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Electrochemical Synthesis of Electrically Conducting Polymers from Aromatic Compounds

Amorphous, electrically conducting polymeric films can be deposited from acetonitrile solutions of specific aromatic compounds containing an appropriate electrolyte. Free-standing films peeled off a platinum electrode have electrical conductivities σ *between* 10^{-3} *and* $1\ \Omega^{-1}\text{-cm}^{-1}$*. Polymers resembling the better-known polypyrrole have been obtained from benzenoid, nonbenzenoid, and heterocyclic monomers. A few characteristic examples are discussed to highlight the characterization efforts. Also discussed are the chemical investigations which have provided some insight into the mechanism of formation and the structure of these conducting polymers.*

Introduction

The electrochemical oxidation of aromatic compounds frequently leads to the deposit of an organic film on the platinum anode [1]. If this film is insulating (as in the case of naphthalene [1a]) the electrochemical current drops off very rapidly, and film growth ceases. If the deposit conducts electricity, however, thick films can be grown and peeled off the platinum electrode [2]. There are two types of conducting organic deposits, crystalline radical cation salts [3] and amorphous polymeric films [2]. Formation of the crystalline salts requires very highly purified substrates and solvents, of which methylene chloride (CH_2Cl_2) and tetrahydrofuran are preferred [3]. This article is concerned with the formation of thick, electrically conducting, amorphous polymeric films from aromatic monomers, and not with the more traditional electro-initiated cationic polymerization of olefinic monomers [4].

Historical background

In a pioneering experiment, Diaz et al. [2] of this laboratory demonstrated that the electro-oxidation of pyrrole in acetonitrile containing an appropriate electrolyte led to the formation of "polypyrrole," an electrically conducting polymer. The continuous films of polypyrrole so obtained seemed to be related to the so-called "pyrrole blacks," the well-known chemical oxidation products of pyrrole [5, 6]. For these earlier pyrrole blacks, it had been concluded that pyrrole, upon oxidation, yielded a chain-type polymer made up of 2,5-pyrrolediyl units. This conclusion was reached based on the resistance of the 2,5-disubstituted pyrrole monomers to polymerization. Furthermore, 2-monosubstituted pyrroles failed to react beyond the dimer stage [5]. In addition, elemental analysis of the electropolymerized polypyrrole films revealed that they contained counter anions from the electrolyte, namely, about one anion for every four pyrrole units [6]. The chemistry of this system has since been studied extensively, though not fully elucidated [6]. An essentially similar behavior has since been found for a variety of other aromatic substances, among them heterocycles [7, 8], as well as benzenoid and nonbenzenoid aromatic hydrocarbons [8, 9].

Properties and physical parameters

Because of the increasing number of systems which have been shown to behave like pyrrole, electrodeposition has become a viable technique for the synthesis of electrically conducting polymeric films. Typically, these films are initially obtained in a black, oxidized (i.e., "doped"), electrically conducting state, from which they can be electrochemi-

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cally converted (i.e., "switched") to a pale-yellow-to-brown, less conducting (neutral) form [10]. This switching is associated with the removal of anions from the polymer. The process can be reversed by application of an appropriate potential, which switches the film back to its conducting state. If the chemical composition of the electrolyte is altered between the switching cycles, the counter anions can be exchanged. In their oxidized state, the polymers are typically stable under ambient conditions to temperatures well above 200°C. In their neutral state, however, they are sensitive to oxygen, and electron scattering (ESCA) studies can be used to follow the oxygen uptake from air. This oxygen sensitivity of the neutral state limits the chemical reversibility and, especially, the reversible electrochromic behavior of these polymers, unless hermetically sealed systems are ensured.

Due to their insolubility, the structures or other physical parameters of these polymers are only scarcely known. Accordingly, the mechanism of the polymerization has remained ambiguous, and these polymers continue to provide a challenge for both traditional and modern characterization methods. The very same reason makes it very difficult to reproduce the properties or physical parameters of a given polymer from batch to batch.

General features

Since vastly different members of the diversified family of aromatic compounds display strikingly similar behavior upon electro-oxidation, it would be more than surprising if the resulting polymeric films were not formed by a rather general polymerization mechanism. Understanding this mechanism would decisively support characterization efforts, since frequently a hypothetical structure can be extrapolated from the reactivity patterns of the reaction intermediates. We have, therefore, conducted a study of a few selected systems, comprising suitable heterocycles (thiophene and carbazole), benzenoid aromatics (triphenylene and pyrene), and a nonbenzenoid variety (azulene).

Polyazulene

Electrochemical oxidation of a 10^{-3} M solution of azulene in acetonitrile containing 0.1 M appropriate electrolyte yields thick, amorphous, electrically conducting films. These can be peeled off the Pt anode to provide free-standing, flexible films with electrical conductivities σ between 10^{-2} and 1 Ω^{-1}-cm^{-1}. Elemental analysis of these films indicates that they contain anions which stem from the electrolyte, at typical concentrations of about one anion for every four azulene units. This situation closely resembles polypyrrole [6]. The electrical conductivities of the polyazulene films depend on the nature of the counter anion, with perchlorate and tetrafluoroborate anions giving the highest values of the selection investigated so far. Table 1 lists the conditions for the synthesis of polyazulene films using different electrolytes, as well as the electrical conductivities of the resulting free-standing films. Figure 1 shows the cyclic voltammogram of a typical 50-nm-thick film of polyazulene-BF_4 attached to a Pt electrode in a 0.1 M solution of tetraethylammonium tetrafluoroborate (TEAFB) in acetonitrile. The peak oxidation potential ($E_{pa} \approx 0.70$ V) of the polymer is shifted by about 0.20 V cathodic relative to that of the monomer. The peak oxidation current values i_{pa} scale linearly with sweep rate between 0.02 and 0.08 V/s, as expected for a surface-attached species. The n value is 2.3, indicating that the polymerization of azulene involves two electrons per monomer. The remaining 0.3 excess charge unit is required for the partial oxidation of the film, which in turn is balanced by uptake of counter anions from the electrolyte. Thus, the electrochemically deposited polyazulene shows electrochemical stoichiometry (as does polypyrrole [6]).

