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The First Fully Characterized 1,3-Polyazulene: High Electrical Conductivity Resulting from Cation Radicals and Polycations Generated upon Protonation

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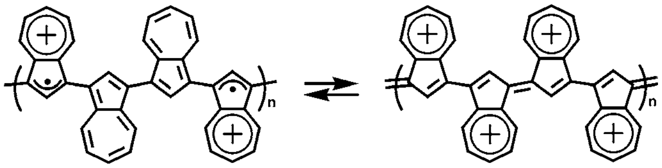
ABSTRACT



1,3-Polyazulene prepared by the chemical polymerization of 1,3-dibromoazulene with Ni(COD)$_2$ was aptly characterized by spectroscopic analysis. The azulene units remain intact in the isolated polymer. Protonation of 1,3-polyazulene by trifluoroacetic acid was found to exhibit high conductivity and paramagnetic properties via the formation of cation radicals and di- and polycations.

There is strong interest in the application of azulenes and polyazulenes as materials with unique optical and electrical properties for design of molecular devices.[1] Most reported polyazulenes were prepared from azulene monomer by electrochemical polymerization,[2] and to the best of our knowledge, only one example was achieved by chemical oxidative polymerization of azulene with iodine and bromine.[3] The magnetic, optical, and electrochemical properties of these polyazulenes have been reported,[4] and a relatively high conductivity in the range of 0.01−1 S/cm was observed in their oxidized states.[2,5] All these reported polyazulenes, however, were practically insoluble in any solvent, thus limiting their characterization and application. 1,2-Polyazulene prepared by heating azulene in trifluoroacetic acid was characterized by ^{1}HNMR spectroscopy that indicated that the polymer has lost the structural feature of azulene.[6] Attempts to aromatize this polymer by oxidation failed to recover the azulene structure but resulted in highly insoluble materials. In this communication, we report the preparation of a soluble 1,3-polyazulene by dehalogenative polycondensation of 1,3-dibromoazulene using an organonickel catalyst. 1,3-Polyazulene was then aptly characterized by ^{1}H NMR spectroscopy and elemental analysis. Most interestingly, the polymer exhibits high conductivity and ferromagnetic properties upon protonation.

Various π-conjugated polymers have been prepared by polycondensations catalyzed by organometallic reagents.[7] In

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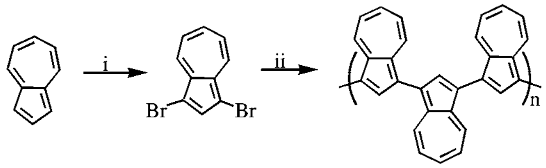
our work, the zero-valent nickel complex Ni(COD)$_2$ was employed as the catalyst for the polymerization as shown in Scheme 1. Ni-Promoted polycondensations often result in polymers with relatively higher molecular weights when the common C−C coupling reactions are not effective. 1,3-Dibromoazulene was obtained in high yield by reacting azulene with NBS in benzene. The polymerization was carried out by a Yomamoto procedure:[8] 1,3-dibromoazulene (1.2 mmol) was added to a DMF solution containing Ni(COD)$_2$ (1.8 mmol), COD (1.8 mmol), and bpy (2.0 mmol) with stirring. Adding the product solution to methanol precipitated the polymer, which was washed successively with an aqueous ammonia solution, a warm solution of EDTA, warm distilled water, and warm methanol. The polymer was finally isolated as a yellow-green powder (84% yield) after drying in vacuo at 70 °C for 8 h. The molecular weight of 1,3-polyazulene was determined by GPC in a THF solution by calibration against polystyrene standards. The average molecular weight (M_n) and polydispersity (PD) were found to be 16 400 and 1.15, respectively. The thermal stability of the 1,3-polyazulene was measured by thermogravimetric analysis. The initial decomposition temperature of 1,3-polyazulene under nitrogen was observed at about 330 °C, and over 60% of its mass was retained after heating to 1000 °C, indicating that the polymer backbone of 1,3-polyazulene has a relatively high thermal stability.

Scheme 1. Synthesis of 1,3-Polyazulene[a]



[a] Reaction conditions: (i) NBS, benzene, rt; (ii) Ni(COD)$_2$, COD, bpy, DMF, 60 °C.

