Visible-light-induced Photocatalysis of Poly(pyridine-2,5-diyl). Photoreduction of Water, Carbonyl Compounds and Alkenes with Triethylamine

Shinjiro Matsuoka, Takao Kohzuki, Yasuhiro Kuwana, Atsushi Nakamura and Shozo Yanagida *
Chemical Process Engineering, Faculty of Engineering, Osaka University, Suita, Osaka 565, Japan

Poly(pyridine-2,5-diyl) (PPy) exhibits heterogeneous and visible-light-induced photocatalysis toward the reduction of water, carbonyl compounds and alkenes in the presence of triethylamine (TEA) as a sacrificial electron donor. The water reductive H_2 evolution is enhanced by colloidal noble metals concurrently photoformed from noble metal halides, and colloidal Ru gives the highest apparent quantum yield of H_2, 0.21 at 450 nm. With regard to the reduction of carbonyl compounds and electron-deficient alkenes, noble-metal-free PPy leads to the efficient and selective reduction to the corresponding alcohols and dihydro compounds, respectively. Carbonyl compounds whose reduction potentials are as negative as −1.83 V *vs.* SCE in acetonitrile are photoreducible. Deuterium incorporation experiments with dimethyl maleate and/or dimethyl fumarate in [O-^{2}H]methanol have revealed that the photocatalysis of PPy should proceed through sequential two-electron transfer reduction, affording dideuteriated dimethyl succinate. Sequential electron transfer and hydride transfer mechanisms are proposed.

In recent years, photochemical reactions using semiconductor particles or organic dyes as photocatalysts or photosensitizers have received much attention not only from the viewpoint of solar energy conversion[1] but also from that of organic synthesis.[2] We previously reported that under visible light irradiation, poly(*p*-phenylene) (PPP) shows heterogeneous photocatalysis for *cis–trans* photoisomerization of simple alkenes[3] and for the photoreduction of water, ketones and alkenes in the presence of triethylamine (TEA) as a sacrificial electron donor.[4] Although colloidal Ru metal formed by the concurrent photolysis of $RuCl_3$ co-catalyses the H_2 evolution, the photoreduction of ketones and alkenes occurs more efficiently without any electron relay such as colloidal noble metals. We recently showed that oligo(*p*-phenylenes) (OPP-*n*) ranging from *p*-terphenyl (OPP-3) to *p*-sexiphenyl (OPP-6) catalyse photoreduction of acetaldehyde to ethanol and of CO_2 to formate, and that the intermediary radical anion of OPP-$n^{\bullet -}$ derived from the singlet state of OPP-*n* and TEA should participate in the electron transfer without any electron relays.[5,6] Such photo-induced charge separation and the accompanying electron transfer on poly(arylenes) like OPP-*n* or PPP can be regarded as promising photochemical processes for light-energy storable synthesis.

Recently, Yamamoto *et al.* reported that the dehalogenation polycondensation of 2,5-dibromopyridine with zerovalent Ni complexes gave poly(pyridine-2,5-diyl) (PPy), which is only soluble in formic acid and hydrochloric acid through protonation.[7,8] The head-to-tail polymerization was estimated by the IR and NMR (^{1}H and ^{13}C) spectra. Based on light scattering measurements, the molecular weight was determined to be 1700 ± 400, which corresponds to a degree of polymerization of 22 ± 5. Since PPy shows a single π–π^* absorption band at λ_{max} = 420 nm in the solid state, which is comparable to that of PPP, and is supposed to have a linear rod-like structure as a novel poly(arylene), we expected PPy to show heterogeneous and visible-light-inducible photocatalysis. In a preliminary paper,[9] we reported that PPy shows some photocatalyses which are superior to those of PPP; water and some carbonyl compounds were photoreduced in the presence of TEA as a sacrificial electron donor, giving good yields of H_2 and the corresponding alcohols, respectively.

In this paper we present a detailed study on heterogenous photocatalyses of PPy. It has now been clarified that the PPy interface provides an effective system for photo-induced charge separation and electron transfer, which is quite different in mechanism from that of PPP, leading to photoreductions of some unsaturated compounds to two-electron-transfer reduction products under visible-light irradiation.

Results and Discussion

Chemical Structure and Physical Properties of PPy Photocatalyst.—Yellow PPy powder was prepared according to the method of Yamamoto.[7] The resulting PPy was subjected to FD–MS and solid-state ^{13}C NMR analysis. FD–MS analysis revealed that PPy consisted of at least 5–19 monomer units and was terminated at each end with hydrogen atoms. The solid-state ^{13}C NMR spectrum with a normal cross-polarization consists of four peaks, suggesting at least four kinds of carbon atoms in PPy [Fig. 1(*a*)]. The cross polarization experiment with a very short (50 μs) contact time, however, demonstrated the presence of three protonated carbons [Fig. 1(*b*)] and the dipolar dephasing experiment revealed the presence of only two non-protonated carbons [Fig. 1(*c*)]. In the structure of pyridine, the α- and γ-carbons are significantly deshielded with respect to benzene, while the β-carbons are shielded. In the proposed structure of PPy, each α-carbon is also γ to the nitrogen in the next ring. As an extension of this, each carbon in the entire structure is either an odd or an even number of bonds from every nitrogen position throughout the polymer. The resultant spectrum is therefore similar to what might be expected for a substituted pyridine. These facts eliminate the possibility of random head-to-head, tail-to-tail, and head-to-tail polymerizations, supporting the proposed structure where each pyridine ring should combine regularly at the 2 and 5 positions.

