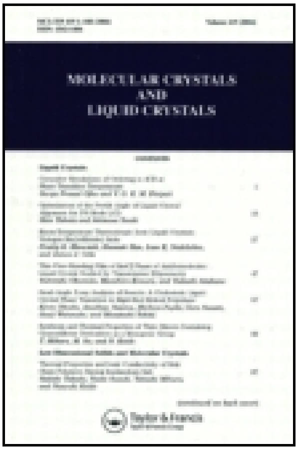

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Polyazulene, A Member of a New Class of Polymers

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POLYAZULENE, A MEMBER OF A NEW CLASS OF POLYMERS

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ABSTRACT: Electrochemical oxidation of azulene in acetonitrile containing an appropriate electrolyte yields thick, electrically conducting polymeric films. Free-standing films of polyazulene peeled off a platinum electrode have electrical conductivities $\sigma = 10^{-2}$ to $1/\Omega{\cdot}\mathrm{cm}$, depending on the counter-anion, with perchlorate or tetrafluoroborate giving the highest values. Similar polymers are obtained from benzenoid or heterocyclic aromatic monomers, for example, pyrene, triphenylene or carbazole. These polymers resemble the better known polypyrrole.

Spectroscopic evidence shows that the polymer consist of aromatic units, and elemental analysis reveals incorporation of counter-anions from the electrolyte; for polyazulene, one per 4 monomeric units. The consequences of alkyl substituents upon the tendency of the monomer to polymerize reveal that the hypothetical structure of polyazulene is best represented by 1,3-linked azulene units. The reaction mechanism involves dimerization of radical cations and deprotonation via a base. The so obtained oligomers oxidize more readily than the corresponding monomers.

INTRODUCTION

The electrochemical oxidation of aromatic molecules in polar solvents containing appropriate electrolytes has been found to yield two characteristically different types of reaction products: Under one set of conditions, especially in carefully purified tetrahydrofuran[1] or dichloromethane[2,3] electrically conducting crystals are being obtained on the anodes, which have been shown[3] to be radical cation salts of arenes (A). Their composition is of the type $(A_2)^{\cdot +}X^-$, whereby X^- is a counter-anion stemming from the electrolyte. Under seemingly similar conditions, especially in commercial grade (i.e., not absolutely dry) acetonitrile as the solvent, amorphous polymeric films deposit on the platinum anode, from where thick, free-standing films can be peeled off. The amorphous polymeric films have a characteristic composition of $\{(A-2H)_4^+ X^-\}_n$. These polymers too conduct electricity, but furthermore they are insoluble in common solvents and temperature stable to often better than 200°C. They are electroactive and can repeatedly be cycled between the conducting (oxidized) and nonconducting (neutral) state with no significant decomposition of material. The switching is also accompanied by a reversible color change from blue-black (oxidized) to yellow (neutral).

Polymers of this type derived from heterocyclic aromatic monomers, in particular pyrrole[4] and thiophene[5] are well known. Polymer formation has also been reported upon electro-oxidation of benzene and biphenyl.[6] We have recently found that azulene in the presence of suitable electrolytes electro-oxidizes in acetonitrile to yield thick, flexible, free-standing, amorphous polymeric films which conduct electricity with conductivities (σ) of the order of $\sigma \approx 10^{-2}$ to $1\ \Omega^{-1}\cdot\text{cm}^{-1}$, depending on the type of counter-anion.[7] Independently Tourillon and Garnier[8] have recently reported the formation of electrically conducting polyazulene via electro-oxidation, but so far only the electrical properties and the elemental composition of polyazulene have been published. Other properties of the polymeric materials, and of polyazulene as well, are difficult to obtain due to their insolubility. Knowledge of the structure of polyazulene would allow extrapolation to the polymerization mechanism. The latter seems to be rather general and to apply to benzenoid, nonbenzenoid and heterocyclic aromatic molecules alike. Of particular interest are the boundary conditions under which the electro-oxidation of aromatics yields either crystalline radical cation salts or instead amorphous polymers.

