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An improved method for the polymerization of ethynylferrocene. Conducting properties of doped polyethynylferrocene

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The catalytic activity of the [Rh(cod)Cl]$_2$ complex (cod = *cis,cis*-cyclo-octa-1,5-diene) with respect to the polymerization of ethynylferrocene (EFc) was examined. A good yield (about 80%) of polyethynylferrocene (PEFc) was obtained in benzene by addition of sodium hydroxide as co-catalyst. PEFc was insoluble in most organic solvents. The conductivity (σ) of the undoped polymer is about 10^{-11} ohm^{-1} cm^{-1}; upon doping PEFc with iodine in tetrahydrofuran the conductivity can be increased to 10–100 ohm^{-1} cm^{-1}. The influence of other doping agents was also examined.

Keywords: Polymerization, ethynylferrocene, conductivity

INTRODUCTION

Recently we found that some rhodium complexes are very active catalysts for the linear polymerization of phenylacetylene[1,2] and propargylamines.[3]

We have now examined the catalytic activity of the [Rh(cod)Cl]$_2$ complex (cod = *cis, cis*-cyclo-octa-1,5-diene) in reactions with ethynylferrocene (EFc).

Polymers of EFc (PEFc) have been considered of interest for many years, owing to the possible interaction between the polyenic chain and the pendant ferrocene group, which exhibits electron–donating properties.

The first polymerization of EFc was carried out by Simionescu *et al.*[4] in the presence of dibenzoylperoxide as a radical initiator. The yield in polymer was about 10 % at 140 °C. The polymer was analogous to the one prepared by Pauskin *et al.*[5] through a polymerization of acetylferrocene in the presence of zinc chloride. Nakashima *et al.*[6] examined the catalytic activity of a series of Ziegler–Natta type catalysts towards EFc: $AlR_3/TiCl_4$ catalysts gave mainly cyclic trimers; $AlR_3/Ti(OBu)_4$ catalysts gave linear polymers in low yield. A similar catalytic system was used by Simionescu *et al.*[7] who found that in the presence of $Al(iso\text{-}C_4H_9)_3/VO(C_5H_7O_2)_2$ (Al/VO=8) EFc is converted into a brown insoluble product. Partially soluble PEFc was obtained by the same authors when using $[NiX_2(PPh_3)_2]$ (X = Cl, Br) complexes as catalysts. Korshak *et al.* carried out radical polymerizations of EFc in the presence of di-*tert*-butyl peroxide[8] and radiation-induced polymerizations in the presence of $[NiBr_2(PPh_3)_2]$.[9]

None of the above methods for the polymerization of EFc is, however, completely satisfactory. The use of oxidizing agents as initiators in the radical polymerizations leads to crosslinked and partially oxidized polymers. Ziegler–Natta type catalysts give mainly mixtures of cyclic trimers and linear polymers and nickel complexes give low yields of soluble uncrosslinked polymers of EFc.

In this paper we report on a new synthesis of PEFc in high yields. The conducting properties and the effect of doping of PEFc were also studied.

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EXPERIMENTAL

Reagents and apparatus

EFc was prepared by Rosemblum's method.[10] $[Rh(cod)Cl]_2$ was a commercial product (Strem Chem. Inc.). Benzene (C. Erba reagent-grade solvent) was dried with calcium chloride and distilled over sodium in a flux of nitrogen, tetrahydrofuran (THF) was dried over $LiAlH_4$ and distilled under nitrogen.

Infrared spectra were run on a Perkin–Elmer model 577 spectrophotometer. NMR spectra were run on a Varian EM 360 spectrometer; ultaviolet spectra (solvent dichloromethane) were obtained on a Perkin–Elmer λ5 spectrophotometer.

The direct-current resistance measurements of doped and undoped polymers were carried out with a Keithley 616 electrometer on pellets (thickness 0.1 cm; diameter 1.3 cm) prepared in the air by means of a Specac hydraulic press P/N 15011 at a pressure of 8 tons. Measured resistance values (ohm) were converted into conductivity σ (ohm^{-1} cm^{-1}).

Polymerization procedure

To 5 cm^3 of anhydrous deoxygenated benzene, 40 mg (0.08 mmol) of $[Rh(cod)Cl]_2$, 1 g of EFc (4.7 mmol) and 1 cm^3 of a methanolic solution of 0.2 mmol dm^{-3} sodium hydroxide were added. The mixture was refluxed for 8 h under nitrogen; the colour turned gradually to red brown and the polymer separated as a powder which was filtered off, dried under vacuum and weighed (yield 80%).

