# Methanolysis of organophosphorus esters promoted by an $M^{2+}$ catalyst supported on polystyrene-based copolymers

**Benoit Didier, Mark F. Mohamed, Elizabeth Csaszar, Kate G. Colizza, Alexei A. Neverov and R. Stan Brown**

**Abstract**: The methanolysis of three neutral organophosphorus esters (a phosphonate, a phosphonothioate, and a phosphorothionate) promoted by several polymer-supported Zn(II) or Cu(II) containing catalysts was studied. The catalysts consist of a Zn(II) or Cu(II) complex with 1,5,9-triazacyclododecane or phenanthroline attached to a porous polystyrene resin. In each case, the polymer supported catalyst showed activity at near neutral ${}_{s}^{s}\mathrm{pH}$ in methanol (8.38) and ambient temperature and provided accelerations of up to a factor of $2.9 \times 10^6$ relative to the background reaction at ${}_{s}^{s}\mathrm{pH}$ 9.05. The solid materials could be reused several times and could be reactivated when the activity diminished. Various polymers of different porosity and extent of cross-linking were studied, with the net result being that larger porosities offer the best reactivity for catalyzed methanolysis of these OP species in methanol. This is explained by different parameters including the accessibility to reactive sites, the increase of concentration of catalytic sites on the surface of the polymer, and some cooperative effects between neighboring catalytic groups.

*Key words:* functionalized polymer, metal containing, methanolysis, organophosphorus pesticides and CW agents, catalyst.

**Résumé :** La méthanolyse de trois esters organophosphorés neutres (un phosphate, un phosphonothioate et un phosphorothionate) ont été étudié en présence de plusieurs catalyseurs contenant du Zn(II) et du Cu(II) compléxés avec du 1,5,9-triazacyclododécane ou de la phénantroline supportés par des matrices polymères poreuses. Dans chacun des cas, le catalyseur supporté par le polymère est actif à température ambiante et à ${}_{s}^{s}\mathrm{pH}$ proche de la neutralité dans le méthanol (8,38) en fournissant des accélérations allant jusqu'à 2,9 x $10^6$ par rapport aux vitesses de réaction obtenues en l'absence de catalyseur métallique à un ${}_{s}^{s}\mathrm{pH}$ de 9,05. Les matériaux utilisés peuvent être réutilisés plusieurs fois ou réactivés lorsque leur activité diminue. Divers matrices polymères de porosité et de degrés de réticulation différents ont été étudiés et il a été observé que les catalyseurs fixés sur les matrices ayant la porosité la plus large ont la plus forte activité catalytique pour la méthanolyse de ces esters phosphoriques dans le méthanol. Ce résultat s'explique par divers paramètres, incluant l'accessibilité des sites réactifs, l'augmentation de la concentration des sites catalytiques à la surface du polymère et de quelques effets de synergie entre des espèces catalytiques voisines.

*Mots-clés :* polymère fonctionnalisé contenant un métal, méthanolyse, pesticides organophosphorés, gaz de combat, catalyse.

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## Introduction

Neutral organophosphorus (OP) compounds with leaving groups having p$K_a$ values less than 8 comprise a very toxic family of compounds that inhibit acetylcholinesterase (1, 2) and thus have uses as chemical warfare (CW) agents, pesticides, and acaricides (3). Among the most nefarious of the CW agents are the phosphonothioate esters that are V-agents, such as VX (**1**) and Russian VX (**2**) and the phosphonoflouridate G-agents such as soman (**3**) and sarin (**4**). Other kinds of OP esters, such as the phosphate triesters and phosphorothionate esters (**5**, **6**), are used as pesticides.

Due to the noxious nature of these materials and the fact that some of them linger in the environment, methods for the decomposition and decontamination of these are continually sought (4). Only a few methods employ metal ions, but generally these are not very effective in water for hydrolysis because of substrate and metal ion solubility problems and also the inherent low activity of the metal ions in promoting solvolysis, which has yet to be overcome in aqueous media. In practice, a decomposition method should be inexpensive, have a high reaction rate, occur at neutral pH and ambient temperature, and convert the toxic starting material into far less toxic or nontoxic products.