For "simple" monomers, such as the five-membered heterocycles pyrrole or thiophene, the gross structural features can be extrapolated from the symmetry and chemical reactivity of the monomers, suggesting that these polymers are mainly made up of α-linked pyrrole or thiophene units. Indeed this hypothesis is supported by chemical evidence, namely by the failure of α-substituted pyrroles to undergo polymerization[9,10] and also from the results of oxidative degradation studies.[11] However, the symmetry of these five membered rings does not allow for unequivocal conclusions pertaining to the reaction mechanism of the dehydropolymerization.

For a more complex monomer such as azulene, it is not straightforward to predict the exact position where the monomer units are connected in the polymer. Knowledge of the connecting pattern, however, would allow one to differentiate between, for example, electrophilic attack of radical cations upon neutral monomer or radical cation dimerization. We have, therefore, tried to obtain structural information about polyazulene using a combination of physical and chemical techniques, namely by applying spectroscopic techniques and by studying the consequences of blocking potential linkage sites with methyl substituents.

EXPERIMENTAL SECTION

All compounds were obtained from commercial sources, except for the following substituted azulenes*: 1-Methyl- and 1-phenylazulene were synthesized according to the literature.[12] Electrochemical measurements were performed in a three electrode, single compartment cell with a platinum working electrode, a gold counter electrode, and a sodium chloride saturated calomel reference electrode (SSCE). The solutions typically contained 10^{-4}–10^{-3}M of the appropriate azulene monomer with 0.1M electrolyte, tetraethylammonium fluoroborate (TEAFB) or tetrabutylammonium perchlorate (TEAPC), in acetonitrile. The acetonitrile (Burdick and Jackson) was used directly without further purification, and deoxygenated by bubbling with argon. All electrochemical measurements were made on an IBM EC225 Voltammetric Analyzer.

RESULTS AND DISCUSSION

Cyclic voltammetric data for azulene and some azulene derivatives are given in Table 1. All monomers exhibit irreversible oxidation peaks, and polymers are obtained only from azulene and 4,6,8-trimethylazulene monomers (Figure 1).

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*We are indebted to Professor P. C. Myhre of Harvey Mudd College, CA, for samples of 4,6,8-trimethylazulene and 4,6,8-trimethylazulene-1-aldehyde, and to R. Twieg of this lab for samples of 1-phenylacetylenylazulene and 1,3-di-trimethylsilylacetylenylazulene.

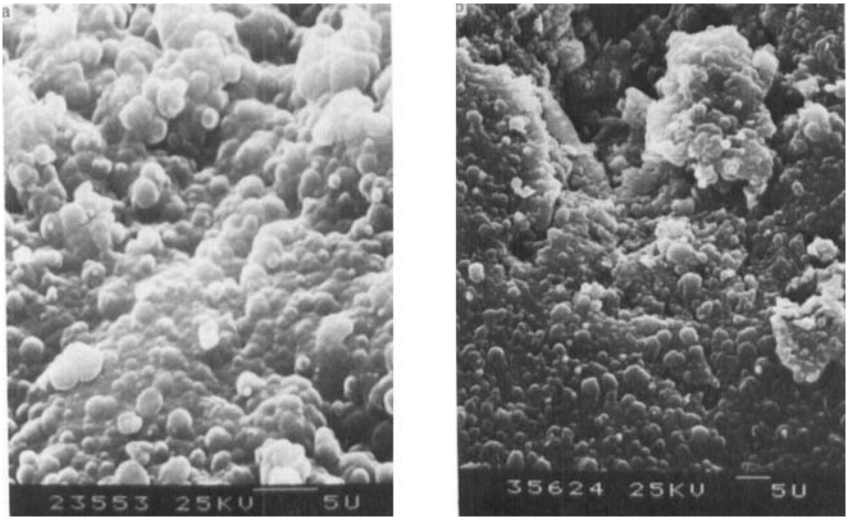


FIGURE 1. Scanning electron micrographs of (a) polyazulene-BF_4 and (b) poly-4,6,8-trimethylazulene-ClO_4.

