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Polymer 41 (2000) 4065–4076

polymer

Electrohydrodynamic polymerisation of water-soluble poly((4-(3-pyrrolyl))butane sulfonate)

P.C. Innis, Y.C. Chen, S. Ashraf, G.G. Wallace*

Intelligent Polymer Research Institute, University of Wollongong, Northfields Avenue, Wollongong NSW 2522, Australia

Received 21 July 1999; accepted 19 August 1999

Abstract

Water-soluble conducting poly((4-(3-pyrrolyl))butane sulfonate) [PPyBS] has been synthesised using an electrohydrodynamic processing technique using high-surface-area porous reticulated vitreous carbon anode and cathodes. Optimisation studies for the synthesis of the homopolymer established maximum molecular weights and electrical conductivities of ca. 10,500 Da and 0.01 S/cm, respectively. It was found that only short electrosynthesis times are needed to initiate polymerisation that then continues to completion simply upon standing.

Keywords: Electrohydrodynamic polymerisation; PPyBS; Conducting polymers

1. Introduction

Applications for conducting polymers can be found in areas as diverse as chemical sensors and biosensors [1], membrane separations [2], biomaterials [3–5] and corrosion inhibition [6,7]. For many of these applications polypyrroles have been of particular interest in that they are readily synthesised from aqueous media and/or at low potentials.

All of the above applications have significant commercial potential; however, this has in most cases, not been fully exploited due to the lack of convenient polymer processing and device fabrication protocols. For example, polymerisation of pyrrole usually results in formation of an insoluble, infusible material not amenable to subsequent fabrication.

In attempts to overcome this problem, solubility has been induced by attaching alkyl [8,9] groups to the pyrrole monomer prior to polymerisation. This does result in markedly enhanced solubility in organic media. Previously we have shown that electropolymerisation could be used to produce alkylated polypyrrole with high (400 g/l) solubility and reasonable (up to 30 S/cm) conductivity [10].

Alternatively, alkylsulfonate groups have been attached to pyrrole to render the polymer water soluble [11]. Both electrochemical and chemical oxidation have been used to produce 3-substituted alkylsulfonated pyrrole [12]. Electrochemical polymerisation was carried out using acetonitrile as solvent to form a solid deposit on the electrode. Alternatively, $FeCl_3$ was used as oxidant. Conductivities in the range 0.001–0.500 S/cm were obtained with polymers in the lower conductivity range obtained from chemical polymerisation. Others [13,14] have prepared homopolymers and copolymers of polypyrrole with alkyl sulfonate groups attached via the N-group. This N-group substitution decreases the inherent conductivity of the polymer.

In the course of this work we have investigated the electrochemical oxidation of alkyl sulfonate pyrrole under hydrodynamic control. Production of the polymer in a flow-through electrochemical cell described by us previously [15] has been investigated.

2. Experimental

2.1. Materials

Sodium [4-(3-pyrrolyl)] butane sulfonate (PyBS) was synthesised at IPRI (see below). Sodium nitrate 99% and methanol (HPLC grade) were obtained from BDH Chemicals. 4-Toluene sulfonic acid sodium salt 98%+ was supplied by Merck–Schuchardt Co. Disodium hydrogen orthophosphate anhydrous (AR grade) was from AJAX Chemicals. Tetrabutylammonium dihydrogenphosphate (1 M) was from Aldrich Chemical Co. All solutions were prepared with de-ionised Milli-Q water.

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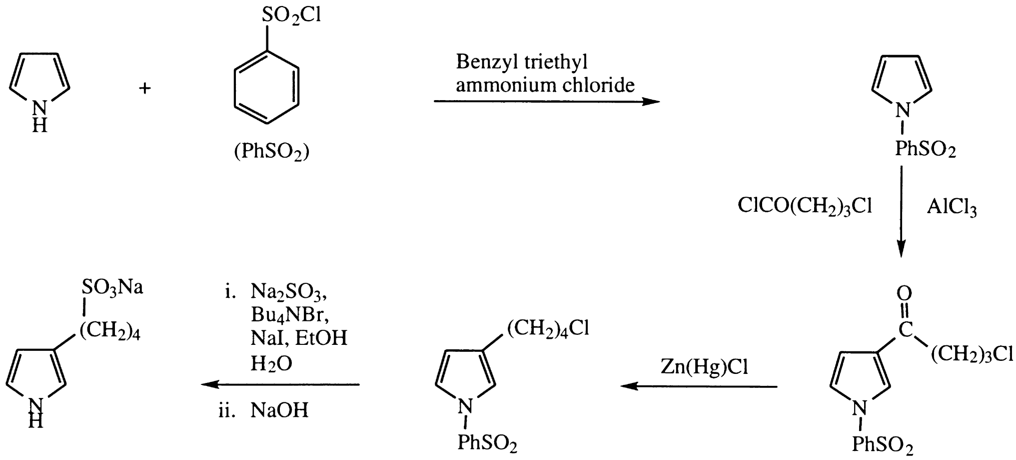
* Corresponding author. Tel.: +61-2-4221-3319; fax: +61-2-4221-3114.
E-mail address: g.wallace@uow.edu.au (G.G. Wallace).

PII: S0032-3861(99)00645-X



Scheme 1.

2.2. Synthesis of 4-(3-pyrrolyl) butanesulfonic acid, sodium salt

3-Alkylsodiumsulfonate pyrrole was synthesised as described previously [11] and as summarised in Scheme 1. The preparation consisted of the following steps:

1. The synthesis of phenylsulfonylpyrrole by the reaction of pyrrole with phenylsulfonyl chloride,
2. The Friedel–Craft acylation of 4-chlorobutyryl chloride with phenylsulfonyl pyrrole,
3. Clemenson reduction of the ketone group, and
4. Conversion of chloride to the sulfonated sodium salt and removal of phenylsulfonyl group by subsequent alkaline hydrolysis afforded the required product.

The product was recrystallised three times from 95% ethanol and characterised by ^{1}H NMR; IR and fast atom bombardment mass spectrometry (f.a.b.m.s).

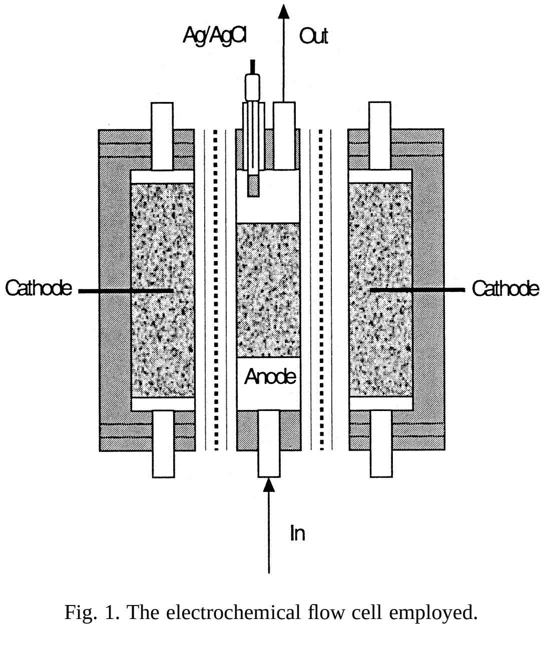


Fig. 1. The electrochemical flow cell employed.

