Polymer-supported Pd(ii) Wacker-type catalysts: 1. Synthesis and characterization of the catalysts

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Polybenzimidazole (PBI) and crosslinked vinyl polymers have been chemically modified with nitrile groups using various methods both homogeneous and heterogeneous. The chemically modified polymers have been used as supports to immobilize palladium(ii) to form the basis of Wacker-type catalysts. A cyanomethylated PBI-supported palladium(ii) complex (PBI-Bz-CH_2CN/$PdCl_2$) is believed to be a coordinately unsaturated species, and it displays remarkable thermo-oxidative stability to ~400°C.

INTRODUCTION

Polymer-supported reactions have become increasingly important in recent years. Polystyrene, polyacrylamide and poly(alkyl methacrylate) bead resins have been used widely and successfully as polymer supports[1-3]. All of these, however, are subject to severe limitations in terms of the temperature at which they can be used. In practice, excessive degradation and depolymerization arise when the temperature is above 150°C. There is now a growing need for much more thermally and oxidatively stable polymers that can be used at temperatures of 250°C and indeed beyond.

In 1961, Carl S. Marvel, one of the foremost researchers in the field of heterocyclic polymer chemistry, reported the first synthesis of all-aromatic, high-molar-mass polybenzimidazoles[4] (PBIs). During the last 30 years, PBI polymers have been applied mainly as engineering materials because of their outstanding thermal and oxidative stabilities. Although, for reasons of economics, at the present time no large-scale commercialization of PBI manufacturing and processing technology is in sight, polybenzimidazole chemistry and its applications are being monitored widely. A few years ago, polybenzimidazole was used as a support for the preparation of polymer-supported hydrogenation catalysts[5-8]. Chemically modified PBIs have also been reported recently for hydrometallurgical applications[9].

We report here on some new chemical modification methods leading to novel polymer-supported palladium(ii) catalysts for Wacker-type reactions.

RESULTS AND DISCUSSION

Cyanomethylated PBI-Bz polymer (PBI-Bz-CH_2CN)

Synthesis. The imidazole ring in a PBI backbone might be used for direct coordination to immobilize

transition metals[5-8]. However, imidazole is a poor ligand for Wacker-type catalysts L_2PdX_2 (see paper 2 in this series[10]), while acetonitrile is reported to be a good one[11]. Hence, to be a useful support for Wacker-type catalysts, PBI polymers must be chemically modified with some suitable functional group, e.g. cyanomethyl. Based on benzimidazole chemistry[12], N-cyanomethylation directly on the imidazole ring seemed possible (*Scheme 1*). For the reaction, sodium hydride was used as an efficient base. This could not be reacted with PBI directly, but was first used with dimethylsulfoxide (DMSO) at 50°C to generate sodium methylsulfinylmethide (MSM). Thereafter, PBI-Bz powder dissolved readily upon reaction with MSM in DMSO to form a deep brown solution. A fluorescent blue colour was noted at the surface of the reactant liquid, which might result from the formation of the PBI-Bz($>N^{\ominus}$) anion (*Scheme 1*). The fluorescent blue disappeared once the bromoaceto-
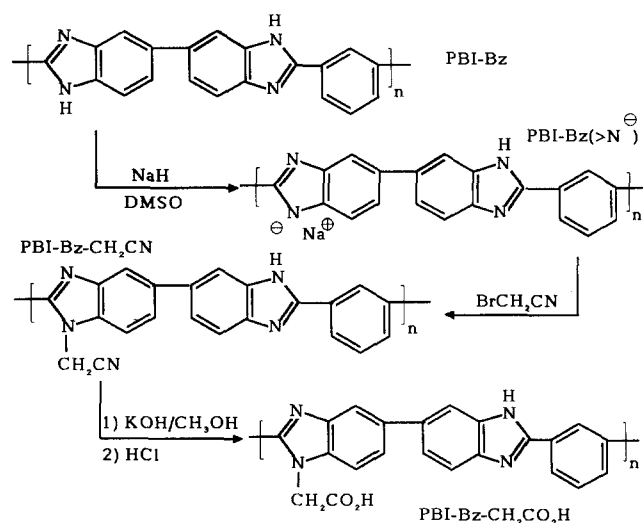
Scheme 1 Chemical modification of PBI-Bz support

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nitrile was added. However, the full reaction is not as fast as the colour change and took a few hours at 65°C.

Characterization. Infra-red spectra of PBI-Bz and cyanomethylated PBI-Bz are shown in *Figure 1* and the i.r. data are summarized in *Table 1*. The absorption at $2211 \, cm^{-1}$ indicates the presence of the nitrile group in the polymer and an H–CH stretching vibration at $2869 \, cm^{-1}$ is distinctive for a methylene ($-CH_2-$) group in the polymer. Both of these absorptions are absent in the case of PBI-Bz. The solid-state ^{13}C n.m.r. spectra are shown in *Figure 2* and the chemical shift data are summarized in *Table 2*. Line broadening was observed. No attempt has been made to assign individual resonances in the rather complicated multiplet from the PBI backbone. However, comparing the spectra of PBI-Bz (a) and cyanomethylated PBI-Bz (b), it can be seen from (b) that the enhanced peak at $\sim 123 \, ppm$ might result from the $-C\equiv N$ groups contained in the PBI polymer, and those at ~ 32 and $\sim 35 \, ppm$ might result from the $-CH_2-$ group, while a peak for PBI-Bz at $\sim 142 \, ppm$ has disappeared in (b). Other peaks are shifted a little closer as the result of cyanomethyl group bonding to the polymer.

