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Synthesis of polyphenylacetylene free-standing films in the presence of rhodium–imidazole catalysts

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A new dinuclear rhodium(I) complex [Rh$_2$(cod)$_2$(imH)$_2$im]PF$_6$ (I) has been synthesized and characterized. The complex is unstable in solution where it undergoes modifications leading to insoluble oligomers. However, it exhibits high catalytic activity towards polymerization of phenylacetylene as compared with other rhodium–imidazole complexes. Free-standing polyphenylacetylene (PPA) films can be obtained under mild reaction conditions. As-grown PPA films are stable and soluble. Two different types of morphologies were found: one exhibits a cell-like structure with microfibrils inside the cell and the other a dense enamel-like smooth surface.

Keywords: Rhodium(I)–imidazole, catalyst, polyphenylacetylene, morphology, thin film

INTRODUCTION

The interest in polyphenylacetylene (PPA) arises from its physicochemical characteristics: the polymer is air-stable, soluble, easily doped either homogeneously or heterogeneously[1,2] and shows non-linear optical properties.[3]

PPAs have been prepared by using a variety of catalysts and reaction conditions.[4] We have partly discussed the utility of [Rh L—Lchel]X coordination compounds [L—L = *cis,cis*-cyclo-octa-1,5-diene (cod) or 2,5-norbornadiene (nbd); chel = nitrogen chelating ligand; X = PF_6^-, ClO_4^-, BPh_4^-] as active catalysts when used in the presence of NaOH cocatalyst.[5,6] Under specific experimental conditions, several of these catalysts gave PPA with a stereoregular structure.[7] Furthermore, we observed that a Rh–cod complex containing an imidazole ligand was active without cocatalyst and provided free-standing PPA films.[1]

This paper reports the preparation and characterization of this new compound and a comparison of its catalytic activity with that of the Rh–imidazole complexes [Rh(cod)(imH)Cl] (imH = imidazole), [Rh(cod)im)]$_3$ (im = imidazolate), [Rh(cod)(mid)$_2$]PF$_6$ (mid = *N*-methylimidazole) and [Rh(cod)(imH)$_2$]BF$_4$ already known in the literature.[8–10] The morphology of the PPA films, investigated by scanning electron microscopy (SEM) will also be discussed.

The particular capability of Rh–imidazole complexes in forming PPA films using simple procedures is a significant topic in polymer science, as it is connected to technological applications of polymeric materials in electronic devices.[11,12]

EXPERIMENTAL

Complexes

The complexes [Rh(cod)(imH)Cl],[8] [Rh(cod)-(mid)$_2$]PF$_6$[9] and [Rh(cod)im]$_3$[10] are known in the literature. The complex, [Rh(cod)(imH)$_2$]BF$_4$ was prepared using standard methods.[8,13] [Rh(cod)Cl]$_2$ is a commercial product (Fluka).

[Rh$_2$(cod)$_2$(imH)$_2$im]PF$_6$·CH$_2$Cl$_2$ (I)

When 0.3 g (0.61 mmol) of [Rh(cod)Cl] was suspended in 20 cm^3 of degassed EtOH, 0.17 g (2.50 mmol) of imidazole was added under nitrogen. A yellow–orange solution was formed immediately. No change was apparent when a concentrated solution of NH$_4$PF$_6$ (0.20 g, 1.23 mmol) in EtOH was added dropwise. After 1 h, about half of the solvent volume was evaporated under vacuum, and substituted by an equal amount of water. A yellow compound precipitated, which was filtered and washed sequentially with H$_2$O, H$_2$O/EtOH, and EtOH/Et$_2$O. The final product was dried in the air and quickly recrystallized from CH$_2$Cl$_2$/n-hexane, giving bright yellow microcrystals. Yield 75%; m.p. 150 °C (partial melting), 164 °C (gas evolution). Elemental analysis: Calcd for C$_{26}$H$_{37}$Cl$_2$F$_6$N$_6$PRh$_2$ (%): C 36.51; H

