance Raman spectroscopy. Some mention will also be made of ^{13}C cross polarization magic angle spinning nuclear magnetic resonance (CPMAS n.m.r.) results.

EXPERIMENTAL

Samples of polypyrrole were produced on a 316 stainless steel polished disc as the anode (10.0 cm diameter) with a steel mesh disc (10.0 cm diameter) as the cathode. Preparation was conducted in a single compartment cell under a blanket of nitrogen gas with 0.3 M pyrrole, 0.5 M sodium *p*-toluene sulphonate or 0.5 M sodium tetrafluoborate, buffered at pH of 4.8, maintained at 20°C. The electrochemical polymerization was carried out under galvanostatic control with a current of 60 mA over 3.5 h. Dedoping was achieved by reversal of the polarity of the electrodes while they were in contact with the conducting electrolyte solution over various time intervals.

Samples of polypyrrole were weighed initially on a five place balance then placed in swelling solvents. Equilibrium swelling was determined by periodic weighing of the swollen polymer until constant weight was established. Excess solvent was carefully removed with tissue paper.

Resonance Raman spectra of polypyrrole samples were measured with an Anaspec Model 33 Raman Spectrometer, fitted with Spectra-Physics Model 164-08 argon ion and 164-111 krypton ion lasers. The 457.9 nm line was produced from an argon ion laser. The 435.0 and 415.0 lines were from a stilbene-3 dye laser pumped with the u.v. output of an argon laser.

The measured frequencies of the ν_2 peaks for various exciting wavelengths were used to calculate the number of conjugated C=C units in the polymer using the relationship established by Baruya *et al.*[6].

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Solid state ^{13}C n.m.r. analysis was performed on a Bruker CXP-100 nuclear magnetic resonance spectrometer. A 90° pulse of 4.9 μs was used. The contact time of the protons and carbons was 1 μs. A recycle time of 1 s was employed. A delay time of 24 μs was used. ^{13}C–^{1}H crosspolarization meaurements were performed at 22.6 and 90 MHz respectively. Magic angle spinning was performed at 54° 7′ at a rotor speed of 3 kHz. The magic angle was set by adjustment of equal peak heights and areas using hexamethylbenzene. Chemical shifts were calibrated with hexamethylbenzene and recorded with respect to tetramethylsilane. All experiments were performed at 25°C.

RESULTS

Molecular weight between crosslinks

Flory[7] derived the following equation from which the average molecular weight between crosslinks, $\bar{M}_x$, can be determined from polymer swelling experiments:

$$\bar{M}_x = V_1\rho_1(V_2^{1/3} - V_2/2)/-\{\ln(1-V_2) + V_2 + \chi_1 V_2^2\} \quad (1)$$

where V_1 and V_2 represent the molar volume fraction of the solvent and the polymer, respectively. ρ_1 is the density of the swelling solvent and χ_1 is the polymer–solvent interaction parameter. The only parameter required for the calculation of $\bar{M}_x$, which is not available experimentally in this case, is χ_1. This parameter is itself generally estimated from swelling experiments, mechanical properties or from the semi-empirical relationship[9,10]:

$$\chi_1 = \beta_1 + V_1/RT(\delta_1 - \delta_2)^2$$

where δ_1 and δ_2 are the solubility parameters of the solvent and polymer, respectively, R is the gas constant and T is temperature. $\beta_1 = 1/Z(1-1/M)$, where Z is the coordination number of the repeat unit and M is the molecular weight of the polymer.

For maximum swelling to occur, $\delta_1 = \delta_2$ (refs 10, 11). In the case of a crosslinked polymer this condition can be determined from a plot of the inverse of the volume fraction of the polymer for a given material against δ_2 of the various swelling solvents. Such a plot yields a bell-shaped curve with a maximum that can be equated with δ_2.

It is also possible to determine the solubility parameter of the polymer using semi-empirical additivity rules[12], where:

$$\delta_2 = \rho \sum E/M_0$$

and where E values are the various molar attraction coefficients summed over the structural configuration of the repeat unit in the polymer chain, ρ is the density of the polymer and M_0 is the molecular mass of the repeat unit.

It was considered to be more realistic to work with dedoped samples, where the electrostatic contributions are negligible and the dopant ions are not using up sites which the swelling solvent can occupy. After examining various solvents it was found that dimethylsulphoxide, DMSO, swelled both the doped and dedoped polymer to the greatest extent. The solubility parameter for DMSO is 12.0 $(\text{cal cm}^{-3})^{1/2}$. Using the semi-empirical approach shown above, the solubility parameter of dedoped polypyrrole is found to be 12.3 $(\text{cal cm}^{-3})^{1/2}$, which is in close agreement with the solubility parameter of DMSO.