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*This article is dedicated to the memory of Professor Keith Yates.*

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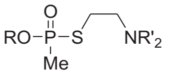
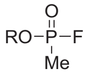
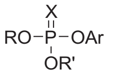
Recent work in our laboratories indicates that neutral (uncharged) esters of phosphates and phosphorothioates (5*a*, 5*b*), phosphonates (5*c*), and phosphonothioates (5*d*) are rapidly solvolyzed in methanol solution in the presence of $La^{3+}$ or a Zn(II)-complex of 1,5,9-triazacyclododecane (**7*a***), forming nontoxic methyl esters. In addition, we have found that the corresponding Cu(II)($^{-}OCH_3$) or Zn(II)($^{-}OCH_3$) complexes of **7a** (6, 7) and **8** (7) catalyze the methanolysis of phosphate triesters and phosphorothionate triesters with a particular propensity for the latter. Routinely we find that a 1 mmol/L solution of the metal species gives accelerations of the methanolysis of these materials by factors of $10^8$–$10^9$ over the background reactions at neutral $^s_s$pH and ambient temperature (8). All these exhibit true catalytic turnover, and all seem to function according to the simple kinetic scheme given in eq. [1]. The disadvantage of complex with **8** is the formation of dimers that are inactive, so it seemed reasonable that fixing the ligands on a solid support could form exclusively monomeric catalysts and prevent the formation of inactive species.





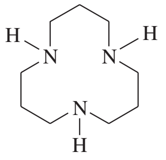


**1**; R=Et, R'=CH($CH_3$)$_2$ **3**; R=CH($CH_3$)(C($CH_3$)$_3$) **5**; X=O, R, R'=alkyl, aryl

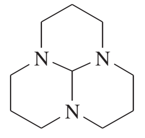
**2**; R=$CH_2CH(CH_3)_2$, R'=Et **4**; R=CH($CH_3$)$_2$ **6**; X=S, R, R' = alkyl, aryl

$$[1]\qquad \text{Substrate} + \text{Mx}^{+}\,(\text{-OR}) \underset{}{\overset{K_b}{\rightleftharpoons}} \text{Substrate:Mx}^{+}\,(\text{-OR})$$

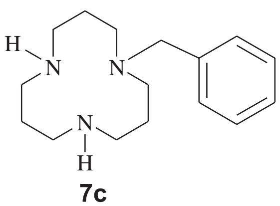
$$\text{Substrate} + \text{Mx}^{+}\,(\text{-OR}) \xrightarrow{\text{kcat}} \text{Substrate:Mx}^{+}\,(\text{-OR})$$



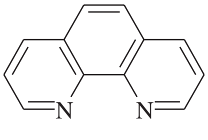
**7a**



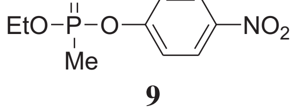
**7b**



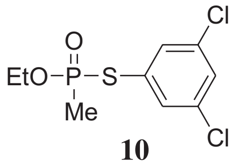
**7c**



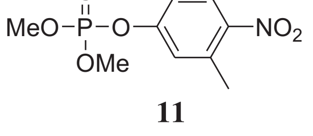
**8**



**9**



**10**



**11**

In some cases, affixing the catalytic group to a solid support can be expected to confer particular advantages of efficiency and cost effectiveness that come from being able to recover and reuse the catalyst. There are several reported studies of the hydrolytic decomposition of organophosphorus compounds promoted by solid supported M(II)-containing catalysts (9–12). In several cases the reactivity of the polymer supported catalyst decreases considerably compared with the activity in solution because of surface and diffusion effects, but in other cases the activity was still acceptable, particularly when the polarity of polymeric matrix was changed (10*b*, 10*c*), the coordination sphere of catalytic complex was modified (10*c*), or a linker was introduced between matrix and catalytic system (9). Nevertheless, all the prior reported studies concentrated on hydrolytic systems where the expected OP products would be acids that may present problems, such as inhibiting the activity of the M(II) through binding of the ionized anionic phosphate or phosphonate. In some cases, such as with the hydrolysis of V-agents, some of the hydrolytic products arise through cleavage of the P-OEt linkage, giving a product that is just as toxic as the starting materials but far more resistant to hydrolysis (1, 2).

