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An investigation into the synthesis of polycarbazole squaraine derivatives

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Summary

The polycondensation of squaric acid with 1,2-(9-Ethylcarbazol-3-yl)ethene and *N*-ethyliminostilbene in polyphosphoric acid yielded insoluble polymers which included substituted phosphate groups on the phenyl rings. The presence of phosphorus in these polymers was identified using solid-state ^{31}P NMR and EDAX techniques. Furthermore the phosphate groups were not ionic, hence no charge-balancing anions were present. Both polymers did not electrically conduct but exhibited dielectric breakdown values of 0.1 and 0.06 $MVcm^{-1}$ respectively.

Introduction

One approach to produce small band gap semiconducting polymers is the synthesis of alternating donor-acceptor systems (1,2), recently achieved by the polycondensation of 1,2-dihydroxy-3-cyclobutene-3,4-dione (squaric acid) and 4,5-dihydroxy-4-cyclopentene-1,2,3-trione (croconic acid) with suitable electron rich molecules such as benzo(1,2-4,5)di(1-alkyl-2-methylene-3,3-dimethylpyrroline) and its thiazole derivative (3,4). These systems were made soluble both in organic solvents and in water by the *N*-substitution of alkyl and alkyl-sulphonate chains respectively. Such materials, although having experimentally reported band gaps down to 0.5 eV, have measured conductivities of only 10^{-5} - 10^{-9} Scm^{-1}. These conductivity values, however, increase to *ca.* 1 Scm^{-1} upon doping with iodine. In conjunction with these results, recent theoretical studies (1,2) have suggested that the above mentioned polysquaraines possess high band gaps and therefore low conductivity. According to these studies, smaller band gap polymers will be achieved

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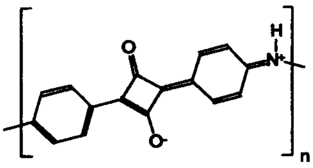
by systems such as 1. An example of this type, which has already been characterized, is poly(*N*-ethylcarbazole) squaraine, 2, where the percentage of -1,2- substituted squarate rings is reported to be between 36-43% (5). This polymer was produced as either a high-yield insoluble black powder by using reaction temperatures > 150 °C, or as a green coloured product which was soluble in DMF, DMSO, and conc. H_2SO_4 by using a reaction temperature of *ca.* 90 °C. This therefore indicated that the green coloured product consisted of only short oligomers. The insoluble polymeric product had an experimentally determined conductivity of $< 10^{-9}$ Scm^{-1}, which did not improve upon doping with iodine.



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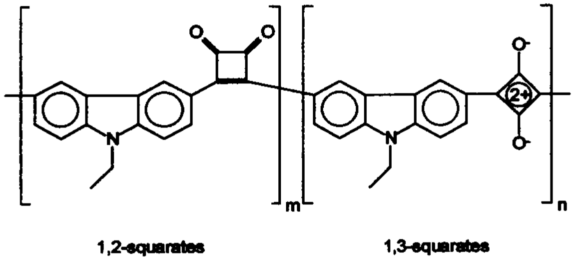

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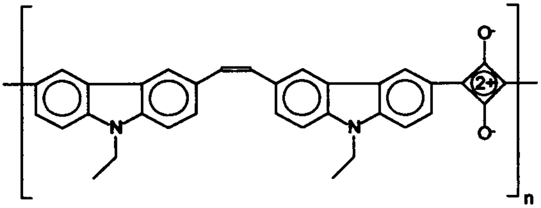
In this present study we initially intended to investigate the electrical properties of the short-chain analogues of two other polycarbazole squaraine derivatives, 3 and 4, before synthesizing their potentially soluble long-chain versions. But, as this paper proves, an unforeseen reaction hinders any further attempts to enhance solubility.