Degree of functionalization. The degree of functionalization of the cyanomethylated PBI-Bz polymer could be calculated from the ratio of the carbon and nitrogen contents determined by elemental microanalysis. It was found that the degree of functionalization was
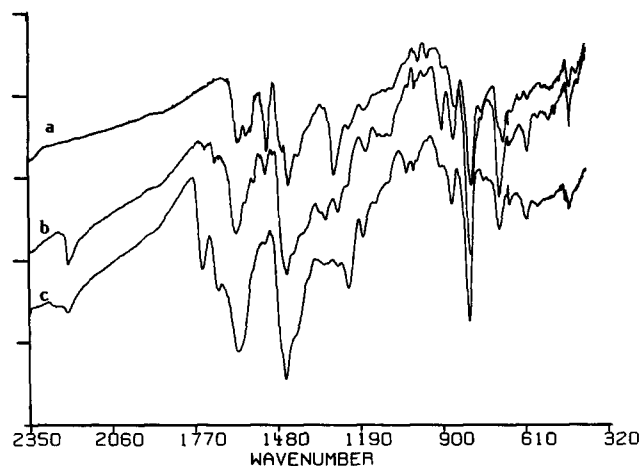
$\sim 60\%$. This result indicates that there are many repeat units in the polymer with only one imidazole ring cyanomethylated (PBI-Bz-CH$_2$CN; *Scheme 1*). Furthermore, the loading of $-CH_2CN$ per gram of polymer can be calculated as well. On average the percentage of N atoms in cyanomethyl groups to the total N atoms of PBI-Bz-CH$_2$CN is 23.4% when the degree of functionalization is 60%. Microanalysis shows that the N content in the polymer is 17.5%, so the weight percentage of N atoms from $-CH_2CN$ in the polymer is $23.4\% \times 17.5\% = 4.1\%$. This means that one gram of polymer contains $0.041 \, g$ or $2.92 \, mmol$ of N atoms from $-CH_2CN$ groups. This corresponds to $2.9 \, mmol$ of $-CH_2CN$ per gram of polymer PBI-Bz-CH$_2$CN.

Other functionalized polybenzimidazole polymers

Carboxymethylated polybenzimidazole (PBI-Bz-CH$_2$COOH). The most convenient method of introducing carboxymethyl groups onto the PBI polymer is by hydrolysis of cyanomethylated PBI-Bz (*Scheme 1*). It is well known that cyanomethyl groups can be hydrolysed to carboxymethyl groups using potassium hydroxide in aqueous methanol[13]. After hydrolysis, the absorption due to the nitrile group at $2211 \, cm^{-1}$ had disappeared, and the broad bands due to COO–H hydrogen bonding between 3450 and $2600 \, cm^{-1}$ appeared. It has been reported that benzimidazole reacts with chloroacetic acid in aqueous solution to form the carboxymethylated derivative. However, this method was unsuccessful in our hands, probably because of the insolubility of PBI.

Grafting of polybenzimidazole with polyacrylonitrile (PBI-GF). It has been reported that N-grafted poly(*p*-phenylene terephthalamide)s (PPTA) can be synthesized
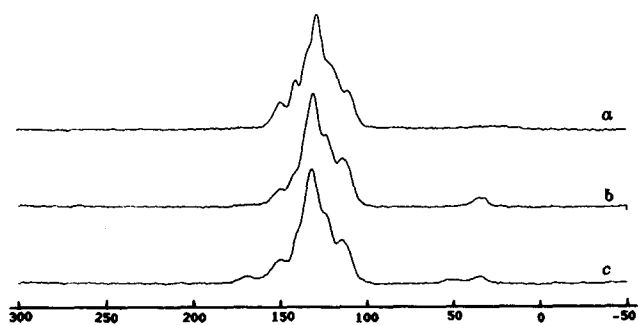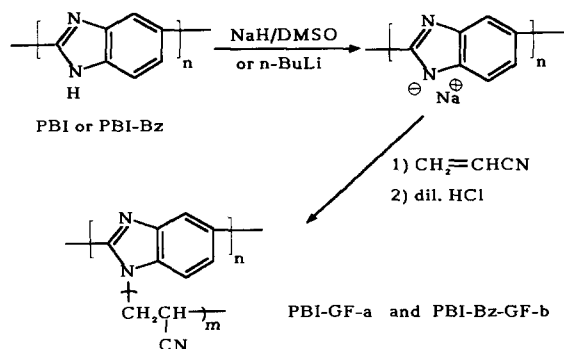

Figure 1 Infra-red spectra of polybenzimidazole and its derivatives: (a) PBI-Bz; (b) PBI-Bz-CH$_2$CN; (c) PBI-Bz-CH$_2$CN/PdCl$_2$

Figure 2 ^{13}C solid-state n.m.r. spectra of polybenzimidazole and its derivatives: (a) PBI-Bz; (b) PBI-Bz-CH$_2$CN; (c) PBI-Bz-CH$_2$CN/PdCl$_2$

Table 1 Infra-red spectral data (KBr discs) of chemically modified PBI polymers containing nitrile group

Polymer	Bands from the functional group (cm^{-1})		Bands from PBI backbone (cm^{-1})			
PBI-Bz	–	–	1620	1511	1439	797
PBI-Bz-CH$_2$CN	$v_{CH} = 2869$ 2927	$v_{CN} = 2211$	1625	1570	1446	800
PBI-GF-a	$v_{CH} = 2870$ 2939	$v_{CN} = 2243$	1624	1572	1442	815
PBI-Bz-GF-b	$v_{CH} = 2879$ 2917	$v_{CN} = 2243$	1629	1526	1449	802

Table 2 Solid-state ^{13}C n.m.r. chemical shifts of functional PBI-Bz (ppm)

Polymer	From $-CH_2CN$ group (ppm)		From PBI backbone (ppm)			
PBI-Bz	–	–	112.6	129.8	142.4	151.3
PBI-Bz-CH$_2$CN	$\delta = 122.6$	(–CN)	113.5	130.4	–	149.8
	$\delta = 31.8, 35.0$	(–CH$_2$CN)				
PBI-Bz-CH$_2$CN/PdCl$_2$	$\delta = 122.0$	(–CN)	114.1	131.1	–	150.9
	$\delta = 169.0$	(–CN–Pd)				
	$\delta = 34.7$	(–CH$_2$–CN)				
	$\delta = 52.0$	(–CH$_2$CN–Pd)				

Scheme 2 Anionic graft polymerization of acrylonitrile onto soluble PBI and PBI-Bz beads (structure of PBI is shown here; PBI-Bz is as shown in *Scheme 1*)

from PPTA and acrylonitrile via metallation of the polymer in solution using sodium methylsulfinylcarbanion dimethylsulfoxide (MSM-DMSO) at low temperature[14]. Using the same method a flexible chain containing nitrile groups was expected to be introduced onto the PBI rigid chain. An acidic proton in the PBI imidazole ring was first removed using MSM-DMSO to form the PBI($> N^{\ominus}$) anion. This was used to initiate the graft polymerization of acrylonitrile onto the PBI backbone. The N-grafted PBI powder (PBI-GF-a) was formed according to *Scheme 2*. The reaction was terminated by the addition of dilute hydrochloric acid.

