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Chemical synthesis and characterization of electroactive and partially soluble polyazulene

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SUMMARY

Simultaneous chemical oxidation and polymerization of azulene by iodine and bromine were carried out. The polyazulene-bromine complex is electrically conductive and partially soluble in organic solvents whereas the polyazulene-iodine complex is much less conductive and insoluble. The physicochemical properties of the polyazulene-bromine complex were characterized by elemental and thermogravimetric analyses, infrared and ultraviolet-visible absorption spectroscopy, cyclic voltammetry and gel permeation chromatography. Experimental evidences suggest that the soluble fraction of the complex consists mainly of azulene oligomers.

INTRODUCTION

Conducting polymers have been electrochemically synthesized from a variety of aromatic molecules which include the heterocyclic monomers such as pyrrole (1), thiophene (2-4), furan (4) and carbozoles (5,6), and the fused ring monomers like azulene (4,6-8) and indene (8). The electrical conductivities (σ) of these polymers vary over a wide range and depend on the monomeric structure. Polypyrrole has the highest conductivity and a value of 10^2 S/cm has been reported (1c). Recently, we have reported a relatively simple chemical method for simultaneous polymerization and oxidation of pyrrole by the halogenic electron acceptors, I_2, Br_2 and Cl_2 (9). This method has also been successfully used for the synthesis of polymers from other heterocycles such as furan (10), thiophene (10) and pyridazine (11). The polypyrrole-halogen complexes obtained from this chemical method is stable in ambient air with electrical conductivity and conduction behaviour comparable to those prepared electrochemically (12). The polypyridazine-I_2 complex also has a σ value comparable to that of electrochemically synthesized polypyridazine (13). However the σ's of the chemically synthesized polyfuran and polythiophene samples remain several orders of magnitude below that of the corresponding electrochemically synthesized polymers (10).

With a few exceptions (14), the conducting polymers synthesized by either electrochemical or chemical methods are insoluble in common solvents. In this paper, we report on the extension of the chemical polymerization method to the fused ring compound, azulene. The resulting polyazulene(PAZ)-Br_2 complex is partially soluble in common organic solvents. The physicochemical properties of this polymeric complex are discussed in this paper.

EXPERIMENTAL

The azulene monomer was obtained from Aldrich Chemicals. All solvents were of reagent grade and were used as received. For iodine induced polymerization, about 1.5g of pulverized I_2 (sublimed, Merck) was added to about 200ml of acetonitrile saturated with N_2. Azulene (0.75 g) was first dissolved in a small amount of acetonitrile and then introduced into the reaction mixture with vigorous stirring under N_2. The reaction mixture turned dark almost instantaneously and black solids gradually precipitated. The reaction mixture was then stirred for at least 6 hours. The product was washed thoroughly with absolute ethanol before being dried under reduced pressure. The yield of the product was about 1.2g. The bromine induced polymerization was carried out in the same manner with 0.75g azulene and 0.8ml Br_2 (BDH Chemical, Reagent Grade). About 1.4g of black precipitate was obtained. Attempts were also made to polymerise azulene with chlorine. However, when azulene was added to acetonitrile solution saturated with chlorine, the solution remained clear yellow with no solid precipitation.

The PAZ-Br_2 and PAZ-I_2 complexes were tested for solubility in common organic solvents and characterized using elemental analysis, electrical conductivity measurements, infrared (IR) absorption spectroscopy, thermogravimetric analysis and cyclic voltammetry. In addition, the soluble fraction of the PAZ-Br_2 complex was characterized using ultraviolet(UV)-visible absorption spectroscopy and gel permeation chromatography (GPC). Cyclic voltammetry was performed on PAZ-Br_2 complex in powder form using a specially modified electrode. A detailed description of this electrode and its performance have been reported earlier (15).