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Table 1 Polymerization reactions of phenylacetylene in the presence of rhodium-imidazole catalysts

Catalyst	Film powder solvent		Time	Yield (%)	MW (a.m.u.)
$[Rh_2(cod)_2(imH)_2im]PF_6$	—		10 min	≈100	20 000
	CH_2Cl_2		20 min	≈100	17 000–22 000
		CH_2Cl_2[a]	1.5 h	90	14 000
		CH_3OH	1 h	70	4500
		$CH_3OH/NaOH$[b]	2 h	20	3500
$[Rh(cod)(imH)Cl]$	CH_2Cl_2		30 min	≈100	14 000
		CH_3OH	1.5 h	75	2300
		CH_3OH	1 h	60	
$[Rh(cod)(imH)_2]BF_4$	—		10 min	≈100	10 000
	CH_2Cl_2		1.5 h	≈100	8000
		CH_2Cl_2[a]	2 h	≈100	7000
		CH_3OH	1.5 h	50	2600
$[Rh(cod)(mid)_2]PF_6$	CH_2Cl_2		1 h	≈100	10 000
		CH_3OH	1.5 h	75	2500
		CH_3OH	1 h	60	
$[Rh(cod)im]_3$	—		1 h	≈100	9500
	CH_2Cl_2		1 h	≈100	10 500
		CH_3OH	1 h	50	2800
		$CH_3OH/NaOH$[b]	1 h	10	3500

[a] PPA film cast from CH_2Cl_2 solution after refluxing.

[b] Cocatalysts NaOH (0.2 mmol) added to the reaction mixture.

4.36; Rh 24.06; CH_2Cl_2 9.9. Found (%) C 36.9; H 4.37; Rh 23.96; CH_2Cl_2 8.5 (determined by gas chromatography).

Polymerization reactions

Film forming

Typical reactions were performed in a nitrogen-filled glovebox. A portion of 2–5 mg of the catalyst in 2 cm^3 of CH_2Cl_2 (dried over $CaSO_4$) were spread on a flat glass vessel: 1 cm^3 (9.1×10^{-3} mol) of freshly distilled phenylacetylene was added and a homogeneous solution was immediately obtained; the polymerization occurred at room temperature within 10 min–1 h (see Table 1) giving, after solvent evaporation, free-standing yellow–brown transparent PPA films. Some reactions were carried out in bulk using the same procedure with no appreciable differences in the reactivity detected.

Reactions at reflux

The catalyst/monomer ratio was the same as that reported for film forming. The solvent was methanol (50 cm^3) and the reaction time approx. 1 h or more (Table 1): the polymer, a yellow powder, precipitated from the reaction mixture as soon as it was formed, and at the end was filtered and washed with methanol, dried under vacuum and weighed.

The elemental analyses of PPA are in agreement with calculated values: Calcd (%) C 94.08; H = 5.92. Found (%): C 94.20; H 6.00.

Doping procedures

PPA films were heterogeneously doped as already reported,[1] by exposure to iodine vapours for 30 min. PPA powders were homogeneously doped by dissolving weighed amounts of polymer and iodine (50%, w/w) in tetrahydrofuran (THF) and ageing the solution for 24 h; the solvent was then evaporated under reduced pressure until a black material was obtained, which was redissolved in CH_2Cl_2 and cast on glass slides to give films.

Methods and instruments

IR spectra were run on a Perkin–Elmer 580B or on a Perkin–Elmer 983G spectrophotometer as KBr pellets (the complexes) or thin films cast from CH_2Cl_2 solutions on NaCl windows (the polymer). Molecular weights (MW) were measured in chloroform solution by a Knauer model