Elemental analysis results were as follows. Calcd for $(C_{12}H_{10}Fe)_n$: C,68.61; H,4.79%. Found: C,67.8; H,4.5%. PEFc was insoluble in chlorinated solvents, acetone, tetrahydrofuran and ethers. The various samples did not melt up to 320 °C.

Methanol can also be used as reaction solvent; however it gives lower yields of PEFc. The catalyst is active also in the presence of air in non-anhydrous benzene, but the elemental analyses of PEFc give lower carbon and hydrogen contents.

Doping procedure

In order to obtain PEFc doped with various percentages of iodine, calculated amounts of iodine in tetrahydrofuran solution (0.75 g in 25 cm^3) were added to 200 mg of PEFc suspended in 30 cm^3 of tetrahydrofuran under nitrogen. The mixtures were aged for 12 h; then the THF was distilled off under vacuum. Doped samples of PEFc were then dried under vacuum for about 5 h. The black powders obtained were ground and pellets prepared as described above.

Similar procedures were followed to dope PEFc with sulphuric acid, silver hexafluorophosphate ($AgPF_6$), sodium tetrahydroborate ($NaBH_4$) and iron(III) chloride. Doping with borontrifluoride, nitric acid and ammonia was carried out by maintaining powdered samples of PEFc in closed vessels in the presence of vapours of the dopant for about 12 h.

RESULTS AND DISCUSSION

In order to determine the possible presence of cyclic trimers, after separation of the polymer, the mother liquors were chromatographed on a silica (SiO_2) column. Unreacted EFc was found in the first fractions by elution with benzene. A small amount of a soluble polymeric fraction of purple colour (analyses and IR spectrum similar to that of PEFc; molecular weight of vapour phase osmometry was found to be 2300 atomic mass units) could be separated by elution with methanol. Cyclic trimers, however, were never identified among the secondary reaction products.

The present polymerization method is preferred to preceding ones[4–9] because the earlier methods give PEFc in lower yield and with elemental analyses in poor agreement with the theoretical values. Partial decomposition of the monomer was suggested to explain the analytical results. The polymer obtained in the presence of the $[Rh(cod)Cl]_2$ complex exhibits instead elemental analyses corresponding to the theoretical values. Therefore no oxidation or decomposition of the monomer takes place in these controlled polymerization conditions.

The IR spectra of EFc and PEFc are given in Fig. 1. The bands at 2100 cm^{-1} ($\nu C\equiv C$) and at 3300 cm^{-1} ($\nu H—C\equiv$) present in the spectrum of EFc (Fig. 1a) are absent in the spectra of PEFc (Fig. 1b), thus confirming that polymerization takes place on the triple bond of the monomer.

The IR spectrum of iodine-doped PEFc shows the appearance of new bands at 1510, 1230, 1200 cm^{-1}, and a broadening of the band at 820 cm^{-1} (Fig. 1c); the broadening of the band at 820 cm^{-1}, assigned to the out-of-plane deformation of the $=C—H$ group, may be due to the overlapping of modes from cyclopentadiene moieties in different chemical environ-

