Conducting Azulene−Thiophene Copolymers with Intact Azulene Units in the Polymer Backbone

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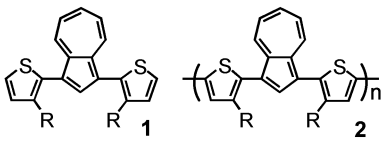
The structural characteristics of azulene and its derivatives[1] account for many of their unique electronic properties such as an appreciable dipole moment (μ = 0.8−1.08 D), low ionization energy, high electron affinity, and a tendency to form stabilized radical cations as well as anions.[2,3] These interesting electronic properties make azulene and its derivatives attractive research targets in the area of materials science.[4−6] Polyazulenes prepared by either electrochemical or chemical oxidation conditions were reported to show electrical conductivities in the range 0.01−1 S cm^{-1}.[7,8] The reported polyazulenes, however, have very low solubility[9] and more undesirably lost the structural features of azulene after polymerization or subsequent oxidation.[10] Polythiophenes are one of the most extensively investigated families of conducting polymers. They exhibit high thermal and environmental stability in both the neutral and doped states, and their properties could be varied over a wide range of solubility, conductivity, processability, and stability depending on their conformational behavior, the type of substituents attached, and their molecular electronic structure.[11−13] Copolymerization is in turn one of the most effective approaches to modify the electronic structure of polythiophenes as it could offer the promise of combining the higher stability associated with thiophene-based polymers with the specific electrical properties of the inserted conjugated moiety. We report here the synthesis of novel conjugated azulene−thiophene copolymers **2** with intact azulene units in the polymer backbone.



a, R = -C_4H_9 (54%)
b, R = -C_7H_{15} (47%)
c, R = -$C_{10}H_{21}$ (58%)
d, R = -$C_{14}H_{29}$ (42%)

The monomers **1a**−**d** were prepared by a Grignard coupling reaction between 2-bromo-3-alkylthiophene and 1,3-dibromoazulene catalyzed by Ni(dppp)Cl_2. The corresponding monomers were then chemically polymerized in chloroform using iron(III) chloride as an oxidizing agent.[14] Polymers **2a**−**d** were dedoped with hydrazine solution and found to be soluble in common organic solvents such as chloroform, THF, dichloromethane, toluene, and xylenes. Results acquired from gel permeation chromatography (GPC) in THF against the polystyrene standards show a number-average molecular weight of these polymers in the range 1.6 × 10^4−4.8 × 10^4. The molecular structures of polymers **2a**−**d** respectively were confirmed by ^{1}H NMR, ^{13}C NMR, and FTIR spectroscopy and elemental analysis.

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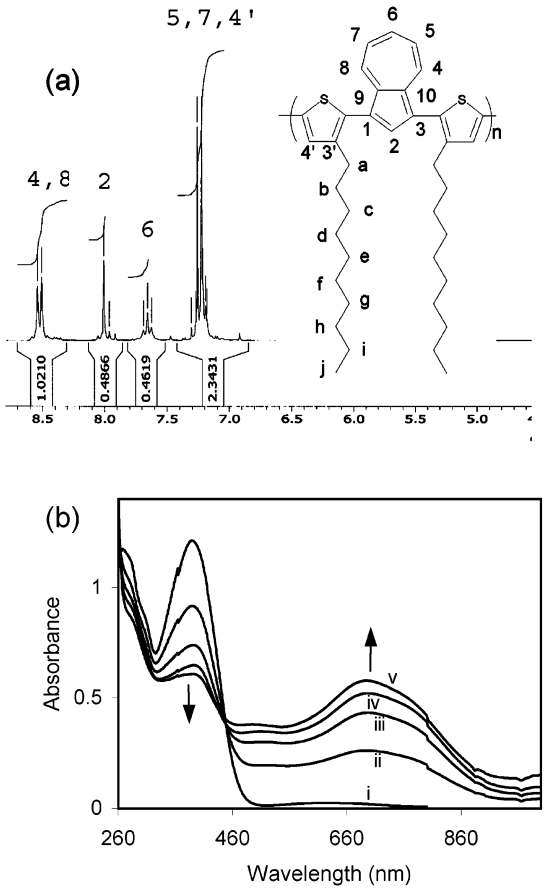

Figure 1. (a) ^{1}H NMR spectrum of the aromatic protons of polymer **2c**. (b) UV−vis spectra of polymer **2c** in chloroform with a TFA concentration of (i) 0%, (ii) 5%, (iii) 10%, (iv) 20%, and (v) 30%,

They display very similar spectral features, and Figure 1a shows the ^{1}H NMR spectra of the aromatic protons of polymer **2c** (R = $C_{10}H_{21}$) as an example. The signals at δ 8.52, 8.00, 7.65, and 7.22 corresponding to the 4,8-H, 2-H, 6-H, and 5,7-H of azulene, respectively, their characteristic splitting patterns, and their proton ratios collectively and strongly support the presence of intact azulene rings in the polymer backbone. Its ^{13}C NMR spectrum showing mainly 10 signals for the aromatic carbon atoms is undoubtedly consistent with the polymer structure and more importantly indicates a high coupling regularity of the polymerization. A thermal analysis reveals that the polymers **2** are stable up to 380−400 °C in air, and an expected side-chain effect of the different alkyl substituents on the polymers was observed in the T_g studies.

