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Studies on Immobilized Polymer-Bound Imidazole-Copper(II) Complexes as Catalysts. 3. Immobilization of Copper(II) Complexes of Poly(styrene-*co*-*N*-vinylimidazole) by Grafting on Silica and Their Catalysis of Oxidative Coupling of 2,6-Disubstituted Phenols[†]

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ABSTRACT: Copper(II) complexes of poly(styrene-*co*-*N*-vinylimidazole) (Cu(II)-PS-Im) were immobilized on modified silica by radical graft copolymerization of *N*-vinylimidazole and styrene and characterized by VIS and EPR spectrometry. In this graft copolymerization, the same reactivity ratios were found as obtained from nongraft copolymerization initiated by AIBN; i.e., $r_1 = 0.07$ and $r_2 = 7.0$ for *N*-vinylimidazole and styrene, respectively. In a batch process under comparable conditions, these Cu(II)-PS-Im complexes grafted on silica are catalytically more active for oxidative coupling of 2,6-dimethylphenol in toluene/methanol (13/2 v/v) than those immobilized on silica by quaternization or adsorption. However, they are three times less active than nonimmobilized Cu(II)-PS-Im or their low molar mass analogue for ligand/Cu = 4, which is primarily attributed to a nonoptimum Cu(II) complex formation. Decreasing reaction rates for still higher ligand/Cu ratios probably result from the high viscosities of the silica suspensions. The specificity for the formation of poly(2,6-dimethyl-1,4-phenylene oxide) is not influenced by the grafting of the catalyst for ligand/Cu = 4. This silica-grafted Cu(II)-PS-Im demonstrates a stable conversion under suitable conditions for at least 150 h in the oxidative coupling of 2,6-di-*tert*-butylphenol in a continuously stirred tank reactor.

1. Introduction

In order to combine the advantages of both homogeneous and heterogeneous catalyst, we have developed a number of immobilized polymer-bound catalysts, e.g., silica-quaternized or -adsorbed Cu(II)-PS-Im (Figure 1c), for oxidative coupling of 2,6-dimethylphenol (DMP) (Scheme I) in toluene/methanol (13/2 v/v).[2] Compared with immobilized polymer-bound pyridine-based[3,4] or 4-(dimethylamino)pyridine (DMAP) based[5] copper(II) complexes, these imidazole-containing catalysts showed intermediate catalytic activity but better specificity for the formation of poly(2,6-dimethyl-1,4-phenylene oxide) (PPO). Moreover, under suitable conditions they proved to be stable catalysts in a continuous phenol oxidation process.[2]

In previous studies we have already investigated nonimmobilized copper(II) complexes of *N*-methylimidazole (Cu(II)-NMIm)[6] and Cu(II)-PS-Im[1] as catalysts (Figure 1a,b) for the same reaction. In both cases mononuclear $[Cu(imidazole)_4]^{2+}$ species at high ligand/Cu ratios were found to be more favorable for higher catalytic activity and better specificity for PPO formation than dinuclear complexes. In addition, toluene/methanol (13/2 v/v) appeared to be a suitable solvent mixture for obtaining both high activity and good specificity.

In general, immobilization of polymeric catalysts by graft copolymerization is a method yielding more effective catalysts than other methods, e.g., adsorption of polymer chains on silica. Therefore, in the present study the preparation and catalysis of silica-grafted Cu(II)-PS-Im (Figure 1d) will be described. Besides, some similarities as well as differences in their catalytic behavior in a batch-type reactor will be pointed out in comparison with silica-quaternized or -adsorbed Cu(II)-PS-Im, as well as nonimmobilized Cu(II)-NMIm or Cu(II)-PS-Im catalytic systems. Finally, application of silica-grafted Cu(II)-PS-Im as a catalyst for oxidative coupling of 2,6-di-*tert*-butylphenol (DTBP) in a continuous reaction process will be reported.

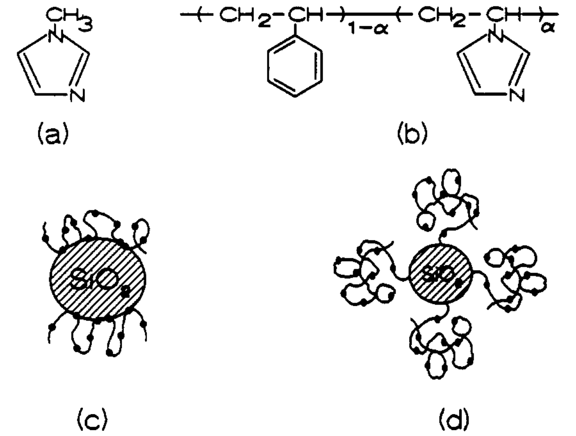
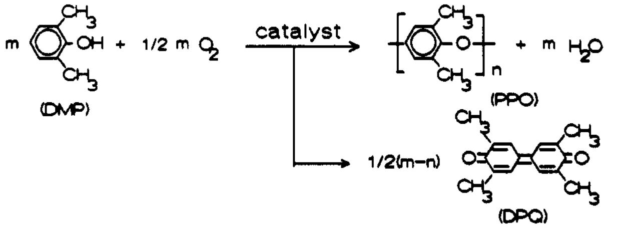


Figure 1. Schematic representation of free and immobilized imidazole ligands in Cu(II) complexes as catalysts: (a) NMIm; (b) PS-Im; (c) silica-quaternized or -adsorbed PS-Im; (d) silica-grafted PS-Im.