The chemical modifications described above employing the MSM-DMSO system involved dissolving the PBI polymer in the solvent. To retain the physical form of a polymer (such as macroporous beads) for further applications, an attempt was made to carry out the same reaction heterogeneously, using tetrahydrofuran (THF) as the medium. The PBI-Bz beads were supplied by the Celanese Corp. and butyllithium (in pentane solvent) was used as the soluble base to remove the proton from the imidazole ring. To protect the polymer beads from attrition, a rotary reactor was used under a nitrogen atmosphere. The latter was also employed in the solution graft reaction. The polymer beads suffered no serious damage during the reaction (*Scheme 2*), which was terminated with dilute HCl to yield polyacrylonitrile grafted PBI-Bz beads (PBI-Bz-GF-b). The infra-red spectral data of PBI-Bz-CH$_2$CN, PBI-GF-a and PBI-Bz-GF-b are summarized in *Table 1*. The absorption band at 2243 cm^{-1} indicates the presence of the nitrile group in the polymer, which is absent in the case of PBI. It is also noticed that the absorptions of the nitrile groups in PBI-GF-a and PBI-Bz-GF-b are the same (2243 cm^{-1})

Table 3 N-Grafting of polyacrylonitrile onto PBI polymer

PBI-GF-a		PBI-Bz-GF-b	
PBI	2.3 g (20 mmol)	PBI-Bz	5 g (16 mmol)
AN	6.5 ml (200 mmol)	AN	5 ml (75 mmol)
Product weight	3.4 g	Product weight	6.7 g
Δwt^a	1.1 g	Δwt^a	1.7 g
Δwt%^{b}	48	Δwt%^{b}	34

^{a} Δwt = increase in weight of product relative to the starting weight of PBI polymer, which correspond respectively to ~21 and 32 mmol of acrylonitrile

^{b} Δwt% = percentage of increase weight to the starting weight of PBI polymer
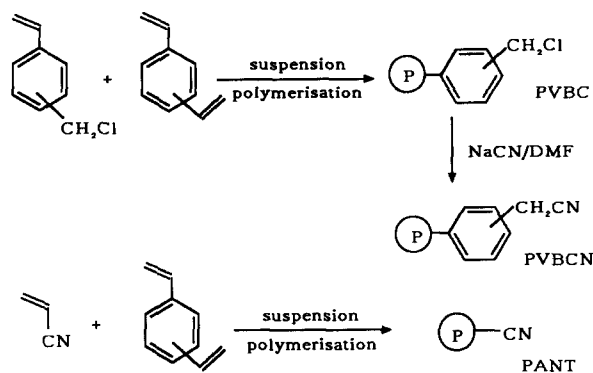
Scheme 3 Synthesis of PVBCN and PANT crosslinked beads

but that due to the nitrile group in cyanomethylated PBI-Bz (2211 cm^{-1}) is slightly different. From *Table 3* it can be seen that the graft polymerization was very successful and the percentage weight increase was ~48 and 34% respectively, corresponding to ~21 and 32 mmol of acrylonitrile respectively. If grafting occurs from all imidazole sites, the degree of polymerization of the grafted chain (m) would be ~1. In practice, however, it is more likely that longer polyacrylonitrile chains are formed on a rather small fraction of the imidazole sites. Unfortunately no experimental evidence is available to confirm this in the present work.

Crosslinked vinyl polymers

Synthesis of crosslinked polymers. For the convenience of further functionalization, vinylbenzyl chloride (VBC) was used as a monomer. VBC is readily polymerized by classical radical-initiated polymerization (*Scheme 3*). The copolymerization with divinylbenzene (DVB) has been

extensively studied[15]. In the present work the suspension copolymerization was carried out following the earlier procedures[16]. Isoamyl alcohol is an efficient porogen and the crosslinking process is efficient, since the polymer quickly becomes insoluble. The yield of beads was high (~93%). The product (nominally 22% crosslinked PVBC) contains 15% Cl corresponding to 4.2 mmol of Cl per gram of polymer and consists of white beads of ~500–800 μm diameter with a surface area of ~60 m² g⁻¹.

Another crosslinked polymer was synthesized by suspension polymerization using acrylonitrile (ANT) with DVB (*Scheme 3*). The procedures and polymerization system were the same as in the case of PVBC. The yield was high (93%). The product contains 9.8% N corresponding to about 7 mmol of nitrile group per gram of polymer. The product (nominally 21% crosslinked PANT) consists of white beads of ~300–500 μm diameter with a surface area of ~120 m² g⁻¹.

Diagnostically useful i.r. absorption bands have been highlighted before[15], and are confirmed here: near 800 cm⁻¹ (C–H out-of-plane bending, overlapped by benzene aromatic skeletal absorptions), near 1600, 1486 and 1450 cm⁻¹ (C=C aromatic ring vibrations), and near 3023, 2930 and 2850 cm⁻¹ (C–H). There are also some characteristic absorptions for PVBC at 1266 and 708 cm⁻¹ (CH₂–Cl), and for PANT at 2238 cm⁻¹ (C≡N).