The protonation of polymers **2** in solution was studied by electronic spectroscopy. An example is the spectra of polymer **2c** in chloroform containing varied concentrations of trifluoroacetic acid (TFA) as shown in Figure 1b. At zero TFA concentration, the polymer exhibits two strong absorption bands at 238 and 386 nm in the UV region of the spectrum associated with the π−π* transition of the thiophene ring and the azulene moiety, respectively. Upon addition of TFA, a new band at 694 nm was observed which was attributed to the formation of azulenium cation radicals[16,17] (refer to later discussion on the EPR study). In fact, an increase in the TFA

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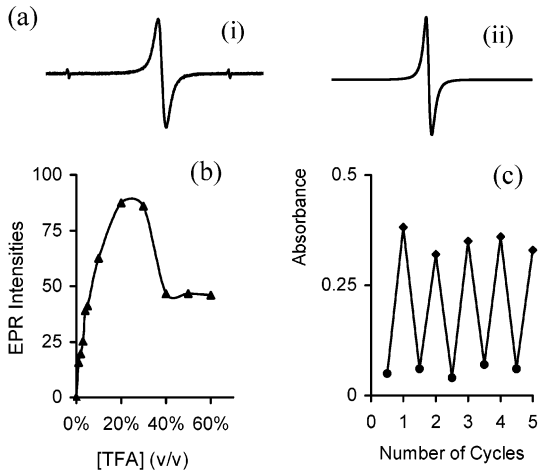
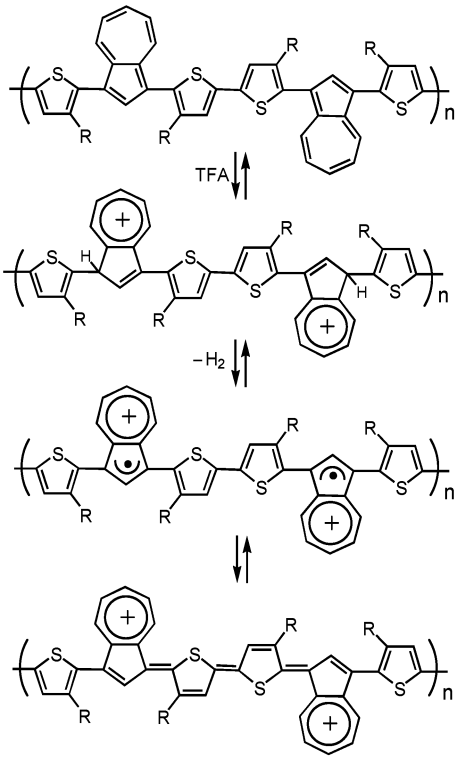


Figure 2. (a) EPR spectra of polymer **2c** (i) in chloroform solution with 5% TFA and (ii) exposed to TFA vapor in the solid state. (b) EPR signal intensity of polymer **2c** in chloroform at different TFA concentrations. (c) Absorbance at 1500 nm of the UV−vis−NIR spectra of neutral (●) and protonated (◆) polymer film of **2c**.

concentration (<30%, v/v) and a rise in absorbance in intensity of the band at 694 nm (1.78 eV) are concomitant with a gradual bleaching of the $\pi-\pi^*$ transition band at 386 nm. A clear isosbestic point is observed at 452 nm consistent with only two interconverting optically different phases are present in the system. The spectra changes became relatively less significant near a TFA concentration of 30% (v/v), suggesting that a saturated population of azulenium cation radicals could be reached at this TFA concentration. More interestingly, the change in their electronic spectrum of these polymers was found to be reversible. The TFA in the protonated polymers could be readily removed by simply washing with water and methanol. The normal UV−vis spectrum of the neutral polymers **2a**−**d** could then be recovered.

Electron spin resonance (EPR) spectra of the protonated polymers **2a**−**d** in chloroform clearly indicate the formation of the azulenium cation radicals.[18−21] For example, a chloroform solution of the polymer **2c** protonated with TFA at room temperature displays an EPR signal centered at $g = 2.0052$ with a width of 4.3 G as shown in Figure 2a. Changes in the EPR spectrum of polymer **2c** in chloroform associated with different TFA concentrations were found to follow a similar tend as those observed in its UV−vis spectra described above. A solution of neutral polymer **2c** gave no EPR response. At relatively low TFA concentrations (<30%, v/v), the intensity of the EPR signal was observed to increase significantly with an increase in TFA concentration (Figure 2b). Further increase in the TFA concentration (>30%, v/v), however, resulted in a drop in the intensity of the EPR signal. This may be attributed to extended protonation of the polymer, resulting in the formation of dications that are silent to electron spin resonance. A plausible sequence of protonation leading to the development of a cation radical followed by a dication is illustrated in Scheme 1. At relatively low TFA concentrations, isolated azulene units in the polymer are first protonated and then oxidized to azulenium cation radicals. This may be similar to the redox mechanism involving the liberation of hydrogen reported for self-acid-doped polythiophenes,[22,23] except that in the series of polymers **2** protonation is expected