Herein we report on the synthesis and analysis of some divinylbenzene (DVB) cross-linked meso- and macro-porous polystyrene resins functionalized with **7a**, **7b**, or 5-amino-1,10-phenanthroline (5-$NH_2$-**8**). After loading the resins with an $M^{2+}$ ion ($Cu^{2+}$ or $Zn^{2+}$), the catalytic activity was determined for the methanolysis of three different OP compounds proposed as simulants for the G-agents (*O*-ethyl-*O*-4-nitrophenyl methylphosphonate (**9**)), the V-agents, (3,5-*O*-ethyl-*S*-3,5-dichlorophenyl methylphosphonothioate (**10**)), and for phosphorothionate pesticides (fenitrothion® (**11**)).

## Experimental

### Materials

Methanol (99.8% anhydr.), DMF (99.8%), sodium methoxide (0.5 mol/L solution in methanol), Cu($CF_3SO_3$)$_2$, Zn($CF_3SO_3$)$_2$, 1,5,9-triazacyclododecane, styrene, 4-(chloromethyl)styrene, divinylbenzene, benzoyl peroxide, boric acid, and sodium hydroxide were purchased from Sigma-Aldrich and used as supplied. THF (extra dry, with molecular sieves, water < 50 ppm) and $HClO_4$ (70% aq. solution) was purchased from Acros Organics and used without further purification. Cellosize, xantham gum, and 5% Pd/C catalyst were purchased from Fluka and *n*-pentanol was purchased from BDH Chemical; these were used as supplied. Merrifield's polymer resin mesoporous (Meso-Ald) (2% crosslinked with DVB, 0.6–0.8 mmol Cl/g, 200–400 mesh) and macroporous (Macro-Ald) (1.2 mmol Cl/g, 100–200 mesh) were purchased from Sigma-Aldrich. PL-CMS MP resin (Macro-PL) (>12% of cross-linking with DVB, 2.8 mmol Cl/g, porosity size 100 Å, particle size 150–300 μm) was purchased from Polymer Laboratories. Fenitrothion (**11**, *O*,*O*-dimethyl *O*-(3-methyl-4-nitrophenyl) phosphorothioate), was a gift from Professors Erwin Buncel and Gary van Loon of this department. *O*-Ethyl-*S*-3,5-dichlorophenylmethylphosphonothioate (**10**) and *O*-ethyl-*O*-4-nitrophenylmethylphosphonate (**9**) were synthesized as reported previously (5*e*, 5*d*).

### Suspension polymerization syntheses of macroporous resins (DVB20, DVB50, and DVB50-hl).

The following procedure was based on the work of Durie et al. (13). An aqueous phase was prepared by dissolving 0.087 g of xantham gum, 0.012 g of Cellosize, and 1.73 g of boric acid in 100 mL of water. This mixture was vigorously stirred to obtain a cloudy solution. Using 20% divinylbenzene cross-linker as an example to make DVB20, the monomer mixture comprised DVB (~80% grade) (1.50 mL, ~20 wt% actual DVB as compared with the other monomers), styrene (4.33 mL), and 4-(chloromethyl)styrene (0.59 mL, ~10% molar ratio with styrene), to which was added benzoyl peroxide (0.080 g) and *n*-pentanol (4.22 mL, ~40 vol% of the entire organic phase). The combined organic phase was added dropwise into the aqueous phase with vigorous stirring. The suspension was then stirred at 80 °C for six hours, cooled, and the polymeric beads were collected by filtration and washed with water (50 mL). The material was washed with methanol (50 mL) and then acetone (50 mL). The yield of polymeric beads was 60% after drying in an oven at 60 °C for 24 h.