Results obtained from ^{1}H NMR and FT-IR spectroscopic studies and elemental analysis confirmed the molecular structure of the isolated 1,3-polyazulene. The ^{1}H NMR spectrum of the polymer shows no aliphatic protons, and the aromatic signals are shown in Figure 1. In the aromatic region, 1,3-polyazulene shows signals similar to those in azulene. The signals centered at δ 8.6, 8.4, 7.6, and 7.1 ppm could in fact be assigned to 4,8-H, 2-H, 6-H, and 5,7-H of the azulene unit, respectively. Their integration ratio of about 2:1:1:2 also agrees with the structure of 1,3-polyazulene. Figure 2 shows a comparison of the FT-IR spectra of azulene and 1,3-polyazulene in the range of 400−4000 cm^{-1}. The IR absorption peaks of 1,3-polyazulene are in general broader, but they correlate clearly with the spectrum of azulene. The characteristic peaks of azulene at 3017 and 2960 cm^{-1} ($\gamma_{=\mathrm{C-H}}$), 1572 and 1390 cm^{-1} ($\gamma_{\mathrm{C=C}}$), and 754 cm^{-1} ($\delta_{=\mathrm{C-H}}$) are mirrored in the FT-IR spectrum of polyazulene at 3011, 2910, 1565, 1395, and 734 cm^{-1}, respectively. The elemental analysis (found: C, 94.31; H, 4.63) is also in good agreement with the expected structure (calcd: C, 95.21; H, 4.79). Thus, there is sufficient experimental evidence to indicate that the azulene units remain intact in the isolated 1,3-polyazulene.

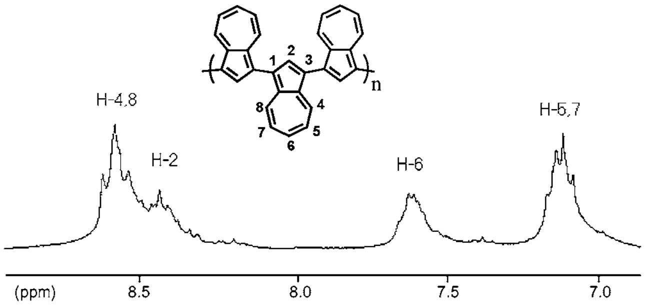


Figure 1. ^{1}H NMR spectrum of poly-1,3-azulene.

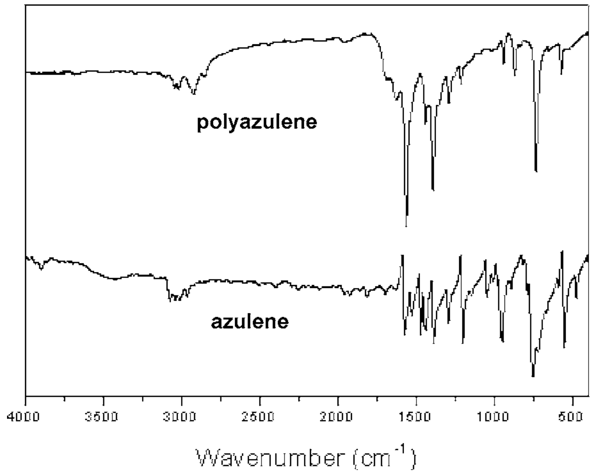


Figure 2. FT-IR spectra of azulene and 1,3-polyazulene.

The 1,3-polyazulene prepared in our work was insoluble in methanol but partially soluble in a variety of organic solvents such as chloroform, THF, xylenes, DMF, and *N*-methylpyrrolidinone, forming a yellow-green solution in each case. In addition, the polymer was also soluble in trifluoroacetic acid (TFA) and concentrated sulfuric acid (concentrated H_2SO_4), resulting in solutions with intense but different colors. A solution of 1,3-polyazulene in concentrated H_2SO_4 was dark-green, while that in TFA was purple. It is interesting to note that the polymer is insoluble in acetic acid and in dilute sulfuric acid. These results suggest that the solubility of 1,3-polyazulene in acid is dependent on the degree of protonation of the polymer and thus the strength of the acid.