Scheme 1. Examples of the Formation of Cation Radicals and Dications upon TFA Protonation of the Copolymers 2



to occur selectively at the azulene units due to the formation of the stable azulenium cation. As the TFA concentration continues to increase, dications would be formed at adjacent azulene units via conjugation in the polymer backbone accompanied by the observed changes in the electronic and EPR spectra.[18,24,25] The formation of the dication was also supported by an increase in absorbance at about 1250 nm in its UV−vis−NIR spectrum (refer to a later discussion on the UV−vis−NIR study).

In a series of EPR studies at room temperature, it was found that in general a chloroform solution of polymer **2c** in the presence of TFA showed only about a 20% decrease in the population of cation radicals after 1 week. In the solid state, a protonated polymer film showed no significant change in the EPR signal after 2 weeks. When a solution of protonated polymer was extracted with water and methanol to remove the TFA, the EPR signal was no longer observed, and the neutral polymer was recovered intact on the basis of NMR and UV−vis spectroscopic analysis. Evidently, the azulenium cation radicals formed were stabilized by the extended conjugation in the polymer backbone. The EPR spectrum of a protonated polymer film of **2c** is very similar to that observed in a chloroform solution. An EPR signal centered at $g = 2.0041$ with a width of 3.3 G was clearly observed (Figure 2a). Conductivity measurements showed that protonated polymer films of **2a**−**d** generally exhibit conductivities <1 S cm^{-1}. For example, the conductivity of a pellet of polymer **2c** reached 0.34 S cm^{-1} after being exposed to TFA vapor for 2 days. It was established that the polymers **2a**−**d** behave like insulator−conductor systems via a protonation−deprotonation process. Their conductivities in fact were observed to be lower than 10^{-12} S cm^{-1} when the TFA was removed from the protonated polymer pellets after washing with water and methanol.

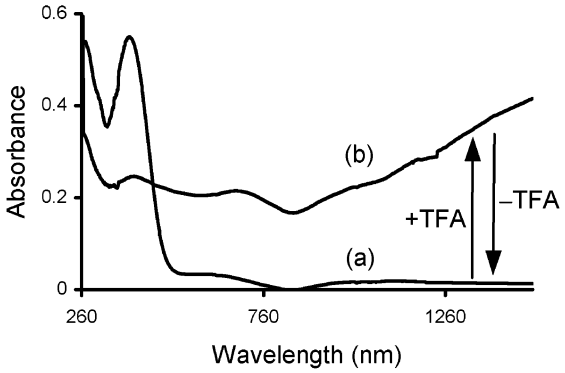


Figure 3. UV−vis−NIR spectra of a thin film of polymer **2c** (a) before and (b) after exposure to TFA vapor.

The UV−vis−NIR spectrum (Figure 3a) of a film of polymer **2c** showed main absorption bands (263 and 383 nm corresponding to the $\pi-\pi^*$ transition of thiophene and azulene) similar to those observed in solution. When the polymer film was exposed to TFA vapor, absorption features in the NIR region are similar to those reported for protonated polyemeraldine.[26] The signals at 263 and 383 nm diminished significantly, and a steadily increasing absorption tail starting from 1000 nm to the NIR region was observed (Figure 3b). Such an extended "free-carrier tail" is often characteristic of charge carriers delocalization in conjugated polymers.[27] The polymer films of **2a**−**d** in general exhibit the reversible protonation−deprotonation process as illustrated in Figure 3. When the dark green protonated polymer films were immersed in water and methanol to remove the TFA, the UV−vis−NIR spectra of the yellow-green neutral polymer films were again recovered. It is noteworthy that such a reversible process could be repeated for many cycles by monitoring the absorbance at 1500 nm as illustrated in Figure 2c. Although the initial absorbance at 1500 nm of the first protonated polymer film was not exactly recovered in subsequent reprotonated films, the largest deviation observed was only about 15%.

In conclusion, a series of novel conductive azulene−thiophene copolymers were successfully synthesized. The 1,3-conjugated azulene unit was shown to remain intact on the basis of spectroscopic analysis. Thus, characteristics of azulene such as its narrow HOMO−LUMO band gap and its tendency to form stabilized radical cations and dications are retained in the conjugated polymers. UV−vis, EPR, and NIR spectra showed that the copolymers showed reversible optical and electronic properties upon protonation and deprotonation due to the formation of azulenium radical cations. The high degree of reproducibility in their reversible processes combined with their high electrical conductivity, thermal stability, and solubility make copolymers **2a**−**d** good models for advanced applications in molecular sensors, switches, and related materials.

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