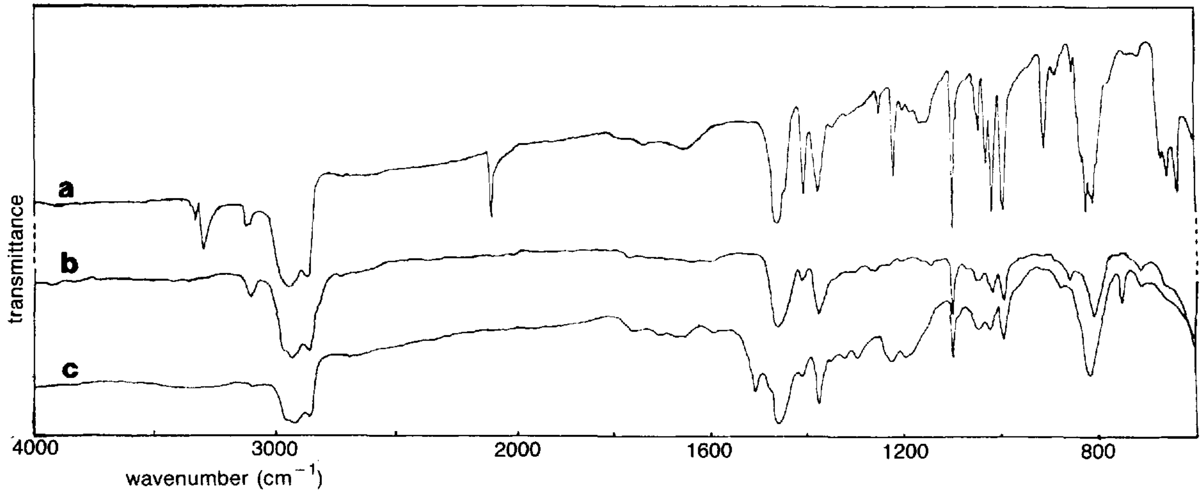


Figure 1 IR spectra (Nujol mulls): (a) ethynylferrocene; (b) polyethynylferrocene (PEFc); (c) iodine-doped (23%, w/w) PEFc.

ments: a similar feature in the IR was observed for polyiodophenylacetylene.[11]

The UV spectra (in dichloromethane) of undoped and iodine-doped PEFc are reported in Fig.2. The polymer shows continuous absorption with a shoulder at 280 nm which shifted to lower wavelengths upon doping: this behaviour has been attributed to a change in the conjugation length of the polymer backbone due to the ionization of the polymer.[12] When iodine is added at 23 % (w/w) a new band at 360 nm appears and by increasing the dopant amount (viz. 50%; 75%) another band at 500 nm appears. These two absorption peaks are assigned to the tri-iodide (I_3^-) and iodine (I_2) species respectively.[13] The absence of absorption at 450 nm may indicate that pentaiodide (I_5^-) species[14] are not present in solution. However, ESCA (electron spectroscopy for chemical analysis) measurements performed on iodine-doped PEFc indicate that I_5^- is the main doping species.[15] Raman spectra performed on other iodine-doped mono(substituted)acetylenes[16,17] provide evidence for the presence of both species (I_3^-, I_5^-) depending on the substituent in the polyenic chain and on the dopant amount. In this case dissociation in solution of I_5^- into I_3^- + I_2 is suggested; measurements are in progress to confirm this hypothesis.

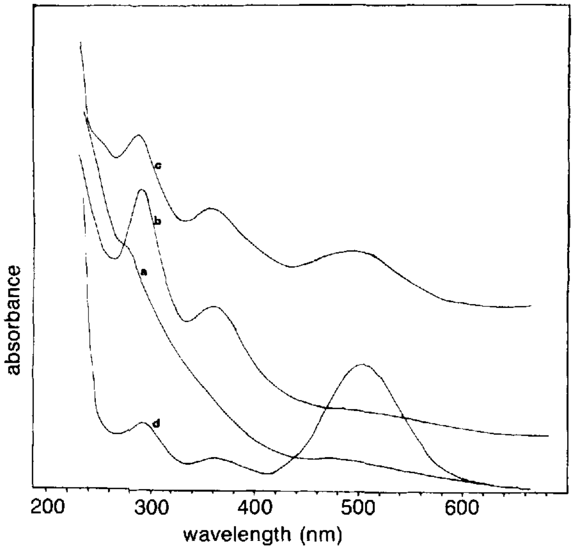


Figure 2 UV spectra (in dichloromethane): (a) polyethynylferrocene (PEFc); (b) iodine-doped (23%, w/w) PEFc; (c) iodine-doped (50%, w/w) PEFc; (d) iodine-doped (75%, w/w) PEFc.

The NMR spectrum of the fraction separated by column chromatorgraphy (see above) is similar to that reported by Nakashima for PEFc obtained with Ziegler–Natta type catalysts. It shows a broad ferrocene signal at about 4–4.3 ppm, but the olefinic protons are not clearly observed.

Conductivity measurements

Conductivity values of about 10^{-11} ohm^{-1} cm^{-1} are found for PEFc. The conductivity increases gradually by many orders of magnitude by doping PEFc with iodine in tetrahydrofuran, reaching a maximum of about 10–100 ohm^{-1} cm^{-1} by addition of high amounts of dopant (75% by weight), when rubber-like materials are obtained (Table 1). The gummy samples slowly release the solvent and become solid; the conductivity then decreases to the value given in Table 1.