RESULTS AND DISCUSSION

Chemical Composition and Solubility

The solubility of the PAZ-halogen complexes was tested in the following solvents : toluene, methylene chloride, chloroform, tetrahydrofuran (THF) and carbon tetrachloride. The PAZ-I_2 complex is completely insoluble, while the PAZ-Br_2 complex shows limited solubility in all the above solvents with the highest degree of solubility obtained with THF and chloroform.

Elemental analysis (C,H,N, halogen) indicates that the PAZ-I_2 complex can be represented as $C_{10.0}H_{6.0}(I_2)_{0.40}$ with better than 99% closure of the mass balance while the PAZ-Br_2 complex can be represented as $C_{10.0}H_{4.9}(Br_2)_{0.72}$ with better than 95% closure. The soluble fraction of the PAZ-Br_2 complex (after solvent evaporation) has a H/C ratio of 4.8/10 and a Br_2/C ratio of 0.75/10. The amount of anion in these complexes is much higher than that of the electrochemically synthesized polyazulene where the typical concentration is about one anion for every four azulene units (6). The H/C ratio in the PAZ-I_2 complex corresponds to that of azulene units connected via two positions of the five-membered ring as proposed by Bargon et al. (6,7). The H/C ratio of the PAZ-Br_2 complex is hydrogen deficient relative to this idealized structure, implying possible crosslinking and/or bromination of the rings. The slight deviation from 100% mass closure for the PAZ-Br_2 complex suggests that the complex may have been 'doped' to a small extent by oxygen as in the case of chemically (9) and electrochemically (16) synthesized polypyrrole.

Thermal and Electrical Properties

The thermogravimetric scans of the PAZ-I_2 and PAZ-Br_2 complexes in nitrogen are compared with that for the azulene monomer in Fig. 1. As

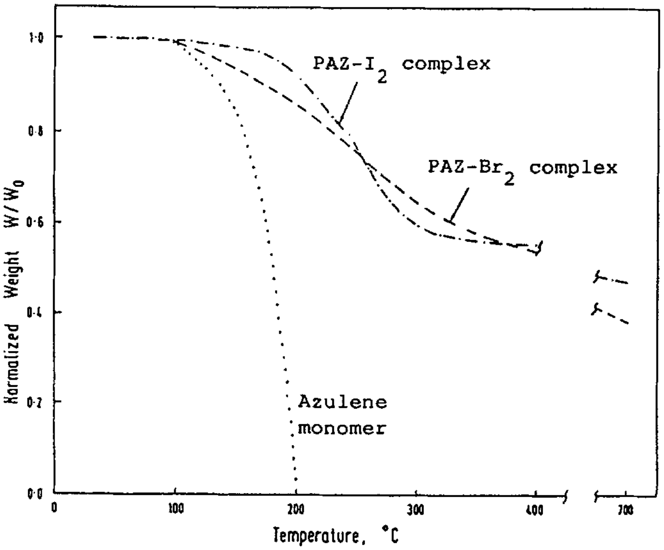

Figure 1 Thermogravimetric scans of polyazulene-halogen complexes and azulene monomer.

expected, the weight loss curve of the azulene monomer is steep with no sample remaining after 200°C. The onset of weight loss for the PAZ-Br_2 complex is at a slightly higher temperature than that for the azulene monomer. The weight loss is also more gradual. The PAZ-I_2 complex is thermally more stable than the PAZ-Br_2 complex but the weight loss shows a step-like curve with the maximum rate at about 240°C.

The electrical conductivity of PAZ-Br_2 complex is about 5×10^{-3} S/cm while that of PAZ-I_2 complex is only of the order of 10^{-6} S/cm. The present PAZ-Br_2 complex is about an order of magnitude less conductive than the electrochemically synthesized polyazulene (4,6). When the PAZ-Br_2 complex is treated with chloroform or THF, the soluble fraction lost most of its conductivity while σ for the remaining insoluble fraction becomes slightly higher than the untreated sample. This loss of electrical conductivity in the soluble fraction of the present PAZ-Br_2 complex is not unlike that of the substituted polythiophene after solubilization (14).