2.3. The electrochemical cell

PPyBS was synthesised electrochemically by passing the anolyte solution through an electrochemical flow-through cell (Fig. 1). The cell consisted of an anode compartment filled with reticulated vitreous carbon (RVC) with a 100 pore per inch (PPI) porosity (surface area 65.6 cm^2/cm^3). This anode was sandwiched between two RVC cathodes of similar dimensions and separated by an anion exchange membrane (Neosepta) to prevent mixing between the anode and cathode compartments. All electrode potentials were measured relative to a Ag/AgCl reference electrode. Princeton Applied Research (PAR) model 363 and 273A Potentiostat/Galvanostats were used for the potentiostatic polymerisation. A MacLab interfaced with a Macintosh computer was employed for recording the PAR model 363 electropolymerisation data and a PC interface was used to record the PAR 273 electropolymerisation data.

2.4. Conductivity

Electrical conductivity was measured for each soluble and deposited polymer fraction after dialysis (12,000 Da cut-off) against water. The polymer was then pressed to a pellet under 6 tons and conductivity was measured using the standard four point probe technique.

2.5. GPC

GPC was performed using a Shimadzu LC-10AT Liquid Chromatograph system or Waters (Millenium^{32} V3.05) in conjunction with Waters Ultrahydrogel 120 and 250 columns. The mobile phase consisted of 80% (0.2 M $NaNO_3$(aq) and 0.01 M Na_2HPO_4(aq)) + 20% methanol. A flow rate of 0.8 ml/min was used. UV–vis spectrophotometric detection

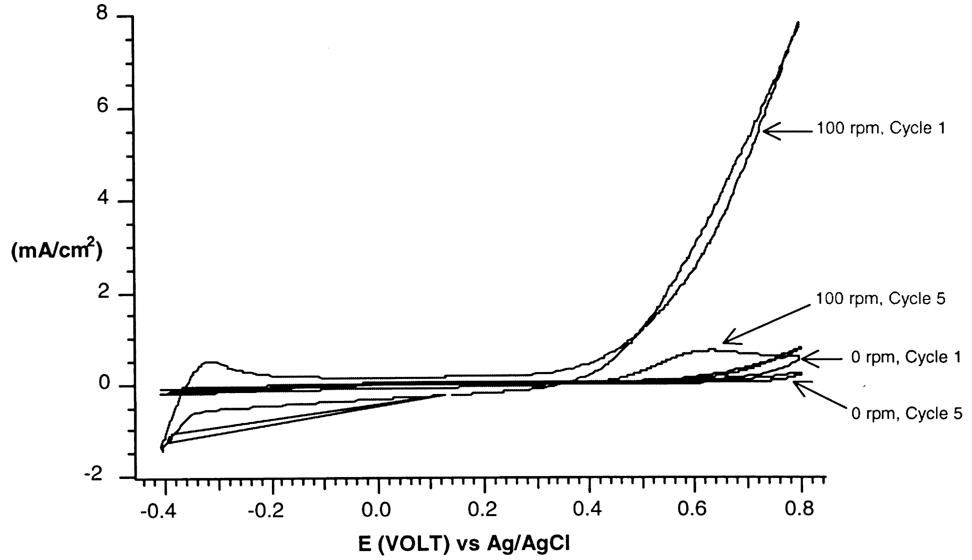


Fig. 2. The effect of electrode rotation on PyBS. Cyclic voltammetric responses of a platinum disc electrode ($D = 5.0$ mm) in an aqueous solution containing 0.10 M PyBS. Potential range: -0.40 to $+0.80$ V vs. Ag/AgCl. Scan rate: 50 mV/s.

($\lambda = 254$ nm) was employed. 50 μl injections were used throughout this work.

2.6. HPLC

The monomer conversion rate was measured by using a Waters 501 HPLC with an Alltima C18 column. The mobile phase was 50% methanol/water (0.005 M tetrabutyl ammonium phosphate), and a flow rate of 0.6 ml/min was used. UV–vis spectrophotometric detection ($\lambda = 236$ nm) was employed. Injection volumes were 50 μl.

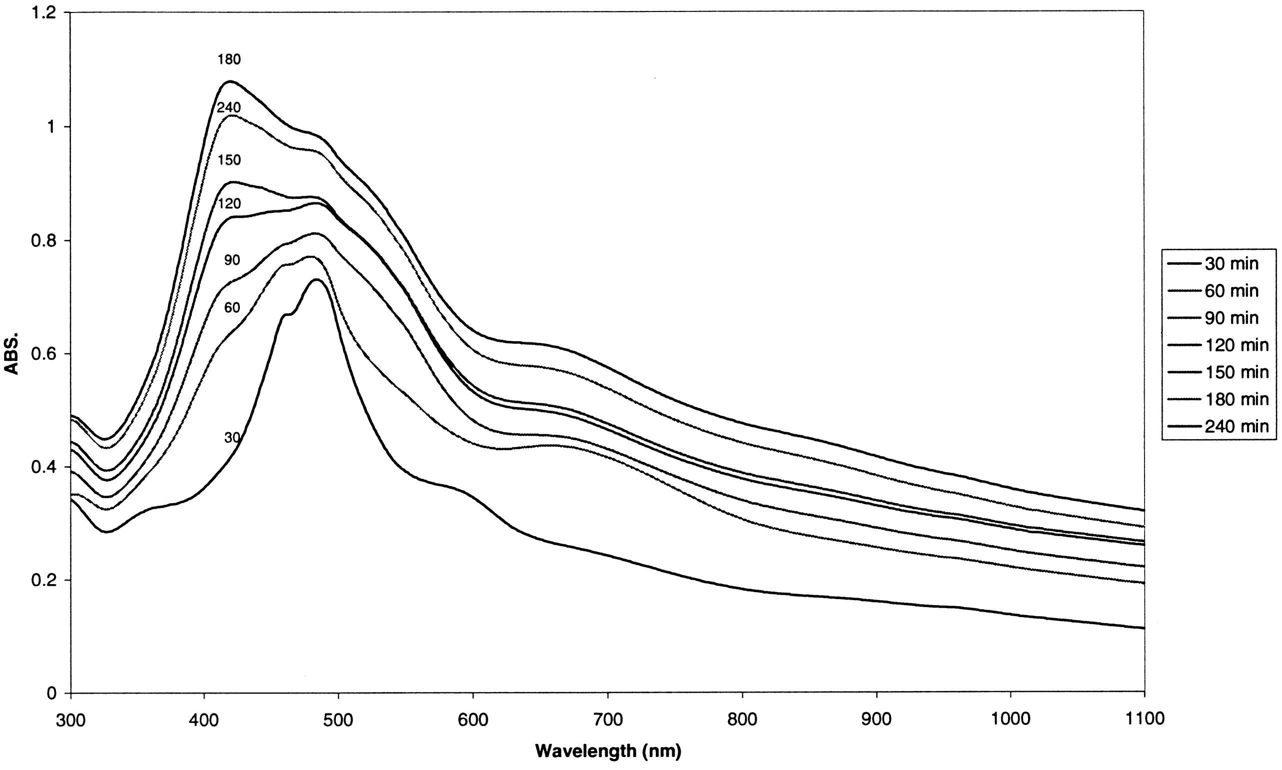


Fig. 3. Uv–vis spectra obtained during polymerisation of PyBS over a 4 h period.

