polymeric materials. The method, termed 'polymer-supported polymerization', is very simple, generally applicable, and does not involve any of the technical requirements of suspension polymerization. Although not an alternative to routine suspension polymerization, the technique provides a highly practical means of preparing beaded resins when direct bead polymerization is not practicable for one reason or another. The general applicability of the method has been demonstrated for free radical, condensation, and coordination polymerizations, and it should be equally applicable for ionic polymerization. The preparations of various beaded resins including those of potential interest in transition metal catalysis and enzyme-like polymers have been described. The overall physico-chemical, and particularly the topochemical, behaviour of the embedded polymer clearly may be influenced by the nature of the prepolymer matrix. This often provides an additionally versatile means of tuning the properties of a given tailor-made functional polymer by the appropriate choice of a suitable prepolymer support. The dimethylamide structure of the presently described prepolymer (**P1**) generally widens the solvent compatibility of the embedded polymer, and is thought to have favourable topochemical effects in, for example, acylation reactions.

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Electrochemical synthesis of polyacetylene tetrachloroferrate $[CH(FeCl_4)_y]_x$ and tetrachloroaluminate $[CH(AlCl_4)_y]_x$

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Polyacetylene can be electrochemically oxidized in $LiClFeCl_3$ nitromethane and $LiClAlCl_3$ nitromethane solutions to give a highly conducting (500 ohm^{-1} cm^{-1}) polymer exhibiting *p*-type conductivity. The limiting composition obtainable in the electrolysis can be expressed by the following formula: $[CH(MCl_4)_{0.05}]_x$ where M=FeAl.

Keywords Conducting polymers; polyacetylene; electrochemical doping; acceptor type doping; metal halide doping

Introduction

Graphite and other macromolecular systems like polyacetylene, poly(*para*phenylene), polypyrrole, etc., are known to react with a large variety of electron accepting compounds to give a whole class of new materials exhibiting high electrical conductivity. There are several groups of compounds that are able to convert polyacetylene into 'an organic metal' and they can be classified as follows: halogens[1], main group transition metals halides[2–4], noble gas fluorides[5] and protonic acids[6].

The chemistry of the 'doping reaction' involves the oxidation of the polymer chain with the concomitant introduction of a proper amount of anions stabilizing the polycarbonium cation formed. This result can be achieved by chemical oxidation or electrochemically through anodic oxidation. The latter process has been successfully applied to the fabrication of light weight rechargeable batteries[7]. Recently some work on the introduction of anions of protonic acids into polyacetylene has been carried out, e.g. ClO_4^-,[7] PF_6^-.[8] In this communication we report that the introduction of Fe^{3+} and Al^{3+} chloroanions into polyacetylene can be achieved through anodic oxidation of $(CH)_x$ in LiCl–$FeCl_3$ and LiCl–$AlCl_3$ solutions.

Experimental

Materials and reagents. The polyacetylene used in all the experiments was prepared using a modification of the method from Ito *et al.*[9] The $(CH)_x$ film had a *cis:trans* ratio of approximately 1:1. $FeCl_3$ and LiCl were vacuum dried at 100°C and 150°C respectively for one hour. $A.C._3$ was kept over calcium chloride and then vacuum distilled. For

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the preparation of $LiFeCl_4$ and $LiAlCl_4$ solutions, required amounts of $FeCl_3$ or $AlCl_3$ were mixed with excess LiCl in a dry argon atmosphere. Nitromethane was transferred into the reactor by distillation under vacuum. The solution obtained was then filtered through a No. 5 frit. The exact concentrations of $LiFeCl_4$ and $LiAlCl_4$ in the filtrate (0.25 M and 0.30 M, respectively) were determined by spectrophotometry.

Electrochemical oxidation. All reactions were carried out in vacuum or in a dry argon atmosphere. A glass reactor with a fritted separator between the anode and cathode compartments was used. $(CH)_x$ film ($2 \times 1.5 \times 0.01$ cm) was attached to a strip of platinum sheet (*ca.* 0.25 cm^2) serving as the anode. A sheet (3 cm^2) of platinum in the case of $LiFeCl_4$ and a sheet of aluminium in the case of $LiAlCl_4$ were placed in the cathode compartment at the distance of *ca.* 1 cm from the $(CH)_x$ electrode. The films were oxidized at a constant voltage of 4.5 V in the case of $LiFeCl_4$ solutions and 4.0 V in the case of $LiAlCl_4$ solutions. In order to avoid contamination, no reference electrode was used during the normal electrolysis. However in a separate experiment it was established that during the doping the polyacetylene electrode was poised *ca.* +0.9 V *versus* SCE. The amount of charge that passed through the system was calculated by the integration of $i = f(t)$ curve. After the reaction the polyacetylene strip was repeatedly washed with dry nitromethane and then pumped for at least 1 hour in order to remove the solvent. In all samples the mass uptake was measured and selected strips were subjected to elemental analysis. In one experiment, designed to verify the hypothesis that under the applied conditions no chemical doping can occur, one sample of $(CH)_x$ was kept in close proximity to the anode but not attached to the source of voltage. As expected, no mass uptake or conductivity changes could be observed for this strip.