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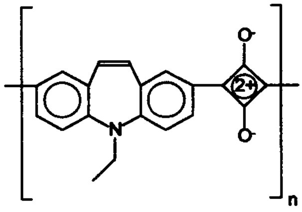

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Experimental

1,2-(9-Ethylcarbazol-3-yl)ethene was synthesized by slowly adding a solution of pyridine (2.5 mL) and 9-ethylcarbazol-3-carbaldehyde (7.85 g) in dry THF (100 mL) to a previously prepared solution of 5 g zinc dust slowly added under argon to an ice cold solution of 4.1 mL $TiCl_4$ in 100 mL THF, and refluxing for 18 h, after which the mixture was quenched with 10% K_2CO_3 solution (100 mL). The resultant solid, after evaporation of the solvent, was extracted with THF and then recrystallized from ethanol. Final purification involved column chromatography using THF : cyclohexane (1:3) as solvent; yield: 3.70 g (51%). 1,2-(9-Ethylcarbazol-3-yl)ethene (0.80 g, 1.9 mmol) was then condensed with squaric acid (0.21 g, 1.9 mmol) according to the literature procedure for polycarbazole squaraine (5) by heating the reactants in polyphosphoric acid for 15 h at *ca.* 120 °C then 4.5 h at *ca.* 150 °C. The product, **3**, was collected as a black powder *via* filtration after dilution and neutralisation (aqueous NH_4OH) of the reaction solvent. Unreacted starting materials were separated from the bulk *via* extraction for three days with refluxing aqueous alcohol; yield = 1.13 g (*ca.* 120%).

Poly(*N*-ethyliminostilbene) squaraine, **4**, was synthesised analogous to the above procedure using *N*-ethyliminostilbene (1.71 g, 7.7 mmol) and squaric acid (0.88 g, 7.7 mmol) and was collected as a black powder; yield = 1.89g (*ca.* 82%).

Infrared spectra were recorded as pressed KBr disks on a Nicolet 205 FT-IR spectrometer. Solid-state ^{31}P NMR spectra were recorded on a Bruker MSL300 nuclear magnetic resonance spectrophotometer operating at 121.5Mhz for ^{31}P. Both samples were spun at the magic angle at 6kHz. Cross polarization from the ^{1}H nuclei was used to obtain the spectra. A cross polarization contact time of 2-15 ms and a recycle delay of 6-30 s was used, depending on the relaxation time of the sample. All peaks were reported relative to phosphoric acid *via* triphenylphosphine set at 9.9 ppm. Energy Dispersive Analysis of X-rays (EDAX) spectra were recorded on a Phillips Scanning Electron Microscope (SEM) 505. 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.

Results and discussion

Polymer **4** was produced at the expected yield for the above synthetic procedure but the unexpected 120% yield for **3** indicated that there were additional reactions occurring with either the polyphosphoric acid or the aqueous NH_4OH, or both. The infrared spectra for polymers **3** (Fig. 1) and **4** both show a medium intensity aryl RO_2PO_2 peak at 1090 and 1050 cm^{-1} respectively. This peak is also present to a lesser extent in the literature spectrum of polycarbazole squaraine (5). Both sets of double bonds were unaffected by the acid with peaks at 1680,1380 and 740 cm^{-1} and 1680,1375 and 755 cm^{-1}, for 3 and 4 respectively, which also indicates that the phosphates are attached to the phenyl rings. Other significant peaks are the 1,3-squarate C-O peaks at 1615 and 1610 cm^{-1}, respectively, and the lesser 1,2-squarate C=O peaks at 1750 cm^{-1}, for both.