Table 1
Analysis of the molecular weight data after 4 h of synthesis

	Solution fraction	Deposited fraction
M_n	7032	9579
M_w	10 410	21 598
PDI (M_w/M_n)	1.480	2.254

2.7. UV–visible spectroscopy

A Shimadzu UV–visible spectrophotometer (UV-1601) was employed throughout this work.

3. Results and discussion

3.1. Stationary/rotated electrode experiments

Initially cyclic voltammetry and rotated ring-disc electrode (RRDE) studies were carried out in a conventional three electrode electrochemical cell. Using cyclic voltammetry the PyBS monomer was found to oxidise at approximately 0.70 V (Fig. 2). Chronamperometric studies confirmed that the monomer was oxidised at this potential. Interestingly, it was observed that while soluble material was produced, an insoluble passivating layer was also deposited on the electrode using either cyclic voltammetric or constant potential conditions. This could be overcome by rotating the electrode, mitigating the deposition of the passivating products (Fig. 2). It was found that with the introduction of hydrodynamic control, currents observed on the initial sweep to anodic potentials were similar to those observed with no rotation. However on subsequent scans the introduction of electrode rotation caused the oxidation currents observed to increase and become constant rather than to decrease. Similar behaviour was observed at all rotation rates investigated (up to 2000 rpm). This suggests that even for the homopolymer there is some initial deposition on the electrode which becomes constant. Without rotation this layer decreases the subsequent electrochemical efficiency; with rotation the electrochemical efficiency on subsequent scans increases slightly.

3.2. Preliminary homopolymer synthesis in the flow-through cell

PPyBS was synthesised electrochemically by passing the anolyte solution through the electrochemical flow-through cell (Fig. 1). Synthesis was carried out under the following conditions:

1. Anoltye: 0.1 M $PBS_{(aq)}$ and 0.2 M $NaNO_{3(aq)}$ (100 ml by SVF).
2. Catholyte: 0.5 M $NaNO_{3(aq)}$ (500 ml by SVF).
3. $E_{applied}$: +0.75 V vs. Ag/AgCl for 4 h.
4. Flow rate: 120 ml/min.

UV–visible spectra were recorded at 30 min intervals throughout the synthesis (Fig. 3). Four absorption peaks were evident. The peak at approximately 500 nm was greatest in magnitude early in the polymerisation. However, peaks at 450 and 400 nm became more prominent as the polymerisation proceeded. The absorption peak at ≈700 nm did increase with polymerisation time. These spectra are similar to those obtained by other workers for sulfonated polythiopheses [16]. After 4 h of synthesis the soluble fraction of the PPyBS was dialysed to remove

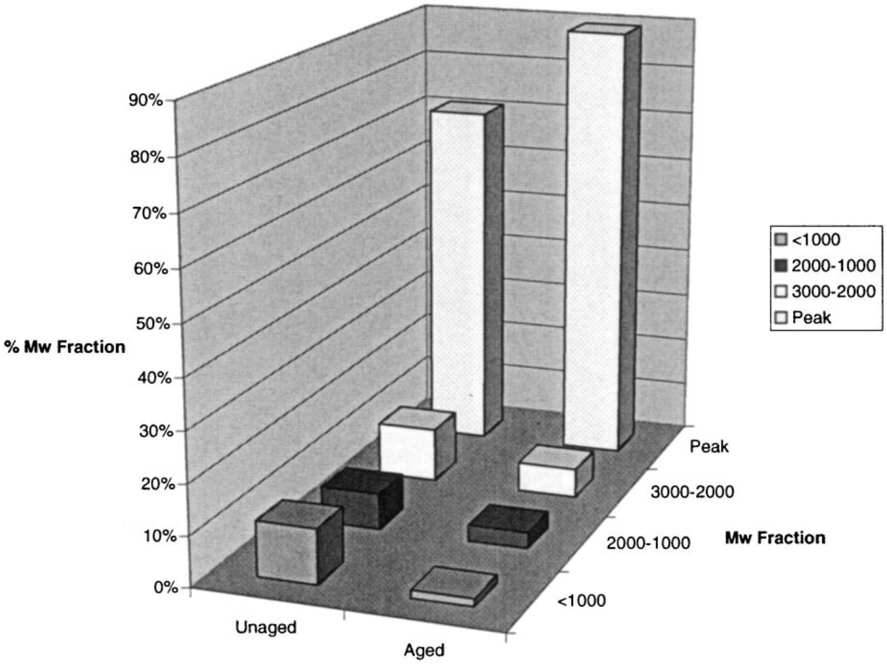


Fig. 4. Effect of ageing on GPC analysis.

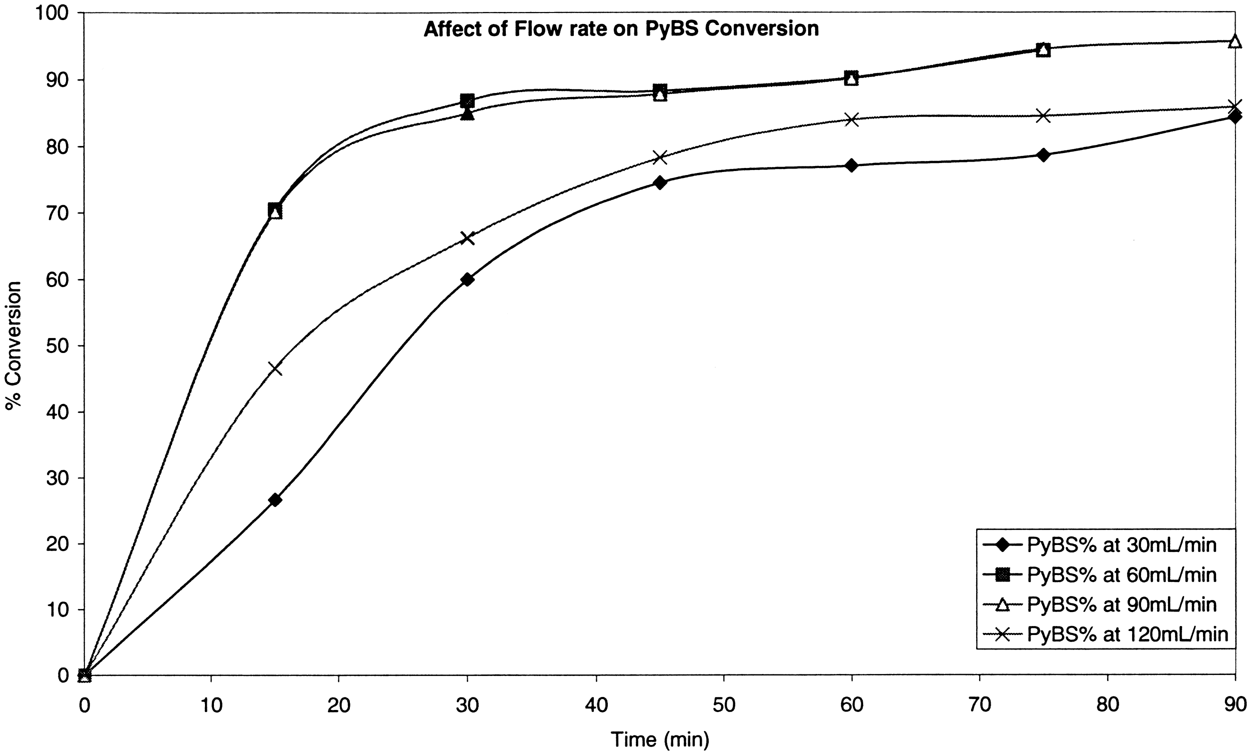


Fig. 5. The effect of electrolyte flow rate on PyBS conversion.

