

Anodic generation of new ionophoric conducting polymers

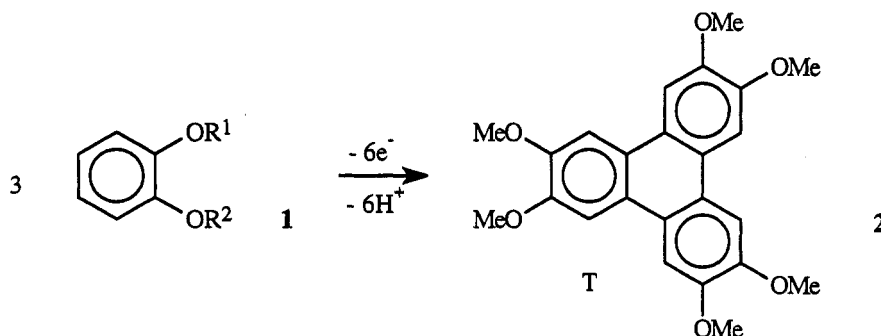
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Abstract : The anodic polymerization of aromatic compounds possessing ether and polyether functions in their structure leads to organic materials endowed with specific complexing properties. One describes the formation of organic polymers with polyether cavities, the experimental conditions necessary to obtain such materials, the mode of dedoping by chemical and electrochemical reagents, the use of those resins as membrane and ionophoric materials specifically devoted to the extraction of inorganic cations, from aqueous and organic solutions, especially at extremely low concentrations.

THE ANODIC TRIMERIZATION OF AROMATIC ORTHODIETHERS

Aromatic orthodiethers (like Veratrole) are known to exhibit either chemically (in 70% sulphuric acid with chloranil or with iron (III) chloride in water) or electrochemically (anodic oxidation at a platinum anode in non nucleophilic media) the formation of the relevant hexamethoxytriphenylene.



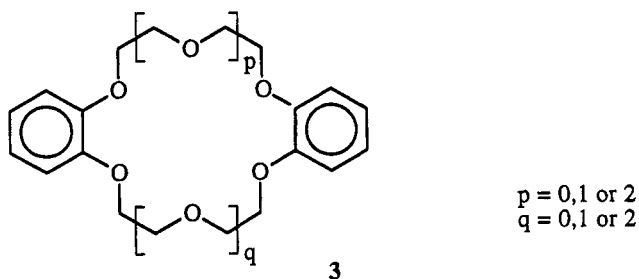
Triphenylenes (T) were reported to present a planar structure and to be thermally quite stable. Therefore hexaalkoxytriphenylenes can be potentially considered (ref. 1) as good models for liquid crystals since they form easily discoid mesophases.

ELECTROACTIVE POLYMERS FROM ANODIC COUPLING OF DIBENZO-CROWN ETHERS

From the previous work described above and devoted to coupling and trimerization reactions, it clearly appears that diaromatic compounds with aromatic rings linked by, at least, a chain including hetero-atoms such as oxygen or less probably nitrogen, may lead to anodic polymerization. As a matter of fact compounds like dibenzo-crown ethers (ref. 2), having two donating substituents in ortho position on each phenyl ring are expected to lead, just like already shown with Veratrole, to specific trimerizations on each ring. When mass transport at the interface is fully established (assuming rather high concentration of crown ether for moderate current densities), the formation of polytriphenylenes may normally occur.

Such a class of electroactive polymers possess obviously a very interesting structure: Presence of triphenylene moieties reversibly oxidized (cf. the electrochemical behaviour of hexamethoxytriphenylene (ref. 3) and tris (N, N¹-ethylenediamino)triphenylene (ref. 4) showing respectively two or four electron transfers in suitable conditions) linked by well-defined polyether rings or chains, which allow possible modifications of the chemical and electrochemical behaviour of the polymers (by specific complexation of metallic cations by monomeric units -before or after the polymerization process-). In this context, such

polymers from crown ethers **3** constitute then a new family of electroactive polymers after other well known ones like polyacetylene. This anodic deposit (oxidized form of the resin) appear to be dependent on its thickness. EPR analysis shows that the polymer is vary with time confirms then a true stability of the intern doping of the polymer. Experimentally found g factors depend neither on the different structures nor on the associated anions and are all equal to 2.0038.