Scheme I



2. Experimental Section

2.1. **Materials.** $CuCl_2(H_2O)_2$ (analytically pure), KOH, and methanol (Uvasol) (Merck) were used as received. *N*-Vinylim-

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Scheme II

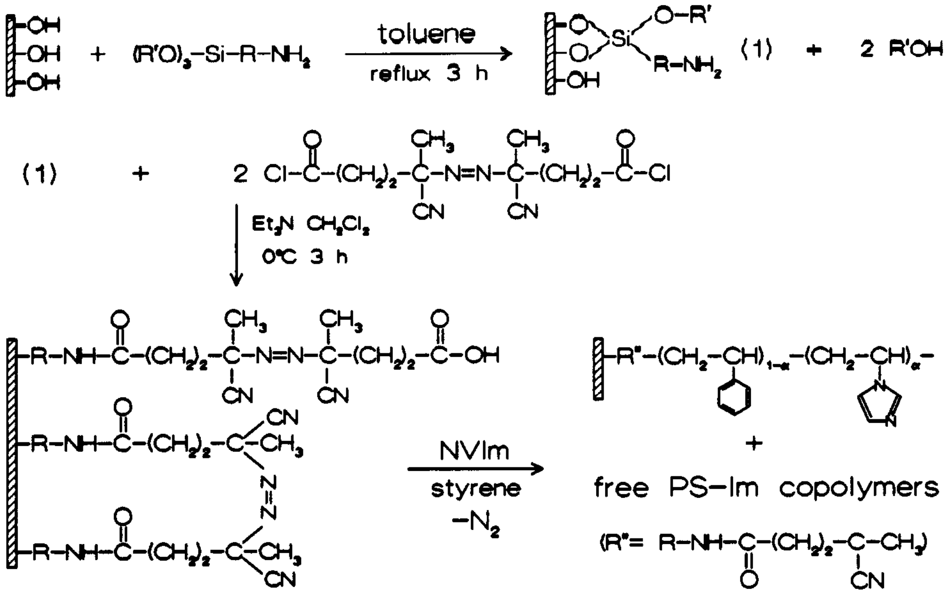


Table I
Graft Copolymerizations of NVIm and Styrene on Aerosil 200V[a]

samples	NVIm, mol %	time, h	α,[b] %	θ,[c] %	conversion, wt % graft	free	total
A	34	6	6.2	23	2.6	2.4	5.0
B	52	6	12	26	3.1	4.1	7.2
C	52	12	12	30	4.2	6.4	11
D	52	24	12	32	4.3	8.6	13
E	62	6	17	27	3.0	3.1	6.1
F	71	6	23	18	1.7	2.6	4.3
G[d]	52	17	10	16	1.3	3.5	4.8

[a] Reactions were carried out under N_2 at 70 °C; amount of Aerosil 200V bound initiator based on total monomers is 0.12 mol % of N=N groups; toluene/monomers = 1/1 (v/v). [b] Chain loading of PS–Im with imidazole groups. [c] Loading degree: wt % of PS–Im on Aerosil 200V. [d] Silica surface of initiator was modified with hydrophobic "$Si(CH_3)_3$" groups.

idazole (NVIm) and styrene (Aldrich) were distilled from KOH under reduced N_2 atmosphere. DMP (Aldrich) was purified by repeated recrystallization from *n*-hexane. DTBP (Janssen) was used without further purification. Toluene (Merck) was dried over Na. The nonporous Aerosil 200V (specific surface $\simeq$200 $m^2{\cdot}g^{-1}$, average sphere diameter 12 nm) containing $\approx$1.0 mmol of "SiOH" per gram of silica was kindly provided by Degussa AG. Hexamethyldisilazane (HMDS) (Janssen) was used as supplied.

2.2. Nonimmobilized PS-Im. Radical copolymerization of NVIm and styrene was performed in toluene using AIBN as an initiator. This copolymerization and the characterization of nonimmobilized PS-Im were carried out as reported previously.[1]

2.3. Aerosil 200V Grafted PS–Im. Scheme II outlines the preparation of silica-bound initiator and subsequent radical graft copolymerization of NVIm and styrene on Aerosil 200V.