Functionalization of poly(vinylbenzyl chloride). Chemical modification of pendent chloromethyl groups in polymers for the synthesis of functional polymers has been extensively studied[15], with nucleophilic reagents in aprotic polar solvents being very useful[17]. In the present work, the chloromethyl groups in crosslinked polystyrene were converted to cyanomethyl groups by reaction with sodium cyanide (*Scheme 3*) to provide a good ligand for Wacker-type Pd(II) catalysts. The polymer backbone absorptions between 1445 and 1605 cm⁻¹ are essentially unchanged, the –CH₂–Cl characteristic vibration at 1266 cm⁻¹ disappears while the –CN absorption at 2251 cm⁻¹ is clearly visible. The residual Cl content in the polymer was just 0.9%, so almost all of the chloromethyl groups were converted to cyanomethyl groups. The product contains 5.3% N, which is equivalent to ~3.8 mmol cyanomethyl groups per gram of polymer.

Preparation of polymer supported palladium(II) complexes

Synthesis. It has been reported that appropriate polymer beads in a chromatographic column can be loaded with metal complex using an excess of palladium dichloride in water (~0.1 g PdCl₂/ml)[18]. However, the solubility of palladium dichloride in water is very limited without the presence of strong acid and the palladium loading achieved using this method proved to be very low (2.7%)[18]. It has also been reported that acetone/water is a good solvent in the preparation of a PBI-supported palladium complex, with about 5% acetonitrile to improve the palladium solubility[5–8]. However, in the present work such a solvent mixture proved to be unsatisfactory as well. In the organic chemistry of palladium, there are some reports describing the use of methanol[19] as a solvent in the preparation of π-allyl palladium complexes from alkenes. Hence, methanol was tried as a solvent for preparation of polymer-supported palladium(II) complexes. The solubility of palladium dichloride in methanol is not particularly high, but it is significantly better than in water and acetone. The coordination reaction of palladium dichloride with the various functional polymers was carried out at room temperature for about 24 h. When the reaction was complete, the colour of the methanol solution of palladium chloride had changed from red-brown to clear light-brown as result of palladium(II) loss to the polymer. After the coordination reaction, the product was extracted with methanol for 24 h to remove any palladium complex that was not chemically bonded to the polymer support.

Characterization. Determination of the organometallic species present in a polymer-supported catalyst is best carried out spectroscopically. The easiest and most widely applied technique is infra-red spectroscopy. The solid-state n.m.r. technique is also an attractive method for characterization of insoluble polymer-supported metal catalysts.

Infra-red spectroscopy analysis. *Table 4* summarizes the infra-red absorption data of the polymers containing nitrile groups supporting palladium(II) complexes. Coordination of the nitrile group to palladium(II) is

Table 4 Infra-red spectral data[a] for polymers containing nitrile groups supporting palladium(II) complexes (cm⁻¹)

Assignment	PBI-Bz-CH₂CN/PdCl₂	PBI-GF-a/PdCl₂	PBI-Bz-GF-b/PdCl₂	PVBCN/PdCl₂	PANT/PdCl₂
ν(C–H)	3154	3079	3055	3024	3025
	3062	2993	3168	2925	2933
	2951	2939		2854	2872
ν(–CN free)	2214 w	2243 w	2244 w	2251 m-sh	2239 m-sh
ν(CN–Pd)	2257 w	2310 w	2308 w	2313 m-sh	2301 w
Δν_CN	16–56 br	67	64	62	62
ν(C=C, C=N)	1617 s-m	1624 s-m	1628 s-m	1605 s	1605 s
		1572 m	1449 s	1448 m	1488 m
	1450 s	1442 s		1447 s	1450 s
	1227 m	1292 m	1300 m	1416 m	
ν(Ar–H)	804 s	815 s	802 s	793 s	799 s
				706 s	710 s
ν(Pd–Cl)	334	325	325	343	350

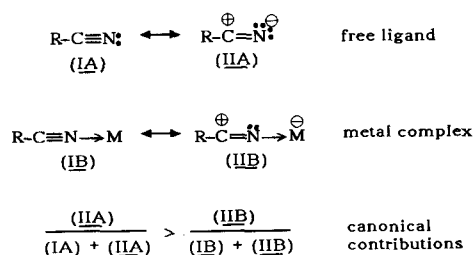[a] m = medium, s = strong, w = weak, sh = sharp, br = broad band

Figure 3 Proposed canonical structures of nitrile ligand — free and metal complexed

Table 5 C≡N stretching frequency shift (cm⁻¹) for nitrile ligand coordinated to Pd(II)

Complex	Vibration of C≡N		
	-C≡N	-C≡N-Pd	$\Delta\nu_{CN}$
PBI-Bz-CH₂CN/PdCl₂	2214	2260	+16-56ᵃ
PBI-GF-a/PdCl₂	2243	2310	+67
PBI-Bz-GF-b/PdCl₂	2244	2308	+64
PVBCN/PdCl₂	2251	2313	+62
PANT/PdCl₂	2239	2301	+62
(CH₃CN)₂PdCl₂	2266	2332	+66