TABLE 1. Cyclic voltammetric data for azulenes in 0.1M TEAFB/CH_3CN: ✓ indicates polymer formation; X indicates no polymer. E_{pa} (✓) *versus* SSCE.

Compound	E_{pa} monomer
azulene	0.91 ✓
4,6,8-trimethylazulene	0.90 ✓
1-methylazulene	0.90 X
1-phenylazulene	0.89 X
4,6,8-trimethylazulene-1-aldehyde	1.33 X
guaiazulene	0.71 X
1-(phenylacetylenyl)azulene	0.90 X
1,3-di-(trimethylsilylacetylenyl)azulene	1.04 X

Any azulene monomer with one or more substituents on the 1- and/or 3-positions on the five-membered ring failed to give polymeric material on electro-oxidation. This is not the case when the seven-membered ring is substituted, however; thus 4,6,8-trimethylazulene polymerizes at the Pt electrode whereas the closely related monomer with an additional 1-substituent on the five-membered ring (4,6,8-trimethylazulene-1-aldehyde) completely fails to polymerize when electro-oxidized. These data suggest that only the five-membered ring positions qualify as linkages between the azulene monomer units in the polymer. Further, the lack of polymer formation with 1-methylazulene suggests the 2-position is also not involved in the polymerization process. It is unlikely that a methyl substituent would either stereochemically or electronically burden the dimerization or polymerization of azulene to any great extent. Therefore, the linkages in polyazulene most likely occur at the 1- and 3-positions. When coupled with data obtained from elemental analysis of polyazulene, the stoichiometry can be elucidated whereby one charge is shared by four azulene units (Figure 2).

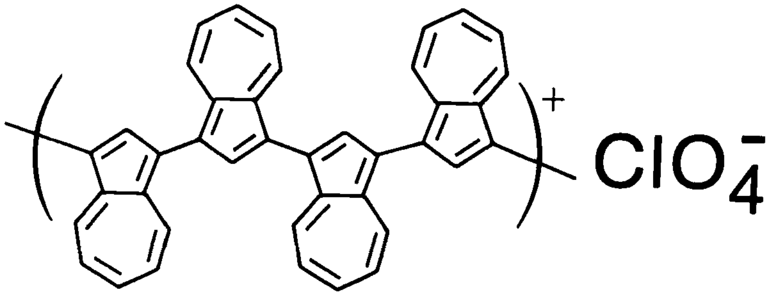


FIGURE 2. A possible structure for conducting polyazulene.

Mechanistic Considerations

From the hypothetical structure outlined above, mechanistic conclusions can be derived in the following manner: Azulene, by virtue of containing a five- and a seven-membered ring has a dipole moment, which is due to the unequal tendency of the two rings to accommodate an electrical charge. Thus the five-membered ring prefers to accept an extra π-electron thereby becoming a 6π-electron system. The seven-membered ring in turn would rather lose an electron, which also gives rise to a 6π-electron system. Quantum chemical LCI-SCF calculations by Zahradnik *et al.*[13] reveal the positions of highest and lowest π electron densities in the neutral azulene monomer and its radical cation, respectively (Figure 3). An electrophilic aromatic attack of the radical cation upon neutral monomer could thus be expected to result in a chain of 1,4-linked azulene units, which is not supported by the above findings, however.

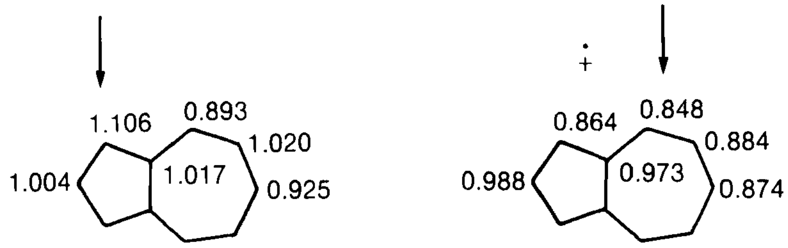
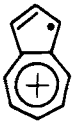


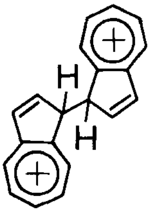
FIGURE 3. π-Electron densities of azulene; see Reference 13.