In Fig. 2 are shown the reflectance spectra measured by a multi-channel photodiode system (MCPD) of the solid states of PPy and PPP. The spectra indicate that the onset and the maximum of the absorption of PPy shift to a longer wavelength than those of PPP, suggesting that PPy should have a more coplanar structure than PPP, and become favourable for utilization of visible light. As for the emission of PPy, the maximum wavelength of the spectrum of PPy shifts to a longer wavelength than that of PPP (Table 1). Furthermore, based on its absorption and emission spectra, the band gap was estimated to be 2.4 eV, which is smaller than that of PPP, 2.9 eV. In order to

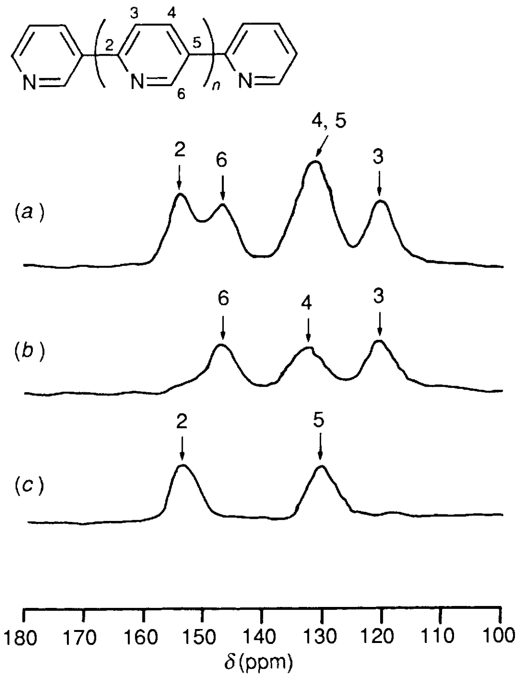


Fig. 1 Solid-state ^{13}C NMR spectra of PPy measured by a normal cross-polarization experiment (*a*), by a cross-polarization experiment with a very short contact time (*b*), and by the dipolar dephasing experiment (*c*)

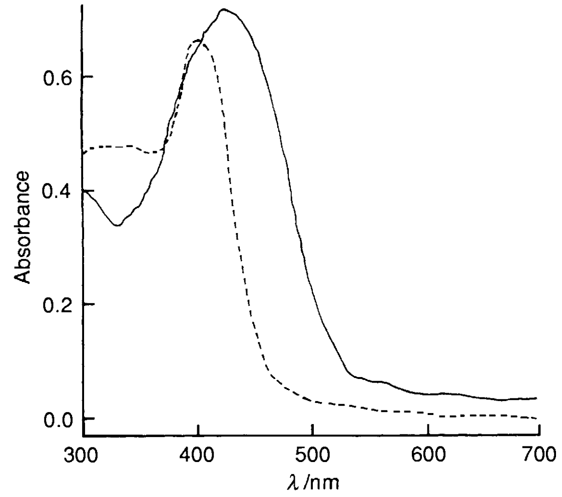


Fig. 2 Reflectance spectra of PPy and PPP measured by a multichannel photodiode system (MCPD): ——, PPy; – – – –, PPP

Table 1 Electronic structure of PPP and PPy

Catalyst	EM_{max}/nm	IP/eV	E_g/eV	E_v/V[a]	E_c/V[b]
PPy	532	5.8	2.4	1.1	−1.3
PPP	485	6.1	2.9	1.4	−1.5

[a] E_v, upper edge of valence band (V) *vs.* SCE; calculated from E_v = IP − 4.7. [b] E_c, bottom of conduction band (V) *vs.* SCE; calculated from $E_c = E_v - E_g$.

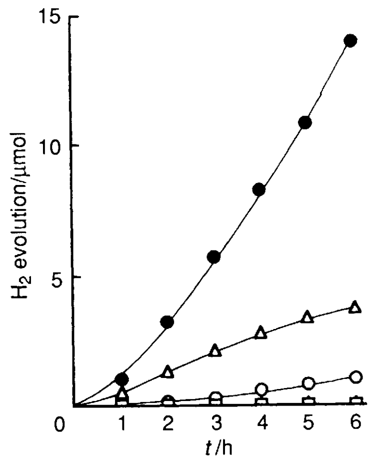


Fig. 3 Effect of noble metal salts on the H_2 photoevolution: ○, none; ●, $RuCl_3$; △, $RhCl_3$; □, K_2PtCl_6

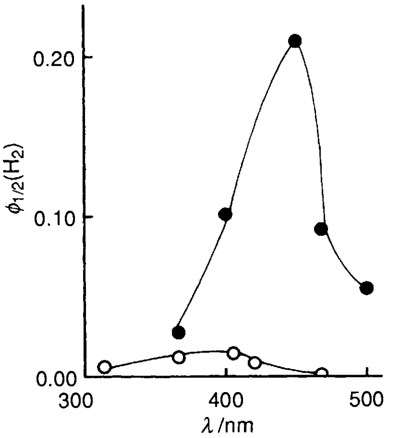


Fig. 4 Action spectra for the H_2 photoevolution in the presence of $RuCl_3$: ●, catalysed by PPy; ○, catalysed by PPP

evaluate the valence band structure of PPy, their ionization potentials (IP) were measured by an atmospheric UV photoelectron analyser (AUP).[4,5] On the basis of AUP results, the IP of PPy was determined to be 5.9 eV. In order to make a quantitative comparison with redox reactions on irradiated PPy photocatalyst, the upper edge of the valence band and the bottom of the conduction band were evaluated in the electrochemical scale by assuming 4.7 eV as a scale factor relating SCE to vacuum,[10] and the results are summarized in Table 1.