The term β_1 takes into account lattice effects[9]. Because polypyrrole is a crosslinked network with infinite molecular weight, $\beta_1 = 1/Z$. The coordination number for the monomer is unknown. Owing to the possibility of crosslinking, it is not unreasonable to assign a value of an intermediate number between 2 and 3 for Z. This represents the two extreme situations: a value of 2 represents an infinite linear chain and a value of 3 corresponds to one crosslink per monomer unit. Although the actual value is more likely to be intermediate between the two, it is not possible to specify, hence only upper and lower limits can be stated.

For $Z = 2$ (linear chain)

$$\chi_1 = 0.5 + 67.21/1.987 \times 293(12.3 - 12.0)^2 = 0.508$$

For $Z = 3$ (fully crosslinked)

$$\chi_1 = 0.333 + 67.21/1.987 \times 293(12.3 - 12.0)^2 = 0.341$$

Thus χ_1 varies from 0.508 to 0.341.

Figure 1 displays the results obtained by swelling polypyrrole in DMSO.

Taking the maximally dedoped mass and applying equations (2) and (3) to obtain the volume fraction of the polymer, V_2, we arrive at a value of $V_2 = 0.305$ ($W_o = 0.03607$ g; W_s (16 h) $= 0.10284$ g).

The equations are:

$$V_s = W_o/P_2 + (W_s - W_o)/P_1 \quad (2)$$

$$V_2 = W_o/\rho_2 V_s \quad (3)$$

Substituting the value of $V_2 = 0.305$ into equation (1) provides estimates of the upper and lower limits of $\bar{M}_x$. For values of χ_1 equal to 0.341 and 0.508, $\bar{M}_x$ values of 1750 and 4300, respectively are obtained. Thus the molecular weight between crosslinks lies in the range of 26 to 64 pyrrole units.

Conjugation length

U.v. spectroscopy. The spectrum of polypyrrole in the range 0.0–4.0 eV was recorded by Street *et al.*[13]. In the reported spectrum the peak at 3.0 eV (corresponding to 410 nm) was ascribed to a $\pi - \pi^*$ transition occurring in the doped polymer. A similar peak was observed in pyrrole, bipyrrole and terpyrrole at 208, 285 and 345 nm respectively. Considering that each pyrrole unit contains two conjugated double bonds and anticipating that the

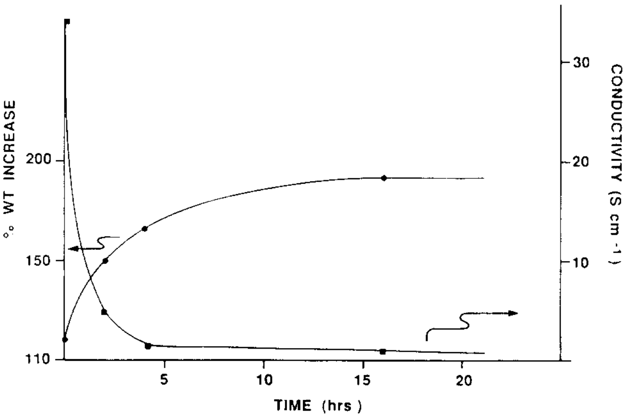

Figure 1 Variation in weight and conductivity as a function of time observed in films of dedoped polypyrrole *p*-toluene sulphonate in DMSO

Table 1 Resonance Raman vibrational frequencies of polypyrrole grown on steel anodes

λe[a] (nm)	ν_2 (cm^{-1})	n_{max}[b]
459.9	1520	12.1
435.0	1530	10.1
415.0	1536	9.0

[a] λe is the laser exciting wavelength

[b] n_{max} is the longest conjugated polyene sequence observed

presence of the ring nitrogen would have little influence on the absorption wavelength, it is possible to relate the conjugation length in polypyrrole to absorption peaks appearing in a long polyene sequence, such as in the case of *trans* polyenes reported in PVC degradation[14]. On this basis the 410 nm peak observed in polypyrrole corresponds to approximately 9–10 conjugated double bonds or 5 pyrrole rings. This implies that the conjugation length may be quite short.

Resonance Raman spectroscopy. Maddams and coworkers[6,14] have reported the frequency shift in the resonance Raman spectra of long conjugated polyenes (as in the case of lightly dehydrochlorinated PVC) to be in the range 1542–1461 cm^{-1} corresponding to polyene sequence lengths, n, of 8–70 nm. This technique is well suited to the analysis of solid insoluble polymers e.g. polypyrrole, if two assumptions are made.

1. The derived equation $\nu_2 = 1461 + 151.24\,e^{-0.07808n}$ cm^{-1} (ref. 7) still applies to mixed *trans/cis* polyene sequences as found in polypyrrole as long as conjugation remains intact.
2. The presence of NH in the pyrrole ring does not shift the position of ν_2 appreciably, so the equation still applies.