The 1- and 3-positions of azulene are indeed known to be attacked readily by electrophiles. Thus the nitration of azulene yields either the 1-nitro or the 1,3-dinitroazulenes.[14]

On the other hand, EPR studies of the radical cation derived from azulene reveal that the highest spin density occurs at the 1- and 3-positions as well.[15] A resonance structure of the radical cation can thus conveniently be drawn as



which lends itself to dimerization via the 1 position. This combination step would generate a doubly oxidized dihydrodimer which would have to lose two protons to become a neutral dimer with appropriate structure.



Subsequent oxidation of this dimer is most likely easier than that of the monomeric azulene, a situation also found with oligomeric thiophenes, pyrroles and p-phenylenes[16] (for example, biphenyl *versus* benzene). Reoxidation of the 1,1′-linked azulene dimer would generate a new radical cation, which with another radical cation of the monomer could yield a doubly oxidized dihydrotrimer. After twofold proton loss and reoxidation, the reaction could go on in a similar fashion to yield a properly 1,3-linked chain of azulene units.

This hypothetical reaction sequence is supported by the observation that in order to sustain the polymerization, it is required that the electrochemical potential has to be maintained at (or near) the oxidation potential of the monomer.

Furthermore, electrochemical oxidation of molecules in solution is determined by the rate with which the substrate diffuses to the electrode region. The electron transfer, i.e., the oxidation itself, is a very fast process. Thus, in the vicinity of the electrode, only radical cations but no neutral azulene monomer will be found. Since the oligomers of azulene are expected to be oxidized more readily than the azulene monomer, they too will occur in the form of their radical cations as well.

To remove the surplus protons in the dehydropolymerization scheme, a suitable proton carrier, i.e., a *base* is required. As such qualify the electrolyte anions and the solvent (acetonitrile). Furthermore, water or other impurities can be expected to affect the base character of the system, which all is consistent with the observation that polymer formation depends chiefly on:

1) the electrolyte anion
2) the solvent
3) the water content thereof.

Ambrose and Nelson[17] have shown that a sterically hindered pyridine can serve as a base during the electro-oxidation of carbazole, which also yields a polymer. This system is of particular interest, since two isomeric dimers can result from the coupling process, namely the 9,9′ linked dimer as well as the 3,3′ linked one. Only the latter has a more favorable oxidation potential than the corresponding carbazole monomer, and thus the polymer has 3,6 linkages between the carbazole monomer units. The 9,9′ linked dimer instead is not reoxidized and terminates this branch of the electro-oxidation. Proper choice of the base can be used to affect the ratio of initial 3,3′ *versus* 9,9′ dimerization.[17]

These findings render the reaction between neutral molecules and radical cations unlikely. Thus the above dehydropolymerization deviates from the conventional schemes of either cationic, free radical or anionic polymerization, which all act upon neutral monomer. The mechanism as discussed here corresponds to a dimerization of radical cations, a known process,[18] but is followed by efficient deprotonation via a base. The deprotonation sets the stage for even more efficient reoxidation and subsequent radical cation combination between an oligomeric and monomeric radical cation, again followed by deprotonation and so forth (Figure 4).