Photoreduction of Water.—Fig. 3 shows a comparison of the photocatalytic activity for H_2 evolution from methanolic aqueous TEA under visible light irradiation ($\lambda > 400$ nm) in the presence of some colloidal noble metals which are simultaneously photoformed in the photocatalytic systems. As a result, the photocatalysis of PPy was enhanced by the presence of noble metal salts. In particular, the photocatalysis of PPy in the presence of colloidal Ru was more than 14 times as effective as that of PPy alone. Photolysis in a $D_2O/TEA/CD_3OD/RuCl_3$ system gave a mixture of D_2, HD and H_2 in a 73:23:4 ratio, indicating that the major source of H_2 should be water. As photoproducts from TEA in the PPy/$RuCl_3$ system, diethylamine (DEA) and a small amount of ethanol were formed concomitantly with H_2, as in the PPP/$RuCl_3$ system.[4,5]

Fig. 4 shows action spectra of PPy- and PPP-catalysed H_2 evolution in the presence of $RuCl_3$, which is based on the quantum yields determined at some wavelength. The quantum yields were all apparent ones, because they were not corrected for light absorption by the suspended PPy catalyst. Surprisingly the quantum yields were almost ten times as high as those of PPP. The action spectrum is almost identical with the absorption spectrum (Fig. 2), and the maximum quantum yield (0.21) was obtained approximately around the band-gap excitation (450 nm) by assuming that two photons produce one molecule of H_2.

Table 2 PPy- and PPP-catalysed photoreduction of aromatic ketones with TEA in methanol[a]

Substrate	$-E_{\frac{1}{2}}^{\mathrm{red}}/\mathrm{V}^{b}$	Catalyst	Conversion (%)	Yield (%)[c] Alcohol **3**	 Pinacol **4**
1a	1.13	PPy	100	93	0
1a	1.13	PPP	98	74	trace
1b	1.17	PPy	100	91	0
1c	1.25	PPy	100	95	0
1d	1.32	PPy	65	63	003
1e	1.48	PPy	35	81	trace
1e	1.48	PPP	87	trace	*ca.*100
1f	1.55	PPy	0	0	0
1f	1.55	PPP	97	45	55

[a] Irradiated methanol at $\lambda > 400$ nm for 6 h. [b] Reported polarographic half-wave reduction potentials *vs.* SCE in methanol.[4,13] [c] Yields are calculated on the basis of the substrates converted.

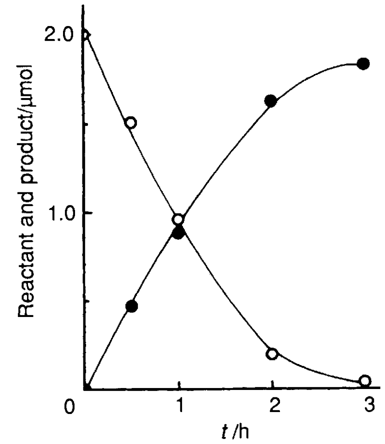
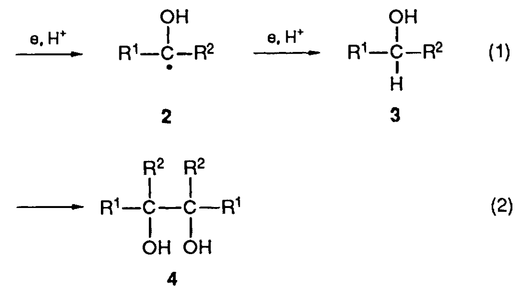


Fig. 5 Time–conversion plots for photoreduction of methyl benzoylformate (**1a**, ○) to methyl mandelate (**3a**, ●) catalysed by PPy



$$R^1-\overset{O}{\overset{\|}{C}}-R^2 \xrightarrow{e,\,H^+} R^1-\overset{OH}{\underset{\bullet}{C}}-R^2 \xrightarrow{e,\,H^+} R^1-\underset{H}{\overset{OH}{C}}-R^2 \qquad (1)$$

1 **2** **3**

$$1 + 2 \longrightarrow R^1-\underset{OH}{\overset{R^2}{C}}-\underset{OH}{\overset{R^2}{C}}-R^1 \qquad (2)$$

4

Substrate	R^1	R^2
a	C_6H_5	CO_2CH_3
b	C_6H_5	*p*-CNC_6H_4
c	*p*-ClC_6H_4	*p*-ClC_6H_4
d	C_6H_5	*p*-ClC_6H_4
e	C_6H_5	H
f	C_6H_5	C_6H_5

Scheme 1

Photoreduction of Carbonyl Compounds.—A series of aromatic ketones (**1**) have been successfully reduced by heterogeneous PPy-photocatalysis in the presence of TEA as a sacrificial electron donor in methanol. Fig. 5 shows time–conversion plots for the PPy-catalysed photoreduction of methyl benzoylformate (MBF, **1a**) under visible light ($\lambda > 400$ nm) irradiation. The reduction of MBF was efficiently achieved, giving methyl mandelate **3a** in 93% yield, while the PPP-catalysed photoreduction of **1a** to **3a** under comparable conditions was found to proceed in 74% yield.[4] The photoreduction proceeded cleanly and no other reduction products were detected after 3 h irradiation.