Small shifts arising from these two assumptions are considered to be relatively unimportant compared with the error associated with lack of resolution of overlapping peaks corresponding to $n-1$, n, $n+1$.

Samples prepared on stainless steel anodes were analysed. These produced results which are displayed in *Table 1*. Effectively, the data show that no resonance was observed for laser exciting wavelengths, λe, longer than 457.9 nm, i.e. the longest observable polyenes correspond to $n = 12$ or 6 pyrrole units.

Solid state ^{13}C n.m.r. spectrum. *Figure 2* shows the ^{13}C n.m.r. spectrum of polypyrrole BF_4. The resonance at 134 ppm corresponds to the aromatic resonances of the pyrrole ring as previously proposed by Clarke *et al.*[15]. The two broad bands on either side of this aromatic peak are spinning side bands probably caused by inhomogeneity in the packing of the sample in the rotor. The peak located on top of the right hand side band at 34 ppm occurs at methylene resonances.

DISCUSSION

Results of the swelling experiments indicate that the average molecular weight between crosslinks is quite large. This is in contrast to previous estimates of the chain lengths in polypyrrole[1]. Short oligomeric chains are unlikely considering the reasonably good mechanical properties of this polymer[16]. A picture that emerges from the current study is that of chains consisting of linear segments of 25–65 monomer units between crosslinks. Within these short conjugated segments (spanning over 6 pyrrole units at most) are interposed. Discontinuities in conjugation may arise by various means: covalently bound oxygen[17], radical defects[18], or formation of sp^3 carbons[15] (such as methylene groups) in the α or β positions. Defects in the α or β positions may arise during the polymerization process proceeding via addition rather than via substitution steps which leads to the formation of long conjugated sequences. This would account for the excess of hydrogens found by elemental analysis without the necessity to invoke short chain lengths. The presence of methylene groups is supported by the solid state ^{13}C n.m.r. data (shown in *Figure 2*), where a resonance observed at 34 ppm is consistent with this structure. Although another source of methylene resonances such as the products of the reaction between the chain ends and the water cannot be completely ruled out, there are probably insufficient chain ends to yield a peak of such relative magnitude.

Batchelder, Bloor *et al.*[19] have recently described the characterization of polypyrrole films by resonance Raman spectroscopy. It was noted that a film grown on Pt at −11°C displays an intense band at 1493 cm^{-1} in addition to one at 1569 cm^{-1}, whereas a film grown on Pt at room temperature has only one strong band at 1576 cm^{-1}. A strong band at this latter frequency also occurs in the case of films grown on Al and Si. By assuming that the relationship between ν_2 and n reported by Baruya *et al.*[6] applies to the bands at 1493 cm^{-1} and 1576 cm^{-1}, which arise from the ν (C=C) mode, n values of 20 and 3.5, respectively, are calculated. These are, of course, average estimates of conjugation lengths. In the case of the 1576 cm^{-1} band the estimate may be subject to an absolute error. This is the result of an extrapolation because the value 1576 cm^{-1} lies outside the limits of the calibration data used in establishing the relationship between ν_2 and n[6]. Nevertheless, it is very evident that the conjugation lengths of samples prepared at room temperature are small, in agreement with the present study.

The film prepared on Pt at −11°C provides a clear exception to this pattern. Although it does contain short conjugated sequences it also has an appreciable concentration of much longer sequences with an average n value of 20 and, hence, a sharp bimodel distribution of sequence lengths. Presumably, the effect of the lower

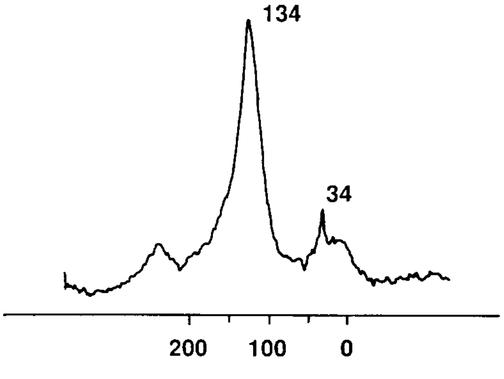

Figure 2 ^{13}C cross polarization magic angle spinning n.m.r. spectrum of solid state polypyrrole tetrafluoborate

preparation temperature is to reduce the incidence of defect structures, thus increasing the average sequence length of some units. Why this occurs in a clear bimodel way, and is not manifest as a broad distribution of sequence lengths, is an open question at present.