Thus, the tendency of azulene to polymerize upon electro-oxidation resembles that of pyrrole,[19] thiophene,[5,10] and benzene or biphenyl,[6] all of which give rise to a chain or network of linked aromatic units. Furthermore, all of these electrochemically produced and conducting polymers from pyrrole, thiophene, and azulene show electrochemical stoichiometry whereby 2.2–2.4 electrons per monomer (X) is lost, and where the excess charge is thought to be consumed in the partial oxidation of the film. Carbazole has an n-value of 2.5–2.8 as reported by Ambrose and Nelson.[17] Thus, all of these appear to follow the general scheme

$$[X]_{n+2} \xrightarrow{-2(n+2)e^-} X'-[X]_n-X'' + (2n+2)H^+$$

Thus, the overall polymerization process resembles the classical ECE mechanism whose key features include:

(a) The polymerization is originally initiated via electrochemical oxidation of the monomer.
(b) The radical cation of the monomer so obtained is a key reaction intermediate.
(c) A dihydrodimer is formed as a subsequent intermediate in an oxidized form.
(d) This oxidized dihydrodimer loses two protons to yield a dimer.
(e) The oxidation potential of the dimer is lower than that of the monomer, a fact which renders the subsequent oxidation of the dimer especially facile.
(f) The dimer becomes electrochemically oxidized.
(g) "Follow-up reaction" of the oxidized dimer lead to an oxidized dihydro-oligomer.
(h) Proton loss eventually yields an oligomer.
(i) Oxidation of any oligomer is more facile than that of either the monomer or dimer.