Although elemental microanalysis are not always perfectly reproducible (the doping ratio could appear to be strongly subordinated to the mode of formation of the polymer and to its history after the synthesis) empirical formulae of poly(**3**) salts can be estimated. If it is corresponding values of the total spin density are of the same order of magnitude as those given by the microanalysis. Polymer IR spectra (KBr pressed pellets) are characteristic of each polymer with absorption bands related to those of the parent substrate. In the case of polymers doped by BF_4^- or ClO_4^- , the absorption bands attributed to these anions are hidden by the polymer bands. In contrast, with PF_6^- as counter-anion, the absorption band of the anion ($\nu=840 \text{ cm}^{-1}$) is clearly identified in the doped polymer spectra. Microwave conductivity measurements performed on a dry film of poly - DB18-C6 doped by BF_4^- afford a room temperature conductivity of $8 \times 10^{-4} \Omega^{-1} \text{ cm}^{-1}$. A high anisotropy was expected due to the assumed structure of the polymers.

A chemical representation of the organic backbone of such a "layer" is given above in the case of poly-DB18-C6 (reduced form). A model of stacking of hexamethoxytriphenylene anodic electrocrystallization (ref. 5) and having the following stoichiometry $(\text{HMT})_2 \text{BF}_4$. this result allows to suppose that, during its growth and just after its formation, the most stable structure of the doped polymer film would have the following general formula $(\text{Ta}_x)_n$ with $x = 0.5$. T represents a triphenylene moiety in the polymer and A the doping counter anion.

Dedoping mode of polycrownethers

The doped polymer can be considered as a redox polymer with a high ratio of triphenylenes as redox centers. The motion of electron through the polymeric matrix is determined at least both by chain flexibility and bulkiness of counter ions in the course of the doping/undoping processes. With thick films, the electron injection from the solid metallic electrode rapidly creates a non-conductive layer which may totally inhibit the completion of the reduction process for the layer in its entirety. On the contrary, reduction by means of reducing reagents like electrogenerated superoxide ion (reduction of air at a graphite cathode in a non aqueous solution), primary and tertiary amines in acetonitrile, solvated electron source in appropriate solvents, benzophenone sodium in tetrahydrofuran and finally tetraalkyl ammonium hydroxide has been easily carried out. Most of the time, reduction by tertiary amines in acetonitrile was found to be particularly easy and fast. The reduction process may lead to a change of morphology of the resin. The black-dark blue aspect of the resin progressively vanishes and then turns to brown and finally yellow. A careful undoping process allows to get a transparent material, very weakly paramagnetic and exhibiting a very low level ($x < 1\%$) of doping. Reduction recipes using ammonium hydroxide are very convenient to carry out the undoping process too.

Electron transfer onto neutral polytriphenylenes. An access to poly-electrides

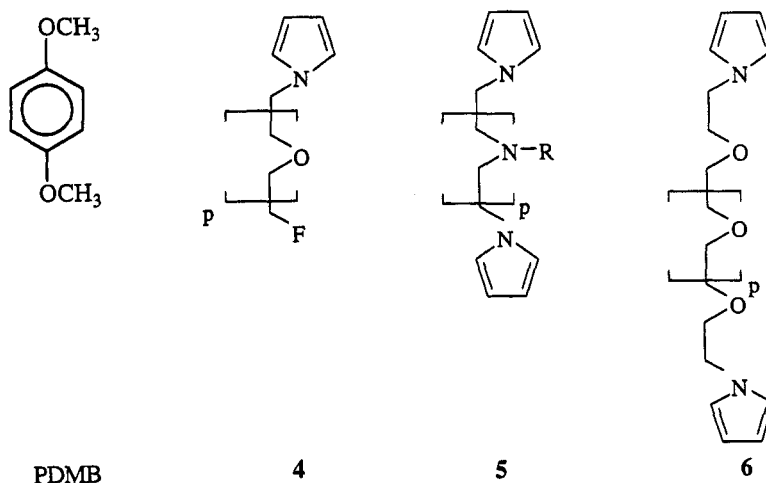
Polyethers possess the remarkable property to dissolve alkali metals in solvents in which they are sparingly soluble such as tetrahydrofuran or ethers. Under those conditions alkali cations, alkali anions and/or

solvated electrons may be produced provided that the complexant is not reduced (ref. 6). For example, cyclic polyethers like "18-crown-6" have been used to dissolve alkali metals in ethers. The cation complexing ability is so strong that both alkali metal and electrides can be obtained upon solvent removal. On the contrary, cation complexants containing π -acceptor groups the LUMO of which can in principle localize the negative charge have not been tested in strong reducing conditions as with alkali metals. Dibenzo 18-crown-6 (structure 3), although of very low LUMO level, could be a prototype of such systems since the negative charge could occupy the low lying prototype of such systems since the negative charge could occupy the low lying antibonding orbitals of the benzene rings. While a large number of polymers containing crown ether cages have been described in the literature (ref. 7) their behaviour in the presence of alkali metals has never been studied.