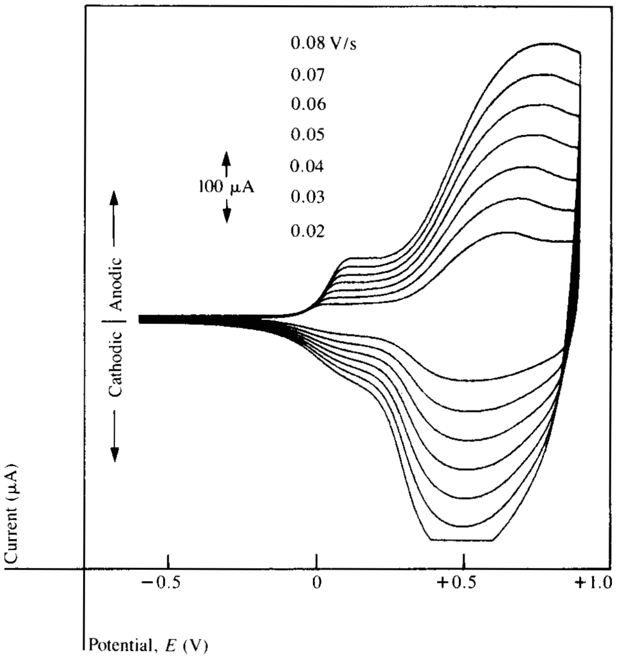


Figure 1 Cyclic voltammogram of [Pt]polyazulene-BF_4 in 0.1 M tetraethylammonium fluoroborate/acetonitrile using a gold counter electrode and a sodium standard calomel electrode (SSCE) as a reference electrode.

Table 1 Electrical conductivity of polyazulene as a function of the counter anion.

Counter anion	σ_{300K} (Ω^{-1}-cm^{-1})
BF_4^-	0.02–1.00
ClO_4^-	0.05
PF_6^-	0.03
p-toluenesulfonate	0.01

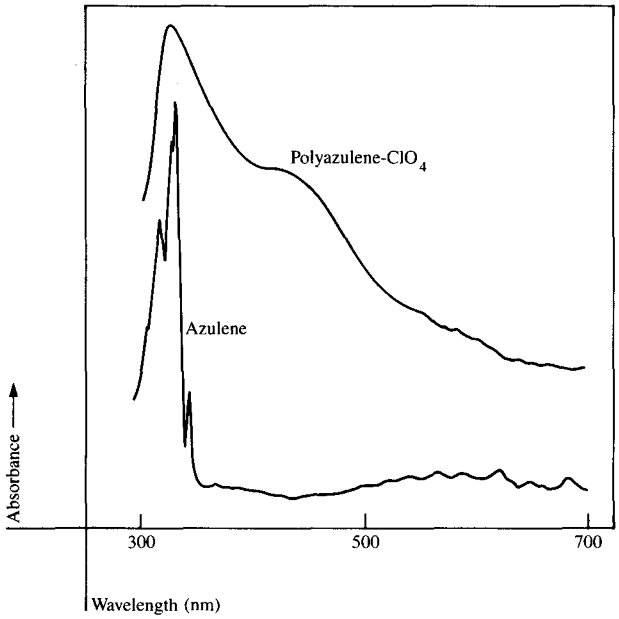


Figure 2 Absorption spectra of azulene and polyazulene on NESA (indium-tin oxide) glass.

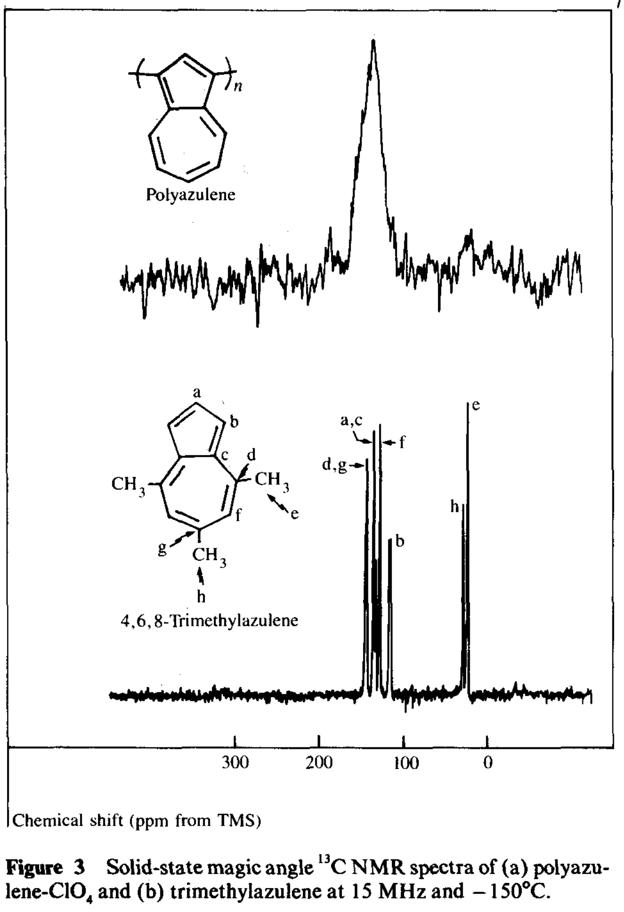


Figure 3 Solid-state magic angle ^{13}C NMR spectra of (a) polyazulene-ClO$_4$ and (b) trimethylazulene at 15 MHz and −150°C.

Excluding the excess oxidation of the polymeric film and the incorporation of counter anions for the moment, the overall polymerization scheme for azulene is best represented by

$$(n + 2)[M] \xrightarrow{-(2n+2)e^-} M' - [M]_n - M'' + (2n + 2)H^{\bullet}.$$

This scheme suggests that polyazulene is made up of a chain of azulene units. The elemental analysis and the electrochemical stoichiometry of the system reveal that excess oxidation of the film occurs; this is balanced by counter anions from the electrolyte at a concentration of one anion for every four azulene units. All samples are found to be hydrogen rich by elemental analysis, a fact that will be addressed in a subsequent study.

Spectroscopic studies

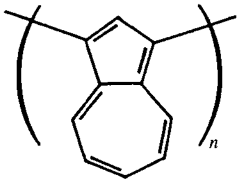
In order to obtain more detailed information, in particular, the location of the azulene unit linkages in the polymer framework, spectroscopic data are required. Such studies are frustrated, however, by the insolubility of the polymeric films.