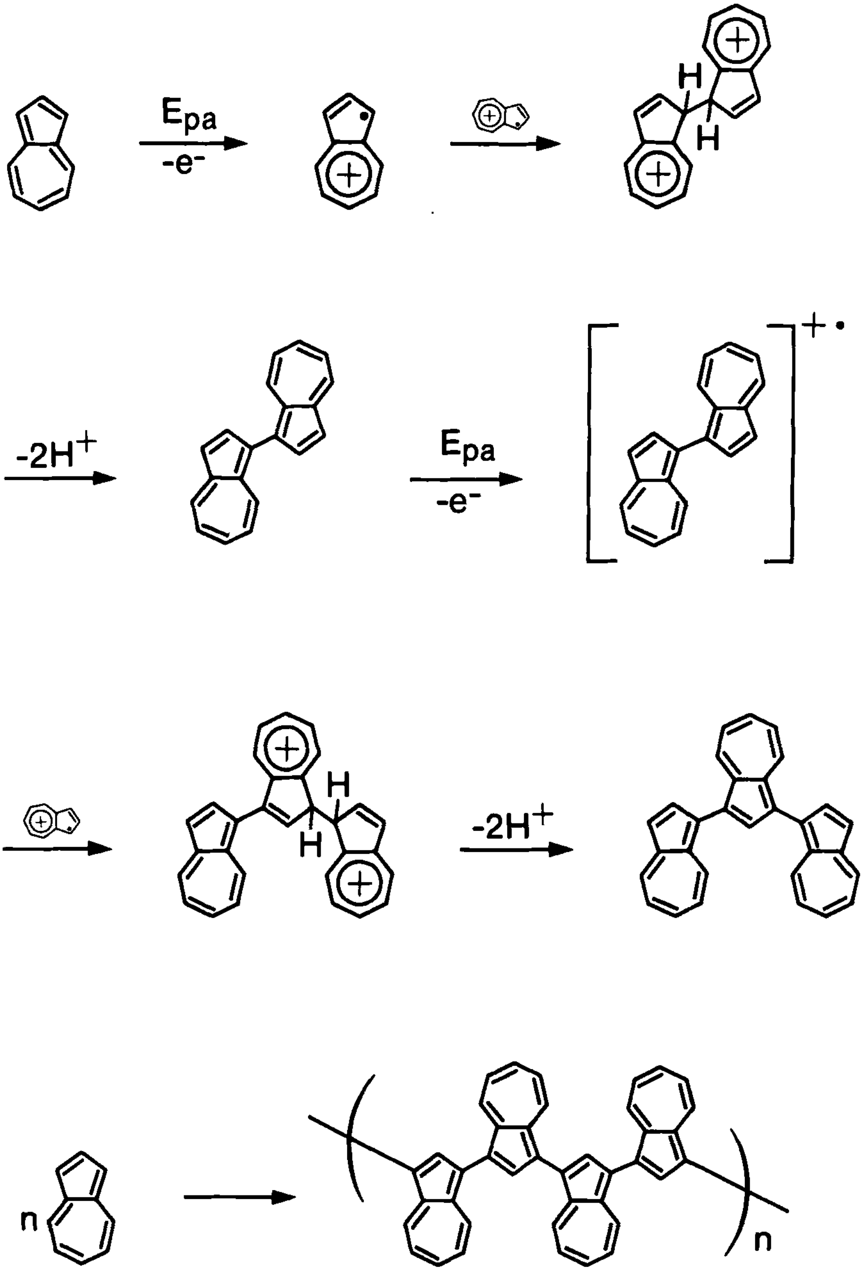


FIGURE 4. Electro-polymerization of azulene.

Spectroscopic Studies

Additional support for the eventual polymer in Figure 4 comes from spectrometric studies. Thus, the UV-visible spectrum of azulene and polyazulene-ClO_4 show similar features, suggesting a related system of π-electrons, and, therefore, that ring integrity is maintained in the polymer (Figure 5). The same interpretation results when considering the ^{13}C solid state NMR spectrum of polyazulene (Figure 6).

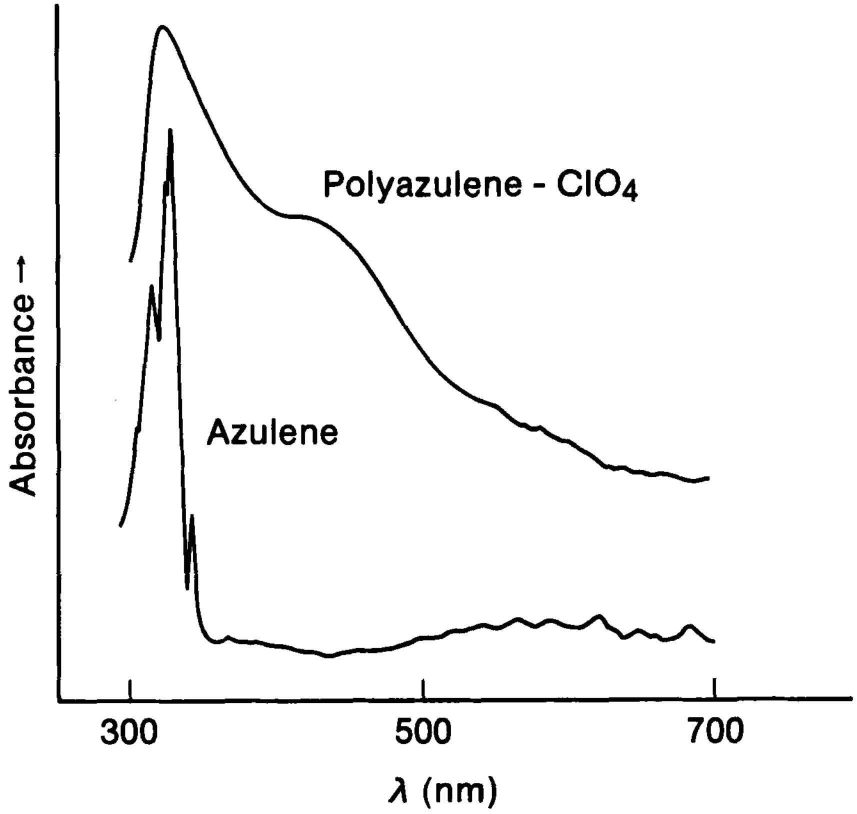


FIGURE 5. Visible spectrum of azulene and polyazulene-ClO_4 (on Nesa glass).