The silica-bound 4,4'-azobis(4-cyanopentanoic acid) was prepared according to a literature procedure.[7] The sample applied in the present case contained 0.14 mmol of "N=N" per gram of silica (calculated from elemental analysis: C, 5.01; H, 0.71; N, 1.18; Aerosil, 92.0). On the average, 0.28 mmol of SiOH and 0.22 mmol of "NH_2" per gram of silica remained on the surface of silica spheres (calculated from elemental analysis: C, 4.13; H, 0.48; N, 0.47; Aerosil, 94.5).

For graft copolymerizations 1.0 g of silica-bound initiator was suspended in 12 mL of toluene under N_2 atmosphere at room temperature. Stoichiometric amounts of monomers were added to the suspension, which was then stirred at 70 °C for 6–24 h. Subsequently, this reaction mixture was centrifuged (decanting the upper layer) and suspended in another 120 mL of toluene/methanol (13/2 v/v) and stirred for at least 3 h. This procedure was repeated three times in order to remove the free copolymers. Then the loaded silica particles were again suspended in 30 mL of toluene and slowly poured into a 15-fold volume of petroleum either 40-60, filtered, dried in high vacuum at 60 °C for 3 days, and characterized by elemental analysis. The free copolymers were precipitated from the supernatant in petroleum/ether (2/1 v/v) and reprecipitated twice from chloroform, then dried, and characterized as above. All results of preparation and characterization of Aerosil 200V grafted PS–Im are compiled in Table I.

For sample G in Table I, the silica surface of the initiator was made hydrophobic with HMDS before the graft copolymerization was started. Trimethylsilylation of the free silanol groups on silica was performed by suspending the silica-bound initiator (2.0 g) in 30 mL of toluene over P_2O_5 under dry N_2 atmosphere and subsequently adding HMDS. Then this suspension was stirred at 20 °C for 14 h. Such a procedure was known to be successful for capping of free silanol groups[8] and did not give rise to destruction of siloxane bonds by formed NH_3 as found by Buszewski[9] at 110 °C in the absence of P_2O_5. The material was separated from solution by centrifuging, washed twice with dichloromethane, and dried under high vacuum at 20 °C overnight.

2.4. VIS and EPR Measurements. VIS spectra of Aerosil 200V grafted Cu(II)–PS–Im in solution were recorded on a Perkin-Elmer Lambda 2 UV/vis spectrophotometer at room temperature (stirring the suspension during measurement). EPR spectra of a frozen solution of Aerosil 200V grafted Cu(II)–PS–Im were recorded on a JES-RE 2X EPR spectrometer at –196 °C.

2.5. Oxidative Coupling in a Batch-Type Reactor. The oxidative coupling polymerization of DMP was carried out in a round flask with stirring, instead of shaking of the cylindrical reaction vessel,[1] to prevent loaded silica particles from sticking on the top wall of the vessel. Immobilized polymeric catalysts were prepared in situ by suspending the Aerosil 200V grafted PS–Im in toluene and adding a $CuCl_2$/methanol solution. The coordination equilibrium period lasted about 24 h. After saturating the reaction system with O_2, the reactions were started by adding hydroxide (as KOH dissolved in methanol) and DMP, subsequently. Steady-state reaction rates R were obtained by measuring O_2 uptake as a function of time with an automatic isobaric gas burette. Relative observed reaction rates (k_{obs}) for a definite substrate concentration were calculated as $k_{obs} = R/[CuCl_2]_0$, assuming that all $CuCl_2$ yields active catalyst. The stirring speed of the reaction solution was sufficient to prevent gas–liquid diffusion of O_2 becoming rate determining. The following standard conditions were applied: $T = 25$ °C; $P_{O_2} = 101.3$ kPa; [DMP] = 0.06 mol·dm^{-3}; [Cu(II)] = 0.33[OH$^-$] = 0.25[imidazole] = 0.83 mmol·dm^{-3}; solvent mixture, toluene/methanol (13/2 v/v); total reaction volume, 0.015 dm^3.

2.6. Continuous Oxidative Coupling Process. Figure 2 shows the setup for continuous oxidative coupling. The diameter

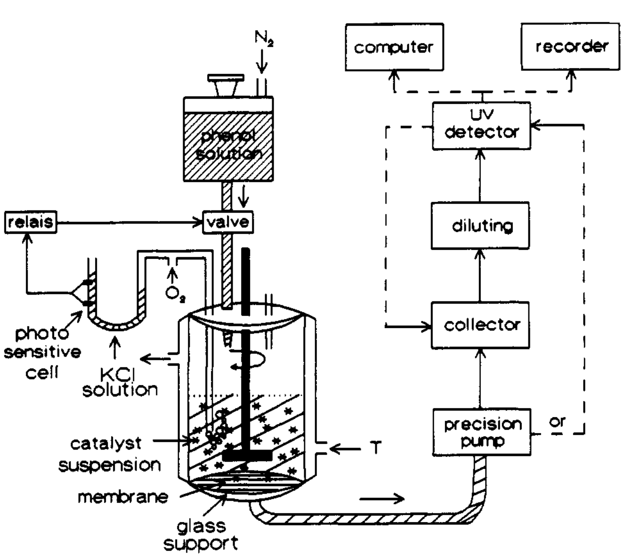


Figure 2. Schematic drawing of the apparatus for the continuous oxidative coupling process of phenols catalyzed by silica-grafted Cu(II)-PS-Im.