The ultraviolet-visible spectra of polyazulene-ClO$_4$ and azulene (Fig. 2) show similar features, suggesting that both compounds are made up of essentially the same framework of π-electrons. This indicates that the integrity of the azulene rings in the polymeric chain is maintained.

The solid-state high-resolution ^{13}C nuclear magnetic resonance (NMR) spectrum of polyazulene-ClO$_4$, obtained at 15 MHz at low temperature under magic angle spinning conditions [11], is shown in Fig. 3, together with that of 4,6,8-trimethylazulene. The latter yields a well-resolved spectrum in which all lines can be assigned to their corresponding carbons by using delayed decoupling techniques. Unfortunately, the spectrum of the polymer consists only of one broad unresolved resonance. The chemical shift of this resonance confirms the previous conclusion that the azulene units are incorporated "intact" into the polymeric chain. However, the expected differentiation between isomeric forms of polyazulene is as yet not possible. The reasons for this lack of resolution are not totally understood, but additional efforts using the neutral form of polyazulene are under way.

Substituent effects

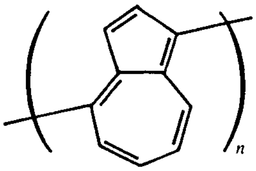
For pyrrole, it is known that blockage of the α positions (the sites where linkage between the pyrrole units occurs in the polymer) suppresses the ability of the monomer to polymerize [5]. We have, therefore, investigated the effect of alkyl substituents on the polymerizability of azulenes. Table 2 reveals that any 1-substituted azulene fails to polymerize electrochemically. Accordingly, both the 1 and 3 positions of azulene must remain unblocked for polymerization to occur. However, 4,6,8-trimethylazulene (TMA), in which three positions of the seven-membered ring are simultaneously substituted, does yield a polymer, albeit of lower conductivity. These substituent effects suggest that the structure of polyazulene is best represented as poly(1,3-azulenediyl) (Structure I).



I

Mechanistic considerations

The finding that the azulene units are connected exclusively via positions of the five-membered ring has the following implications for the reaction mechanism: The originally formed radical cation, in principle, has two likely options. It can act as an electrophile and attack neutral azulene, or it can act as a radical and dimerize (i.e., combine with a second radical cation). The hypothetical structure expected for the polymer would be different and thus would depend on the type of polymerization mechanism. Electrophilic attack should cause a linkage between the position of the *lowest* π-electron density in the *radical cation* (i.e., the 4,6- or 8-position of the seven-membered ring [12]) and the site of *highest* π-electron density in *neutral* azulene (i.e., the 1 or 3 position of the five-membered ring [12]). Figure 4 outlines the π-electron distribution for azulene (Structure II) and its radical cation (Structure III) as calculated by Zahradnik using HMO methods [12]. Accordingly, electrophilic addition of azulene radical cations to neutral azulene should result in poly(1,4-azulenediyl) (Structure IV), which was not found. Therefore, the conclusion drawn from substituent effects, i.e., that polyazulene has a poly(1,3-azulenediyl) structure (Structure I; see also Fig. 5), supports the concept of radical cation dimerization. This should lead to linkages between the 1 positions of the five-membered rings (the position of highest spin density in the azulene radical cation [13]) and the corresponding 1′ position of the other radical cation. Subsequent proton loss of the resultant dication (Structure V in Fig. 5) of the dihydrodimer would lead to the 1,1′-biazulyl (Structure VI). Upon reoxidation, the radical



IV

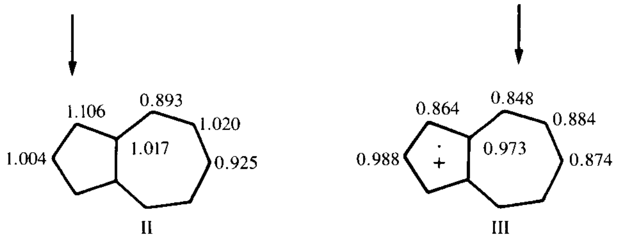


Figure 4 π-Electron densities in azulene and its radical cation. Arrows mark positions of highest density in neutral azulene and lowest density in the radical cation, respectively.

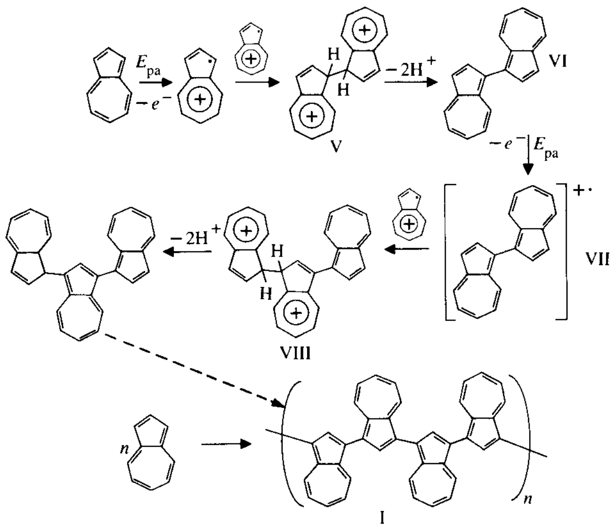


Figure 5 Proposed mechanistic scheme for the electropolymerization of azulene. Roman numerals adjacent to structures are referred to in the text.

Table 2 Cyclic voltammetric data for azulenes in 0.1 M TEAFB/CH_3CN (E_{pa} vs. SSCE).

Compound	*Monomer E_{pa}* (V)
Azulene	0.91^a
4,6,8-Trimethylazulene	0.90^a
1-Methylazulene	0.90^b
1-Phenylazulene	0.89^b
4,6,8-Trimethylazulene-1-aldehyde	1.33^b
Guaiazulene	0.71^b
1-(Phenylacetylenyl)azulene	0.90^b
1,3-Di-(trimethylsilylacetylenyl)azulene	1.04^b

[a] Polymer formation.
[b] No polymer formation.