PPy- and PPP-catalysed photoreductions of various carbonyl compounds (**1a–f**) are summarized in Table 2 together with their reduction potentials in methanol. In the case of PPy photocatalysis, carbonyl compounds **1a–e** were all photoreduced to the corresponding alcohols **3a–e** in good yields without forming pinacols **4a–e**. It is clear that PPy is more effective and selective for the formation of alcohols than PPP, and that carbonyl compounds whose reduction potentials are more positive than −1.48 V *vs.* SCE can be photoreduced in this system. It is worth noting that benzaldehyde (**1e**) was exclusively reduced to benzyl alcohol (**3e**) in the PPy-catalysed-photoreduction system, while the PPP-catalysed photoreduction gave only the pinacol (**4e**). In addition, no photoreduction of benzophenone (**1f**) occurred with PPy, but both the alcohol **3f** and the diol **4f** were formed competitively in the PPP system. As was observed in the PPP-catalysed photoreductions, the presence of colloidal Ru was unfavourable for the PPy-catalysed photoreduction of carbonyl compounds.

The first one-electron-transfer reduction gives intermediary hydroxyl radical **2** after protonation, the reduction potential of which is critical in determining whether the second electron-transfer or the radical-coupling reaction occurs (Scheme 1).[11]

We previously reported that the PPP-catalysed photoreduction of aromatic ketones to both alcohols and pinacols should occur *via* disproportionation of **2**.[4] However, the exclusive formation of alcohols without pinacols in the PPy system strongly indicates that the disproportionation mechanism is not responsible for the present system. In other words, it suggests the contribution of a sequential two-electron transfer reduction as was reported in the photoreduction with quantized ZnS[12] and CdS.[13]

Photoreduction of Alkenes.—Fig. 6 shows sequences of PPy-catalysed photolysis of dimethyl maleate (*Z*) and dimethyl fumarate (*E*) in methanol with TEA as an electron donor under $\lambda > 400$ nm irradiation. In the photolysis of the maleate, the formation of dimethyl succinate was observed, accompanying the formation of the fumarate as a photoisomerization product, whereas the photolysis of the fumarate led only to the formation of the succinate. None of the photolyses occurred in the absence of any one of PPy, TEA and light.

In order to obtain insights into the mechanism of two-electron reduction, we carried out deuterium incorporation experiments in the PPy-catalysed photolysis of the maleate or the fumarate in [*O*-^{2}H]methanol. The results in Table 3 show the deuterium distribution in the recovered maleate, fumarate and succinate, which were analysed by GC–MS at 50% conversion of the maleate or the fumarate. With respect to the photoreduction of the maleate, it was found that the succinate

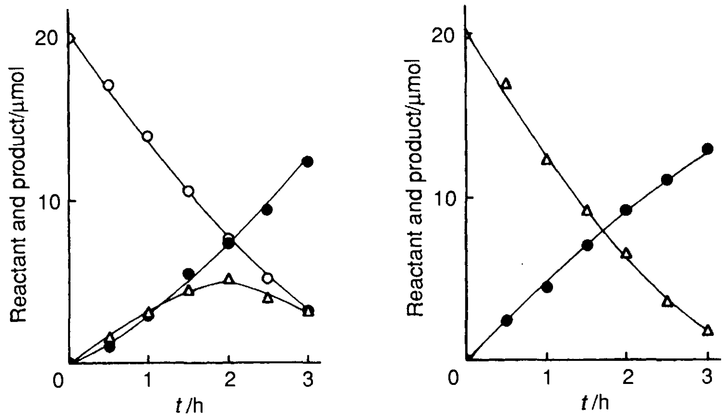


Fig. 6 Time-conversion plots for photoreduction of dimethyl maleate (○) and dimethyl fumarate (△) to dimethyl succinate (●) catalysed by PPy

Table 3 Deuterium distribution in the recovered substrates and reaction products after PPy-catalysed photolysis under irradiation at $\lambda > 400$ nm[a]

	Deuterium content (%)[b]									
	Maleate *cis*			Fumarate *trans*			Succinate			
Substrate	$[^2H_0]$	$[^2H_1]$	$[^2H_2]$	$[^2H_0]$	$[^2H_1]$	$[^2H_2]$	$[^2H_0]$	$[^2H_1]$	$[^2H_2]$	$[^2H_3]$
Maleate	100			97	3		5	15	64	16
Fumarate				100			7	16	70	7

[a] Analysed when the conversion is 50%. [b] Determined by GC–MS analysis.

Table 4 Solvent effects on Py-catalysed photoreduction of ketones to alcohols with TEA[a]

	CH_3CN			Cyclohexane	
Substrate	$-E_{\frac{1}{2}}^{\mathrm{red}}/\mathrm{V}$[b]	Conversion (%)	Yield[c]	Conversion (%)	Yield[c]
1b	1.42	100	93	0	0
1c	1.67	100	97	0	0
1d	1.75	97	91	0	0
1f	1.83	26	88	0	0
1f[d]	1.83	47	57	0	0

[a] Irradiated at $\lambda > 400$ nm for 6 h. [b] Polarographic half-wave reduction potentials *vs.* SCE in AN.[13,14] [c] Yields are based on converted ketones. [d] PPP was used as a photocatalyst.

which incorporates two deuterium atoms comprises 64% of the total succinate, and that deuterium is not incorporated in the recovered maleate. Similarly, in the case of the fumarate, the succinate incorporating two deuterium atoms was obtained in 70% yield. These results are in contrast to the PPP-catalysed photoreductions, where one deuterium atom is exclusively incorporated in both the recovered maleate and the succinate, suggesting that the two reactions follow different mechanisms.