of pores in the applied poly(tetrafluoroethylene) membrane is 20 nm. However, the grafted polymer chains bound to silica prevent the loaded silica particles from passing through the membrane.[5] Moreover, leaching of Cu(II) from the polydentate coils as well as detachment of grafted polymeric ligands from silica appeared to be negligible.[5] The standard conditions were $T = 25$ °C; $P_{O_2} = 101.3$ kPa; $[\mathrm{DTBP}]_0 = [\mathrm{DTBP}] = 0.02\ \mathrm{mol{\cdot}dm^{-3}}$; $[\mathrm{Cu(II)}]_0 = 0.67[\mathrm{OH^-}]_0 = 0.25[\mathrm{imidazole}]_0 = 0.21\ \mathrm{mmol{\cdot}dm^{-3}}$; solvent mixture, toluene/methanol (13/2 v/v); total reaction volume, 0.15 $\mathrm{dm^3}$; flow rate, 0.2 $\mathrm{cm^3{\cdot}min^{-1}}$. The coordination equilibrium period lasted about 24 h and was followed by an addition of hydroxide (as KOH dissolved in methanol).

2.7. Determination of DPQ. In batch-type experiments, once the reaction was complete the reaction mixture was immediately diluted with chloroform and subsequently the overall catalytic specificity was determined by measuring the concentrations of the side product 3,5,3′,5′-tetramethyl-4,4′-diphenoquinone (DPQ) with a PYE Unicam SP-8-200 UV/vis spectrophotometer at 421 nm ($\epsilon = 74\,000\ \mathrm{dm^3{\cdot}mol^{-1}{\cdot}cm^{-1}}$) because PPO and DPQ are practically the sole products from DMP.

For continuous experiments, DTBP was used as a substrate since it yields only one main product, viz., its DPQ, which could be detected by UV/vis spectrophotometry at 426 nm ($\epsilon = 65\,000\ \mathrm{dm^3{\cdot}mol^{-1}{\cdot}cm^{-1}}$) after strong dilution with chloroform. From these data the stability of the catalyst could be derived.

3. Results and Discussion

3.1. Graft Copolymerization. The preparation and the type of initiator bound to Aerosil 200V (Scheme II) are different from those reported by Verlaan et al.[3] and Koning et al.[5] On the average, 28% of free SiOH remained on the silica surface instead of 40% of free SiOH in Koning's case; this lower value seems to be more favorable for high catalytic activity.

In order to obtain silica-grafted PS-Im having a reliable and narrow range of chain loading (α) with imidazole groups, the final conversions of graft copolymerizations were kept below 15%. Because of the similar α values of both silica-grafted and free copolymers,[5] we took the α values in Table I from free PS-Im by elemental analysis and applied them to the immobilized copolymers. By use of the Fineman and Ross method, the reactivity ratios of monomers were calculated to be $r_1 = 0.07$ and $r_2 = 7.0$ for NVIm and styrene, respectively. The same values were also obtained for nongrafted copolymerization initiated by AIBN.[1]

Finally, very long times of graft copolymerization (>12 h) seem not to yield higher loading degrees (θ) of PS-Im on silica but produced more free copolymer in solution (Table I, samples B-D), as was also found for graft polymerizations of methyl methacrylate and was explained in terms of radical recombination on silica surface and the Trommsdorff effect in the surrounding medium.[7]

Table II
Effect of OH/Cu on Catalysis under Standard Conditions

catalyst	OH/Cu	10^3k_{obs}, $\mathrm{s^{-1}}$	DPQ, %
Aerosil 200V	0	0	
grafted	1	1.2	12
Cu(II)-Ps-Im	2	2.3	12
(sample B)	3	6.5	12
	4	3.2	

Table III
Effect of Ligand/Cu on Catalysis under Standard Conditions

catalyst	ligand/Cu	10^3k_{obs}, $\mathrm{s^{-1}}$	DPQ, %
Aerosil 200V	0	0	
grafted	1	0.56	11
Cu(II)-Ps-Im	2	4.4	12
(sample B)	4	6.5	12
	10	5.4	14
	22	1.1	

3.2. Catalysis in a Batch-Type Reactor. As found in the cases of nonimmobilized Cu(II)-NMIm[6] and Cu(II)-PS-Im,[1] no reaction takes place in the absence of base with immobilized polymeric catalyst (Table II). However, in the present case a maximum in catalytic activity is found for silica-grafted Cu(II)-PS-Im around OH/Cu = 3 instead of OH/Cu = 1 and 2 for Cu(II)-NMIm[6] and Cu(II)-PS-Im,[1] respectively. Apparently, on immobilizing Cu(II)-PS-Im on silica, its stability against base improves. The main role of hydroxide is to produce phenolate anions from DMP,[10,11] whereas an excess of base somehow induces catalyst destruction by forming copper hydroxides.[1,2,6] A control experiment proved that detachment of grafted polymeric ligands by base from silica does not take place under standard conditions even in the absence of neutralizing DMP.