ᵃ Broad band from 2230 to 2270 cm⁻¹

characterized by an increase in the C≡N stretching frequency. For the palladium complexes formed here, such a shift is clearly seen. In general coordination would be expected to weaken the ligand bond next to the coordinate bond, and cause the appropriate ligand i.r. absorption band to shift to a lower frequency. However it is interesting to note that in the case of RCN–Pd, the C≡N vibration band shifts to higher frequency (about +65–70 cm⁻¹). X-ray studies[20] have indicated that the bond length of RC≡N is 1.16 Å, while after coordination to Pd(II) the bond length is decreased[21] to 1.14 Å. These data support the i.r. band shift to higher frequency. In terms of the accompanying resonance structure[22] (*Figure 3*) this result suggests that structure (**IIA**) contributes more to the total structure of the free C≡N than does structure (**IIB**) to the total structure of the complex. Furthermore, in the coordination of RC≡N to palladium(II), the nitrogen is the coordinating atom. There is no back-donation of electrons from the metal to nitrogen. Hence after coordinating to Pd(II), the C≡N stretch frequency increased. The frequency shift data are collected in *Table 5*. The spectroscopic properties of all the polymer complexes (Δν: +62–65 cm⁻¹) correlate well with those of the homogeneous analogue (CH₃CN)₂PdCl₂ (Δν: +66 cm⁻¹)[12,23] except for PBI-Bz-CH₂CN/PdCl₂ (Δν: +16–56 cm⁻¹). It seems therefore that the palladium–nitrile bond is slightly weaker in PBI-Bz-CH₂CN/PdCl₂ than in the other supported complexes. *Figure 4* shows a comparison of infra-red spectra in the C≡N stretching region for PBI-Bz-CH₂CN/PdCl₂ and cross-linked PVBCN/PdCl₂. For PBI-Bz-CH₂CN/PdCl₂ a broad band between 2230 and 2270 cm⁻¹ is observed while for PVBCN/PdCl₂ a relatively sharp peak is seen at 2313 cm⁻¹. The broad band also tends to indicate that the microenvironment of the PBI-Bz-CH₂CN/PdCl₂ complex (on a rather rigid polymer chain) is variable while that of the PVBCN/PdCl₂ (on a flexible polymer chain) is relatively well defined.

Solid-state ¹³C n.m.r. spectroscopy. *Figure 2* shows the solid-state ¹³C n.m.r. spectra for PBI-Bz-CH₂CN and PBI-Bz-CH₂CN/PdCl₂. Line broadening was observed. No attempt has been made to assign individual resonances in the rather complex multiplet from the PBI backbone. However, the peaks at ~35 and ~123 ppm in the spectrum of PBI-Bz-CH₂CN (b) can be assigned to methylene carbon and nitrile carbon, respectively, in non-coordinated –CH₂CN. The new resonances at ~52 and ~169 ppm in the spectrum of PBI-Bz-CH₂CN/PdCl₂ (c) can be assigned to the methylene carbon and the nitrile carbon of –CH₂CN coordinated to Pd. Note also that the non-coordinated characteristic resonance at ~35 ppm is also retained. These residual free nitrile groups were also evident in the infra-red spectra.

Palladium loading on polymer support. In the supported palladium complex, the molar ratio of palladium:chlorine should be 1:2 and the palladium content can, in principle, be calculated from chlorine content:

$$X = YM_{Pd}/2M_{Cl}$$

where X = Pd content (to be calculated), Y = Cl content (from microanalysis) and M = atomic weight. However, this is still an indirect measurement of palladium loading on the polymer and would not be applicable for all cases in the present work (e.g. PBI-Bz-CH₂COO$_x$PdCl$_{2-x}$ (x = 1 or 2)). Atomic absorption spectroscopy (a.a.s.) provides a direct measurement of palladium loading. Comparing the values of Pd content by calculation from Cl microanalysis and by a.a.s., it can be seen from *Table 6* that the agreement from the two techniques is reasonably good.

Possible structure of supported Pd(II) complexes

Those catalyst structures for which direct analytical data are available indicative of the Pd, Cl and CN contents are Catal-1 (PBI-Bz-CH₂CN/PdCl₂), Catal-5 (PVBCN/PdCl₂) and Catal-6 (PANT/PdCl₂), and the Pd/Cl/CN ratios for these are around 1/1.5/1.7, 1/3/12.5 and 1/2.5/12 respectively. It is clear from these that no clear-cut conclusions can be drawn about the respective structures from the experimental CN/Pd ratios, since in some cases there is poor usage of nitrile ligands, probably arising from inaccessibility problems in the crosslinked polymers. The Pd/Cl ratios, however, are all reasonably close to 1/2 and along with the i.r. spectral
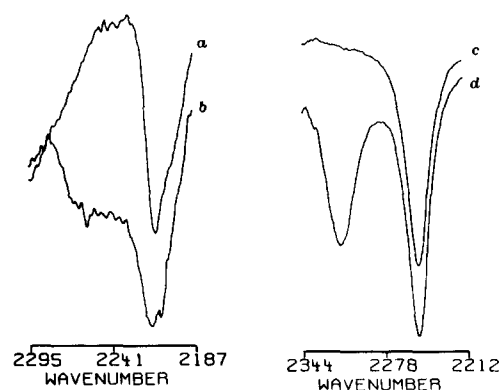

Figure 4 Infra-red absorption frequency shift of cyanide group on coordination to Pd(II): (a) PBI-Bz-CH₂CN; (b) PBI-Bz-CH₂CN/PdCl₂; (c) PVBCN; (d) PVBCN/PdCl₂

Table 6 The loading of palladium on the various polymer-supported complexes

| | Pd loading on polymer | | | | |
| | % | | (mmol g^{-1}) | | |
Catalysts[a]	MA[b]	AAS[c]	MA[b]	AAS[c]	Colour
Catal-1 (PBI-Bz-CH$_2$CN/PdCl$_2$)	13.5	18.6	1.3	1.7	dark-brown
Catal-2 (PBI-Bz-CH$_2$COO/Pd)[d]	–	28.1	–	2.7	dark-brown
Catal-3a (PBI-GF-a/PdCl$_2$)	17.8	16.5	1.7	1.6	brown-yellow
Catal-3b (PBI-Bz-GF-b/PdCl$_2$)	16.9	15.9	1.6	1.5	brown-yellow
Catal-4 (PBI-Bz/PdCl$_2$)	7.4	–	0.7	–	pink (beads)
Catal-5 (PVBCN/PdCl$_2$)	5.3	3.3	0.5	0.3	pink (beads)
Catal-6 (PANT/PdCl$_2$)	7.6	6.0	0.7	0.6	pink (beads)