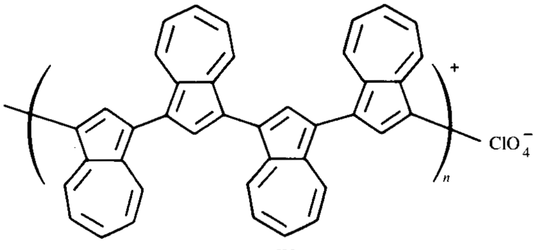
Table 3 Cyclic voltammetric data for 10^{-4}–10^{-5} M thiophenes measured in 0.1 M TEAFB/CH_3CN using Pt vs. SSCE.

Compound	*Monomer* E_{pa} (V)	*Polymer* E_{pa} (V)
Thiophene	2.06	0.96
2,2′-Bithiophene	1.32	1.00
2-(3-Thienyl)pyridine	1.69; 2.35	
3-Methylthiophene	1.86	0.72
3-Thiopheneacetic acid	1.94	
3-Thiophenemalonic acid	2.02	
3-Bromothiophene	2.10	1.06
3-Thiopheneacetonitrile	2.22	1.12
3,4-Dibromothiophene	2.23	1.33
3-Thiophenecarboxylic acid	2.28	
3-Thiophenecarboxaldehyde	2.35	

cation of the dimer (Structure VII) should show the same pattern of spin-density distribution as the azulene radical cation. This means that the highest π-electron density in the radical cation of the dimer is expected to occur in the 3 (or 3′) position. This site should, therefore, combine with the 1 position of the azulene radical cation to result in dihydrotrimer (VIII). Proton loss, reoxidation, and an extension of the above concept should lead to poly(1,3-azulenediyl) (I), in agreement with the findings derived from the substituent effects.

At the anode surface, radical cation dimerization is indeed a likely process. There, the radical cation concentration is high, whereas the concentration of neutral azulene is low, rendering reactions between radical cations more probable than their reactions with neutral species. This is due to the fact that electron transfer is likely to be faster than the diffusion of the neutral molecules into the vicinity of the electrode. Thus, the situation encountered is very different from typical polymerization reactions occurring in the bulk, where the concentration of neutral monomers is always much higher than those of the reactive intermediates.

The initial dimerization product of two radical cations is the dication of the dihydrodimer (V in Fig. 5). The formation of this product is quite likely a reversible step, but it becomes irreversible if two protons are removed subsequently, yielding the 1,1′-biazulyl (VI). Consequently, the radical-cation combination is very sensitive to the presence of proton acceptors, even in trace amounts, and in particular to the presence of bases, nucleophiles, or water. This sensitivity to trace amounts of "impurities" is especially pronounced if polymeric radical cation salts [3] (see Structure IX) are the desired reaction products rather than the polymers, as discussed here.



IX

The oxidation potential of VI is lower [0.60 V vs. standard sodium calomel electrode (SSCE)] than that of azulene. This is a characteristic feature of many families of homologous oligomers of aromatic compounds [14]. Due to this fact, the dimer or any higher oligomer is more easily oxidized than the monomer. However, since the concentration of radical cations of the monomer in the vicinity of the anode is always high, the most likely reaction pathway for the radical cation of the dimer or of a higher oligomer will be combination with azulene radical cations to the next higher dihydro-oligomer dication. Proton loss and subsequent reoxidation thus account for the polymerization reaction, which is essentially a cascade of electron transfer reactions (E) and chemical steps (C). For this process, an extension of customary electrochemical abbreviation [15], the symbolism $E(CE)_n$, is suggested. Excess oxidation of the polymer and complexation of counter anions from the electrolyte lead to polyazulene, as outlined in Fig. 5.

Polythiophene

It is a well-established fact that thiophene can be chemically polymerized to an electrically conducting polymer [16]. This reaction has recently received renewed attention [17, 18]. In light of the electrochemical polymerization of pyrrole to conducting polymeric films [2], successful electropolymerization of thiophene is not surprising. It provides a system closely related to pyrrole (and thus polypyrrole), but in certain respects it is easier to study. For example, a wide variety of substituted thiophenes are commercially available, whereas 3-mono- or 3,4-disubstituted pyrroles are difficult to synthesize. We have, therefore, investigated the electropolymerization of a family of 3-substituted and 3,4-disubstituted thiophenes, and have obtained polymers from about half a dozen monomers. Indeed, not all thiophene monomers investigated yield conducting amorphous polymer films (Table 3). Those which do represent a data set that allows one to test some concepts about the molecular framework of this polymeric form of heterocycles, as well as about the bonding structure and conduction mechanism in polythiophenes [7].

A plot of the peak oxidation potentials of the substituted thiophene monomers vs. their respective polymers in a 0.1 M TEAFB/CH_3CN solution yields a linear correlation (Fig. 6). The oxidation potentials of the monomers (Fig. 7), in turn,

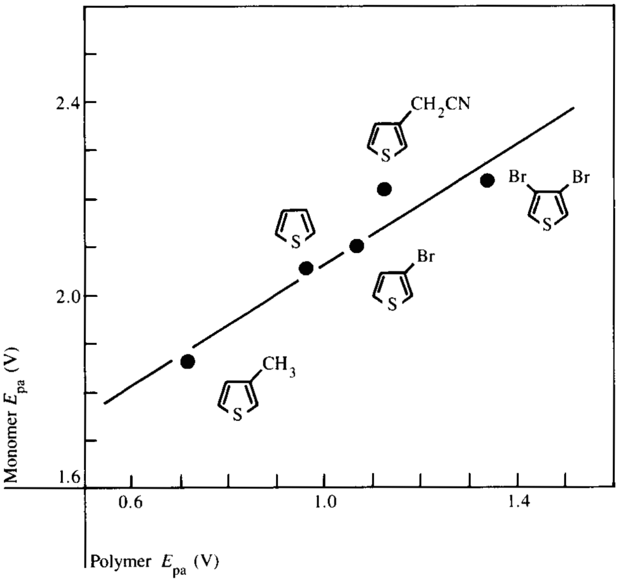


Figure 6 Peak oxidation potentials of thiophene monomers vs. their respective polymers in 0.1 M TEAFB/CH_3CN solution.