In previous studies with nonimmobilized catalytic systems, we found higher reaction rates for higher ligand/Cu ratios, because of the apparent formation of more mononuclear $[\mathrm{Cu(imidazole)_4}]^{2+}$. Enhancement of reaction rates was obtained even for ligand/Cu > 30 in the case of Cu(II)-NMIm[6] but only up to 10 for Cu(II)-PS-Im due to the overlap of polymer coils in concentrated solution.[1] However, with silica-grafted Cu(II)-PS-Im as catalyst, high ligand/Cu ratios require a large number of loaded silica particles. Then the high viscosity of the silica suspension probably limits diffusion of reactants. Consequently, no increase in reaction rate is observed for ligand/Cu > 4 (Table III).

With silica-grafted Cu(II)-PS-Im as catalyst, the percent DPQ of about 12% is independent of the applied OH/Cu and ligand/Cu ratios (Tables II and III). This differs from the cases of Cu(II)-NMIm[6] and Cu(II)-PS-Im,[1] for which increasing ligand/Cu ratios are always accompanied by a decrease in percent DPQ down to 6%, resulting from the transformation of dinuclear complexes into more specific mononuclear species.

We also investigated the kinetics of oxidative coupling polymerization of DMP catalyzed by Aerosil 200V grafted Cu(II)-PS-Im as a function of substrate concentration. Under standard conditions so-called saturation kinetics are observed and the double-reciprocal Lineweaver-Burk plot of reaction rate versus DMP concentration is given in Figure 3. A straight line intersects the Y axis in

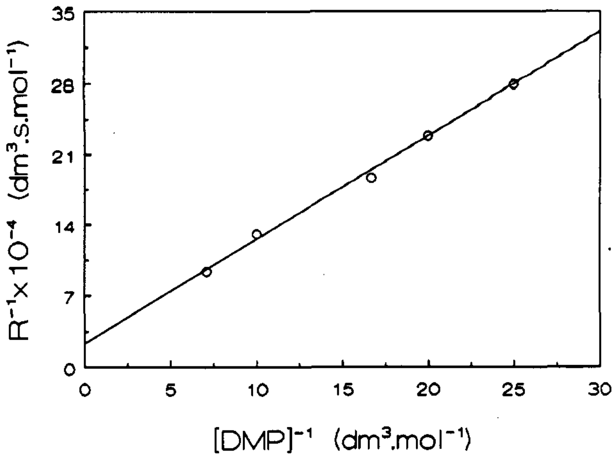
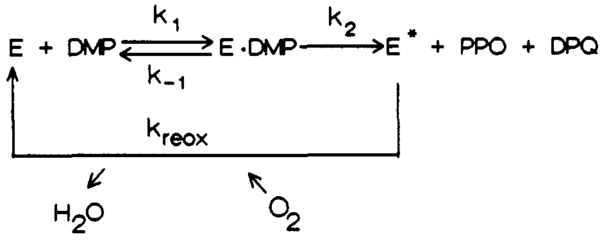


Figure 3. Double-reciprocal Lineweaver–Burk plot of steady-state reaction rate versus substrate concentration under standard conditions for Aerosil 200V grafted Cu(II)–PS–Im (sample B) as catalyst.