excess monomer and supporting electrolyte, and GPC analysis was performed. There was a significant fraction of polymer deposited at the RVC anode surface. It was found that this fraction could be removed by washing the RVC anode in ca. 300 ml of water. This fraction was also dialysed and molecular weight analysis performed.

The molecular weight determinations, Table 1, show that the solution fraction has a relatively tight molecular weight distribution (PDI 1.48). The deposited fraction of the PPyBS was of a higher molecular weight polymer and had a broader molecular weight distribution (PDI 2.25). Using GPC it was found that the relative concentration of the PPyBS in the synthesis solution decreased dramatically after the first 30 min of synthesis. Analysis of the GPC data at 0.5, 1, 2, 3 and 4 h intervals showed no significant molecular weight variations. These results indicate that the bulk of the water-soluble polymer was formed in the early stages of electrosynthesis. The decrease in PPyBS concentration may be due to the polymer depositing at the anode (RVC) surface during prolonged electrosynthesis.

The molecular weight distributions of the polymer were observed to vary within the first 24 h after synthesis (Fig. 4). GPC analysis within minutes of sampling showed a significant amount ($\approx$10%) of monomer present in the solution. However, this excess monomer is subsequently converted to polymer upon standing for one day. Given that the polymer system has significant post-synthesis reactivity, all samples were left to stand over 24 h before performing any further characterisation.

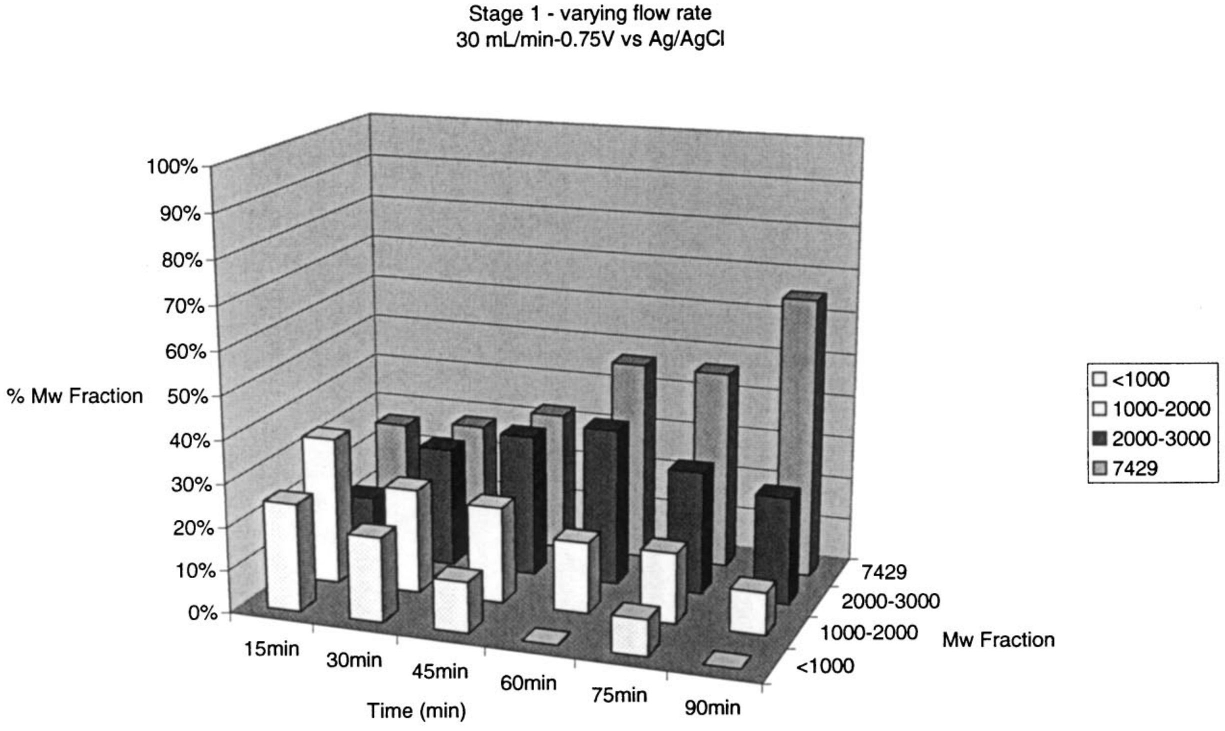
3.3. More detailed studies in the flow-through cell

In order to avoid the loss of polymer product by deposition on the RVC electrode surface the electropolymerisation process was then optimised over a shorter synthesis time (90 min). The effect of flow rate, applied potential, concentration of [PyBS] and electrolyte composition on the formation of PPyBS was investigated. The optimisation process has been divided into four stages. For each experiment, polymer yield, molecular weight (GPC), UV–visible spectra, monomer consumption (HPLC) and electrical conductivity were measured. A total synthesis time of 90 min was used for each experiment with sampling intervals every 15 min for GPC, HPLC and UV–vis determinations. Yield and electrical conductivity were determined after 90 min of synthesis and dialysis. The polymerisation time was arbitrarily chosen.