The short conjugation length in polypyrrole has important consequences on the mechanism of electrical conduction in polypyrrole. The most commonly accepted mechanism is attributed to bipolarons. Theoretical studies have indicated that the optimum size for bipolarons in polypyrrole is of the order of four pyrrole units[20]. If this is the case, then bipolarons are unable to move very far along the chain. Hence they must hop from one chain to the next to provide electrial conduction. In essence, the bipolarons are pinned between two defects. Experimentally, it has been shown that temperature dependence of conductivity is of the form $\sigma(T)=\sigma_0 \exp[-(T_0/T)^{1/4}]$ (ref. 21), which implies a variable range hopping mechanism. The thermoelectric power is small and positive[21] in line with the idea that conduction may not be entirely metallic in nature. Pfluger *et al.*[22] indicate that long conjugation lengths are not required to explain the observed ultraviolet photo-emission spectra of polypyrrole, although they do not discount the possibility of long conjugated sequences being present. Electron diffraction studies[23] indicate a low degree of order in polypyrrole. All these observations are consistent with short conjugation lengths in polypyrrole. Hence it must be questioned whether polypyrrole should be viewed as a linear metallic chain structure as has been frequently done in the past.

CONCLUSIONS

Although the application of the Flory–Huggins theory of polymer solutions to calculate the average molecular weight between crosslinks is only an approximate method, it does provide us with an estimate of $\bar{M}_x$. However, owing to the uncertainty in χ_1 only a range of values for $\bar{M}_x$ can be estimated. This was found to be in the range of 25–65 monomer units.

Maximum conjugation lengths in polypyrrole determined from u.v. and resonance Raman spectroscopy agree with each other and are much smaller than the averge molecular weight between crosslinks. This result has serious ramifications on the mechanisms of electrical conduction in polypyrrole. It supports a variable range hopping mechanism, whereby conduction occurs via hopping from one chain to the next and backbone conduction probably only plays a minor part. The short conjugation lengths probably arise from the formation of sp^3 centres created during the polymerization process or via other defect structures such as covalently bound oxygen or radical centres.

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REFERENCES

1 Nazzal, A. and Street, G. B. *J. Chem. Soc., Chem. Comm.* 1984, 83
2 Yakushi, K., Lauchlan, L. J., Clarke, T. C. and Street, G. B. *J. Chem. Phys.* 1984, **79**, 4774
3 Flory, P. J. 'Principles of Polymer Chemistry', Cornell University Press, Ithaca, NY, 1953
4 Flory, P. J. *J. Chem. Phys.* 1942, **10**, 51
5 Huggins, M. L. *Ann. N.Y. Acad. Sci.* 1942, **43**, 1
6 Baruya, A., Gerrard, D. L. and Maddams, W. F. *Macromolecules* 1983, **16**, 478
7 Flory, P. J. *J. Chem. Phys.* 1950, **18**, 108
8 Huggins, M. L. *J. Chem. Phys.* 1941, **9**, 440
9 Bristow, G. M. and Watson, W. F. *J. Chem. Soc. Faraday Trans.* 1958, **54**, 1731
10 Rodriguez, F. 'Principles of Polymer Systems', McGraw-Hill, New York, 1983
11 Hildebrand, J. H. and Scott, R. L. 'The Solubility of Nonelectrolytes', 3rd edn. Reinhold, New York, 1950
12 Hoy, K. L. *J. Paint Tech.* 1970, **42**, 76
13 Street, G. B., Clarke, T. C., Krounbi, M., Kanazawa, K. K., Lee, V., Pfluger, P., Scott, G. C. and Weisser, G. *Mol. Cryst. Liq. Cryst.* 1982, **83**, 253
14 Maddams, W. F. In 'Degradation and Stabilization of PVC' (Ed. E. D. Owens), Elsevier, London, 1984
15 Clarke, T. C., Scott, J. C. and Street, G. B. *IBM J. Res. Develop.* 1983, **27**, 4
16 Bloor, D., Hercliffe, R. D., Galiotis, C. G., Young, R. J. in 'Electronic Properties of Polymers and Related Compounds' (Eds M. Mehring and S. Roth), Series in Solid State Sciences, **63**, 179, Springer, Berlin, 1985
17 Nishakawa, O. and Kato, H. *J. Chem. Phys.* 1985, **85**, 11
18 Scott, J. C., Pfluger, P., Krounbi, M. and Street, G. B. *Phys. Rev. B* 1983, **28**, 2140
19 Cheung, K. M., Smith, B. J. E., Batchelder, D. N. and Bloor, D. *Synth. Met.* 1978, **21**, 321
20 Bredas, J. L. *Mol. Cryst. Liq. Cryst.* 1985, **118**, 49
21 Kanazawa, K. K., Diaz, A. F., Gill, W. D., Grant, P. M., Street, G. B., Clarke, T. C. and Kwak, J. F. *Synth. Met.*, 1980, **1**, 329
22 Pfluger, P., Gubler, V. M. and Street, G. B. *Solid State Comm.* 1984, **49**, 911
23 Geiss, R. H., Street, G. B., Volksen, W. and Economy, J. *IBM J. Res. Develop.* 1983, **27**, 321