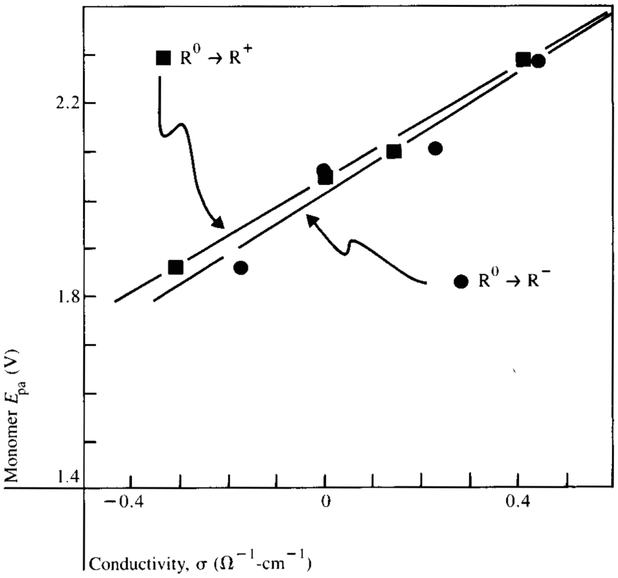
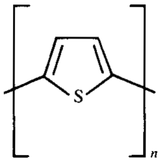


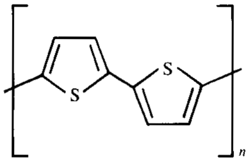
Figure 7 Electrochemical oxidation of β-substituted thiophene monomers, where substitution in the β position is Me, H, Br, and COOH, from left to right.

Table 4 Electrochemical data for some conducting polythiophene films. Structures corresponding to the roman numerals are found in the text.

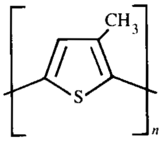
Structure	*Anion*	*Conductivity* (Ω^{-1}-cm^{-1})	*Charge fraction*
Xa	$(BF_4)^-$	0.02	0.06
Xa	$(PF_6)^-$	0.02	0.06
Xb	$(HSO_4)^-$	0.10	0.22
XI	$(PF_6)^-$	1.	0.12

yield linear plots vs. the σ-Hammet constants [19] for para-substituents in the reaction types $R^0 \rightarrow R^+$ and $R^0 \rightarrow R^-$. These correlations indicate that substituents affect the electronic bonding scheme in both the monomers and polymers in the same way. Accordingly, the electronic structures of the monomers and their polymers must be alike, which is consistent with the earlier assertion that polythiophene [20], like polypyrrole [5, 20], is made up of α,α′-linked heterocycles. The poly(2,5-thiophenediyl) structure (Structure Xa) is also consistent with the chemical synthesis concept [17] starting from 2,5-dibromothiophene.


Xa


Xb

As is reflected in Table 4, poly(3-methylthiophene) (Structure XI) has a lower peak oxidation potential and a higher electrical conductivity than the parent polythiophene. In our studies, the highest level of fractional excess oxidation, 0.06, was found for polythiophene-PF_6 (Structure Xa) obtained from monomeric thiophene. Respective values of 0.22 and 0.12 were found for polythiophene-HSO_4 (Structure Xb) derived from 2,2′-bithiophene and for poly(3-methylthiophene)-PF_6 (Structure XI). Independently, Tourillon and Garnier [21] have reportedly obtained fractional excess oxidation around 0.25 for these three polymers by using carefully purified substrates; the electrical conductivities for their samples are said to be two orders of magnitude higher than the values reported here [i.e., $\sigma \approx 100$ Ω^{-1}-cm^{-1} for poly(3-methylthiophene)-PF_6]. We have so far been unable to reproduce these results.


XI

The increase of electrical conductivity of the polymer derived from a methyl-substituted thiophene over that of the parent polythiophene is a rather specific example which is not paralleled in the analogous pyrrole system. Table 5 reveals that poly(3-methylpyrrole) (Structure XIII) has a

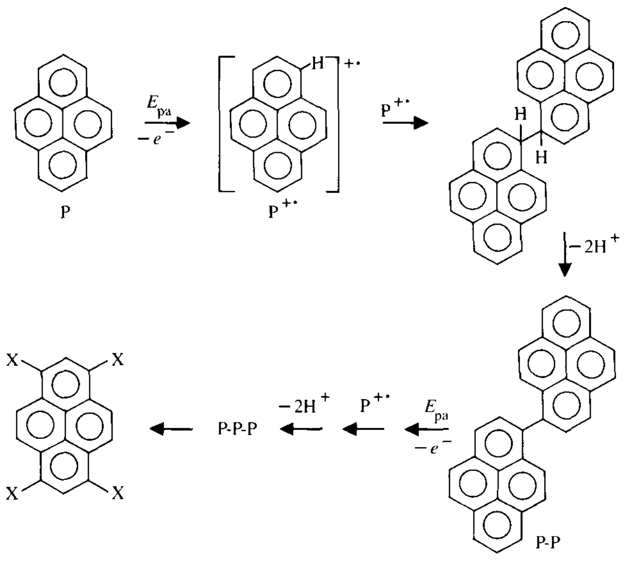
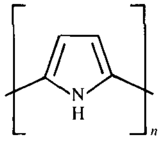


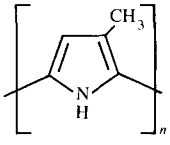
Figure 8 Proposed mechanistic scheme for the electropolymerization of pyrene, P. Roman numerals adjacent to structures are referred to in the text.

Table 5 Electrochemical data for some conducting polypyrrole-BF_4 films. Structures corresponding to roman numerals are given in the text.

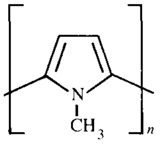
Structure	*Polymer* E_{pa} (V)	*Conductivity* (Ω^{-1}-cm^{-1})	*Charge fraction*
XII	−0.15	100	0.25
XIII	−0.25	4	0.25
XIV	−0.50	10^{-3}	0.25



XII



XIII

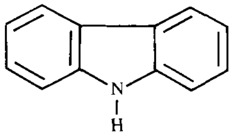


XIV

25-fold *lower* conductivity than the parent polypyrrole (Structure XII) at an identical level of fractional excess oxidation (0.25). Similarly, poly(3,4-dimethylpyrrole) [22] and poly(3,4-dimethylthiophene) [21, 22] show a significantly lower conductivity than the unsubstituted parent polymers. Table 5 also shows the data for poly(N-methylpyrrole) (Structure XIV). Apparently, a delicate balance exists between the electronic and steric effects; this balance can render substituted polymers of the five-membered heterocycles either more or less conducting than their parents.