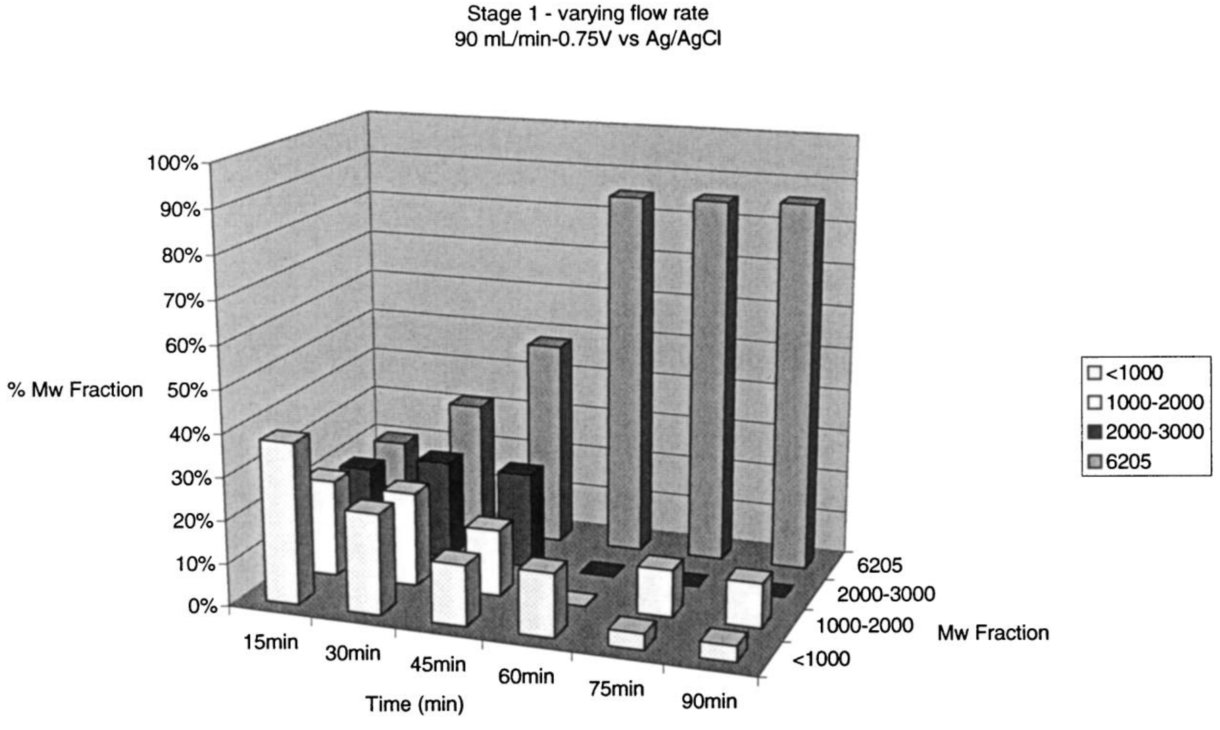
3.3.1. Stage 1. Optimisation of flow rate

The optimum flow rate was determined by varying the flow rate from 30 to 120 ml/min in 30 ml increments using 0.1 M PyBS, 0.2 M $NaNO_3$ feed solution and a polymerisation potential of 0.75 V.

The effect of flow rate on the conversion of the PyBS monomer to PPyBS over the range 30–120 ml/min was investigated using both HPLC and GPC techniques (Fig. 5). The use of flow rates at 90 and 120 ml/min was found to give better monomer conversion than the lower flow rates and had similar rates of monomer conversion. Conversions



(a)



(b)

Fig. 6. The effect of flow rate of (a) 30 and (b) 90 ml/min on the molecular weight fraction distribution of PPyBS.

of greater than 85% were achieved within the first 30 min of synthesis. At the lower flow rates the rate of monomer conversion decreased.

The effect of flow rate on the formation of PPyBS was monitored using GPC (Fig. 6). The molecular weight distributions have been grouped into four classes of less than 1000, 1000–2000, 2000–3000 Da and the maximum observed (peak) molecular weight. Each class has been

Table 2
The effect of flow rate on electrical conductivity of polymer

Flow Rate (ml/min)	Conductivity (S/cm)
30	1.90×10^{-3}
60	2.50×10^{-3}
90	10.0×10^{-3}
120	2.30×10^{-3}

expressed as a percentage of the total polymer observed in the GPC analysis. At 30 ml/min (Fig. 6(a)) there were approximately equal amounts of each polymer fraction present. This trend was reversed after 60 min of synthesis when the lower molecular weight fractions were converted to higher molecular weight species. After 90 min of synthesis there were still significant amounts of lower molecular weight fractions, although continuing the synthesis for a longer time may have reduced this. A similar trend was observed when using a flow rate of 60 ml/min. Using a flow rate of 90 ml/min (Fig. 6(b)) the lower molecular weight fraction was almost completely removed. Interestingly, the molecular weight of the largest fraction at 6200 Da did not increase significantly after consumption of the lower molecular weigh components. The rapid increase in molecular weight that was observed for the 30–90 ml/min sample occurs when the monomer had undergone 80% or better conversion. At 120 ml/min the trends observed at the lower flow rates are reversed, with the lower molecular weight fractions becoming more significant with increasing synthesis time.

The effect of flow rate on electrical conductivity is shown in Table 2. The highest conductivity of 0.01 S/cm was observed when a flow rate of 90 ml/min was employed. The observed electrical conductivity was dependent upon the molecular weight distribution, with the lower conductivities arising from the presence of the lower molecular weight fraction.

Although the highest peak molecular weight was achieved at the lowest flow rate of 30 ml/min this also resulted in the formation of a significant amount of low molecular weight polymer, poor monomer conversion, reduced product purity and lower conductivity. From the above results it was determined that an electrolyte flow rate of 90 ml/min was the optimal, maximising monomer conversion, molecular weight and conductivity.

Table 3
The effect of applied potential on monomer conversion after 90 min and electrical conductivity of polymer

Applied potential (V vs Ag/AgCl)	Conversion (%)	Conductivity (S/cm)
0.55	83	1.60×10^{-4}
0.65	95	1.80×10^{-3}
0.75	96	1.00×10^{-2}
0.85	91	8.60×10^{-5}
0.95	93	7.00×10^{-6}

3.3.2. Stage 2. Optimisation of applied potential

The influence of applied potential over the range 0.55–0.95 V (100 mV increments) on the synthesis was investigated using the optimum flow rate of 90 ml/min, 0.1 M PyBS and 0.2 M $NaNO_3$. The rate of conversion was similar when potentials of 0.65 V or greater were applied (Table 3).

The effect of applied potential on the molecular weight distribution over the synthesis period was determined (Fig. 7). With application of 0.55 V (Fig. 7(a)) a high proportion of low molecular weight species remained throughout the synthesis. Upon application of 0.65 V the low molecular weight species produced during the early stages of synthesis were slowly converted into a high molecular weight product. Similar trends were observed when 0.75, 0.85 or 0.95 V (Fig. 7(b)) was applied. The time required to achieve conversion of 90% (or better) for the highest molecular weight fraction decreased from 60 min at 0.75 V to 15 min at 0.95 V.