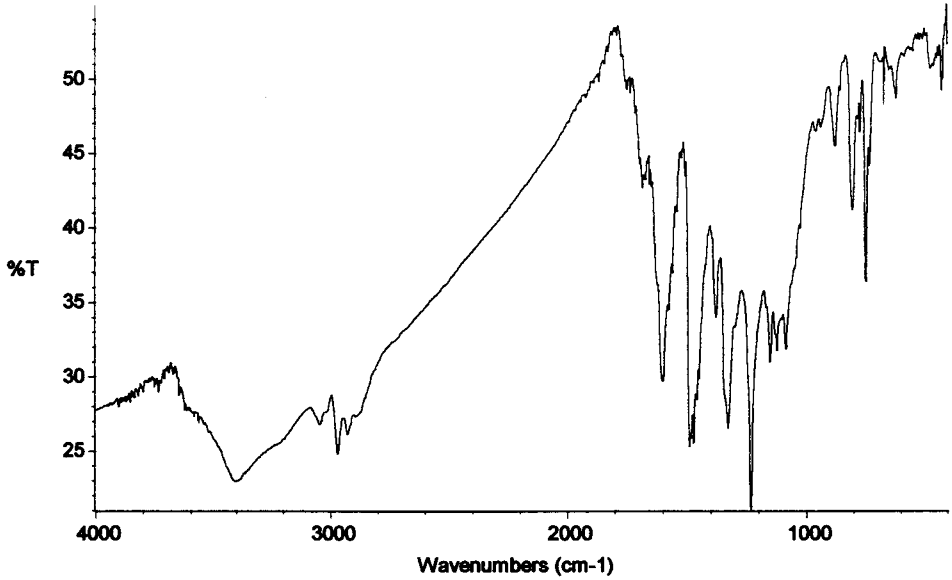

Fig. 1 Infrared spectrum for polymer 3

Solid-state ^{31}P NMR confirmed the presence of phosphorus in both samples with several major peaks observed in the spectra (Fig. 2). With each peak representing a unique phosphorus centre (6), it is evident that there are several different phosphorus conformations present in each polymer matrix, although both show very similar phosphorus arrangements due to the similarity of chemical shifts and peak intensities in the spectra. It is quite possible that the phosphates are crosslinking the polymer chains, but no preferred stacking arrangements are present, as indicated by the X-ray powder diffraction patterns of 3 and 4 which show the polymers are completely amorphous. It was also considered that the phosphates could be ionic with the charge balanced by complexed NH_4^+ anions. To test this theory both polymers were resynthesized and neutralized using aqueous KOH. The similar products were then examined for potassium using EDAX