Since the PAZ-Br_2 complex is electrically conductive, it would be of interest to characterize its electrochemical behaviour. The cyclic voltammogram of the PAZ-Br_2 complex in a 0.5M aqueous NaBr solution with Pt counter electrode and a Ag/AgCl reference electrode is shown in Fig. 2. A sweep rate of 1000 mV/s was used. Well defined oxidation and reduction peaks were obtained with a redox potential of about 0.1V. This value is substantially more positive than the value of -0.4V obtained for chemically synthesized polypyrrole-Br_2 complex in the same electrolyte and using the

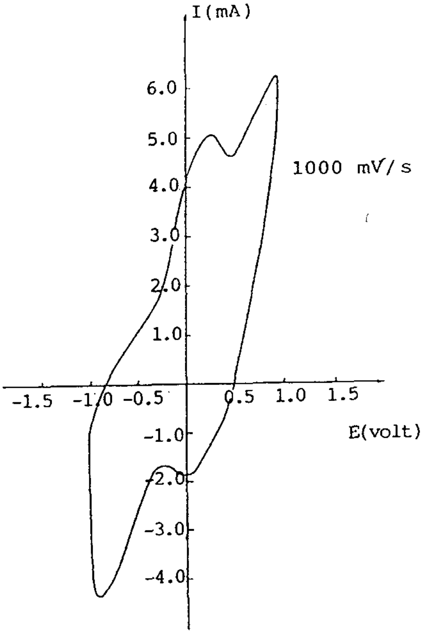

Figure 2

Cyclic voltammogram of polyazulene-Br_2 complex in 0.5M aqueous NaBr solution.

same reference electrode (15). This redox potential, however, is still somewhat lower, for example, than that observed for the electrochemically prepared PAZ-BF_4 complex when cycled in 0.1M tetraethylammonium fluoroborate/acetonitrile electrolyte (6).

Absorption Spectroscopy

The IR absorption spectra of the PAZ-Br_2 complex and the chloroform-soluble fraction show similar features as those obtained by Burzynshi et al. (17) with electrochemically prepared polyazulene, except for the transitions due to the counter anion. The characteristic bands of oxidized polyazulene such as those at about 1465, 1450, 1320, 1290, 1220, and 1180 cm^{-1} (17) are present in both the PAZ-Br_2 complex and the chloroform-soluble fraction. The bands for both the whole complex and chloroform-soluble fraction are broader than those for the monomer, consistent with the amorphous nature of the complex. The strong C-H deformation band at 765 cm^{-1} of the monomer, which is characteristic of the crystalline state (17), is absent from the spectra of both the PAZ-Br_2 complex and the chloroform-soluble fraction. Another difference between the spectra of these two samples and that of the monomer is the presence of a long absorption tail from 4000 to about 1750 cm^{-1} in the polymer samples. This absorption tail probably results from the tail of the absorption band located in the red and near-IR region of the oxidized PAZ. An IR absorption tail of similar nature has also been observed in electrochemically oxidized PAZ complexes (17) and in chemically (9) as well as electrochemically (16) oxidized polypyrrole.

The UV-visible absorption spectra of the PAZ-Br_2 chloroform-soluble fraction and the azulene monomer are given in Fig. 3. The two spectra