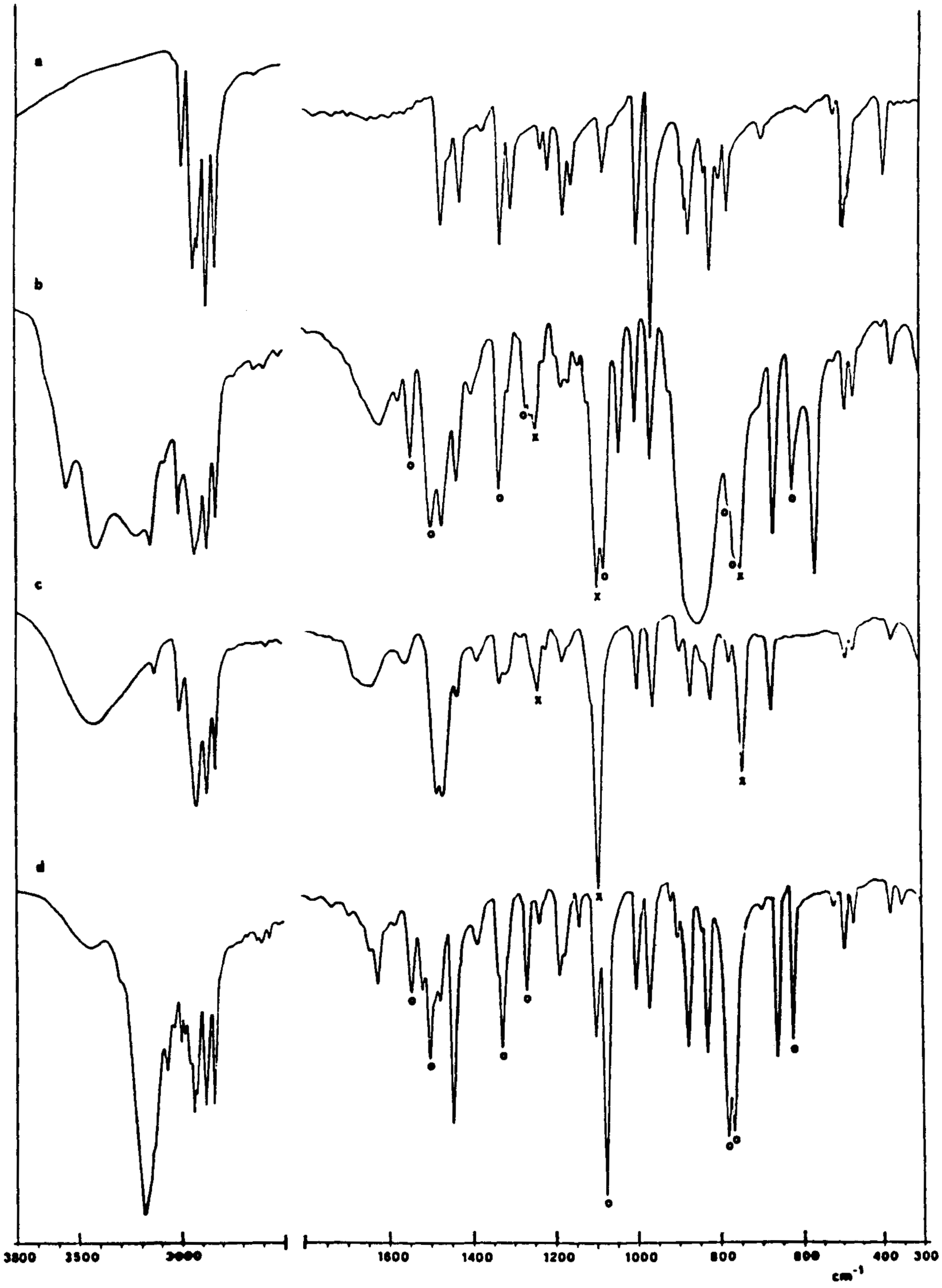


Figure 1 IR spectra of (a) $[Rh(cod)Cl]_2$, (b) $[Rh_2(cod)_2(imH)_2im]PF_6 \cdot EtOH$, (c) $[Rh(cod)im]_3$, (d) $[Rh(cod)(imH)Cl]$; ×, exo-bidentate imidazolate bands; ○, imidazole ligand bands.