Table 1 Conductivity of undoped and iodine-doped PEFc

	I_2 (%, w/w)					
	0	23	37	50	60	75[a]
σ ($\mathrm{ohm^{-1}\ cm^{-1}}$)	2.2×10^{-11}	1.5×10^{-9}	1.1×10^{-7}	4.2×10^{-6}	6.0×10^{-5}	2.3×10^{-4}

[a] Under the conditions given in the doping procedure, even after long periods (~ ten days) of drying, rubber-like materials with conductivity in the range 10–100 $\mathrm{ohm^{-1}\ cm^{-1}}$ were obtained at this high percentage of dopant. The value reported in this table refers to samples which become solid after a long period ageing in air (~ one month).

Table 2 Conductivity, σ ($\mathrm{ohm^{-1}\ cm^{-1}}$) of PEFc doped with various doping agents

Doping agent	Weight of dopant (%)	Doping procedure	Time (days)[a]		
			0	5[b]	13[b]
Borontrifluoride	60	THF	2.4×10^{-7}	2.3×10^{-7}	5.8×10^{-8}
Sulphuric acid	60	THF	2.7×10^{-8}	3.1×10^{-8}	3.7×10^{-8}
Iron(III) chloride	50	THF	2.3×10^{-8}	—[c]	—
Sodium tetrahydroborate	60	THF	1×10^{-8}	1×10^{-8}	—
$AgPF_6$	60	THF	6.8×10^{-9}	9.2×10^{-9}	5.2×10^{-7}
Nitric acid	3	Vapour	$5{,}3\times10^{-8}$	3.4×10^{-8}	3.0×10^{-8}
Boron trifluoride	2	Vapour	1.7×10^{-11}	—	2.4×10^{-11}
Ammonia	2	Vapour	3.9×10^{-12}	—	1.0×10^{-11}

[a] Time at which the conductivity measurements were made on the same sample stored in air. [b] Samples stored in air. [c] Not determined.

Conductivities of PEFc doped with various doping agents are reported in Table 2. By doping with sulphuric acid, nitric acid and boron trifluoride, the colour of the polymer changes from brown to dark green. A green colour is characteristic of iron(III) in the ferricinium ion; therefore an oxidation of the polymer appears to take place with these doping agents. Sodium tetrahydroborate ($NaBH_4$) is a reducing agent, and a dark yellow to orange colour was observed during doping. A dark brown to black colour was observed instead after doping with iodine. Perchloric acid ($HClO_4$) must be avoided because an explosive mixture was obtained when a small sample of PEFc was doped with this reagent. Boron trifluoride or ammonia vapours do not increase the conductivity of PEFc which instead is sensitive to nitrogen oxide (NO_x) (Table 2).

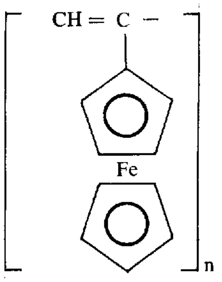
The various doping agents examined in Table 2 increase the conductivity of PEFc only by three to four orders of magnitude. The doped samples maintained their conductivity for at least two weeks. In some cases, as for $AgPF_6$, an increase in conductivity with time was observed, which probably can be correlated with absorption of water vapour from the atmosphere.

CONCLUSION

PEFc is a polymer, similar to various polyacetylenes, in which the π-system of the main chain can interact with the ferrocene pendant group (Scheme 1).

P or n doping agents create positively or negatively charged solitons, polarons or bipolarons in polyacetylene and in other conjugated polymers.[18,19]

In PEFc the p doping agents induce oxidation of the ferrocene pendant group: preliminary ESCA measurements of iodine-doped samples reveal that by increasing the amount of iodine the iron(III)/iron(II)



Scheme 1

($Fe^{3+}|Fe^{2+}$) ratio increases. The electrons are transferred from the iron atom of the pendant group to the doping agent. The same oxidation process takes place with other dopants (see above), when we observed a variation of the polymer colour from brown to dark green. The electronic delocalization between the main chain and the pendant groups reduces the number of charge defects on the polyenic backbone without hindering the increase of conductivity over many orders of magnitude.

Investigations on the conducting mechanism are in progress.

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