[a] Designations Catal-1 to Catal-6 are to allow easy cross-correlation with ref. 10
[b] Calculated from Cl content by microanalysis
[c] Found by atomic absorption spectroscopy
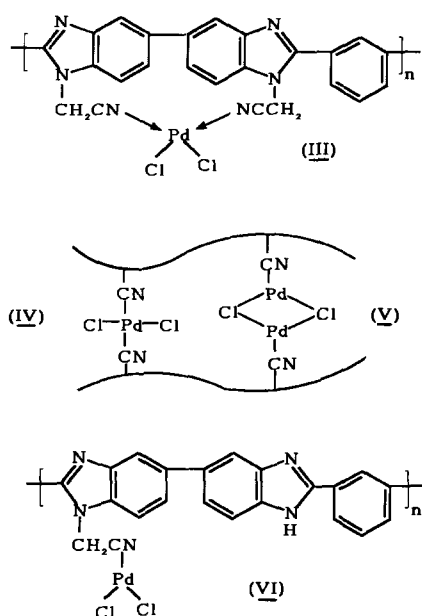[d] PBI-Bz-CH$_2$COO/Pd = (PBI-Bz-COO)$_x$PdCl$_{2-x}$, x = 1 or 2

Figure 5 Possible structures of Pd(II) complex in PBI-Bz-CH$_2$CN/PdCl$_2$: (III) 'chelate complex'; (IV) and (V) 'crosslinking complexes'; (IV) 'coordinately unsaturated complex'

Figure 6 Computer modelling structural data for the possible repeat unit in PBI-Bz-CH$_2$CN

Figure 6. Here it can be seen that the smallest distance between the two nitrile N atoms is 5.7 Å[21,24–27] and the bond angle C–N–Pd is 171.7° (ref. 26). Clearly therefore structure (III) is impossible, and the most likely form therefore is the coordinately unsaturated species (VI) (*Figure 5*). The presence of a high proportion of this species could also explain the anomalous i.r. spectrum.

Thermo-oxidative stability of polymer-supported complexes

One of the major objectives of the present study was to produce supported complexes with enhanced thermo-oxidative stability. While there is no doubt about the adequate properties of polybenzimidazoles, which are well documented[4], it could be argued that introduction of additional (aliphatic) substituents and metal complex centres might severely reduce the inherent stability of these supports. This indeed was one of our own concerns, and to check this we examined what has proved to be our most active catalyst (PBI-Bz-CH$_2$CN/PdCl$_2$) using thermogravimetric analysis. For comparison we have also examined the starting PBI-Bz polymer and its cyanomethylated derivative, PBI-Bz-CH$_2$CN. The results shown in *Figure 7* are very compelling. PBI-Bz itself is essentially stable in air to ~450°C and introduction of cyanomethyl groups has little effect. Indeed, even when the Pd metal complex is formed on the polymer, PBI-Bz-CH$_2$CN/PdCl$_2$, stability in air is still retained until ~400°C. Interestingly the latter species retains a significant residue (~25 wt%) even at 1000°C, which we presume is essentially an inorganic Pd species. It is quite evident from these results that this polymer-supported Pd complex is remarkably stable and it encourages us to believe that application of these and other complexes supported on PBI polymers really do offer exciting

data, which correlate well with the low-molecular-weight model complex (CH$_3$CN)$_2$PdCl$_2$, it seems that a structure analogous to this model arises with the polymer catalysts. The case of PBI-Bz-CH$_2$CN/PdCl$_2$ is anomalous however. The Pd/Cl ratio lies within the same range as the other species, but the Pd:CN ratio is much lower, implying a relatively highly efficient use of nitrile ligands. In addition the i.r. spectrum of this species is also anomalous. Superficially a 'chelate complex' (III) or a 'crosslinking complex' (IV) or (V) might be expected, with perhaps (III) favoured over (IV) and (V) (*Figure 5*). PBI-Bz-CH$_2$CN is a highly rigid species with little scope for the intermolecular movement of chains necessary to satisfy the strict stereochemical requirement of structures (IV) and (V). In addition the chlorine bridge binuclear species (V) demands a Pd:Cl of unity. Regarding structure (III) however, earlier it was argued that the most likely structure for PBI-Bz-CH$_2$CN is a form with only one cyanomethyl group per repeat unit (*Scheme 1*). Furthermore, simple computer modelling calculations provide the hypothetical structure data shown in
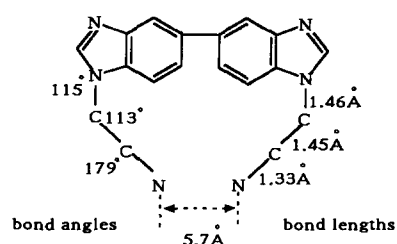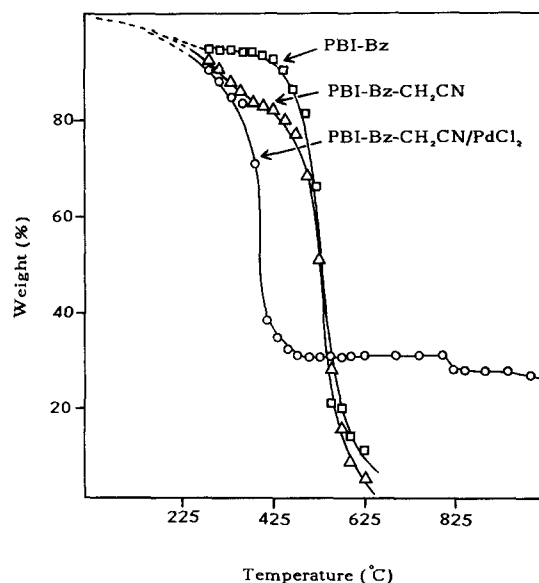
Figure 7 Thermogravimetric analytical data for PBI polymers with and without complexed Pd(II)

prospects for novel catalysts operating in hostile oxidative environments.

Polymer-supported Pd(II) complexes as Wacker-type catalysts

In part 2 of this series of papers[10] we report in detail on the use of these polymeric catalysts in the ketonization of terminal alkenes using air as the oxidant. Interestingly all of the species show catalytic activity, with PBI-Bz-CH$_2$CN/PdCl$_2$ being the most active.