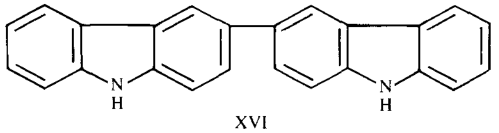
Polycarbazole

Electrochemical oxidation of 10^{-3} M carbazole (Structure XV) in acetonitrile containing 10^{-1} M tetra-n-butylammonium perchlorate (TBAPC) at +1.3 V (vs. SSCE) yields an amorphous conducting film which adheres to the Pt anode. Unlike polypyrrole, polythiophene, or polyazulene, these films are very brittle and crack easily. They show very low electrical conductivities of between 10^{-4} and 10^{-3} Ω^{-1}-cm^{-1} at 300 K. Furthermore, our elemental analysis data $(C_{12}H_{13}N)(ClO_4)_{0.45}$ reveal that these films are very rich in hydrogen and contain a high level of perchlorate anions. The films are most likely a mixture of low-molecular-weight oligomers, unlike the crystalline radical cation salts obtained by Chiang et al. in very pure THF solvent [3a]. The formation of film deposits on the electrode during oxidation of carbazole had previously been observed by Ambrose and coworkers, who considered the films to be insulators [23].

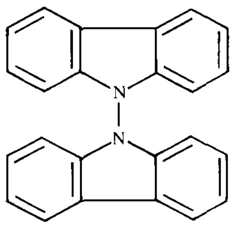


XV

The carbazole system, though yielding a very poor polymer or only oligomers, is of interest from a reaction-mechanistic point of view. Chemical oxidation studies have already shown [24] that the chief oxidation products are four isomeric dicarbazyls and a small amount of trimer [25]. According to Tucker and Maitland [24] the reaction medium affects the isomer distribution drastically: In the presence of sulfuric acid using dichromate as the oxidant, only the 3,3′-dicarbazyl (Structure XVI) is obtained, whereas in the absence of sulfuric acid, the 9,9′-dicarbazyl (Structure XVII) is also formed. Electrochemical oxidation studies of Ambrose et al. [23] revealed that the 3,3′-dicarbazyl is typically the far-dominating electro-oxidation product. The 9,9′-dimer was only formed very early during electrolysis, before the proton concentration buildup. Addi-



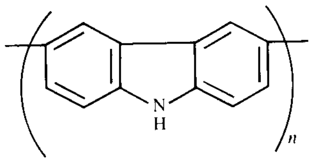
XVI



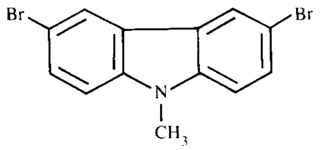
XVII

tion of H_2SO_4 suppressed the formation of the 9,9′-dimer altogether, whereas addition of base (pyridine) as a proton scavenger increased its yield significantly. These same authors showed further [23] that the 3,3′-dimer has a lower oxidation potential than the parent carbazole; the 9,9′-dimer has a higher oxidation potential than the parent carbazole.

For polymer formation, subsequent reoxidation of the dimer is essential. The 9,9′-dimer does not meet this requirement due to its high oxidation potential; therefore, it would not further polymerize. Consequently, "polycarbazole" must be derived from the 3,3′-dimer and must have essentially a poly(3,6-carbazolediyl) structure (Structure XVIII). Consistently, previous chronoamperometric and chronopotentiometric oxidation studies have shown that the *n* values for carbazole oxidation fall in the range of 2.5 to 2.8. For authentic 3,3′-dicarbazyl the *n* value is 1.92. It is most likely that oxidation of the 3,3′-dimer yields the same type of conducting "polymer" as obtained from carbazole; this would further substantiate the previously mentioned structure. Upon electro-oxidation, N-alkyl-substituted carbazoles typically do not proceed beyond the dimer state [23]. Recently, however, Wellinghoff et al. [26] have obtained linear polymeric products via chemical polymerization starting from N-methyl-3,6-dibromocarbazole (Structure XIX).



XVIII

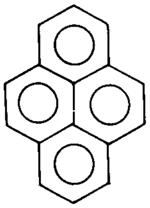


XIX

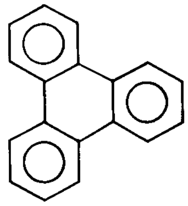
These chain molecules dissolve in nitrobenzene, can be cast into a film, and turn conducting upon doping with I_2/Br_2. The electrical conductivities of the air-stable, black, doped films are around 1 Ω^{-1}-cm^{-1}. Their structure follows readily from the synthetic concept, poly(N-methyl-3,6-carbazolediyl), in agreement with the considerations outlined previously for polycarbazole. High molecular weight chains of the parent polycarbazole should be accessible in a similar fashion.

Polypyrene and polytriphenylene

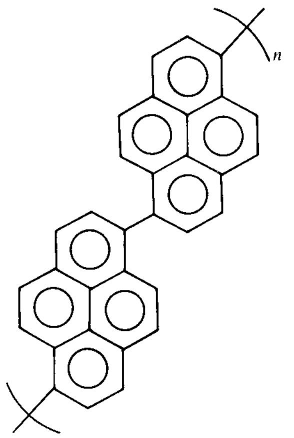
In their earlier electro-oxidation studies of a variety of polyaromatic hydrocarbons, Peover and White [1b, 27] had already found that pyrene, P (Structure XX; see also Fig. 8) and triphenylene (Structure XXI) caused deposition on the electrode of insoluble films which they considered to be insulating. However, we have found these deposits to be conducting; the conductivities of polypyrene-ClO_4 films after they have been peeled off the anode are between 10^{-1} and 1 Ω^{-1}-cm^{-1}. Table 6 lists the electrochemical and elemental analysis data for polypyrene in comparison with polyazulene and polycarbazole. Their polymeric structures are unknown at present, but can be predicted on the basis of the concept of radical cation dimerization previously discussed. For example, polypyrene is expected to be made up of 1,6-pyrenediyl (Structure XXII) and/or 1,8-pyrenediyl (Structure XXIII) units, as outlined in Fig. 8. The mechanism for formation is also presented in the figure.



