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Towards processible poly(pyrrol-2-ylsquaraines)

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Summary

In an attempt to produce a processible poly(pyrrol-2-ylsquaraine) by forming a copolymer of poly(pyrrol-2-ylsquaraine) with polymethylmethacrylate, two synthetic routes were utilised. The first included forming the polysquaraine and then polymerising the attached methacrylate groups to form the desired product and the second proceeded *via* the preformed methacrylate polymer, containing *N*-alkylpyrrole side chains, which was then condensed with squaric acid. Difficulties arose in the first route when the polysquaraine product was found to be insoluble, hence preventing any further polymerisation but partial solubility during the second procedure did allow bissquaraines to be formed and, as a consequence, the resultant product exhibited fluorescent properties. Yet the desired processible poly(pyrrol-2-ylsquaraine) was not achieved.

Introduction

In a recent study we discovered that poly(1-octadecylpyrrol-2-ylsquaraine) (*P-Py*) was soluble in chloroform (1). This enabled the material to be both analysed by a variety of chemical techniques and deposited as a Langmuir-Blodgett (LB) thin film. Spectroscopic analysis revealed that *P-Py* consisted of a mixture of 1,3- and 1,2-squarate units with the average number of repeat units being in the order of 10s of units. Surface studies on deposited thin films of *P-Py* showed that the long alkyl chains did not promote any molecular ordering. Instead, the films were very convoluted with the minimum thickness being *ca.* 16 Å which indicated that the alkyl chains were arranged almost parallel to the substrate surface. The use of specific long alkyl chains would therefore

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seem unnecessary for molecular ordering in favour of shorter chains which would still allow solubility of the polyarylene backbone. Concurrent experiments on the depositional characteristics of *P-Py* by other techniques have indicated that due to the relatively short polymeric lengths of the backbone, this material does not form uniform dip-coated or spin-coated films. Poly(pyrrolylsquaraines) are worth studying because these systems exhibit both second-order (1) and third-order (2) nonlinear optical effects but these polymers need to be processed in a more practical form.

In an attempt to improve the processibility of poly(pyrrolylsquaraine) we decided to produce a copolymer by grafting it onto a well-known processible polymer, polymethylmethacrylate (*PMMA*). In this case we do not necessarily define processibility as meaning solubility, instead a means by which the polymer can be fabricated, either by chemical and / or thermal treatment, into a useful form. To achieve this, two experimental approaches were considered. The first (i) was to synthesise poly{[2-(*N*-pyrrolyl)ethyl methacrylate]squaraine} and then polymerise the methacrylate groups to form the *PMMA* backbone, and the second (ii) through the use of poly[2-(*N*-pyrrolyl)ethyl methacrylate] which would then be condensed with squaric acid to form the desired product, *P-Sq* (Fig. 1). However, before proceeding *via* route (i) it was necessary to determine the solubility of the precursor polysquaraine, hence poly{[2-(*N*-pyrrolyl)ethyl acetate]squaraine} (*P-PES*) was synthesised as a working model. Additional considerations included the fact that the bond lengths of the monomeric unit in the methacrylate chain would not allow the appropriate incorporation of the squarate groups so as to link neighbouring pyrroles, thus cross-linking is essential for the stable formation of the desired polysquaraines; idealized products are shown in Fig. 1. Furthermore, in route (ii) the required solvent for the polycondensation reaction with squaric acid was 1-butanol (2), which as a solvent did not satisfactorily solubilize poly[2-(*N*-pyrrolyl)ethyl methacrylate], but does however boil at a temperature just above the T_g of the PMMA derivative.