A comparison of the electronic spectra of 1,3-polyazulene in different solvents is shown in Figure 3. The extended π-conjugation in the polymer results in a red shift (about 76

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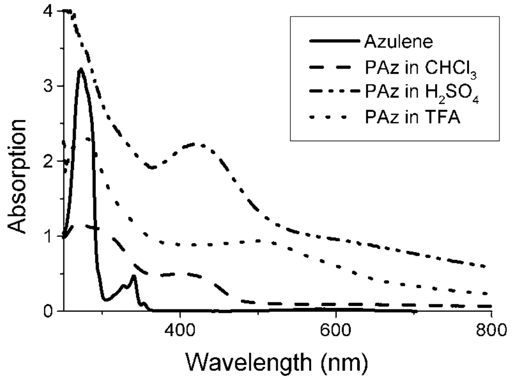
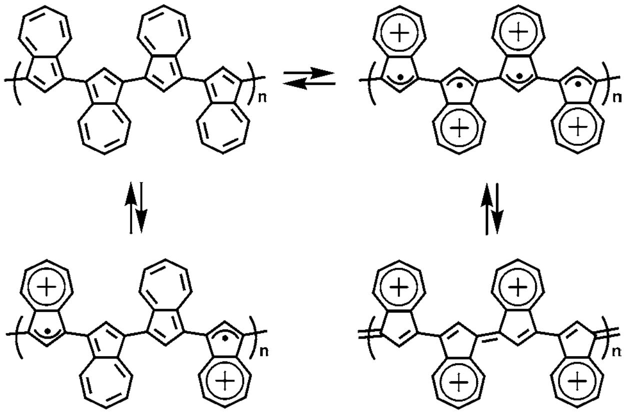


Figure 3. UV−vis spectra of azulene and 1,3-polyazulene.

nm) of the $\pi-\pi^*$ absorption band going from azulene (341 nm) to 1,3-polyazulene (417 nm). Compared with the large red shifts (200−250 nm) of polythiophene and poly(3-alkylthiophene),[9] 1,3-polyazulene shows a significantly smaller red-shift, reflecting the less effective *meta*-conjugation. The UV−vis spectra of 1,3-polyazulene in concentrated H_2SO_4 and TFA are significantly different, although its solubility in both solvents should involve protonation.[10] The solution in concentrated H_2SO_4 shows a λ_{max} at 435 nm with a shoulder at about 630 nm, while that in TFA exhibits a λ_{max} at 508 nm. These results substantiate that different protonation species of the polymer were present in the two acid solutions. The absorption at the longer wavelength is believed to correspond to the formation of azulenium cation radicals or the σ dimers,[11] and more extensive protonation would then lead to the formation of di- and polycations as illustrated in Scheme 2. Findings from EPR studies (Figure 4) are in good agreement with the above observation. A solution of 1,3-polyazulene in concentrated H_2SO_4 shows only a very weak EPR signal centered at $g = 2.0020$ with a peak-to-peak line width (ΔH_{pp}) of 2.49 G, which is considered to be derived from the cation radical by trace protonation and/or oxidation of azulene. On the contrary, a solution of 1,3-polyazulene in TFA gave a sharp EPR signal centered at $g = 2.0016$ with a ΔH_{pp} of 5.86 G, indicating that more free cation radicals (polarons) are generated from TFA protonation followed by oxidation.

Scheme 2. Examples of the Formation of Cation Radicals and Di- and Polycations upon Protonation of 1,3-Polyazulene.



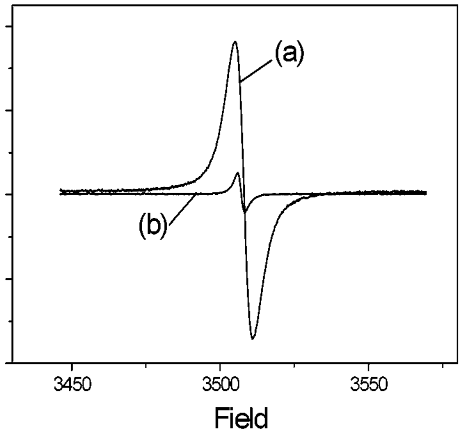


Figure 4. EPR spectra of 1,3-polyazulene in (a) TFA and (b) concentrated sulfuric acid.

Irreversible oxidations were observed above 0.5 V in azulene and its derivatives, and the current was attributed to the generation of azulenyl cation radicals.[12] However, in a cyclic voltammetry experiment conducted on the polyazulene prepared in our work, a quasireversible oxidation appeared at 0.7 V (vs Ag/Ag^+). The observation of the corresponding reduction current may be due to the stabilization of the azulenyl cation radicals by the conjugated polymer backbone.