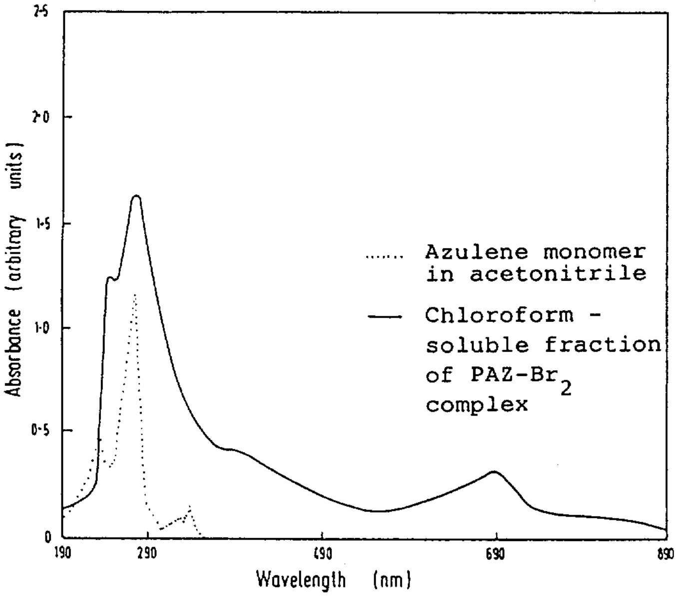

Figure 3 UV-visible absorption spectra of polyazulene-Br$_2$ chloroform-soluble fraction and azulene monomer.

display similar features from 190 nm to about 330 nm, suggesting that the azulene ring structure remains intact in the polymeric complex. The polymer absorption spectra however shows a shoulder at about 390 nm and a long tail with a broad peak centered at about 690 nm. The absorption shoulder is probably indicative of the effective conjugation length while the absorption tail probably results from charge transfer interaction between the polymer and the dopant. The peak at 690 nm is substantially reduced when THF or toluene is used as solvent. UV-visible absorption spectra of the electrochemically synthesized polyazulene-ClO_4 film also shows similar features, with a broad shoulder at about 420 nm and an absorption tail extending into the visible region (7). The slightly shorter absorption shoulder observed in the present PAZ-Br$_2$ complex is consistent with the oligomeric nature of the soluble fraction (see below). A careful study on the evolution of the red and near-IR absorption tail for the PAZ-ClO_4 complex during electrochemical oxidation has also been reported recently (8).

Gel Permeation Chromatography

Since the PAZ-Br$_2$ complex is partially soluble, attempts were made to estimate the molecular weight of the soluble fraction. The GPC chromatograms of the THF soluble fraction of PAZ-Br$_2$ complex and the azulene monomer are compared in Fig. 4. As expected, the retention time of the polymeric complex is shorter than that of the monomer. Based on the commonly used standards of polystyrene, the average degree of polymerization of the THF-soluble fraction is estimated to be about 7. However the use of polystyrene standards for estimating the molar mass of conducting polymers of substituted thiophenes has been shown to be grossly inaccurate (14). Thus we can only conclude that the THF-soluble fraction

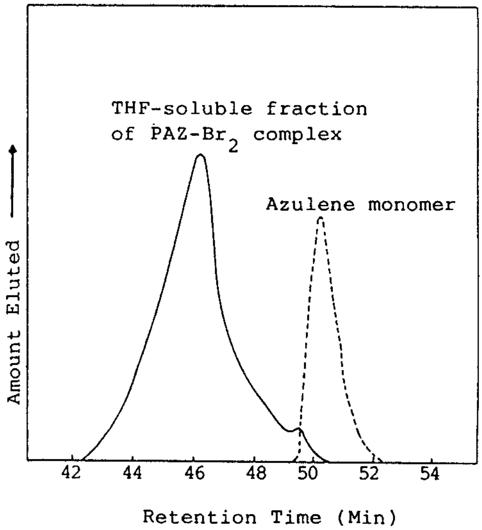

Figure 4 GPC chromatograms of polyazulene-Br$_2$ THF-soluble fraction and azulene monomer.

of the PAZ-Br$_2$ complex consists mainly of oligomers while the degree of polymerization for the insoluble fraction is expected to be substantially higher.

CONCLUSION

We have successfully synthesized a partially soluble, electroactive polyazulene-bromine complex using a simultaneous chemical polymerization and oxidation method. This complex is stable under ambient conditions and can undergo electrochemical redox reactions. The same chemical method used with pyrrole produces a totally insoluble polypyrrole-halogen complex, but of much higher conductivity (9). GPC measurements of the THF-soluble fraction of the PAZ-Br$_2$ complex suggest that the soluble fraction is oligomeric in nature. Unfortunately, this soluble fraction lack any substantial electrical conductivity.

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