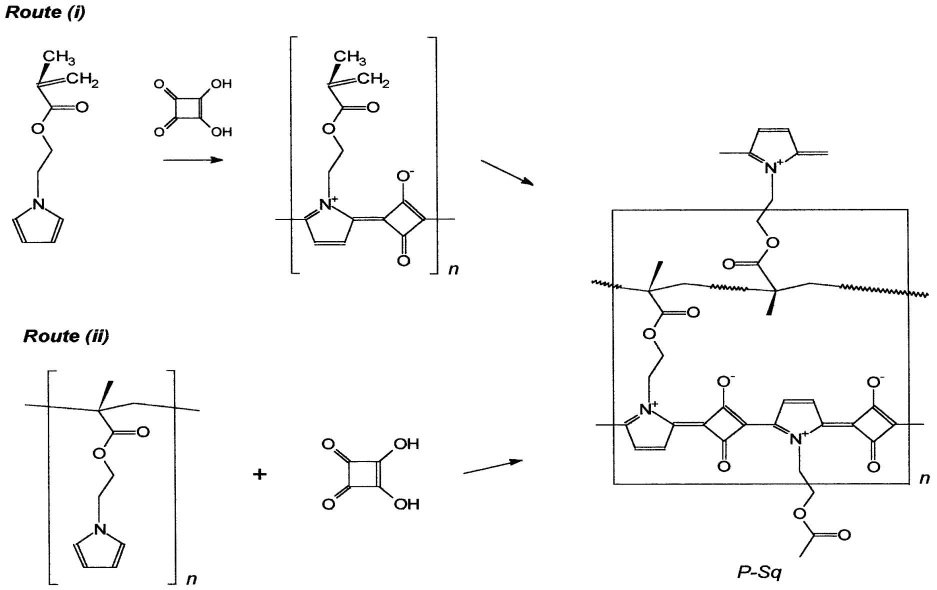


Fig. 1 Schematic diagram outlining the two synthetic procedures considered and the idealized product.

Experimental

2-(*N*-pyrrolyl)ethyl acetate and poly[2-(*N*-pyrrolyl)ethyl methacrylate] were synthesised according to the literature procedures (3,4) respectively. Poly[2-(*N*-pyrrolyl)ethyl methacrylate] was produced with an average molecular weight of 52 900.

Poly{[2-(*N*-pyrrolyl)ethyl acetate]squaraine} (*P-PES*) was synthesised according to the literature procedure for the synthesis of poly(1-methylpyrrolylsquaraine) (2) by refluxing equimolar amounts of squaric acid (513 mg, 4.5 mmol) and 2-(*N*-pyrrolyl)ethyl acetate (688 mg, 4.5 mmol) in butan-1-ol (50 mL) for 2 h. The crude products were collected by filtration upon cooling of the reaction solution. Low molecular weight materials were separated from the polymer *via* extraction for 12 h with refluxing ethyl acetate. The polymer was collected as an insoluble, dark blue powder; yield = 620 mg (59%).

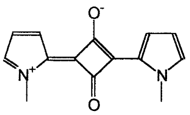
The squaraine derivative of poly[2-(*N*-pyrrolyl)ethyl methacrylate] (*P-Sq*) was synthesised using the above procedure by refluxing equimolar amounts of squaric acid butan-1-ol (50 mL) for 2 h. The product was collected by filtration upon cooling of the reactant solution as an insoluble, bright red-violet powder; yield = 210 mg (which relates to 41% squarate content, assuming 100% recollection of the methacrylate polymer).

Infrared spectra were recorded as pressed KBr disks on a Nicolet 205 FT-IR spectrometer. Fluorescence measurements were made on a Perkin Elmer luminescence spectrometer LS50. X-ray powder diffraction patterns were recorded using a Philips PW1700 System diffractometer (Cu Kα X-radiation). Dielectric breakdown measurements were taken on an Astec 15 KV Nondestructive Insolation Tester Model 615. Samples for differential scanning calorimetry (DSC) were run on a Setaram DSC92 heated at 8 °C min^{-1} from 20-200 °C. X-ray Photoelectron Spectroscopy (XPS) data was collected on a PHI Model 560 XPS, SAM, SIMS 1 Multitechnique Surface Analysis System incorporating a model 25-270AR Cylindrical Mirror Analyser (CMA). Static Secondary Ion Mass Spectroscopy (SIMS) was recorded using a PHI Model 2500 SIMS 1 system over the mass range 0 - 100 amu. The primary ions used were generated in a Model O4-303 Diffy ion gun. 4 KeV Ar^{+} ions, 5 nA over 1 cm^{2} for a total data acquisition time of 5 mins ensured a total ion dose of *ca.* 10^{13} ions per cm^{2} (Static SIMS limit). Scanning Electron Microscopy (SEM) pictures were obtained on Pt coated samples using a JEOL 6400 operating at 15 kV.