EXPERIMENTAL

Materials and equipment

Sodium hydride (60% dispersion in mineral oil), butyllithium (2.5 M solution in pentane), bromoacetonitrile (97%) and acrylonitrile (99%) were supplied by Aldrich. Palladium dichloride was supplied by the Johnson Matthey Chemical Co. Ltd. Dimethylsulfoxide (DMSO) (Aldrich) was purified by heating and distilling from CaH$_2$ at low pressure. Tetrahydrofuran (THF) (Aldrich) was purified by refluxing over and distilling from LiAlH$_4$. Vinylbenzyl chloride (VBC) was a gift from the Dow Chemical Co. Divinylbenzene (DVB), a mixture of isomers (DVB 55%, ethylvinylbenzene (EVB) 45%), was supplied by BDH. Azobisisobutyronitrile (AIBN) was supplied by BDH. Isoamyl alcohol was supplied by Fisons. PBI-Bz beads were a gift from the Celanese Corp., with bulk density 0.2 g ml^{-1} and specific surface area 30 m^2 g^{-1}. PBI-Bz and PBI powders were synthesized in the author's laboratory[28]. PBI-Bz powder has the same structure as PBI-Bz beads.

Infra-red spectra were obtained by using a Nicolet 20 SXB *FT*-i.r. spectrometer and KBr pellets. Solid-state ^{13}C n.m.r. spectra were recorded with a Bruker MSL-100 spectrometer. Analyses of carbon, hydrogen and nitrogen were performed with a Carlo Erba 1106 analyser, while the analysis of chlorine was carried out by a standard chemical method. Palladium metal analyses were obtained using a Philips PU9100X atomic absorption spectrometer. Thermogravimetric analyses

(t.g.a.) were performed with a Du Pont 990 thermogravimetric balance. Each polymer sample was heated in an air flow (50 ml min^{-1}) using a temperature programme of $+5°C$ min^{-1}. Thermograms were recorded as percentage weight as a function of temperature.

Synthesis of cyanomethylated PBI-Bz-CH$_2$CN (Scheme 1)

A typical reaction was performed as follows using quantities of starting materials in the molar ratio of PBI-Bz:sodium hydride:bromoacetonitrile of 1:2:3. A three-necked 250 ml glass flask equipped with a magnetic stirrer was charged with purified DMSO (100 ml) and sodium hydride (1.3 g, 60% in mineral oil, 32 mmol). The mixture was stirred at 50°C under nitrogen atmosphere for 5 h and PBI-Bz polymer powder (5 g, 16 mmol) was added in DMSO (100 ml). The mixture was stirred overnight at 50°C. A fluorescent blue colour was formed at the surface of the reactant liquid. Bromoacetonitrile (3.4 ml, 48 mmol) was added in DMSO (10 ml) by a syringe. The fluorescent blue disappeared once the bromoacetonitrile was added. The reaction was continued at 65°C overnight. After cooling to room temperature, the reactant solution was poured into methanol (500 ml). A precipitate formed immediately and was collected by filtration. The product was washed with water and finally with acetone. It was dried in a vacuum oven at 40°C overnight. The polymer was extracted with acetone for 24 h to remove low-molecular-weight organics and again vacuum dried at 40°C overnight. Typically the product was a dark-brown coloured powder and the final yield was 75% (4.7 g, about 12.2 mmol) based on the quantity of PBI-Bz. Microanalysis: calculated (%), C 74.6, H 3.4, N 21.8; found (%), C 64.6, H 3.4, N 17.5. Infra-red: $v_{C-H}=2927$, 2869 cm^{-1}, $v_{CN}=2211$ cm^{-1} (see *Table 1*). ^{13}C solid-state n.m.r.: $\delta_{CN}=122.6$ ppm, $\delta_{CH_2CN}=31.8$ ppm (see *Table 2*).

Synthesis of carboxymethylated PBI-Bz (PBI-Bz-CH$_2$COOH) (Scheme 1)

A typical reaction was performed as follows. A three-necked 100 ml glass flask equipped with a magnetic stirrer was charged with cyanomethylated PBI-Bz (3.9 g, about 10 mmol) and potassium hydroxide (13 g) dissolved in methanol (80 ml). The mixture was stirred at 60°C for 60 h. The polymer was then collected by filtration and stirred in hydrochloric acid (15%) for 4–6 h. The product was filtered again and washed with water. Finally, it was extracted with methanol overnight to remove low-molecular-weight organics, and vacuum dried at 60°C overnight. A typical product was brown-yellow in colour and the final yield was 55% (2.1 g) based on the weight of the starting polymer. Microanalysis: found (%), C 61.3, H 3.7, N 13.5. Infra-red: $v_{COOH}=3450$ to 2600 cm^{-1} (broad band).

Homogeneous grafting of PBI with polyacrylonitrile (PBI-GF-a) (Scheme 2)

A typical reaction was performed as follows. A three-necked 250 ml glass flask equipped with a mechanical stirrer was charged with purified DMSO (100 ml) and sodium hydride (0.8 g, 60% dispersion in mineral oil, 20 mmol). The mixture was stirred at 50°C under a nitrogen atmosphere for 5 h and then PBI powder (2.32 g, about 20 mmol) was added. The mixture was stirred overnight at 50°C. Acrylonitrile (6.5 ml, about

Table 7 Suspension vinyl polymerizations

	PVBC	PANT
Monomers	Vinylbenzyl chloride	Acrylonitrile
	45 ml (317 mmol)	15 ml (228 mmol)
	Divinylbenzene	Divinylbenzene
	30 ml (115 mmol)	20 ml (77 mmol)
Other chemicals		
Initiator	AIBN 1.5 g	AIBN 1.0 g
Porogen	Isoamyl alcohol	Isoamyl alcohol
	56 ml	26 ml
Solvent	Toluene 19 ml	Toluene 9 ml

200 mmol) was added via a syringe. The reaction was continued at 50°C for 4 h under a nitrogen atmosphere. Finally, hydrochloric acid (5%, 50 ml) was added to terminate the reaction. The resulting solution was poured into water (500 ml). A precipitate formed immediately. The polymer was collected by filtration and washed with water and acetone. It was dried in a vacuum oven at 40°C overnight. Finally, the polymer was extracted with acetone for 24 h to remove low-molecular-weight organics and again dried in a vacuum oven at 40°C overnight. Typically the product was a yellow powder and the final yield was ~120% (2.8 g) based on the starting weight of PBI (2.3 g). Microanalysis: found (%), C 65.2, H 5.4, N 23.1. Infra-red: $v_{CH} = 2939$, 2870 cm^{-1}, $v_{CN} = 2243 \text{ cm}^{-1}$.