Conductivity measurements were carried out with polymer pellets of known thickness (ca. 5 mm) using the four-point probe method. The neutral 1,3-polyazulene was essentially nonconducting (estimated to be $<10^{-11}$ S/cm). The dc conductivity of the polymer, however, increased significantly to 1.22 S/cm after being exposed to iodine vapor at room temperature for 4 days. A dc conductivity of 0.74 S/cm was observed for another sample of the polymer exposed to TFA vapor for 2 days. 1,3-Polyazulene was thus found to exhibit a high conductivity upon protonation similar to an observation made for polyaniline.

EPR spectral studies of iodine-doped and TFA-protonated powdered samples of 1,3-polyazulene were then used to provide additional information on the mechanistic changes upon doping and protonation, respectively. Consequently, a better understanding of the origin of conductivity may be elucidated. No EPR signal was observed before doping or protonation, but well-resolved signals were recorded after

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the processes. EPR analyses clearly suggest two different doping mechanisms. In the case of iodine doping, the spectrum of the sample shows an asymmetric EPR signal with a g factor value at 2.0026 and a peak-to-peak line width (ΔH_{pp}) of 18.62 G. As for the TFA-protonated sample, a symmetric signal with a g value at 2.0017 and a ΔH_{pp} value of 1.58 G was observed instead. These above results indicated that the paramagnetic center (PC) was different in the two cases. The spectral asymmetry and broadening in iodine doping can be associated with the strengthened spin−spin (both dipolar and exchange) interaction due to a high radical concentration upon iodine doping.[13]

The stability of the paramagnetic cation radicals formed after TFA protonation of 1,3-polyazulene and the reversible processes upon oxygen and nitrogen diffusion into the amorphous polymer powder could also be readily monitored by EPR studies. Using a common standard (1,2-diphenyl-2-picryl-hydrazyl for g value and Mn^{2+} salt for intensity) and the same spectrometer for a series of experiments, only about a 3% decrease in signal intensity with essentially no changes in the g value was observed for TFA-protonated samples exposed to air for 3 weeks. It is believed that the relatively long-lived cation radicals were stabilized by the formation of the azulenium cation due to the unique dipolar nature of azulene and the extended conjugation in the polymer backbone. When a TFA-protonated sample was exposed to oxygen, the intensity of its EPR signal decreased rapidly and broadened to a peak-to-peak line width (ΔH_{pp}) of 3.14 G. The signal was hardly detectable after 5 min. The paramagnetic dioxygen molecules could have attached to the polymer, and the exchange interaction between spins of immobile dioxygen molecules and mobile polarons during their collisions would result in the broadening of the observed EPR.[14]

Removal of oxygen from the TFA-protonated polymer seemed to be a slower process. A sample exposed to oxygen for 5 min was monitored by EPR measurements under a nitrogen flow at intervals of 10 s. The EPR signal returned to the original intensity only after >10 min as demonstrated in Figure 5. It is also interesting to note that the oxygen−nitrogen diffusion processes are reversible and could be repeated for many cycles.

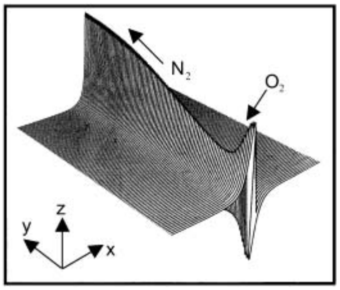

Figure 5. EPR spectral change with oxygen diffusion and nitrogen diffusion: x, axis of field (G); y, time (s); and z, intensity.

The quenching of the cation radicals unexpectedly did not affect the conductivity of the polymer significantly. A sample of powdered 1,3-polyazulene exposed to oxygen for 30 min still showed a conductivity of 0.57 S/cm. This suggests that protonation of 1,3-polyazulene by TFA may have resulted in the formation of both cation radicals and di- and polycations in the polymer backbone that collectively contribute to the high conductivity observed. The relatively small effect observed after quenching the cation radicals with oxygen may indicate that the cation radicals (polarons) play a relatively less significant role in the observed conductivity. The di- and polycations (bipolarons) make a more important contribution to the polymer's conducting properties.[15] The high electrical conductivity of 1,3-polyazulene achieved readily upon protonation makes it and its derivatives good models for advanced applications in molecular sensors, switching, and related materials.

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