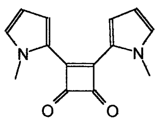
Results and Discussion

P-PES was produced as an insoluble dark blue powder which would also be the case if 2-(*N*-pyrrolyl)ethyl methacrylate was polycondensed with squaric acid. In this respect, polymerisation of the methacrylate group by normal solution methods (after the polysquaraine was formed) would not be possible. Additionally, conductivity experiments on a pressed disk of *P-PES* indicated that the sample did not conduct. Several recent papers, both theoretical (5,6) and experimental (7,8), have suggested that polysquaraines possess low band gaps and therefore high conductivity. To date, none of the poly(pyrrolylsquaraine) series have shown any signs of this effect. Instead, poly(1-methylpyrrol-2-ylsquaraine) displays a slow dielectric breakdown from 0.025 to 0.9 MV cm^{-1}. For comparison, common nonconducting organic polymers generally have values between 1-9 MV cm^{-1} at 20 °C (9). The reason for poly(1-methylpyrrolylsquaraine) exhibiting a slow breakdown is attributed to the fact that within the polymer matrix there is approximately one water molecule present per squaraine unit (2).

P-Sq, made using the second procedure, was collected as a bright, red-violet powder which was insoluble in all common organic solvents. The production of squarates in this material was expected to be low due to the insolubility of poly[2-(*N*-pyrrolyl)ethyl methacrylate] in the reactant solution hence limiting the condensation of squaric acid to the attainable pyrrole sites. However, subsequent inspection (under an optical microscope) of crushed fragments of *P-Sq* revealed that the red-violet colouration was consistant throughout the polymer bulk. Infrared analysis of the product material showed evidence of 1,3-squarates but any 1,2-squarates were masked by the stronger C=O peak from the polymethacrylate chain. DSC analysis of the collected material gave a single endothermic peak (-17.471 mJ or -0.324 mJ/mg) between 66.5-85 °C. The X-ray powder diffraction patterns of both the starting polymer and the product were essentially identical in showing the expected broad amorphous peaks, although the latter showed an increased intensity across the region 4.8-3.4 Å (*d*-spacing). Additionally, the red-violet colour of this material would suggest that only bis(pyrrolyl)squaraines had formed; any further polymerisation of the pyrroles would have resulted in a dark blue colouration.



1,3-squarates



1,2-squarates

One technique which did provide essential molecular information was XPS. An initial wide scan survey spectrum (at a pass energy of 100 eV) identified the major elements present (except hydrogen) in the bulk polymer down to 0.1 atom percent and confirmed the presence of only C, N and O. Prior to XPS analysis the sample was crushed to expose fresh surfaces representative of the bulk. High resolution (25 eV pass energy) multiplex scans of the C, N and O peaks were recorded. The peak shapes of which were indicative of the chemical states present. A semiquantitative estimate of the magnitude of the various species present in the spectra of each element was resolved by linear least-squares curve-fitting techniques using as a guide, peak shapes and widths of similar peak fitting results obtained from reference polymer materials recorded under identical experimental conditions. This data, along with microanalysis† and experimental yield

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† Found for *P-Sq*: C, 66.4; H, 6.8; N, 7.4%. *P-Sq* in Fig. 2 requires C, 66.6; H, 6.6; N, 7.2%.

results confirm the presence of *ca.* 40% squarate content in the bulk polymer. Further comparative analysis of the specific C, N and O groups present in the polymer gave the molecular configuration as consisting of unreacted 2-(*N*-pyrrolyl)ethyl methacrylate groups, 1,3-substituted bis[2-(*N*-pyrrolyl)ethyl methacrylate]squaraine units and 1,2-substituted bis[2-(*N*-pyrrolyl)ethyl methacrylate]squaraine units in the ratio of 1 : 0.185 : 0.148 respectively. A yield of 41%, based on the formation of these dimers, should almost be considered average in comparison to other bis(pyrrolyl)squaraine yields.

Granular particles of this material were also studied using a SEM in order to elucidate any physical changes due to the presence of squarate groups. Fig. 2 shows that although the particles still appear amorphous, some prefered layering can be seen. The material is quite stable under electron beam irradiation in the SEM, unlike pure PMMA. Further evidence of the stability of the polymer backbone is provided by the fragmentation pattern observed with SIMS. According to Briggs *et al* (10), the major positive ion peaks for PMMA are found at m/z = 41, 55, 59 and 69 amu. 41 amu ($C_3H_5^+$) is a common backbone fragment to many polymers, however, all other PMMA ions are lesser peaks in the observed pattern, with 59 amu being absent. Characteristic peaks for this material were m/z of 80 amu for the squarate $C_4O_2^+$ and 65, 78 and 93 amu for pyrrole ion fragments ($C_4H_3N^+$ $C_5H_3N^+$ and $C_6H_7N^+$ respectively). Therefore the squarate units are definitely bound to the polymer as they affect the cleavage of the PMMA backbone.