Scheme III



agreement with the well-known equation

$$\frac{1}{R} = \frac{1}{k_2[E]_0} + \frac{K_m}{k_2[E]_0[DMP]}$$

Therefore, this reaction can be described by a Michaelis–Menten mechanism as given in Scheme III. E is the active Cu(II)–PS–Im complex; E* is the Cu(I) complex; $[E]_0$ is overall concentration of the active Cu(II) ions; k_2 is the rate constant of the rate-determining step; $K_m = (k_{-1} + k_2)/k_1$, the Michaelis–Menten constant. From the straight line in Figure 3, k_2 and K_m^{-1} (K_m^{-1} is a measure of the accessibility of active site for substrate) have been calculated, yielding $k_2 = 0.052\ s^{-1}$ and $K_m^{-1} = 2.3\ dm^3{\cdot}mol^{-1}$. These values imply that the reduction in reaction rate, after grafting, as compared to that for nonimmobilized Cu(II)–PS–Im with $k_2 = 0.15\ s^{-1}$ and $K_m^{-1} = 1.7\ dm^3{\cdot}mol^{-1}$, is caused either by a decrease of the intrinsic activity of catalytic sites (k_2) or by a decrease of $[E]_0$ ($[E]_0 < [CuCl_2]_0$) due to imcomplete complexation of $CuCl_2$. Fortunately, the latter possibility could be excluded by the following result. After centrifuging the silica-grafted Cu(II)–PS–Im from solution (standard conditions except addition of DMP), Cu(II) ions were found by atomic absorption to be less than 10^{-2} ppm in aliquots of the supernatant solution. This result proves that less than 0.025% of Cu(II) ions is present outside grafted PS–Im coils, i.e., $[E]_0 = [CuCl_2]_0$. So, the reduction in reaction rate is only related to the decreased k_2.

3.3. Explanation of the Reduced Activity after Grafting. Table IV demonstrates that grafting of PS–Im on silica does not affect the catalytic specificity (percent DPQ) of its Cu(II) complexes. However, the relative observed reaction rates (k_{obs}) for silica-grafted Cu(II)–PS–Im are three times lower than those for nonimmobilized Cu(II)–NMIm and Cu(II)–PS–Im. Several possible explanations will be considered, taking into account that the reduction in reaction rate can be completely attributed to lowering of k_2.

Table IV
Comparison for Different Catalytic Systems under Comparable Conditions

catalysts	ligand/ Cu	OH/ Cu	10^3k_{obs}, s^{-1}	DPQ, %
Cu(II)–NMIm	4	1	21	14
Cu(II)–PS–Im	4	1	19	15
Aerosil OX50 quaternized Cu(II)–PS–Im (α = 12%; θ = 5.9%)	4	3	4.0	10
Aerosil OX50 adsorbed Cu(II)–PS–Im (α = 35%; θ = 9.5%)	4	3	4.1	14
Aerosil 200V grafted Cu(II)–PS–Im (sample C)	4	3	7.3	11
(sample D)	4	3	7.1	11
(sample G)	4	3	6.9	11
Aerosil 200V grafted Cu(II)–PS–Py (α = 25%; θ = 38%)[a]	2	1	<1.0	>40[b]
Aerosil 200V grafted Cu(II)–PS–DMAP (α = 30%; θ = 28%)[c]	4	1	16	19

[a] In 1,2-dichlorobenzene/methanol (ODCB/MeOH) (13/2 v/v) and for [DTBP] = 0.18 mol·dm^{-3} (ref 4). [b] For nonimmobilized Cu(II)–PS–pyridine in ODCB/MeOH (13/2 v/v) (ref 17). [c] In ODCB/MeOH (13/2 v/v) (ref 5).

First, water enrichment, owing to free hydrophilic silanol groups on the silica surface, might retard the catalytic process.[12] However, this interpretation is not supported by the experimental result for sample G, having less free silanol groups (Tables I and IV). In fact, no enhancement in reaction rate is observed by using sample G for catalysis. Another effect of the free silanol groups could be adsorption of some imidazole ligands of PS–Im on silica, resulting in a decrease of the effective ligand/Cu ratio. The shortage of available imidazole ligands is not favorable for the complete formation of the most active mononuclear $[Cu(imidazole)_4]^{2+}$ species,[1,6] which might cause a decreased k_2. However, this possibility is not in agreement with the experimental result for sample G in Tables I and IV either. On the contrary, the basic NH_2 groups (0.22 mmol) left on the silica surface would prevent the interaction between silanol and imidazole groups.

By using sample B in Table I as an example, the available area for a polymer chain on a silica surface was calculated to have a radius of 37.3 Å ($\bar{M}_n$ of grafted PS–Im assumed to be the same as that of free copolymer, viz., 46 000 g·mol^{-1}). On the other hand, in terms of Flory's statistical theory ($R_g^2 = \langle r^2 \rangle/6$ and $\langle r^2 \rangle = C_\infty n l^2$ assuming a Θ state), we calculated the radius of gyration of free PS–Im yielding R_g = 68.3 Å by taking C_∞ = 10 and l = 2.5 Å. Apparently, the values of 37.3 and 68.3 Å imply that some overlap of polymer coils on the surface of silica spheres should take place, which may affect the structure of the Cu(II) complexes.