### Characterization of porosity

To characterize the porosity of the beads, we followed a procedure reported by Chemin et al. (14) where the volume of porosity and the accessible porous volume for methanol were characterized by a measurement of the apparent density of the polymeric beads in different solvents. Around 2 g of dry polymeric beads were weighed in a tared 50 mL volumetric flask, after which 40 mL of solvent were introduced. For the measurement with hexane, the flask was placed in an ultrasonic bath for 10 min, after which the mixture was allowed to stand for 2 h at room temperature. The volume was adjusted with hexane and the flask was weighed again. This procedure gives an apparent volumetric weight of beads in the given solvent (e.g., hexane, water, and methanol) by using the following formula:

$$[2] \qquad \rho^{s}{}_{a} = \frac{W_{p}}{100-(W_{2}-W_{1})\times \frac{1}{\rho_{s}}}$$

where $W_p$ is the weight of polymer in g, $W_1$ is weight of the flask with beads, $W_2$ is the weight of the flask with the beads filled with the solvent, $\rho_s$ is the density of the solvent, and $\rho^{s}{}_{a}$ is the apparent density of the beads in the solvent (in g/mL). The pore volume ($P\%$) or the accessible porous volume in methanol was calculated with the following equation:

$$[3] \qquad P(\%) = \left(1-\frac{\rho^{w}{}_{a}}{\rho^{s}{}_{a}}\right)\times 100$$

where $\rho^{w}{}_{a}$ is the apparent density of the beads in water in g/mL, and $\rho^{s}{}_{a}$ is the apparent density of the beads in hexane for total pore volume or in methanol for accessible porous volume in methanol.

### 5-Amino-1,10-phenanthroline

5-Amino-1,10-phenanthroline was prepared via a modification of a previously published route (15).

### *N*-benzyl-1,5,9-triazacyclododecane

The title compound was made as described in ref. 16.

### Modification of polymeric resins with 7a or 7b

Commercial Macro-Ald resin (0.50 g, 0.6 mmol of Cl, 1 equiv.) was swelled in 10 mL of THF for 1 h. 1,5,9-Triazacyclododecane (**7a**) (0.12 g, 0.7 mmol, 1.15 equiv.) was added and the mixture was heated at reflux and stirred carefully overnight. The polymer was recovered by filtration and washed with THF (3 × 10 mL) and dried in oven at 60 °C for 24 h.

The modification with the immediate precursor of **7a**, triazatricyclo[7.3.1.0]tridecane (**7b**), was done by the same procedure using the same molar ratios, after which the recovered polymer was subjected to hydrolysis using a solution of 10 mL each of ethanol and water containing 1.07 g of sodium hydroxide heated at reflux overnight to liberate the 1,5,9-triazacyclododecane-functionalized resin. In all cases the final polymer functionalized with **7a** was subsequently treated with a solution of THF–methanol (50:50 *v*/*v*, 20 mL) containing 200 μL of sodium methoxide (0.5 mol/L) for 15 h to remove all traces of acid and residual exposed chloromethyl functionality.

### Modification of polymeric resins with 5-amino-1,10-phenanthroline

Polymer-bound phenanthroline was prepared via a modification of a published route (15). Commercial PL-CMS MP resin (0.824 g, 2.31 mmol of Cl, 1 equiv.) and solid 5-amino-1,10-phenanthroline (0.724 g, 3.71 mmol, 1.6 equiv.) were added to a 100 mL round-bottomed flask equipped with a reflux condenser and a small magnetic stirbar. To the flask was added 50 mL of anhydrous DMF and the mixture was gently stirred, to avoid crushing of the polymer, and heated to reflux. After 1 h of heating, triethylamine (520 μL, 3.7 mmol) was added to the reaction mixture and the mixture was allowed to continue refluxing. An additional 230 μL (1.65 mmol) of triethylamine was added after 24 h of heating and the two phase mixture was left to reflux for another 48 h. After cooling, the polymer was filtered and washed with 20 mL of DMF and 100 mL of methanol. The resin was left to stir gently in boiling DMF for three hours followed by filtration and rinsing with methanol. To remove residual DMF, the polymer was boiled in acetone at 60 °C overnight, collected, filtered, and washed with acetone and then methanol. The functionalized polymer was treated with a 20 mL solution of sodium methoxide (5 mmol/L) in methanol for 15 h to remove any traces of acid and residual exposed chloromethyl functionality.