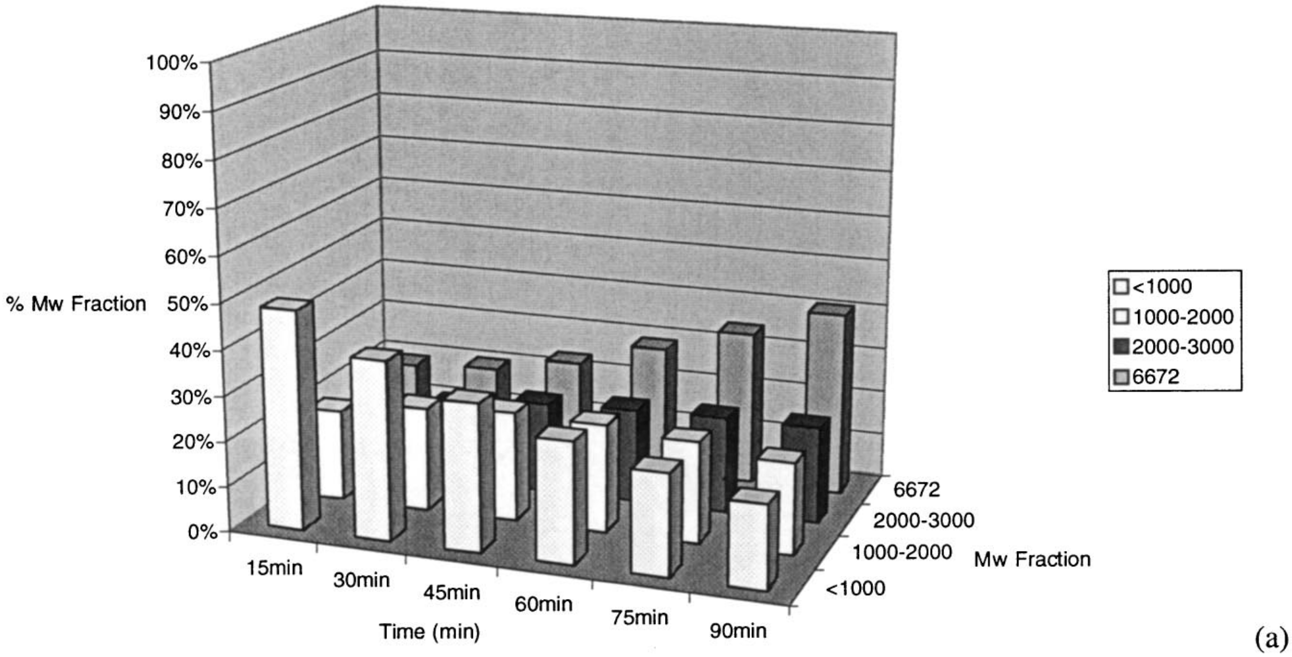
The optimum electrical conductivity (after 90 min) was found to be 0.01 S/cm when a potential of 0.75 V (Table 3) was employed. When higher potentials were employed lower conductivities were obtained. This can be attributed to over-oxidation of the polymer as evidenced by a decrease in intensity of bands at 480–500 nm and at ≈700 nm and an increase in absorption around 400 nm.

The formation of PPyBS can be achieved quickly when a potential between 0.65 and 0.95 V is applied. The molecular weight increases with increased applied potential. However, at potentials higher than 0.75 V there is evidence of significant polymer over-oxidation as illustrated by the UV–vis spectra and conductivity data. The results presented above suggest that the formation of PPyBS is sensitive to applied potential and that prolonged synthesis past the point where the available monomer or low molecular weight oligomer is consumed is detrimental. This suggests that conductivity could be further improved if the synthesis was terminated at the point where these degradative processes are initiated.

3.3.3. Stage 3. Variation of PyBS concentration

The effect of varying the PyBS monomer concentration from 0.05 to 0.10 and 0.15 M was investigated using an applied potential of 0.75 V and a flow rate of 90 ml/min, with 0.2 M $NaNO_3$ as the supporting electrolyte. The influence of monomer concentration on conversion after 90 min of synthesis is shown in Table 4. With the synthesis conditions employed here the use of 0.1 M PyBS results in maximum conversion.

The distribution of the molecular weight fractions during electropolymerisation is shown in Fig. 8 for 0.05, 0.10 and 0.15 M PyBS. Using 0.05 M PyBS (Fig. 8(a)), there is rapid conversion to the highest molecular weight fraction of 8900 Da with the electropolymerisation complete after approximately 45–60 min. Using 0.1 M PyBS (Fig. 8(b)),



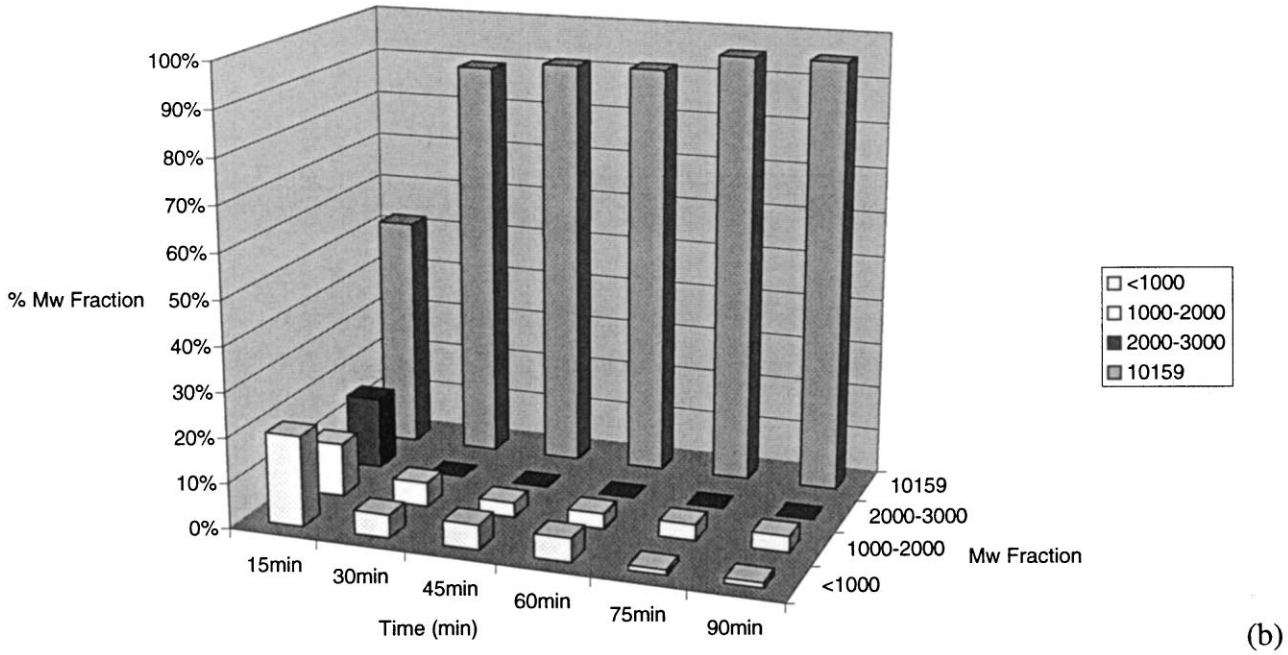


Fig. 7. The effect of applied potential (a) 0.55 and (b) 0.95 V on the molecular weight fraction distribution of P(PyBS).

the conversion is slower but conversion to higher weight polymer is obvious. Using 0.15 M PyBS (Fig. 8(c)), the reaction is clearly incomplete with a large amount of intermediate molecular weight species present.

The effect of monomer concentration on electrical conductivity is shown in Table 4. Under these conditions the optimal conductivity was found to be at 0.10 M PyBS. The conductivity of the sample synthesised at 0.05 M PyBS was noted to be the lowest and was probably due to over-oxidation of the polymer caused by the rapid consumption of the monomer in the early stages of synthesis, as illustrated by Fig. 8(a). At 0.15 M PyBS the electrical conductivity was slightly higher than the 0.05 M PyBS condition but was significantly lower due to incomplete conversion of the polymer under the synthesis conditions being used. It appears that lower molecular weight fractions disrupt the bulk conductivity of the samples prepared.