11 osmometer at 30 °C. Scanning electron micrographs (SEM) of PPA samples were obtained with a SEM–Cambridge 100 instrument.

RESULTS AND DISCUSSION

Chemistry of the complex [Rh(cod)(imH)$_2$]PF$_6$

The compound, [Rh(cod)(imH)$_2$]PF$_6$, we intend to test in order to extend the series of cationic rhodium complexes used as catalysts for the polymerization of phenylacetylene, is known in the literature.[8] This compound formed without difficulty in solution by reacting [Rh(cod)Cl]$_2$, imidazole and NH$_4$PF$_6$ in the presence of an excess of the two latter reagents. However, during work-up, this complex easily looses imidazole and rearranges to a new product of approximate formula [Rh$_2$(cod)$_2$(imH)$_2$im]PF$_6$·S$_n$ (S = solvent; $n = 1, 2$) (**I**). In agreement with the proposed structure, ^{1}H NMR spectra in CDCl$_3$ indicate the presence of two imidazoles, one imidazolate for two molecules of cod. The complex (**I**) may be visualized as being formed by deprotonation of one of the imidazole ligands. The values of its measured molecular weight strongly depend on the concentrations (*C*) of the solutions. In CH$_2$Cl$_2$ at 45°C, a MW of 764 a.m.u. was found at C = 0.57% (w/w) which decreases to 614 at C = 0.29% (w/w) and to 370 at C = 0.06% (w/w). The observed MW decrease is associated with enhancement of the solution conductivities (at the lowest concentration reported above, the complex is a 1 : 1 electrolyte).

Complex **I** is not very stable itself in solution. Although it can be recovered unchanged following rapid recrystallization from CH$_2$Cl$_2$ and n-hexane, it leaves a not-negligible residue of an almost insoluble material, with higher Rh/N and Rh/PF$_6$ ratios than the parent compound, which does not melt below 300 °C. (A similar behaviour is also observed for the BF$_4$ derivative, which we

Table 2 Attribution of absorption IR bands for the complexes reported in Fig. 1 (a–d)

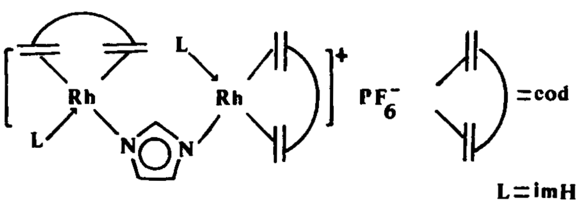
Ligand	a	b	c	d
		3552		
im		3410 br	≈3440 m,br	≈3435 w,br
		3220 br } ms		≈3138 s,br
		3150	3135 vw	
		3080 sh		3064 w
		3012		
	2992		3004	3000 w
cod	2940 } s	2933 } ms	2931 m	2940
cod	2875	2874	2874	2880 } ms
cod	2830	2830	2829	2836
im,imH		≈1615 w,br	1700–1600 sh,br	1636 w
		1570 vw	≈1555 w,br	1618 w
				1595 sh
				1578 vw
imH		1538 w		1536 w
			1510 w	
imH		1490 ms	1480	1492 m
cod	1466 m	1466 ms	1468 } m	1468 w
cod	1422 m,w	1429 w	1429 w	1436 s
			1377 w,br	
imH,cod	1325 m	1327 m	1328	1330 m
		1315 sh } w	1320 m	
cod	1300 mw	1305 sh	1305 sh	
imH		1263 sh		1260 mw
		1251 sh		
		1240 w	1235 w	1230 w
	1210 w			