### Metal complexation of polymer bound ligand

A 0.1 mol/L solution of $M(OTf)_2$ was prepared in methanol and the polymer was immersed in this solution for 4 h after which it was separated by filtration, washed with methanol, and dried in oven at 60 °C for 24 h. A final step placed the material into a basic methanol solution (20 mL of methanol with 200 μL of 0.5 mol/L sodium methoxide) to obtain the active catalytic species of complexed M(II):($^{-}OCH_3$).

### Analysis of the M(II) loading

The metal-loaded polymer (around 0.01 g) was immersed

**Table 1.** Characteristics of functionalized polystyrene resins synthesized and complexed with Copper (II).

| Name | Triaza-precursor | Cl[a] | $M^{(II)b}$ | Total pore volume (mL/g)[c] | Pore volume access $CH_3OH$ (mL/g)[c] |
|---|---|---|---|---|---|
| DVB20 | **7b** | 0.7 | 0.009 (Cu) | 0.4 (0.1) | 0.27 (0.02) |
| DVB50 | **7b** | 0.7 | 0.033 (Cu) | 0.6 (0.1) | 0.49 (0.03) |
| DVB50-hl | **7a** | 3.9 | 0.09 (Cu), 0.11 (Zn) | NA[d] | NA[d] |
| Macro-PL | **7b** | 2.8 | 0.13 (Cu) | 0.8 (0.1) | 0.48 (0.05) |
| Macro-PL-(II) | **7a** | 2.8 | 0.23 (Cu), 0.14 (Zn) | 0.8 (0.1) | 0.48 (0.05) |
| Macro-Ald | **7a** | 1.2 | 0.15 (Cu), 0.02 (Zn) | 0.8 (0.1) | 0.31 (0.05) |
| Meso-Ald | **7b** | 0.7 | 0.014 (Cu) | NA[d] | NA[d] |

[a] Chlorine loading in mmol/g.
[b] Metal ion loading in mmol/g.
[c] Error limits given in brackets.
[d] NA = not available.

in 2 mL of nitric acid solution in methanol (5% *v*/*v*) for 30 min. The methanol solution was carefully decanted away from the polymer, reserved, and the acid wash was repeated with this material four times. The combined methanol washes were stripped of solvent to produce ~0.2 mL of a residue, which was diluted with water in a volumetric flask (25 or 50 mL). The concentration of $M^{2+}$ in this solution was obtained by atomic absorption spectrometry using a Varian Spectra AA-20 Plus spectrometer. The spectrometer was calibrated with known [$M^{2+}$] solutions (0.5–5 ppm for copper, and 0.1–0.5 ppm for zinc).

### Kinetics

All kinetics experiments with the polymers were conducted in 2.5 mL of a methanol solution buffered with *N*-*iso*-propylmorpholine ($6.8 \times 10^{-3}$ mol/L) at ${}^s_s\text{pH} = 9.0 \pm 0.4$. The rates of methanolysis of **9** and **11** (0.03 mmol/L) catalyzed by heterogeneous M(II)-**7** complex (0.08 g to 0.75 g; $1 \times 10^{-3}$ mol/L < [M(II)-**7**] < $30 \times 10^{-3}$ mol/L suspended in the buffered methanol) were followed by monitoring the appearance of *p*-nitrophenol (or 3-methyl-4-nitrophenol) at 312 nm or the disappearance of starting material at 264 nm, using a Cary 100 UV–vis spectrophotometer with the cell compartment thermostatted at 25.0 ± 0.1 °C. The rates of methanolysis of **10** (0.3 mmol/L) were followed by monitoring its disappearance at 253 nm.