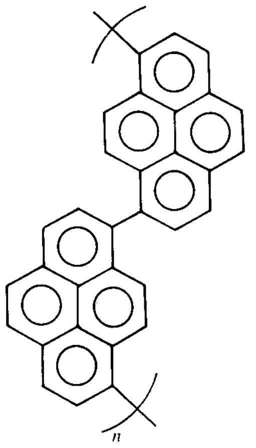
XX



XXI



XXII



XXIII

General considerations

The systems discussed here are all polymeric electro-oxidation products derived from either benzenoid, nonbenzenoid, or heterocyclic aromatic compounds. Therefore, among any family of these three categories, there are members which electropolymerize to conducting polymers. Those which do have many features in common. Similarly, the polymers so obtained, apart from their electrical conductivity data, appear to be rather similar. This fact is very well reflected, for example, in the scanning electron microscope pictures (SEMs) shown in Figs. 9(a)–(d). The SEMs display the respective granular appearances of polyazulene-p-toluenesulfonate, polypyrene-BF_4, polytriphenylene-BF_4, and polycarbazole-BF_4. The sizing marker reproduced at the bottom of each figure is 5 μm.

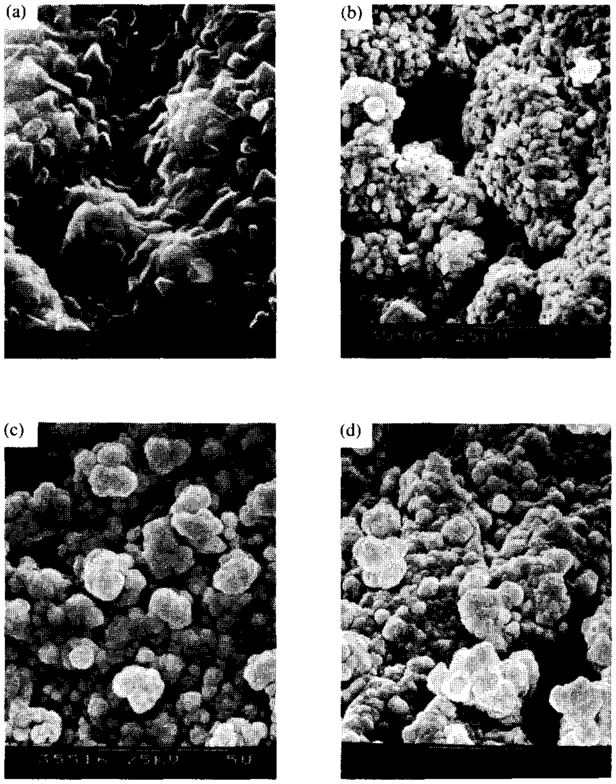


Figure 9 Scanning electron micrographs of (a) polyazulene-p-toluenesulfonate; (b) polypyrene-BF$_4$; (c) polytriphenylene-BF$_4$; and (d) polycarbazole-BF$_4$.

In spite of all these similarities, not all aromatic monomers yield conducting polymers; this depends on a number of parameters, but perhaps most significantly on the reactivity of their parent radical cations. It is well established [15] that radical cations with a high degree of charge delocalization are relatively stable. Stability increases further if the radical cation is stabilized by a functional group or if its reactive sites are blocked by substituents. Apart from these latter stabilizations, the higher the charge spin density in a specific position, the higher the tendency to dimerize, and therefore the higher the reactivity of radical cations. Accordingly, it has been observed that during an oxidation study of a series of oligomeric pyrroles, only the monomeric pyrrole yielded a conducting polymeric film upon electro-oxidation [28]. However, bipyrrole and terpyrrole only gave rise to red-brown coloration of the solutions in the region near the electrode surface, despite the fact that they both exhibit irreversibility. No continuous films were obtained. Similarly, attempts to produce polymer films at the low oxidation potentials of the oligomeric pyrroles in the presence of monomeric pyrrole were unsuccessful; film formation occurred only at potentials higher than 1.1 V (i.e., above the oxidation potential of the pyrrole monomer [28]). These results also reflect the fact that an abundance of monomeric pyrrole radical cation is necessary for sustained polymer growth.

In this same study [28] it had also been shown that a homologous series of oligomers for such systems which do undergo polymerization to conducting polymers (pyrrole, thiophene, p-phenylene) are typically associated with a set of oxidation potentials E_{pa} which relate linearly to $1/N$. Here, N is the number of monomer units in the oligomer. Similarly, the onset of absorption for the series of homologous oligomers shifts within the series pyrrole, bipyrrole, terpyrrole, and polypyrrole; it also relates linearly to $1/N$ [28, 29]. Such behavior implies that increasing the number of monomer units in the oligomer also extends the degree of conjugation of the π system. For this requirement to be met, both electronic and steric prerequisites must be satisfied. In particular, isomeric dimers can have a more or less significant degree of electronic interaction between the two molecular halves. Simpson has worked out an independent systems approach [30] to assess the amount of delocalization of energy across a π bond of low bond order. This concept has been applied to the 1,1′- and 2,2′-biazulyl dimers by Heilbronner and coworkers [31]. These same authors have also assessed the degree of steric crowding around the dimer linkage, especially in the 3,3′-diguaia-azulyl, which has a twist angle of $>60°$. The latter serves as a model system for the poly(4,6,8-trimethyl azulene) studied here.

Apart from steric crowding, which is aggravated by substituents, Figs. 10(a)–(e) illustrate the degree of steric interference in isomeric dimers derived from (a) naphthalene, (b) azulene, (c) carbazole, and (d) pyrene. Whereas biphenyl (e) is a well-studied system, less specific information is available about some of the other dimers. The figure helps one to visualize the rather different levels of steric crowding. Thus, biphenyl is reported to be nonplanar in the gas phase [32] with a dihedral twist angle of 41.6°, though an essentially planar conformation has been found in the crystal [33].