Table 2 *cont.*

Ligand	a	b	c	d
		1195 sh		
cod	1172 w	1180 } w	1174 w	1180 wm
cod	1150	1160	1160 sh	1167 sh
		1136 vw		1134 w
		1105 sh	1105 sh	
im		1090 s	1090 s	1091 mw
imH	1077 w	1071 s		1067 s
		1035 w		
cod	994 m	998 w	994 w	994 w
cod	960 s	960 w	995 w	962 mw
	885 sh		890 w	
	880 sh			
PF_6^-		≈850 vs,br		
	868 w		865	867 mw
	832 vw		836 sh } w	836 sh
	817 m		815	821 mw
imH	775 w	≈770 sh	787 sh	
imH		≈755 sh	772 vw	771 m
im		743 ms	740 vw	756
cod		≈695 sh		
	690 w			
im,imH		660 ms	667 w	651 mw
imH		614 w		613 mw
PF_6		560 m		
	513 w			513 vw
cod	487 m	481 w	481 w	485 w
im,imH	475 sh	460 w	463 w	462 w
	385 w			
im,imH		366 w	368 w	372 w
			345	

were not able to isolate at the first stage of reaction, i.e. the $[Rh(cod)(imH)_2]BF_4$ complex.) The enhanced degree of oligomerization of the complex cation is connected with a decrease in colour intensity and catalytic activity. Different poorly soluble cationic species are formed by heating complex **I** in the most common solvents, and seem to be analytically associated with loss of cod.

From saturated DMF solutions of complex **I**, solid $[Rh(cod)im]_3$ precipitates after a few hours at room temperature.



Complex 1

IR spectra

Figure 1 provides several pertinent spectra for the reaction products, together with that of $[Rh(cod)Cl]_2$, taken as a reference compound. As can be inferred from a comparison among these spectra, complex **I** (Fig. 1b) spectrum shows absorptions characteristic for bidentate cod (compare with Fig. 1a) and both monocoordinated and exobidentate bridging imidazole. All the diolefin absorption peaks of the $[Rh(cod)Cl]_2$ complex (Fig. 1a) are well reflected in the new compound, which furthermore shows absorptions due to exobidentate imidazolate, indicated in Fig. 1 by × (1090 s, 743 ms cm^{-1}; compare with Fig. 1c) and to imidazole ligands, labelled in Fig. 1 by ○, (1538w, 1490(ms), 1327(m*), 1263(sh), 1074(s), ≈770,755(sh); 614(w), cm^{-1}). Characteristic in

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* Cod absorption contributes to the intensity of the 1327 cm^{-1} peak.

Fig. 1(b) is the articulate pattern in the 3650–3050 cm^{-1} region and the absorption at 3150 cm^{-1}. The two characteristic peaks of the PF_6 group (strong, broad in the 850 cm^{-1} region and sharp at 560 cm^{-1}) prove the ionic nature of complex **I** (Table 2).

The insoluble products formed during the recrystallization of **I** maintain roughly the IR spectrum of the parent compound, but with an increased relative intensity of the bands associated with the imidazolate ligands and absence of the band at 1035 cm^{-1}.

(*a*) Treatment of **I** with hot dichloroethane produces general broadening of IR bands and modifications in the spectral pattern of cod.

(b) Recrystallization of **I** from hot acetone gives a product whose spectrum is very similar to that of $[Rh(cod)im]_3$, but differs due to the presence of the PF_6^- ion and is of reduced intensity with respect to complex **I**. Other minor differences are new bands at 3200 (w, br), 1700 (m, br) 618(w) cm^{-1} and enhanced intensity of the band at 770 cm^{-1}.

Catalytic reactivity

The polymerization behaviour of phenylacetylene in the presence of rhodium–imidazole catalysts is reported in Table 1. All the complexes examined are active in bulk or in CH_2Cl_2 for the preparation of films which are air-stable, soluble and can be obtained with approx. 100% yield. The reactions run at reflux in methanol lead to a PPA yield of 60–75% in 1–2 h and longer reaction times do not markedly improve the polymer amount. The presence of NaOH, which was required as cocatalyst to enhance the polymerization rate and yield when other rhodium(I) catalysts were used,[5,6] is not recommended in the reactions carried out with the complexes tested here. Attempts to substitute cod with nbd were also unsuccessful.