Kinetic experiments with the Zn(II) complex of *N*-benzyl-1,5,9-triazacyclododecane (**7c**/Zn(II)) were conducted in methanol under self-buffered conditions where the ligand, $Zn(OTf)_2$, and $NaOCH_3$ were formulated in stock solutions in a 1:1:0.5 molar ratio (${}^s_s\text{pH} = 10$). The kinetics of the methanolysis of phenyl acetate ($1.0 \times 10^{-4}$ mol/L) and **9** ($3.6 \times 10^{-5}$ mol/L) were monitored at 280 and 320 nm, respectively, as a function of $[\mathbf{7c}/\text{Zn(II)}]_{\text{total}}$. The $k_2$ value for the catalyzed methanolysis was determined as twice the gradient of the $k_{\text{obs}}$ vs. $[\mathbf{7c}/\text{Zn(II)}]_{\text{total}}$ plot, the factor of two being introduced because the active form is $[\mathbf{7c}/\text{Zn(II)}{:}^{-}OCH_3]$, which is present at 1/2 the concentration of the total Zn(II) complex.

## Results and discussion

### Functionalized polymer preparation

The chloromethylated polystyrene support matrix was chosen for its desirable (17) physical and chemical properties, which include chemical inertness, structural stability that enables a controllable porosity that ensures accessibility of reagents to the internal catalytic domains, and the $ClCH_2$-functionalities that can be modified to attach various catalytic systems to the matrix. Three different commercial polymers were used in this study, one mesoporous (Meso-Ald) and two macroporous (Macro-Ald and Macro-PL). Macro-PL is defined by its manufacturer as macroporous but has an average size porosity of 10 nm and does not correspond to the IUPAC definition (18) that distinguishes three porous domains: microporosity (<2 nm), mesoporosity (2–50 nm), and macroporosity >50 nm).

Three other polystyrene resins were synthesized in this work by radical suspension polymerization wherein a mixture of monomer and a radical precursor (benzoyl peroxide) was dissolved in a solvent and was finely dispersed in an aqueous phase. Three different monomers in varying proportions were used, styrene and 4-(chloromethyl)styrene to ensure the reactive function of polymer and divinylbenzene to obtain cross-linking of the polymeric matrix. The solvent (pentanol) containing the monomeric phase was used as the porogen (17, 19) because it is known to permit a large porosity (19, 20). During the polymerization process, a phase separation occurs between the growing polymeric chain and the porogenic agent, and the matrix forms around the space where the solvent is occluded creating the porous structure. Two polymers were synthesized, one (DVB20) with 20 wt% of divinylbenzene and another (DVB50) with 50 wt%. In all cases the porogen was introduced to make up 40% of the volume of the organic phase. A third matrix was prepared with the same amount of DVB as for DVB50 but with only 4-(chloromethyl)styrene as the other monomer, to obtain a polymer with high loading (designated as DVB50-hl).

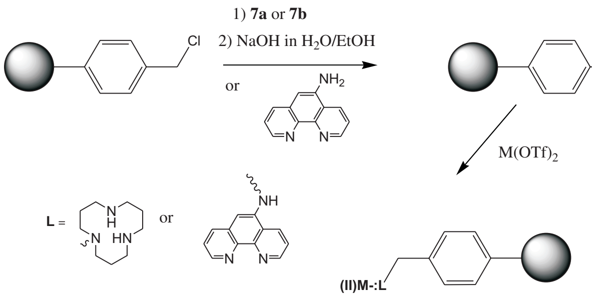
The porosities of the resins were characterized by measuring their apparent densities in different solvents (hexane, water, and methanol). From those values one calculates, from eqs. [2] and [ 3], the volume of total porosity and porous volume accessible to methanol (14). Data are reported in Table 1. The results show slightly higher pore volumes for the commercial polymers than for the synthesized polymers. However, the ratio of this volume to that accessible to methanol is 70%–80% for prepared polymers and somewhat less for the commercial polymers, ~60% for Macro-PL and ~40% for Macro-Ald. This result shows that a majority of pores are not accessible to methanol in Macro-Ald. For

**Table 2.** Apparent second-order rate constants of the complex **8**/$Zn^{2+}$ in solution and of different polymer resins functionalized with **8**/$Zn^{2+}$, determined at ${}^{s}_{s}$pH = 9 in methanol, buffered with *N-iso*-propylmorpholine, $T$ = 25 °C, [**10**] = $3 \times 10^{-4}$ mol/L, and [**9**] = [**11**] = $3 \times 10^{-5}$ mol/L.