Heterogeneous grafting of PBI-Bz beads with polyacrylonitrile (PBI-Bz-GF-a) (Scheme 2)

A typical reaction was performed as follows. A 250 ml glass flask was charged with anhydrous THF (150 ml), butyllithium (15 ml solution of 2.5 M in pentane, about 38 mmol) and PBI-Bz beads (5 g, about 16 mmol). The mixture was stirred on a rotary reactor[29] under a nitrogen atmosphere at room temperature for 24 h. Then acrylonitrile (5 ml, about 75 mmol) was added via a syringe under a nitrogen atmosphere. The reaction was continued at about 35–40°C for 24 h. Finally, hydrochloric acid (5%, 20 ml) was added to terminate the reaction. The beaded product was collected by filtration and washed with acetone. Finally, the polymer was extracted with acetone for 48 h to remove low-molecular-weight organics and dried in a vacuum oven at 40°C overnight. Typically the product consisted of light yellow-green beads and the final yield was ~120% (6 g) based on the weight (5 g) of starting PBI-Bz beads. Microanalysis: found (%), C 64.3, H 4.2, N 15.5. Infra-red: $v_{CH} = 2917$, 2879 cm^{-1}, $v_{CN} = 2243 \text{ cm}^{-1}$.

Preparation of crosslinked vinyl polymers (PVBC, PANT and PVBCN) (Scheme 3)

Polymerization. A suspension solution (600 ml aqueous 3 wt% Biozan R Gum, Hercules Powder Co.) was charged into a 1000 ml polymerization reactor equipped with a hot water jacket and an efficient stirrer. The solution was stirred at 75 ± 5°C. Vinylbenzyl chloride (45 ml, 317 mmol), divinylbenzene (30 ml, 115 mmol), isoamyl alcohol (56 ml), toluene (19 ml) and AIBN (1.5 g) were pre-mixed then poured into the stabilizer solution, which was continuously stirred at 170 rpm (*Table 7*). The reaction was continued under a nitrogen atmosphere for 6 h at 75°C and the contents of the reactor were then poured into warm water (about 4 litres, 70°C) and left

standing overnight. The product (PVBC) polymer beads were collected by filtration and washed with water and acetone alternately several times. Finally, the beads were steeped in acetone overnight and extracted with this solvent for 24 h to remove low-molecular-weight organics. The product was dried in a vacuum oven at 60°C overnight and the final yield was 93% based on the total weight of monomers. Typically the product was white beads with surface area $\sim 60 \text{ m}^2 \text{ g}^{-1}$. Microanalysis: calculated (%), C 78.4, H 6.8, Cl 14.8; found (%), C 77.9, H 6.7, Cl 15. Infra-red: $v_{CH} = 2925$, 2852 cm^{-1}, $v_{CCl} = 1266 \text{ cm}^{-1}$.

The synthetic procedure for crosslinked polyacrylonitrile (PANT) was the same as for the preparation of PVBC (*Table 7*). The final yield of product was 93% based on the total weight of monomers. Typically the product was white beads (surface area $\sim 120 \text{ m}^2 \text{ g}^{-1}$). Microanalysis: calculated (%), C 82.6, H 7.3, N 10; found (%), C 81.3, H 7.1, N 9.8. Infra-red: $v_{CH} = 2932$, 2872 cm^{-1}, $v_{CN} = 2238 \text{ cm}^{-1}$.

Crosslinked poly(vinylbenzyl cyanide) (PVBCN) via modification of PVBC (Scheme 3). The reaction was performed as follows. PVBC polymer beads (20 g, containing Cl ~ 85 mmol) were soaked in DMF (200 ml) in a 500 ml glass flask for two days to allow the polymer beads to swell. Sodium cyanide (7.5 g, 150 mmol) was added in water (10 ml). The mixture was stirred in a rotary reactor in an oil bath at 100°C for 48 h. After cooling the flask the polymer beads were collected by filtration and washed with methanol and water. The polymer beads were steeped in methanol overnight, then extracted with methanol for 36 h. The product was dried in a vacuum oven at 60°C overnight. Typically the final beads were light yellow in colour and the final yield was 18.8 g. Microanalysis: calculated (%), C 86.9, H 7.1, N 6.1, Cl 0; found (%), C 86.5, H 7.1, N 5.3, Cl 0.9. Infra-red: $v_{CH} = 2929$, 2855 cm^{-1}, $v_{CN} = 2251 \text{ cm}^{-1}$.

Preparation of polymer-supported palladium(II) complexes

The reaction was performed as follows using palladium chloride with the various appropriately functionalized PBI polymers. For the PBI-Bz-CH$_2$COOH support, palladium acetate was used instead of palladium chloride.

Typically a 150 ml glass flask equipped with magnetic stirrer (when using polymer beads a rotator was used in place of a flask and stirrer) was charged with the functionalized polymer (~ 1.5 g), anhydrous methanol (100 ml) and palladium chloride (0.5 g, 3 mmol). The mixture was stirred at room temperature for 24 h. The colour of the solution changed from red-brown to clear light brown. The product was collected by filtration and washed with methanol, and then extracted with methanol for 24 h to remove the palladium complex that was non-chemically bound to the polymer. Finally, the product was vacuum dried at 60°C for 15 h.

ACKNOWLEDGEMENTS

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