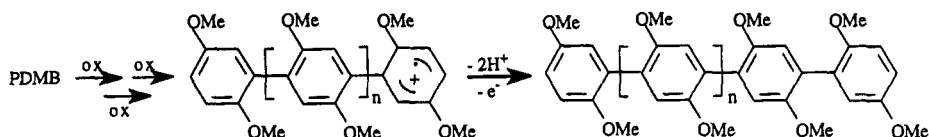
For the first time a polyelectride (ref. 8) was prepared: for that, poly DB 18C6 (doped or undoped) was treated by alkali metals in liquid ammonia or methylamine. Moreover films (whatever their doping level) were carefully dried by evaporation overnight in a vacuum higher than 1×10^{-5} Torr.

ELECTROCHEMICAL POLYMERIZATION OF PARADIALKOXY-BENZENES AND RELATED COMPOUNDS

A substrate such as paradimethoxybenzene (PDMB) has been studied widely in organic electrochemistry.



Thus, PDMB were shown to lead to rather stable cation radical (ref. 9). It has been underlined that their decomposition in nucleophilic media (ref. 10) like methanol or acetonitrile containing cyanide ions may afford the corresponding quinone (ref. 11) or acetal (ref. 12). Those conditions obviously quench any polymerization reaction. On the other hand, it can be easily foreseen that one favours phenyl-phenyl bond formation by using carefully dried solvents such as acetonitrile. The interest of the method is to focus on the synthesis of a new family of resins parent of polyparaphenylene (PPP) with the property to be electroactive and also electronically conducting at the doped stage.

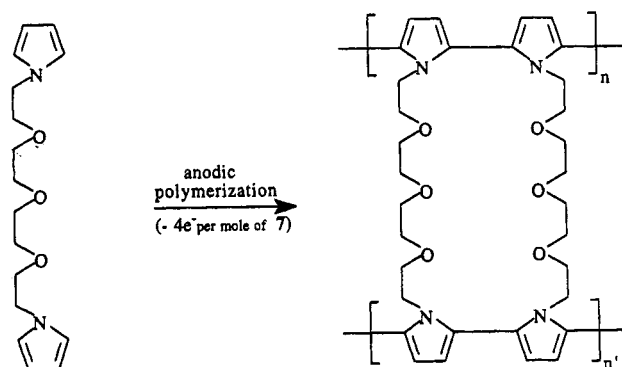


POLYMERIZATION OF N-SUBSTITUTED PYRROLES

The oxidation of 3-substituted pyrroles (grafting of azacrownethers) has been already reported (ref. 13,14). As part of the present study, the anodic coupling of pyrroles N-substituted by polyether chains has been

achieved. Thus, monopyrroles such as **4** lead to polymers, the interest of which is obviously modulated by the length of the poly-oxa-chain and the presence of functional groups F in terminal position. For example F can be a functional group like carboxylic or sulfonic groups (ref.15). Structures possessing two pyrrole moieties like **5** and **6** can be easily oxidized. Anodic polymerization of monomers with aza groups appeared more delicate to handle and to achieve. Conditions of their polymerization were defined (absolutely necessary presence in the anolyte of strong acid such as trifluoroacetic acid which aims to anodically deactivate the anolyte of strong such as trifluoroacetic acid which aims to anodically deactivate by protonation the amino-group(s). Resins (from **5**, $p=1$) produced by such a way appeared to possess a peculiar acid-basic response (ref. 16) fully reversible and roughly depending on the pH of the solution : consequently, analog polyaza resins could be built anodically and accordingly used as sensors.