The optimal monomer concentration was found to be

Table 4
The effect of PyBS monomer concentration on monomer conversion after 90 min and the electrical conductivity of polymer

[PyBS] (M)	Conversion (%)	Conductivity (S/cm)
0.05	83	1.50×10^{-3}
0.10	96	1.00×10^{-2}
0.15	89	1.4×10^{-4}

Table 5
The effect of electrolyte type on conversion of monomer after 90 min and electrical conductivity of the polymer

Electrolyte	Conversion (%)	Conductivity (S/cm)
None	100	5.0×10^{-5}
0.1 M pTS	90	6.2×10^{-3}
0.1 M $NaNO_3$	96	1.00×10^{-2}

0.10 M PyBS as this condition gave the highest electrical conductivity and an intermediate molecular weight of 6200 Da. Although the lower monomer concentration (0.05 M) yields higher molecular weight polymer, the over-oxidation effects that result from the monomer being rapidly consumed in the early stages of synthesis offset this advantage. The highest monomer concentration of 0.15 M exhibited incomplete reaction of the monomer and intermediates. These effects could possibly be avoided if the synthesis time was modified to suit the available monomer to either avoid over-oxidation or incomplete conversion.

3.3.4. Stage 4. Variation of supporting electrolyte

The effect of changing the electrolyte, from 0.2 M $NaNO_3$ to 0.2 M pTS and the use of no additional electrolyte on conversion of monomer was determined (Table 5). An unexpected result was obtained in that the best conversion was found to be in the absence of supporting electrolyte. The use of pTS electrolyte was found to give the most inefficient monomer conversion.

The effect of the supporting electrolyte on the molecular weight distribution was determined. When $NaNO_3$ was used as the supporting electrolyte, formation of a large amount of intermediate oligomers, followed by the conversion of these oligomers to higher molecular weight material was observed (Fig. 9(a)). When pTS was used these intermediate species were less prevalent and the system tended to form the high molecular weight fraction (Fig. 9(b)). Interestingly, when pTS was used, no polymer fraction at 2000–3000 Da was observed. In the case of no electrolyte, no intermediate species were present after 15 min of synthesis, with all of the material converted through to the highest molecular weight fraction (Fig. 9(c)).

The type of electrolyte employed during synthesis had a dramatic effect upon conductivity, as shown in Table 5. The highest electrical conductivity (0.01 S/cm) was observed when $NaNO_3$ electrolyte was used, pTS (0.006 S/cm) was similar. The UV–vis obtained indicated that with both of these electrolytes some over-oxidation (peak at 400 nm) had occurred. The conductivity values obtained with no electrolyte were the lowest at 5.0×10^{-5} S/cm.

Under the conditions investigated the $NaNO_3$ electrolyte gave a polymer with the highest electrical conductivity. The polymer obtained using pTS as electrolyte had a considerably higher molecular weight than that obtained using $NaNO_3$; however, conductivity was of the same order. Given the evidence for the over-oxidation of the polymer in the presence of pTS after 90 min of synthesis, shorter synthesis times may result in better conductivities and a higher molecular weight product. In the case of no electrolyte, this system is inherently predisposed to over-oxidation and as a result should only be used with very short synthesis times (i.e. <15 min). This approach is feasible given the high rate of conversion that can be achieved within the cell.

3.4. Polymer synthesis at shorter times and lower potentials

From the above experiments it was clear that with an applied potential of 0.75 V, a flow rate of 90 ml/min and using 0.1 M PyBS and 0.2 M $NaNO_3$ the conversion of monomer to polymer was nearly complete after 60–70 min (Fig. 6). In an attempt to improve the electrical properties of the final product a shorter synthesis time of 60 min was investigated in order to prevent over-oxidation effects that may occur upon depletion of the monomer.

Using this approach there was no increase in electrical conductivity, after dialysis, as was initially anticipated with the conductivity dropping to less than 10^{-4} S/cm. This would imply that the proposed over-oxidation effects at times up to 90 min were not as significant as first anticipated. This observation is confirmed by UV–vis where the over-oxidation absorption band at ca 400 nm does not dominate the final product after 90 min of synthesis. The lower conductivity may also be due to the presence of low molecular weight fractions.

Data presented in Fig. 7(a) also indicated that the synthesis of PPyBS at 0.55 V was incomplete and that the reaction would have benefited from an extended synthesis time. Synthesis at a lower potential should also prevent the over-oxidation observed in the UV–vis spectra discussed above. Synthesis over 2.5 h gave excellent monomer to polymer conversion (98%). The molecular weight distribution for the polymer produced under these conditions was much improved with a higher molecular weight (M_w 10,675 Da, PDI 1.61) than was observed at shorter synthesis times. The product purity was also greatly improved with only one major synthesis product (93%) being observed. However, no increase in electrical conductivity was observed (0.2×10^{-4} S/cm).

The synthesis of PPyBS in the absence of supporting electrolyte was repeated over 15 min at +0.55 V to determine if the electrical conductivity could be improved. Under these conditions the monomer conversion before standing