The VIS spectrum of silica-grafted Cu(II)–PS–Im in solution (sample D, standard conditions except addition of DMP) showed a broad absorption of the Cu(II) complex in the range 600–850 nm, which might indicate the presence of both mono- and dinuclear Cu(II) complexes.[6] In addition, Figure 4a presents an EPR spectrum of a frozen solution of silica-grafted Cu(II)–PS–Im (ligand/Cu = 4). Obviously, the optimum mononuclear species $[Cu(imidazole)_4]^{2+}$ ($g_\perp$ = 2.04, $g_\parallel$ = 2.24, $A_\parallel$ = 179 G, and A_N = 15.1 G) is present.[1,13] Unfortunately, the turbid sample

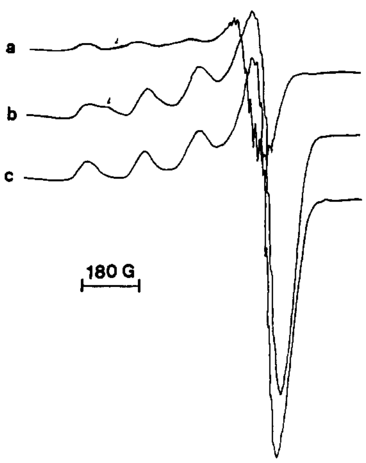


Figure 4. EPR spectra of frozen solution of (a) Aerosil 200V grafted Cu(II)-PS-Im (sample D), standard conditions except addition of DMP, receiver gain, 2.0×10^2; (b) Cu(II)-PS-Im with ligand/Cu = 2 (ref 1); (c) Cu(II)-PS-Im with ligand/Cu = 4 (ref 1).

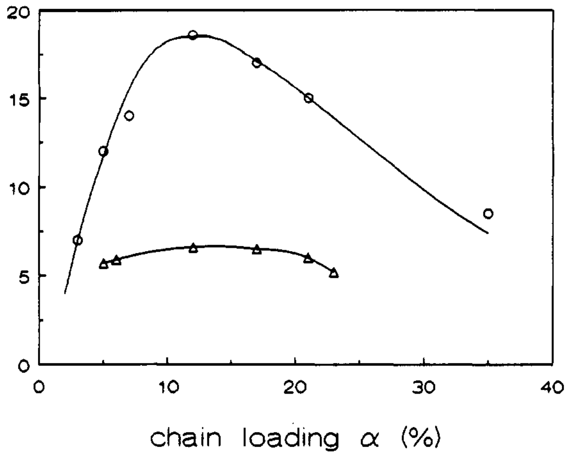


Figure 5. Effect of chain loading (α) on reaction rate under standard conditions: (○) for nonimmobilized Cu(II)-PS-Im and [Cu(II)] = [OH$^-$] = 0.25[imidazole] = 3.32 mmol·dm^{-3}; (△) for Aerosil 200V grafted Cu(II)-PS-Im.

of Cu(II)-PS-Im grafted on silica can not give clear signals of other possible Cu(II) species in its EPR spectrum.

The EPR spectrum of grafted Cu(II)-PS-Im at position (↓) (Figure 4a) looks similar to that of nonimmobilized Cu(II)-PS-Im with ligand/Cu = 2 (Figure 4b) rather than to that with ligand/Cu = 4 (Figure 4c). In cases of nonimmobilized Cu(II)-PS-Im with ligand/Cu = 2, we have already reported the coexistence of [Cu(imidazole)$_4$]$^{2+}$ and the less active mononuclear [Cu(imidazole)$_{1-3}$]$^{2+}$ species, thus yielding half of the optimum reaction rate.[1] Therefore, in the present case of silica-grafted Cu(II)-PS-Im under standard conditions with ligand/Cu = 4, the decrease in reaction rate after grafting is primarily attributed to the incomplete transformation of Cu(II) ions into the optimum complex [Cu(imidazole)$_4$]$^{2+}$, probably owing to overlap of polymer coils on the silica surface (see above) and partial aggregation of imidazole groups. In other words, steric hindrance of overlapping polymer chains on the silica surface and nonuniform distribution of imidazole ligands are not favorable for the complete formation of the symmetrically planar [Cu(imidazole)$_4$]$^{2+}$ complex. The resulting [Cu(imidazole)$_{1-3}$]$^{2+}$ species will produce rather low intrinsic activities of catalytic sites (k_2).

We have already tried to promote the transformation of [Cu(imidazole)$_{1-3}$]$^{2+}$ species into the optimum complex by adding extra low molar mass imidazole ligands, viz., NMIm with NMIm/Cu = 2-4. However, in the presence of extra NMIm a decreased reaction rate was observed under standard conditions with OH/Cu = 3. This seems to indicate that the extra added NMIm ligands extract some Cu(II) ions from silica-grafted polymer coils to form some low molar mass complexes, rather than promoting the formation of [Cu(imidazole)$_4$]$^{2+}$ species. The Cu(II)-NMIm complex is known to be unstable at OH/Cu = 3.[6]

It seems from the above discussion that lowering the loading degree (θ) of PS-Im on silica might prevent overlap of polymer coils on silica surface, thus permitting a higher activity of the catalyst. Unfortunately, no enhancement in reaction rate was found by applying the sample G as catalyst having a value of θ = 16% (Tables I and IV) instead of 26% for sample B. In fact, for a value of only θ = 13% the radius of the available area for a polymer chain on a silica surface would be $\sqrt{2} \times 37.3 = 52.2$ Å (referring to sample B in Table I, for which 37.3 Å was calculated), which is still smaller than the value of R_g = 68.3 Å. Therefore, overlap of polymer coils on the silica surface may still occur for sample G. Rather low loading degrees (θ) of PS-Im on silica, e.g., $\theta < 6.5\%$ in the present case, are required to prevent overlap of grafted polymer coils. However, this would involve a 4-fold increase of the number of the loaded silica particles for a constant ligand/Cu ratio. Then, the high viscosity of the silica suspension and possible interparticle complexation would limit the diffusion of reactants. So, increasing reaction rates would not be observed either.