Macroelectrolysis of **7** were performed on a large scale by using industrial type cells in order to obtain polymer deposits onto graphite grains allowing therefore an easy handling for building of filters. At the right current density, (intensiostatic electrolyses) polymer deposited in thin and stable layer at the carbon surface should possess a high number of in situ formed complexing cavities for allowing as well as possible specific inorganic cation extractions.



USE OF ELECTROGENERATED POLYMERS AS CATION EXCHANGE RESINS

The work-and related general ideas-here presented aim to produce materials with redox and/or electronic conductivity reaching an acceptable level. For example, deposits on graphite felts or other cheap industrial carbons were carried out as already discussed previously and then conducting resins (at least very thin film) can be undoped chemically and electrochemically. The main interest of resins is to use them for extracting selectively inorganic acceptors like metallic ions from aqueous or organic solutions. Let us recall that the neutral resins after treatment by tetraalkylammonium hydroxide can be considered as a classical cation exchange material P able to insert fast and selectively a given cation M^+ .

Extracting capability of polyether resins towards inorganic cations

The first evidence for the extraction of ions by polyetheral resins moderately doped was given (ref.17) in the case of alkali metal ions. Especially, it has been demonstrated that cation extraction was, in that case, often accompanied by a decay of the p-doping level of resin. Experimentally, from concentrated KBF_4 solutions, a maximum extraction ratio corresponding to K^+ , one alkali cation per two ligand moieties was reached. It looks like well known 2:1 complexes exhaustively described in solution where K^+ plays the role of the meat in the heart of the sandwich. The capacity of extraction relevant to different resins depends on the number of accessible sites per volume unit and the diffusion rate of concerned cations through the polymer. The extraction of Ag^+ , Sr^{2+} and Cs^+ in undoped poly DB18C6 has been achieved. A very similar property could be found with other resins the monomers of which are not expected to give strong complexes in solution. Thus, polyetheral polymers exhibit an astonishingly strong ability to extract a large palette of cations even if the selectivity is *a priori* much lower than that observed in certain cases with several polydibenzo-crown ethers in solution. It is remarkable to note that the "cauliflower" - like structure

of the of the undoped materials is totally modified by insertion of strontium, platinum and gold ions. Lastly, the large external changes at the polymer interfaces after extraction could be also fully visualized by means of scanning tunnelling spectroscopy. Absorption of Cs^+ in large amount does not lead to a dramatic modification of surface aspect. On the contrary, maintaining resin in the contact of silver salts affords a very large change of the surface relief.

Extraction of inorganic cations at extremely low concentration

Most of the materials described along this presentation were found to behave efficiently as cation exchange resins. Preliminary data concerning exchange kinetics and thermodynamics were also presented. However, the principal feature exhibited by those materials is undoubtedly their capability to extract inorganic cations at very low concentration ($c < \text{ppb}$). This property was found to be effective principally in neutral solutions. The efficiency of poly DB18C6 to extract cations vanishes when solution $\text{pH} < 4$. Several studies (ref. 18) were carried out with poly DB18 C6 for various radiotracers ($^{137}\text{Cs}^+$, $^{60}\text{Co}^{++}$, $^{110}\text{Ag}^+$, ^{22}Na , $^{85}\text{Sr}^{++}$). Another example of the affinity of polyetheral resins can be drawn from polypyrroles (such as poly 7). Thus, poly 7 deposited on coke and undoped by tetraalkylammonium hydroxide has exhibited an efficient extraction ratio at very low concentration. With $^{60}\text{Co}^{++}$, $^{137}\text{Cs}^+$ and $^{40}\text{K}^+$ a good extraction selectivity was found in the case of cobalt ions. However, a progressive desorption of K^+ was noted and could not be satisfactorily explained (ref. 19). On the other hand, silver retention by electrogenerated resins was also studied owing to the interest of extraction of metastable silver ion from primary circuits of nuclear plants. $^{110}\text{Ag}^+$ could be extracted fast at a fairly good level whatever the undoping mode chosen for the resin.

CONCLUSION

The present lecture aims to account for the interest of anodic polymerization of all kinds of aromatic systems possessing ether and polyether functions. Synthesis of such ionophoric materials (crystals, oligomers, polymers) appear possible by means of electrochemical technique. The nature and morphology of the deposits at different kinds of anode can be modulated by means of a large palette of experimental conditions. The interest of such ionophoric materials seems to grow especially when applications are focused on membranes, deposits and composites.

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