| Polymer | $M^{(II)-}$ loading (mmol/g) | $k_2$ (**10**) ($(mol/L)^{-1}s^{-1}$) | $k_2$ (**9**) ($(mol/L)^{-1}s^{-1}$) |
|---|---|---|---|
| DVB50-hl **8**/$Zn^{2+}$ | 0.065 | 0.49 | 0.31 |
| Macro-PL **8**/$Zn^{2+}$ | 0.035 | 1.17 | 0.80 |
| Macro-PL-(II) **8**/$Zn^{2+}$ | 0.098 | 11.75 | 0.61 |

**Note:** Error limits considered to be ±20%, based on the errors in the determination of metal loading and uncertainties in the duplicate rate measurements.

**Fig. 1.** Scheme of the modification of polystyrene resins.



Macro-PL, the advertised pore size is 10 nm but the porosity for Macro-Ald, although not specified, seems to be smaller according to the criteria here.

All the polymeric matrices were functionalized by nucleophilic substitution of the benzylic chloride by 1,5,9-triazacyclododecane (**7a**) or its immediate precursor triazatricyclo[7.3.1.0]tridecane (**7b**) as shown in Fig. 1.

Using **7b**, the polymer must then be subjected to base catalyzed hydrolysis with sodium hydroxide in water–ethanol, to obtain the 1,5,9-triazacyclododecane functionalized polymer. Once functionalized, all the polymers are treated with a sodium methoxide THF–methanol solution to deprotonate the highly basic triazacyclododecane and to react with any residual benzylic chloride that might affect the future characteristics of the material. The subsequent steps involve the $M^{2+}$ loading ($Cu^{2+}$ or $Zn^{2+}$), wherein the polymeric matrix was immersed in an 0.1 mol/L $M(OTf)_2$ solution in methanol. In the case of copper, the loading is visually characterized for the **7a** functionalized polymer by an immediate green-blue colouring of the solid, which remained so after a final washing with methanol.

The $M^{2+}$ loading was quantified by immersing a known quantity of the resin in a known volume of a 5% solution of nitric acid in methanol, which protonates the ligand and releases metal ion into the solution, as judged by the loss of colour of the solid in the case of copper. The solution was then analyzed by atomic absorption spectroscopy and the results are presented in Table 1. The data show that, in all cases, there is an incomplete conversion of chloride into metal complex. The best result was obtained with Macro-Ald with a conversion of 13% of the available chloride. The low conversion likely stems from the fact that some of the Cl is buried inside the polymer in sites inaccessible to the triaza ligand although the functionalization was done in THF, which is known to swell polystyrene appreciably. Since the metallation step was done in the nonswelling solvent methanol, it is possible that some of the ligand sites could not be accessed, which could also contribute to the relatively low amount of $Cu^{2+}$ on the polymer. In fact, we have chosen to do the metallation under nonswelling conditions as this is the medium where all the subsequent catalytic reactions are performed, and the metal ion loading was determined under non-swelling conditions in aqueous acid. Another possibility for some materials is a difference in reactivity of **7a** and its precursor **7b**, since it is generally observed that materials prepared with the latter always have a slightly lower $Cu^{2+}$ loading. Indeed, the only difference between Macro-PL and Macro-PL-(II), where the polymeric matrix is the same for each, is the triazacyclododecane precursor, which is **7b** for Macro-PL and **7a** for Macro-PL-(II). It could be that there is a higher reactivity with the more flexible **7a** relative to **7b** or that the hydrolysis step required for the latter in ethanol–water is not very efficient because of the low affinity between polystyrene resin and this solvent mixture. As a final note, we observed that the polymers prepared for this study have much lower conversion of chloride into the $Cu^{2+}$-loaded resin (<3%) relative to the commercial resins. This is possibly due to the high level of cross-linking, since it is known (21) that a higher level decreases the reactivity of functional groups on a rigid polymeric backbone.