Of the two naphthalene dimers shown, the 2,2′-dimer has a crowding level similar to that in biphenyl; the same holds for the 2,2′-bipyrenyl dimer. The 1,1′-binaphthyl system, however, has been investigated via a few experimental studies [34] which reveal the dihedral twist angle to be around 70°. More recently, force-field method calculations have shown that the torsional potential has a minimum about 90°, with a very shallow bottom within ±25° of the center [35]. The effects of steric hindrance in these two binaphthyl systems are reflected in both their optical absorption spectra [36] and their oxidation potentials. Thus, in a 0.1 M TEAFB/CH$_3$CN solution, the E_{pa} values (vs. SSCE) are naphthalene, 1.78 V; 1,1′-binaphthyl, 1.70 and 1.92 V (second wave); and 2,2′-binaphthyl, 1.59 and 1.89 V. Thus, the

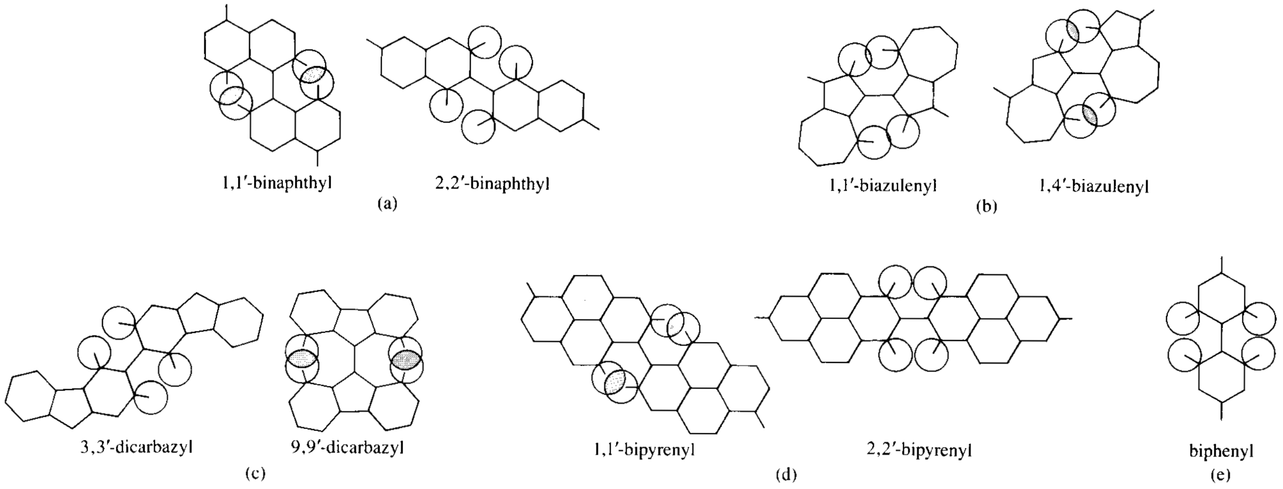

1,1′-binaphthyl 2,2′-binaphthyl (a)
1,1′-biazulenyl 1,4′-biazulenyl (b)
3,3′-dicarbazyl 9,9′-dicarbazyl (c)
1,1′-bipyrenyl 2,2′-bipyrenyl (d)
biphenyl (e)

Figure 10 Steric crowding in selected dimers of aromatic units of (a) naphthalene, (b) azulene, (c) carbazole, (d) pyrene, and (e) biphenyl.

Table 6 Properties of polymeric perchlorates derived from aromatic monomers. The monomer compositions are shown in parentheses after their names. The polymer conductivities are obtained at 300 K (σ_{300K}) and the polymer densities are given as flotation densities.

Monomer	*Monomer* E_{pa} (V)	*Polymer composition*	*Polymer* E_{pa} (V)	σ_{300K} (Ω^{-1}-cm^{-1})	*Density* (g-cm^{-1})
Azulene ($C_{10}H_8$)	0.91	$(C_{10}H_{6.5})(ClO_4)_{0.25}$	0.65–0.70	10^{-2}–1	1.35
Pyrene ($C_{16}H_{10}$)	1.23	$(C_{16}H_{12})(ClO_4)_{0.31}$	1.1	10^{-1}–1^{a}	1.34
Carbazole ($C_{12}H_9N$)	1.30	$(C_{12}H_{13}N)(ClO_4)_{0.45}$	0.95	10^{-3a}	1.36

[a] Pressed films.

first oxidation potential for the sterically hindered 1,1′-binaphthyl is little different from that of naphthalene, whereas that for 2,2′-binaphthyl is significantly lower. Similarly, the absorption spectrum of the slightly hindered 2,2′-binaphthyl is radically different from that of either the 1,1′-binaphthyl or naphthalene, which have closely related spectra [36].

It is known that coplanarity is not a prerequisite for a polymer to become electrically conducting [37]. However, in a series of homologous systems, coplanarity should assist in improving the electrical conductivity of a molecular chain-type molecule. Evidence for such behavior is found, for example, in the electrical conductivity differences between polyazulene and poly(4,6,8-trimethylazulene) (see Fig. 3), as just discussed.

The concept of radical cation dimerization forecasts a structure that consists essentially of aromatic units linked together at the sites of highest reactivity (charge density) of the intermediate radical cations. Which particular aromatic compound will undergo oxidative electrodehydropolymerization to a conducting polymer will depend on the reactivity pattern of the radical cation, the electronic structure of the cation, and the electronic structure of the resulting connection scheme in the resultant oligomers. Steric crowding could either suppress the polymerization altogether or lower the electrical conductivity by varying degrees.

For these polymers to be conducting, excess oxidation with uptake of counter anions (doping) is essential. All polymers discussed here have been obtained from the electrochemical synthesis with counter anions incorporated from the beginning. Chemically synthesized polymers, however, have to be doped after synthesis.

The concepts discussed here have been considered in part before. Systems such as azulene, however, allow one to differentiate the validity of competing concepts better than the traditional heterocyclic or benzenoid aromatic monomers, to which the application of these concepts had previously been restricted.

The study of conducting polymers is still in a state of flux, and the conduction mechanisms are, on the whole, little understood. The concepts formulated here try to address only certain aspects of the polymerization mechanism, without elucidating upon questions such as why excess oxidation of the polymeric chain or network occurs or how it leads to electrical conductivity.

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