Photoreduction of Carbonyl Compounds in Aprotic Solvents.— The PPy-catalysed photoreduction of carbonyl compounds **1b–d,f** with TEA was carried out in cyclohexane and in anhydrous acetonitrile (AN), and preferential formation of the coupling products **4b–d,f** was expected because the absence of protic species should retard the protonation process in the formation of alcohols **3b–d,f** (Scheme 1). Interestingly, efficient photoreduction to alcohols was observed in anhydrous AN, but not in cyclohexane (Table 4). These facts suggest that the more polar solvent contributes to stabilization of charge-separated states of the PPy assembly and/or resulting electron-transferred intermediates, and that TEA should play an important role not only as an electron source but also as a proton source, as shown in Scheme 2.

$$\mathrm{PPy} + \mathrm{Et_3N} \xrightarrow{h\nu} \mathrm{Et_3N^{\bullet +}} + \mathrm{PPy^{\bullet -}}$$

$$\mathrm{Et_3N^{\bullet +}} \xrightarrow{-\mathrm{H}^+} \mathrm{Et_2N\dot{C}HCH_3} \xrightarrow{-\mathrm{e}} \mathrm{Et_2N^+{=}CHCH_3}$$

Scheme 2

It is worth noting that benzophenone (**1f**) was efficiently photoreduced to **3f** in AN, although the photoreduction was never observed in methanol (see Table 2) and the polarographic half-wave reduction potential of **1f** in AN is −1.83 V *vs.* SCE, which is more negative than that (−1.55 V *vs.* SCE) in methanol. The observation is quite in contrast to the PPP-catalysed photoreduction of **1f**, where the conversion of **1f** in AN was lower than in methanol. The lower conversion in the PPP/AN system may be explained as being due to the negative shift of the reduction potential of **1f** in AN. Accordingly, the selective formation of **3f** in the PPy/AN system strongly suggests that the PPy-catalysed photoreductions proceed through the

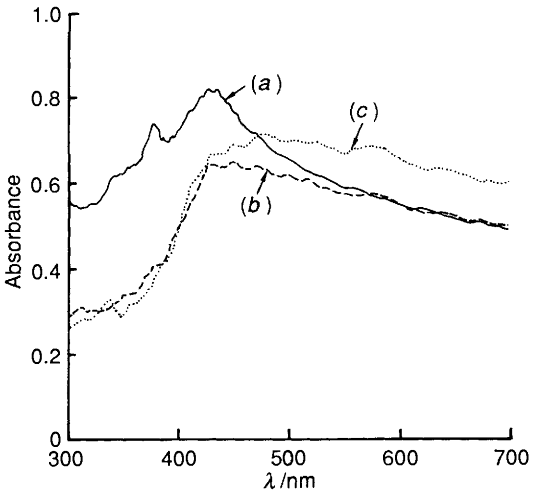


Fig. 7 Reflectance spectra of PPy suspended in TEA/AN solution before (*a*) and after visible-light irradiation for 1 h (*b*) and 3 h (*c*)

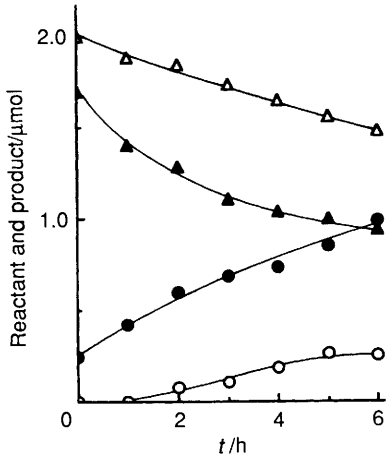


Fig. 8 Time-conversion plots for photoreduction of benzophenone (**1f**; △, ▲) to benzhydrol (**3f**; ○, ●) catalysed by PPy: △, ○, without pre-irradiation; ▲, ●, with pre-irradiation

formation of hydride species derived photochemically from PPy.

Mechanism for PPy-catalysed Photoreductions of Organic Substrates.—In order to clarify the nature of the reducing intermediates from PPy, we analysed PPy suspensions in AN under visible-light irradiation in the presence of TEA by a multichannel photodiode system (MCPD). As shown in Fig. 7, after one or three hours irradiation, the absorption at shorter wavelength decreased and the absorption at longer wavelength gradually increased. The rise of absorption at longer wavelength implies the appearance of a conjugated π-electron structure in the irradiated PPy.

Careful examination of PPy-catalysed photoreductions revealed that the photoreductions of substrates whose reduction potentials are more negative than the conduction band of PPy have an induction period for the formation of the products as exemplified by the photoreduction of **1f** to **3f** (see Fig. 8). Interestingly, as soon as **1f** was added to the pre-irradiated PPy system, 0.25 μmol of **3f** was detected even before irradiation and then **3f** was formed linearly after irradiation.

It is known that 1-benzyl-1,4-dihydronicotinamide (BNAH) has potential as a NADH model compound to reduce *p*-benzoquinone derivatives or aromatic aldehydes, yielding alcohol derivatives through a hydride transfer mechanism.[15,16] With this in mind, the formation of hydrogenated PPy as an active intermediate in the PPy-catalysed photoreductions was postulated. We propose their formation as depicted in Scheme 3.