3.4. α Effect on Catalytic Activity. As shown in Figure 5, a maximum reaction rate is observed at α = 12% with nonimmobilized Cu(II)-PS-Im. This effect of chain loading (α) of PS-Im with imidazole groups on catalytic activity was discussed in a previous paper[1] in terms of strain in the polymer chain segments between neighboring ligands.[14,15] However, after grafting of PS-Im on silica, this effect nearly disappears (Figure 5). In section 3.3, the overlap of polymer chains on the silica surface and the aggregation of some imidazole ligands were described. In this case, the Cu(II) ions may be coordinated by imidazole ligands from different polymer chains. Then, strain in the polymer chain segments between neighboring ligands will hardly change with increasing α. This is different from the case of isolated free polymer coils, wherein the Cu(II) ions solely coordinate with imidazole ligands attached to the same polymer chain.

3.5. Comparison with Other Immobilized Catalysts. It appears from Table IV that silica-grafted Cu(II)-PS-Im is catalytically more active than silica-quaternized or -adsorbed Cu(II)-PS-Im. Grafted polymer chains are longer and more extended than the loops and tails of quaternized or adsorbed chains,[16] which was considered to be favorable for catalytic acitivity.[5]

Finally, the present grafted imidazole-containing catalysts show better catalytic specificity for PPO formation and intermediate catalytic activity compared with grafted pyridine or DMAP-based catalytic systems under proper conditions (Table IV). In view of the high basicity of the DMAP ligand, one can understand the higher activity of the DMAP-based catalytic system. Unfortunately, the strong basicity of DMAP prevents successful application of this DMAP-type catalyst in a continuous phenol oxidation process.[5]

3.6. Stability of Catalysts. Aerosil 200V grafted Cu(II)-PS-Im has been applied as catalyst for the oxidative coupling of DTBP in a continuously stirred tank reactor (CSTR) (Figure 2). Under standard conditions with (OH/Cu)$_0$ = 1.5, a stable DTBP conversion is observed for at

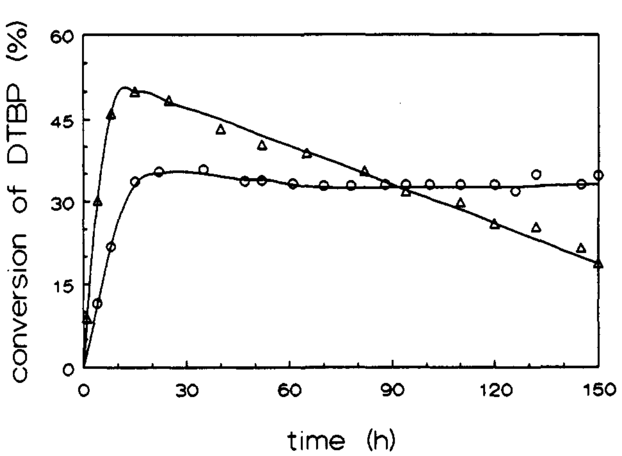


Figure 6. Stability of Aerosil 200V grafted Cu(II)–PS–Im (sample F) as a catalyst for oxidative coupling of DTBP in CSTR under standard conditions: (○) $(OH/Cu)_0 = 1.5$; (△) $(OH/Cu)_0 = 3$.

least 150 h (Figure 6). This result not only demonstrates successful application of an immobilized polymeric catalyst in a continuous process but also confirms that phenolate anions, produced from initial hydroxide and DTBP, are regenerated during the oxidative coupling and do not escape from the catalytic intermediate. This fact should be taken into account when considering the mechanism of oxidative coupling of phenols catalyzed via Cu(II)–amine complexes. However, the decreasing conversion in the case of $(OH/Cu)_0 = 3$ as shown in Figure 6 indicates that higher initial base concentrations are not suitable anymore for a continuous catalytic process, probably because of gradual destruction of some base-coordinated catalysts over a long period. Only in the initial stage the rate is enhanced for a higher OH/Cu ratio, as expected from the results in batch processes (see Table II).

In the near future, the optimum conditions for continuous oxidative coupling derived from the present study will be applied to DMP as substrate in order to prepare PPO-type oligomers.

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