PPA films show molecular weights in the range 22 000–10 000 a.m.u., which are hence higher than those of PPA powders obtained from the reactions at reflux (4500–2500 a.m.u.). These results suggest that polymerization conditions (i.e. solvent and/or heating) hinder chain growth in the formation of PPA powders. Chain termination events are more probable at higher temperatures. Also, the nature of the solvent must be implied, given that no films are obtained in methanol at room temperature.

The IR spectra of PPA samples (performed on films cast from CH_2Cl_2 solutions), coming either from free-standing films or from powders, show very similar features independent of the catalyst used. Many questions about the correlation of IR bands with the polymer structure are still unresolved;[7,14] however, there is general agreement to attribute an intense absorption at 740 cm^{-1} to a 'cis' rich polymer backbone configuration. In our PPA samples the 740 cm^{-1} band is always stronger than the 760 cm^{-1} band attributed to a '*trans*'-rich polymer.[15] A stereoregular structure for the new PPA samples that have been prepared is suggested by comparison of the ^1H and ^{13}C-NMR spectra with those already reported,[7] i.e. the new PPA samples shown in Table 1 have a stereoregular structure.

Investigations on the morphology of PPA free-standing films have been carried out by scanning electron microscopy (SEM). The surface of as-grown films exhibits mainly two different kinds of structure, independent of the reaction catalyst: (a) dense enamel or glass with random wrinkles and fissures probably due to sample handling (Fig. 2a); (b) cell-like, with the diameter of the cells $\approx 9\,\mu m$ (microns), as can be seen in the picture considering the cell delineated by the two straight markers (Fig. 2b). The cross-section of the films has been examined also: in Fig. 2(c) the edge is the straight line separating the dark (surface) from the bright (bulk) part of the picture. No orientation of the material or fibrils can be detected on the enamel surface. In Fig. 2(d) the bulk of the cell-like structure is shown: the cells are located at the surface of the film, while in bulk a compact structure is formed which seems to be built up from clumped, unoriented fibrils.

Examples of film morphology are reported in the literature, mainly regarding polyacetylene,[16–18] polypyrrole[19,20] and polythiophene.[21] The morphology of the surface of as-grown polymers generally consists of microgranular particles or randomly oriented fibrils: the as-grown films exhibit lower conductivity than that of the stretched samples, whose morphology turns to fibrils with high alignment.[16–18] To our knowledge, polyconjugated organic polymers usually do not show the morphology of PPA films; recently reported SEM images of polycyclooctatetraene, synthesized by the liquid-phase ROMP (ring-opening metathesis polymerization) route, show similar morphology.[22] Some preliminary attempts of making oriented PPA have produced films with a network of fibrillar and enamel-like zones.

The conductivity of heterogeneously iodine-doped PPA films prepared with rhodium–