As shown in the photocatalysis of *p*-terphenyl (OPP-3),[5] the excited state of PPy should be quenched by TEA to produce the radical anion of PPy. Some pyridine units in **P** would be enough for giving a kind of polaron state. When further pyridine units in the same chain undergo the photochemical quenching with TEA or reductive electron transfer from $[Et_3N]^{\bullet+}$, a kind of bipolaron state (**Q**) may be formed.[17,18] Yamamoto and his group showed on the basis of light scattering measurements that electrons in the PPy polymer can move easily along the rod-like system. Therefore, the formation of **R** is conceivable. Protonation of **R** gives **A**, **B**, **C** and **D**. The protonation to **A**, **B**, **C** and **D** may be assisted by the proton released during the oxidation of TEA in aprotic solvents (see Scheme 2). These compounds can be regarded as photo-Birch reduction products from PPy.[19] However, we have now speculated that they should have reducing ability. In particular, the hydrogenated PPy, **A** or **C**, can be regarded as a BNAH analogue. In fact, the reaction of benzophenone (**1f**) with the PPy suspension which was pre-irradiated with TEA gave the alcohol (**3f**) without irradiation.

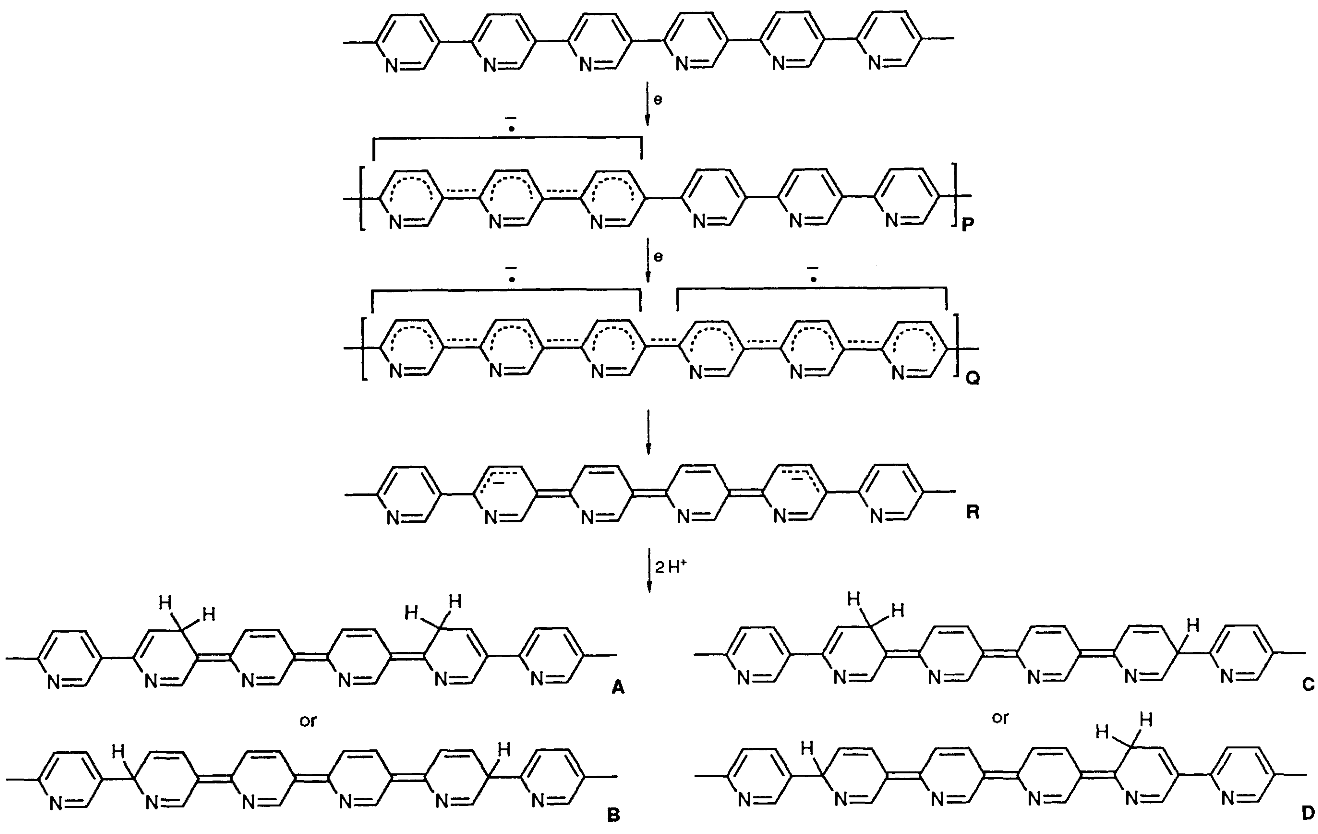
The mechanism for the PPy-catalysed photoreductions may be rationalized in two ways; the direct electron transfer mechanism from the radical anion **P** formed by the reductive quenching of the excited PPy with TEA, and the hydride transfer mechanism mediated by the hydrogenated PPy. The former mechanism should be favourable for substrates whose reduction potentials are less negative than the conduction band potential of PPy. Continuous electron transfer becomes possible, giving the two-electron-transfer products. As for the substrates whose reduction potentials are much more negative than the conduction band of PPy, photo-Birch reduction of PPy should become predominant, leading to the operation of the latter mechanism.