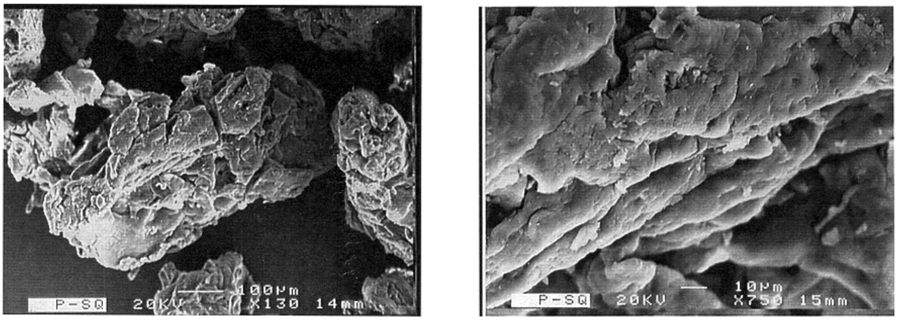

Fig. 2 SEM pictures of a ganular particle of the product of route (ii).

Fig. 4 shows the solid-state fluorescence spectrum for the compound, illuminated with both green and ultra-violet light, which displays two fluorescence maxima at 583 and 632 nm. Such properties can only be due to the presence of the reacted squaraines. This is an intriguing result because bis(1-octadecylpyrrol-2-yl)squaraine, which exists as an aggregated mixture of 1,2- and 1,3-squarates (1), does not fluoresce. Additionally, the collected material from the poly{[2-(*N*-pyrrolyl)ethyl acetate]squaraine} reaction, which was found by mass spectroscopy techniques to be predominantly bis[2-(*N*-pyrrolyl)ethyl acetate]squaraine, also fluoresced [$\lambda_{max}(CHCl_3)$ = 548 nm, $\lambda_{em}(CHCl_3)$ = 563 nm). The presence of the proximal ester groups must promote specific aggregates which in turn fluoresce.

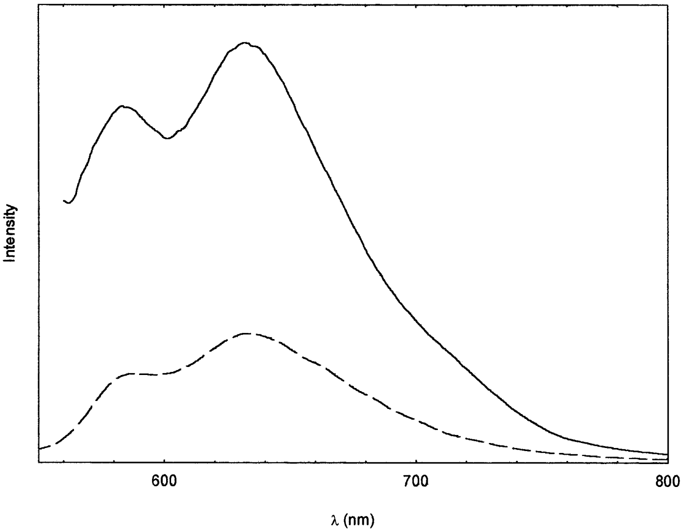

Fig. 4 Solid-state fluorescence spectra for the product of route (ii); excitation wavelengths at 545 nm (—) and 322 nm (----).

In conclusion neither of the suggested synthetic routes were successful in producing a more processible poly(pyrrolylsquaraine). However, the second route did provide some promising results with respect to the bis(pyrrolyl)squaraine moiety. The next logical step of course is to synthesise longer alkyl derivatives of poly[2-(*N*-pyrrolyl)ethyl methacrylate] so as to promote easier crosslinking and / or allow neighbouring pyrroles to react. Due to the unexpected fluorescence results it is advantageous at the moment to continue our squaraine copolymer studies using ester-containing polymers.

Acknowledgements

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