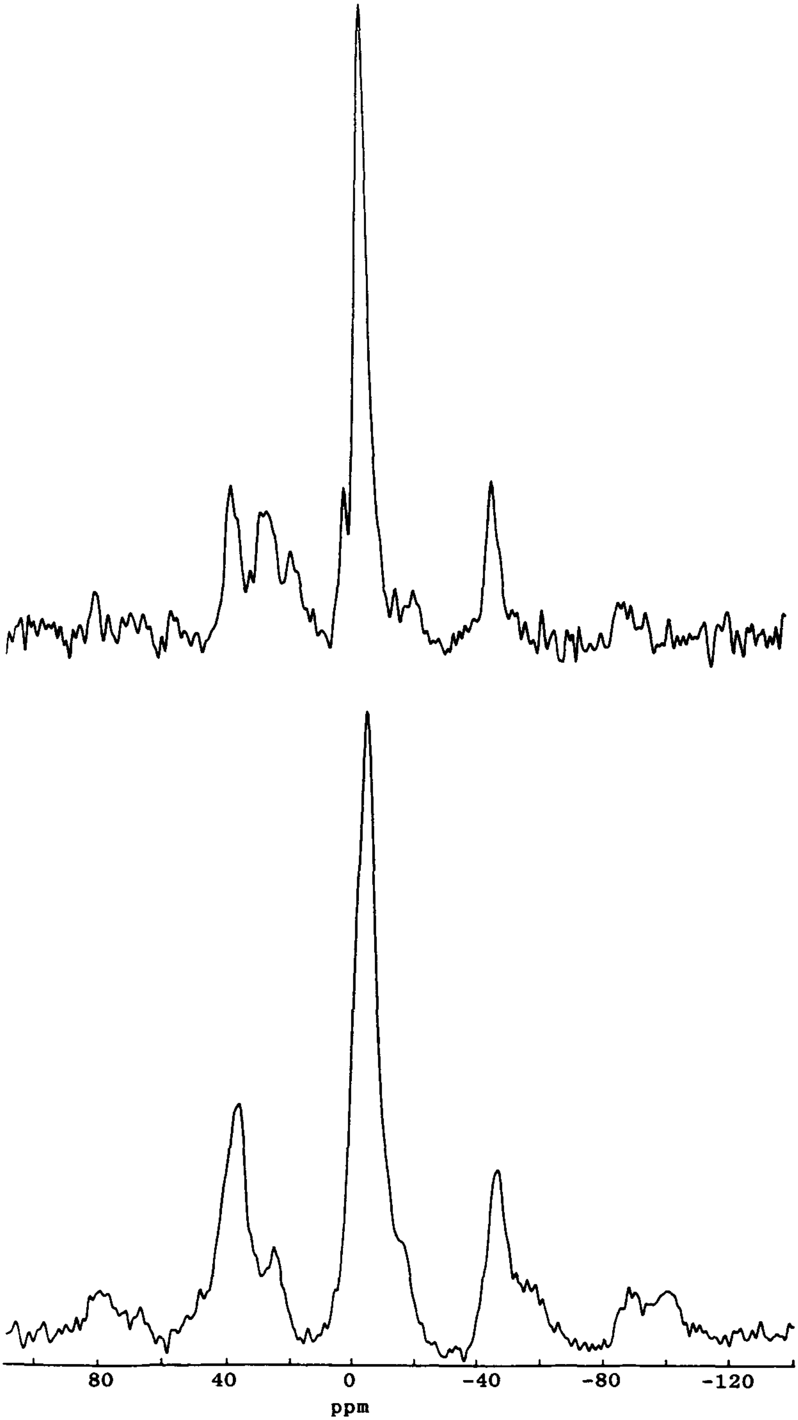

Fig. 2 Solid-state ^{31}P NMR for polymers 3 (top) and 4 (bottom).

experiments on a SEM. In both cases these experiments showed only the presence of phosphorus, no potassium was found.

Conductivity measurements using the four-probe technique on pressed disks of polymers **3** and **4** indicated a bulk resistance $<10^{-9}$ Scm^{-1}. In addition to this, dielectric breakdown experiments gave values of 0.1 and 0.06 $MVcm^{-1}$ respectively. Common nonconducting organic polymers generally have values between 1 - 9 $MVcm^{-1}$ at 20 °C (7). Subsequent attempts were made to synthesize polymers **2**, **3** and **4** using other known squaraine synthetic procedures (3,8). These methods essentially require higher boiling point solvents, catalytic amounts of a mineral acid and the continuous removal of water during the reaction. But apart from the observation in some cases of a weak blue coloration in the reactant solutions, these procedures yielded mixtures consisting solely of the starting materials. Furthermore, in an attempt to reduce the phosphate content of these polymers during the reaction, additional synthetic procedures included the dilution of polyphosphoric acid with volume percentage amounts of butan-1-ol. Yet this made no difference to the final product. Once produced the resultant polymers were very resistant to any further chemical reactions (primarily due to their inherent insolubility). For this reason the phosphates could not be removed or replaced after production of the polymers.

A common approach to enhance the solubility of polyarylene backbones is the substitution of long alkyl chains (9). However, the collected yellow-brown products of the reactions between both *N*-decylcarbazole and *N*-octadecylcarbazole with squaric acid in polyphosphoric acid were again essentially the respective starting materials. The intention of this paper was not to present any new compounds, but rather to investigate why polymer **2** does not conduct when it is an analogue of the theoretically conductive polymer **1**. As we have shown, this is due to the presence of substituted phosphates, obtained from the reaction solvent, which have also potentially cross-linked the polyarylene backbone chains and as a consequence caused insolubility. Therefore, we conclude that a completely new approach to produce soluble polycarbazole squaraines, and hence type **1** polymers, is required.

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