Conclusions

Dehalogenation polycondensation of 2,5-dibromopyridine with zerovalent Ni complexes gives insoluble yellow poly(pyridine-2,5-diyl), whose structure, resulting from regular head-to-tail polymerization, was confirmed by high resolution solid-state ^{13}C NMR spectroscopy. The solid-state characteristics of the PPy photocatalyst were elucidated by spectroscopic analysis, and the visible-light-induced heterogeneous photocatalysis was demonstrated in photoreductions of water, carbonyl compounds and electron-deficient alkenes. PPy showed much more efficient and selective two-electron transfer photocatalysis than PPP, although the band gap and the conduction band potential of PPy are inferior to those of PPP. The PPy structure is favourable for formation of a coplanar chain, because no repulsion exists betwen the hydrogen atom at the 6 position and the nitrogen atom of the adjacent pyridine ring. The much more coplanar geometry of PPy should contribute not only to the stabilization of the radical anions, **P** and **Q**, through delocalization, but also to the formation of the hydrogenated PPy, **A**, **B**, **C** and **D** through the intermediate **R**, which are all stabilized by the coplanar quinoid-like structure. The hydrogenated PPy plays an important role especially in the reduction of aromatic ketones with very negative reduction potentials. Further investigation on the photo-induced hydride transfer reduction is now in progress.

Experimental

Materials.—2,5-Dibromopyridine, zinc powder, $NiCl_2$, $RuCl_3 \cdot 1–3H_2O$, $RhCl_3$, K_2PtCl_6 and triphenylphosphine (PPh_3) were extra pure (EP) grade from Tokyo Kasei and were used without further purification. Ketones were obtained from the following sources; benzophenone [Guaranteed reagent (GR)



Scheme 3

grade] and 4,4′-dichlorobenzophenone (GR grade) from Wako Pure Chemical Industries, and *p*-chlorobenzophenone (GR grade) from Tokyo Kasei. Methyl benzoylformate, *p*-cyanobenzophenone and benzaldehyde were extra pure (EP) grade from Nacalai Tesque. Dimethyl maleate, dimethyl fumarate and dimethyl succinate were GR grade from Tokyo Kasei. PPP was prepared by Yamamoto's method.[20] TEA was purified by fractional distillation before use. Methanol and acetonitrile (AN) were distilled before use.

Analysis.—Analysis of alkenes was carried out by gas chromatography using a Shimadzu GC-12A apparatus equipped with a flame ionization detector, and a Shimadzu capillary column (25 m × 0.2 mm) of OV-1. As an internal standard methyl benzoate was used. Analysis of ketones, alcohols and pinacols was carried out by liquid chromatography using a Cosmosil-ODS column, and UV detector (at 230 nm) (Tosoh; UV-8000). As eluent, a solution of methanol and buffered aqueous solution (KH_2PO_4–NaOH; pH7) (6:4 mixture) was employed with a flow rate of 0.5 cm^3 min^{-1}.

Other analyses were identical with those reported in previous papers.[4,5]

Synthesis of PPy.—PPy was synthesized by Yamamoto's method[7] as follows. $Ni(PPh_3)_4$ was prepared *in situ* from $NiCl_2$ (48 mmol), Zn (48 mmol), and PPh_3 (192 mmol) in *N*,*N*-dimethylformamide (200 cm^3) at 60 °C for 2 h under an argon atmosphere. To the resulting solution of $Ni(PPh_3)_4$ was added 2,5-dibromopyridine (40 mmol) and the solution was stirred at 60 °C for 2 days. The precipitates formed were filtered, washed repeatedly with warm aqueous EDTA (pH 3), warm aqueous NaOH (pH 9), hot toluene, and dried under vacuum. Synthesized PPy was characterized by ^{13}C NMR and FD–MS analyses. Furthermore, neither Ni nor Zn were detected in the prepared PPy by X-ray fluorescence analysis.

Photoreduction of Water.—As reported in the PPP and OPP-*n*-catalysed photoreactions,[4,5] distilled water, TEA, methanolic $RuCl_3$ solution (6 × 10^{-3} mol dm^{-3}) (each 0.5 cm^3), and PPy (10 mg) were placed in a Pyrex tube (8 mm in diameter). After purging with argon gas, the tube was closed off with a gum stopper, and irradiated at 25 °C under magnetic stirring with a 300 W halogen lamp fitted with a sodium nitrite solution filter. The inner gas was analysed by GLC.

Photoreduction of Organic Substrates.—To 2 cm^3 of methanolic TEA (1 mol dm^{-3}) and PPy (10 mg) solution in a Pyrex tube (8 mm in diameter) was added an organic substrate in an amount to make a 1 mmol dm^{-3} solution for carbonyl compounds and a 10 mmol dm^{-3} solution for alkenes. The resulting PPy-suspended solution was worked up under the same conditions as the water photoreduction. With respect to the photoreduction of benzophenone (**1f**) with the hydrogenated PPy, 2 cm^3 of an AN solution containing PPy (10 mg) and TEA (1 mol dm^{-3}) was irradiated for 12 h under an argon atmosphere, and then 1.0 × 10^{-2} cm^3 of an AN solution of **1f** (0.2 mol dm^{-3}) was added to the Pyrex tube.

Determination of Deuterium Isotopic Distribution.—Photoreduction of dimethyl maleate was performed in [*O*-^{2}H]methanol as described above. When 50% of the substrate disappeared, the irradiation was stopped, the reaction suspension was filtered off, and the filtrate was evaporated. The residue was analysed by GC-MS.