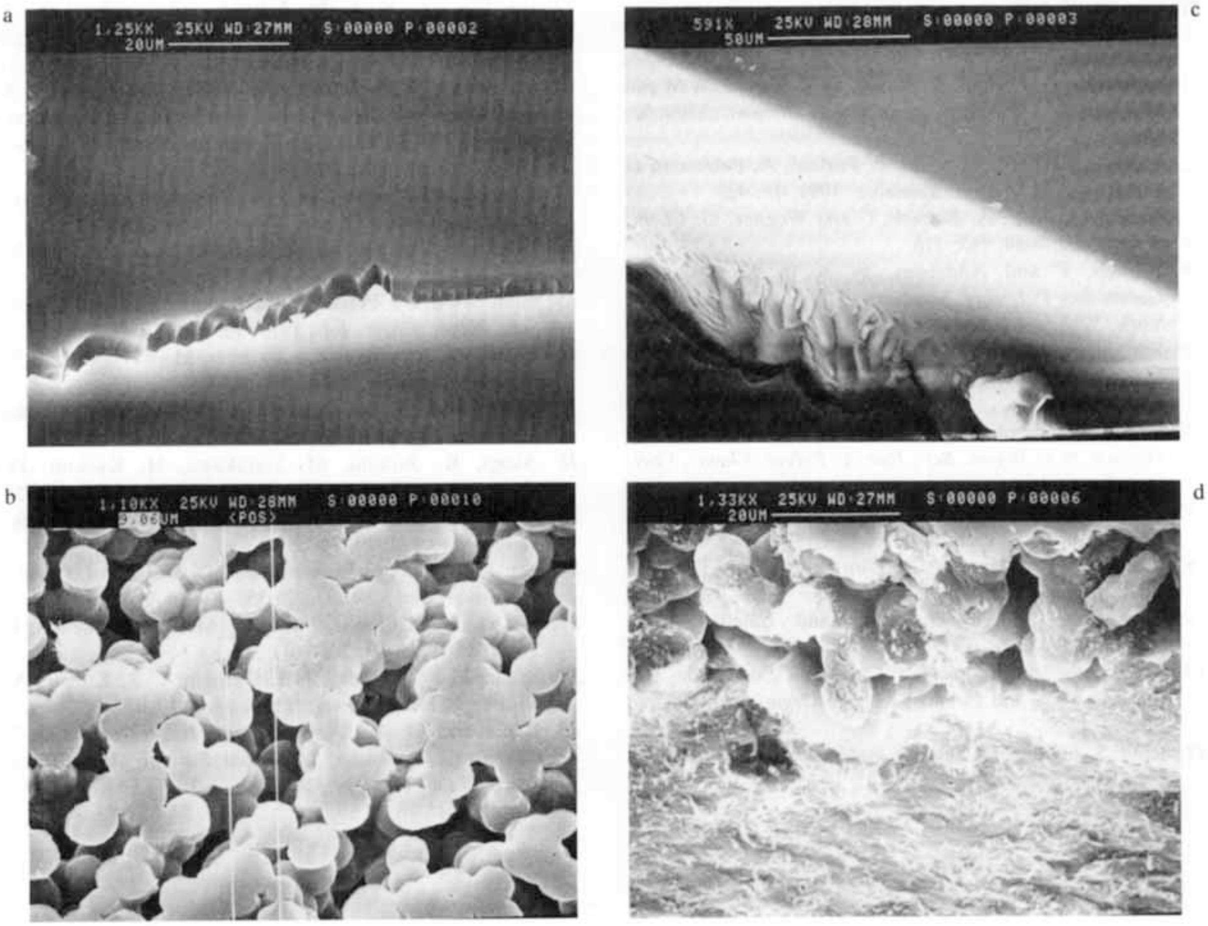

Figure 2 Scanning electron micrograph of PPA free-standing films: (a) enamel-like surface; (b) cell-like surface; (c) enamel-like edge fracture; (d) cell-like fracture (bulk).

imidazole complexes was found to be lower than that of homogeneously iodine-doped PPA powders, confirming the results already reported.[2] This behaviour was attributed to limited iodine penetration at the surface of PPA films, as indicated by angle-resolved XPS measurements.[23] This effect may be correlated to the glassy surface and bulk of PPA films.

CONCLUSIONS

Rhodium–imidazole complexes are very active catalysts for PPA free-standing film production, under mild reaction conditions. The usual catalyst/monomer molar ratio is very low, roughly 1:1000. The presence of NaOH as cocatalyst is not necessary; on the contrary it hinders the reaction rate and yield. Among the tested Rh(I) imidazole complexes, the new dinuclear $[Rh_2(cod)_2(imH)_2im]PF_6$ gives PPA with the highest MW (in the range 17 000–22 000 a.m.u.), and total monomer conversion in 10 min. The morphology of PPA films surface seems to be correlated to the polymerization reaction conditions, rather than to the catalyst structure. The cells contain microfibrils (Fig. 2d), which upon clumping yield a compact and dense surface with homogeneous appearance. These preliminary results will be further investigated, in order to correlate mojphology and electrical properties of PPA.

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