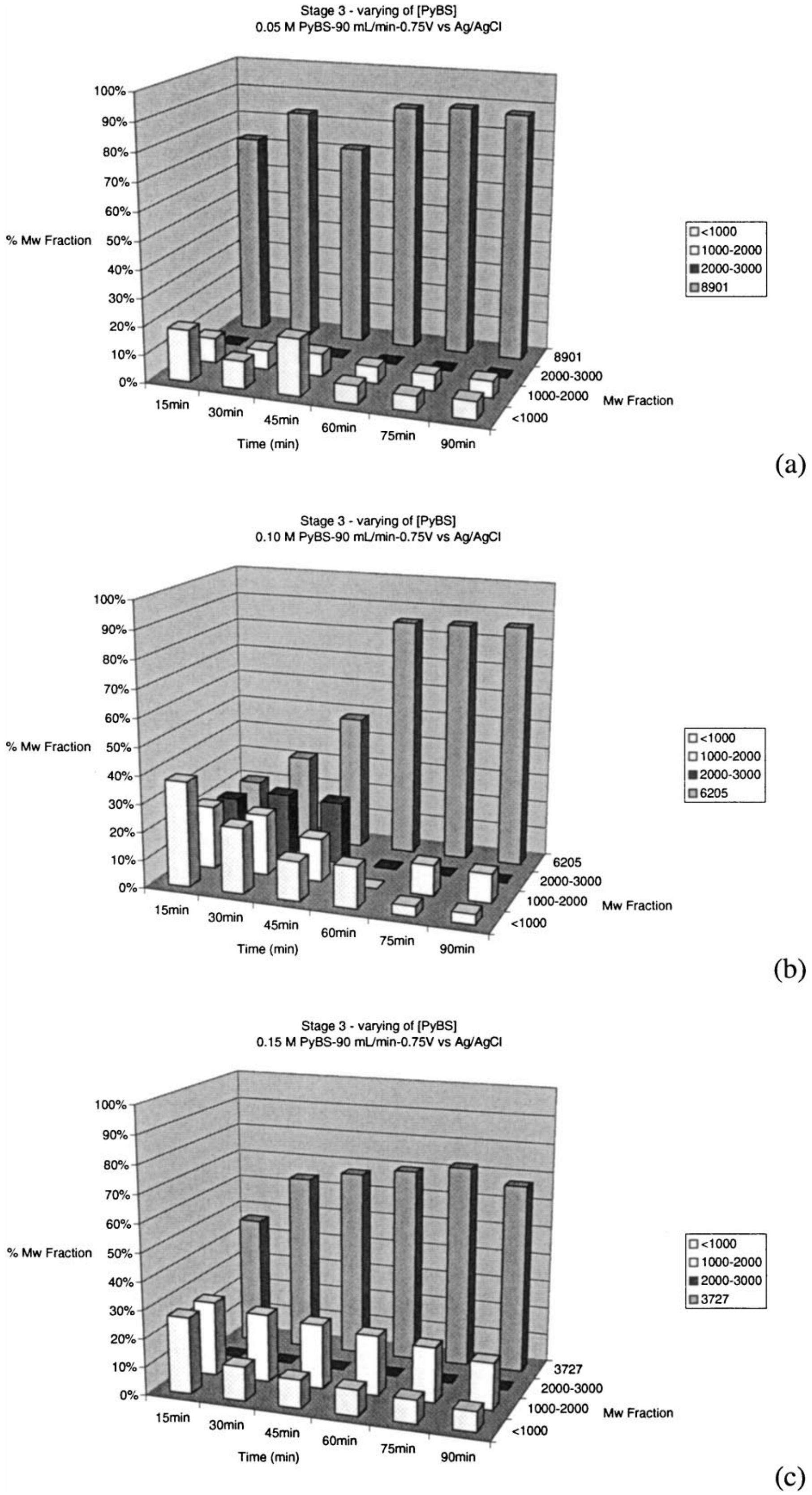


Fig. 8. The effect of PyBS monomer concentration (a) 0.05, (b) 0.10 and (c) 0.15 M on the molecular weight fraction distribution of P(PyBS).

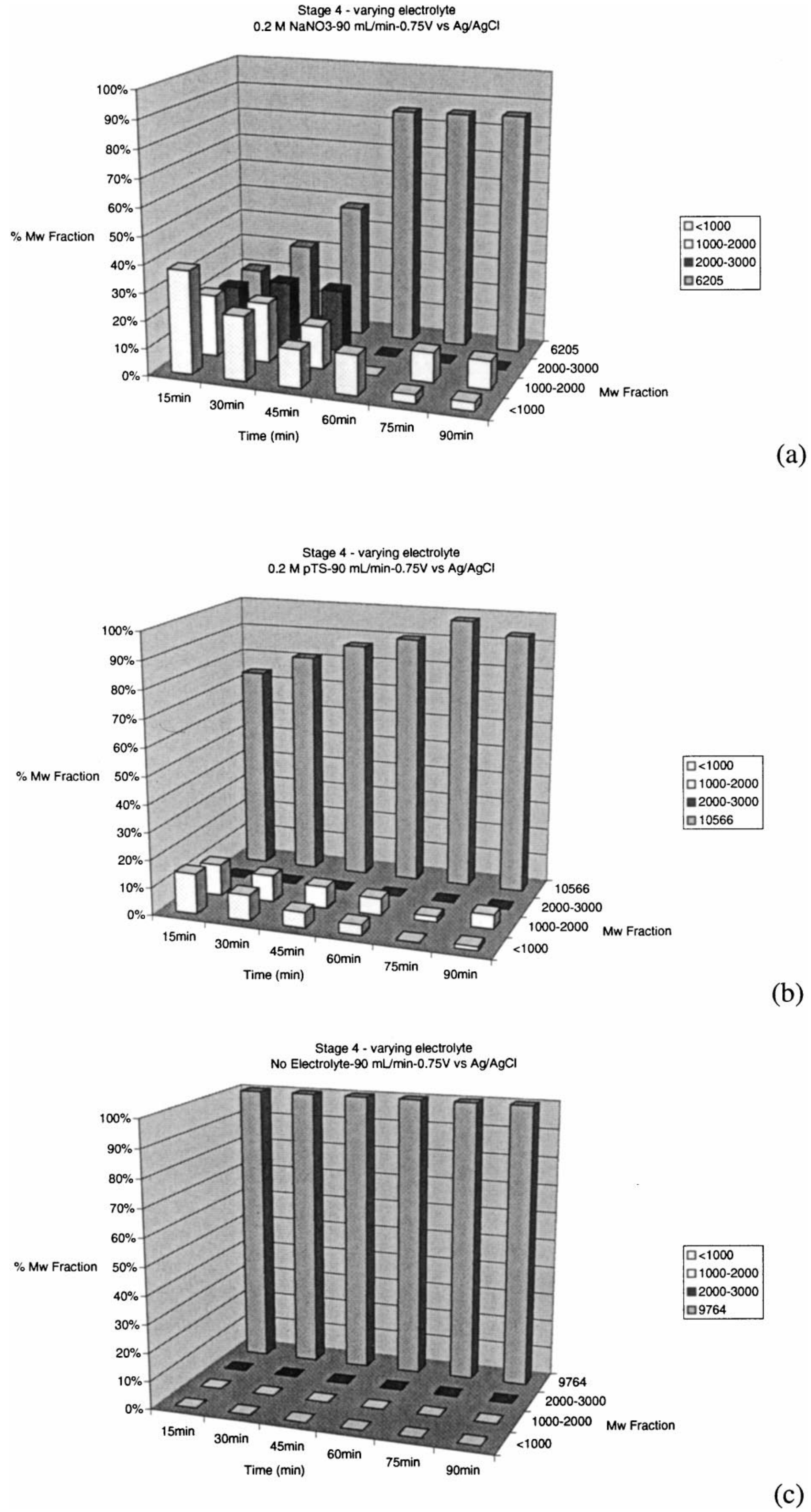


Fig. 9. The effect of (a) $NaNO_3$, (b) pTS and (c) on electrolyte on the monomer weight fraction distribution of P(PyBS).

was observed to be approximately 50%, increasing to 80% after standing for 24 h. A peak M_w of 8007 Da (PDI 1.18) was determined which was slightly higher than was observed when synthesised over 90 min (M_w 6672, Fig. 7(a)). Under these conditions electrical conductivity was observed to decrease to $<10^{-5}$ S/cm, presumably due to the presence of a large number of reaction intermediates.

4. Conclusions

PPyBS can be produced electrochemically using the flow-through cell. The maximum molecular weights obtained are of the order of ≈10,500 Da. Using selected synthesis conditions, low molecular weight fractions could be minimised and over-oxidation avoided. However, under no condition studied was the maximum molecular weight increased. Maximum conductivities of the order of 0.01 S/cm were obtained. When no supporting electrolyte was used it was found that the PyBS monomer was extremely reactive. After only 15 min of electrosynthesis the solution could be left to stand overnight with almost all of the monomer being consumed.

Similarly, excess monomer present after longer synthesis was observed to undergo continued reaction over 24 h after the electrosynthesis was terminated. This reactivity of the monomer once polymerisation is instigated has the potential to provide an interesting route to the formation of copolymers and other novel materials. Studies are currently under way.

Acknowledgements

The Australian Research Council and MM Cables (Australia) are thanked for financial support.

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