Measurement of Reflectance Spectra of the Hydrogenated PPy.—Reflectance spectra were recorded on a Photal (Otsuka Electonics) with a spectromultichannel photodetector (Model MCPD-100). A 3 cm^3 AN solution containing PPy (1.2 mg) and TEA (1 mol dm^{-3}) was placed in a quartz cell (4 cm^3). After the solution was purged with argon gas and cooled on an ice bath, the cell was closed off with a gum stopper and then measured by MCPD before and after visible-light irradiation.

Acknowledgements

We thank Dr. Allen R. Palmer at Chemagnetics Inc. for his kind measurement of solid ^{13}C-NMR and Dr. H. Sakaguchi at Osaka University for X-ray fluorescence analysis. This research was supported by a Grant-in-aid for Scientific Research from the Ministry of Education, Science and Culture, Japan (No. 03203119). The research was also conducted as a theme of the Research Society for CO_2-fixation sponsored by the Institute of Laser Technology under the commission of The Kansai Electric Power Company Inc. The financial aid given by Yazaki Memorial Foundation for Science and Technology is also gratefully acknowledged.

References

1 A. J. Bard, *J. Phys. Chem.*, 1982, **86**, 172; K. Kalyanasuadram and M. Gratzel, *Photochem. Photobiol.*, 1984, **40**, 807.
2 T. Sakata, in *Homogeneous and Heterogeneous Photocatalysis*, ed. E. Pelizzetti and N. Serpone, Reidel, Dordrecht, 1986, p. 397.
3 S. Yanagida, M. Hanazawa, A. Kabumoto and C. Pac, *Synth. Met.*, 1987, **18**, 785.
4 S. Yanagida, A. Kabumoto, K. Mizumoto, C. Pac and K. Yoshino, *J. Chem. Soc., Chem. Commun.*, 1985, 474; T. Shibata, A. Kabumoto, T. Shiragami, O. Ishitani, C. Pac and S. Yanagida, *J. Phys. Chem.*, 1990, **94**, 2068.
5 S. Matsuoka, H. Fujii, C. Pac and S. Yanagida, *Chem. Lett.*, 1990, 1501; S. Matsuoka, H. Fujii, T. Yamada, C. Pac, A. Ishida, S. Takamuku, M. Kusaba, N. Nakashima, S. Yanagida, K. Hashimoto and T. Sakata, *J. Phys. Chem.*, 1991, **95**, 5802.
6 S. Matsuoka, T. Kohzuki, C. Pac and S. Yanagida, *Chem. Lett.*, 1990, 2047.
7 T. Yamamoto, T. Ito and K. Kubota, *Chem. Lett.*, 1988, 153; T. Yamamoto, T. Ito, K. Sanechika, K. Kubota and M. Hishinuma, *Chem. Ind.* (*London*), 1988, 337.
8 T. Yamamoto, T. Maruyama and K. Kubota, *Chem. Lett.*, 1989, 1951; T. Yamamoto, T. Maruyama, T. Ikeda and M. Sisido, *J. Chem. Soc., Chem. Commun.*, 1990, 1306.
9 S. Matsuoka, T. Kohzuki, A. Nakamura, C. Pac and S. Yanagida, *J. Chem. Soc., Chem. Commun.*, 1991, 580.
10 J. L. Bredas, R. Silber, D. S. Boudreaux and R. R. Chance, *J. Am. Chem. Soc.*, 1983, **105**, 6555.
11 O. Ishitani, S. Yanagida, S. Takamuku and C. Pac, *J. Org. Chem.*, 1987, **52**, 2790.
12 S. Yanagida, Y. Ishimaru, Y. Miyake, T. Shiragami, C. Pac, K. Hashimoto and T. Sakata, *J. Phys. Chem.*, 1989, **93**, 2576; S. Yanagida, M. Yoshiya, T. Shiragami, C. Pac, H. Mori and H. Fujita, *J. Phys. Chem.*, 1990, **94**, 3104.
13 T. Shiragami, C. Pac and S. Yanagida, *J. Chem. Soc., Chem. Commun.*, 1989, 831; *J. Phys. Chem.*, 1990, **94**, 504.
14 P. J. Wagner, R. J. Truman, A. E. Puchalski and R. Wake, *J. Am. Chem. Soc.*, 1986, **108**, 7727.
15 S. Fukuzumi and T. Tanaka, *Chem. Lett.*, 1982, 1513; S. Fukuzumi, N. Nishizawa and T. Tanaka, *J. Org. Chem.*, 1984, **49**, 3571.
16 S. Fukuzumi, M. Ishikawa and T. Tanaka, *J. Chem. Soc., Chem. Commun.*, 1985, 1069; *Tetrahedron*, 1986, **42**, 1021; *Chem. Lett.*, 1989, 1227.
17 K. Tanaka and T. Yamabe, *Adv. Quantum Chem.*, 1985, **17**, 251.
18 J. L. Bredas and G. B. Street, *Acc. Chem. Res.*, 1985, **18**, 309.
19 J. A. Barltrop, *Pure Appl. Chem.*, 1973, **33**, 179.
20 T. Yamamoto and A. Yamamoto, *Chem. Lett.*, 1977, 353; T. Yamamoto, Y. Hayashi and A. Yamamoto, *Bull Chem. Soc. Jpn.*, 1978, **51**, 2091.

Paper 1/05345K
Received 22nd *October* 1991
Accepted 20th *December* 1991