Results

The results for the elemental analyses and mass uptake measurements of electrochemically oxidized polyacetylene in the LiCl–$FeCl_3$/nitromethane solutions are listed in *Table 1*. For sample No. 10 the number of moles of lithium deposited at the cathode was determined analytically and within experimental error, was equal to the number of moles of $FeCl_4^-$ anions introduced into the polyacetylene in the course of the reaction (7.3×10^{-2} and 7.5×10^{-2} mmoles, respectively). In some cathode deposits minute amounts of elemental iron were detected. A typical conductivity value for a $[CH(FeCl_4)_{0.05}]_x$ sample was *ca.* 500 Ω^{-1} cm^{-1}.

Electrolysis of the $AlCl_3$–LiCl system gave similar results. The only marked difference was the unusually high instability in air of the prepared samples. Conductivity of the freshly prepared samples dropped by more than three orders of magnitude on the two hours exposure to air.

Discussion and Conclusions

The equilibrium of a Lewis acid (such as $AlCl_3$ and $FeCl_3$) with LiCl in a nonaqueous aprotic solvent can be described by the following reaction[10]:

$$LiCl + AlCl_3 \rightleftarrows Li^+ + AlCl_4^-$$

This equilibrium is the source of $AlCl_4^-$ and $FeCl_4^-$ in the system and as a result, in the anodic oxidation of $(CH)_x$, the insertion of the above anions between the polymer chains occurs. This conclusion is strongly supported by chemical analysis and Mössbauer spectroscopy data. The chemical analysis shows the Fe:Cl ratio very close to 1:4. The Mössbauer spectrum shows the existence of only one type of iron with Mössbauer parameters characteristic of $FeCl_4^-$.[11] Maximum doping levels in chemically and electrochemically doped samples differ significantly. In the first case it reaches 12 molar %[3], in the second case it is equal to *ca.* 5 molar %. As can be clearly seen from *Table 1* the passage of charge above 5% doping does not produce heavier doping but only causes a severe decrease in the current yield. However, for the samples that 'received' the amount of charge corresponding to *ca.* 5% doping level, the current yield approaches 100%. The phenomenon of a lower maximum doping level for electrochemical doping in comparison with the chemical doping has been observed for some dopants like polyiodine anions[12] or PF_6^-.[8] This is not, however, a general rule since we observe the same maximum doping level for chemical and electrochemical doping in the case of ClO_4^-.[13]

Finally, we would like to stress that to date all anions inserted electrochemically into graphite or polyacetylene belong to a group of very stable *versus* oxidation species. No anions of $FeCl_4^-$ or $AlCl_4^-$ were successfully intercalated into graphite by electrochemical means[14]. In both cases the anion is being oxidized before the intercalation starts. Since polyacetylene is more easily oxidized than graphite, in principle, a much wider range of anions, than in the case of graphite, can be inserted into it by electrochemical methods. The present work shows that this is indeed the case.

Table 1 Mass uptake, elemental analysis and current yield measurements of electrochemically oxidized polyacetylene

Sample no.	Composition from mass uptake assuming $FeCl_4$	Composition from elemental analysis	Composition from current passed assuming 100% yield	Current yield (%)
1	$[CH(FeCl_4)_{0.05}]_x$		$[CH(FeCl_4)_{0.091}]_x$	55
2	$[CH(FeCl_4)_{0.049}]_x$		$[CH(FeCl_4)_{0.062}]_x$	79
3	$[CH(FeCl_4)_{0.051}]_x$	$[CH_{1.01}(FeCl_{3.88})_{0.051}]_x$	$[CH(FeCl_4)_{0.064}]_x$	80
4	$[CH(FeCl_4)_{0.043}]_x$	$[CH_{1.01}(FeCl_{3.88})_{0.051}]_x$	$[CH(FeCl_4)_{0.050}]_x$	86
5	$[CH(FeCl_4)_{0.044}]_x$	$[CH_{1.05}(FeCl_{3.76})_{0.046}]_x$	$[CH(FeCl_4)_{0.050}]_x$	88
6	$[CH(FeCl_4)_{0.043}]_x$		$[CH(FeCl_4)_{0.049}]_x$	88
7	$[CH(FeCl_4)_{0.046}]_x$	$[CH_{1.07}(FeCl_{3.95})_{0.041}]_x$	$[CH(FeCl_4)_{0.050}]_x$	92
8	$[CH(FeCl_4)_{0.046}]_x$		$[CH(FeCl_4)_{0.050}]_x$	92
9	$[CH(FeCl_4)_{0.046}]_x$		$[CH(FeCl_4)_{0.050}]_x$	92
10	$[CH(FeCl_4)_{0.050}]_x$		$[CH(FeCl_4)_{0.050}]_x$	100

Typical elemental analysis as presented here for sample No. 7: %C = 56.39, %H = 5.04, %Fe = 10.80, %Cl = 27.05, Total: 99.28%

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