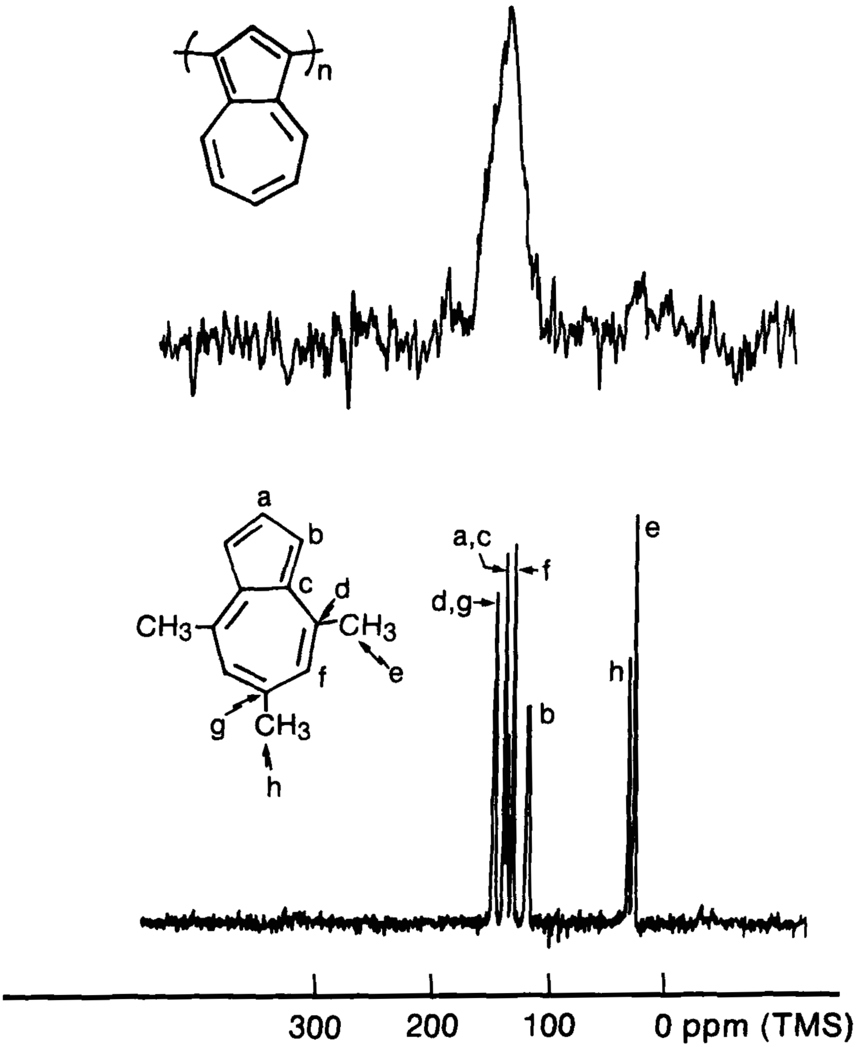


FIGURE 6. Solid state magic angle ^{13}C nmr spectrum of (a) polyazulene-ClO_4 and (b) trimethylazulene monomer at -150°C.

Figure 6b shows the 15 MHz solid state NMR spectrum of 4,6,8-trimethylazulene monomer, whose lines were assigned by analogy to azulene monomer[20] and by delayed decoupling techniques.[21] The ring carbon atoms resonate in the 130-150 ppm range, whereas the methyl carbon atoms resonate upfield at 31 and 36 ppm, relative to TMS. In comparison, the NMR spectrum observed for unsubstituted and oxidized polyazulene-ClO_4 also occurs in the 130-150 ppm range, confirming prior assertions of intact azulene units in the polymer. Unfortunately, the lines of the polymer are broad, thus masking any detailed structural information. The origin of the broadening is unknown. Further studies are in progress.

CONCLUSIONS

Spectroscopic data and chemical substitution of azulene indicate that polyazulene forms via linkages at the 1- and 3-positions with ring integrity maintained. The conducting polymers obtained from azulene, pyrrole, thiophenes, and carbazole all show electrochemical stoichiometry, and the polymerization pathway seems to be universal for the above polymers of which the key features include: (a) dimerization of radical cations; (b) proton loss to yield a neutral dimer; (c) oxidation of dimer or higher oligomer; (d) reaction of oxidized oligomer with radical cation; (e) dehydro-oligomerization.

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