The modification of polymeric resins with 5-amino-1,10-phenanthroline was done following a published procedure (15). The loading of zinc after this modification was low (see Table 2) with 0.035 mmol/g compared with 0.14 mmol/g for zinc loading to Macro-PL-(II) functionalized with **7a**. Subsequently we changed the functionalizing solvent to DMF, in which the 5-amino-1,10-phenanthroline is more soluble than in dioxane. The solvent change increased the loading about three-fold, giving a loading of ~0.1 mmol/g, which is close to that found with **7a**.

## Catalytic studies

Study of the catalytic activity of the materials was conducted by determining the rate of change in the UV–vis absorbance for loss of substrate and formation of product in methanol solutions containing known amounts of the solid resins. Polymer (0.05 g to 0.75 g) was put into 2.5 mL of methanol solution buffered by *N-iso*-propylmorpholine ($6.8 \times 10^{-3}$ mol/L) at ${}^{s}_{s}$pH ~ 9 (the range of ${}^{s}_{s}$pH values is between 8.6 and 9.8) (22), which is slightly above neutrality (${}^{s}_{s}$pH = 8.4 (22)). For practical reasons owing to the high absorptivities of the turbid media, the heterogeneous mixtures were not stirred continuously; rather, the cell was shaken every 2 to 5 min and the particles were allowed to settle prior to measurement of

**Table 3.** Apparent second-order rate constants of the complex **7a**/$M^{2+}$ in solution and of different polymer resins functionalized with **7a**/$M^{2+}$, determined at $^{s}_{s}\mathrm{pH} = 9$ in methanol, buffered with *N-iso*-propylmorpholine, $T = 25$ °C, [**10**] = $3 \times 10^{-4}$ mol/L, and [**9**] = [**11**] = $3 \times 10^{-5}$ mol/L.

| Catalyst | $k_2$ (**10**) ($(\mathrm{mol/L})^{-1}\mathrm{s}^{-1}$) | $k_2$ (**9**) ($(\mathrm{mol/L})^{-1}\mathrm{s}^{-1}$) | $k_2$ (**11**) ($(\mathrm{mol/L})^{-1}\mathrm{s}^{-1}$) |
|---|---|---|---|
| $^{-}OCH_3$ | 2.17[a] | 2.7[b] | $(7.2 \pm 0.2) \times 10^{-4}$ [b] |
| **7a**/$Cu^{2+}$ [c] | — | 243[b] | 12.2 [b] |
| DVB20 **7a**/$Cu^{2+}$ | 3 | 0.18 | 0.05 |
| DVB50 **7a**/$Cu^{2+}$ | 3.1 | 0.07 | 0.02 |
| DVB50-hl **7a**/$Cu^{2+}$ | — | 0.17 | 0.04 |
| Macro-PL **7a**/$Cu^{2+}$ | 0.47 | 0.02 | 0.005 |
| Macro-PL-(II) **7a**/$Cu^{2+}$ | — | 0.14 | 0.05 |
| Macro-Ald **7a**/$Cu^{2+}$ | 0.21 | 0.017 | 0.006 |
| Meso-Ald **7a**/$Cu^{2+}$ | 0.17 | 0.005 | 0.0003 |
| **7a**/$Zn^{2+}$ [d] | 95.2 | 46.8 | — |
| DVB50-hl **7a**/$Zn^{2+}$ | 0.95 | 0.33 | — |
| Macro-PL-(II) **7a**/$Zn^{2+}$ | 0.38 | 0.09 | — |
| Macro-Ald **7a**/$Zn^{2+}$ | 0.2 | 0.015 | — |

**Note:** Error limits considered to be ±20%, based on the errors in the determination of metal loading and uncertainties in the duplicate rate measurements.

[a] Ref. 7.

[b] Ref. 5*c*.

[c] $M^{2+}$ complex of 1,5,9-triazacyclododecane in methanol.

[d] Ref. 5*d*.

the absorbance. In an attempt to quantify the amount of $M^{2+}$ in the solution, the known amount of the heterogeneous resin was converted to concentrations as if it were completely dissolved (this is termed [bound $M^{2+}$]). Under this assumption, the metal concentration varied between 1 and 30 mmol/L, while those of the substrates were 0.3 mmol/L for **10** and 0.03 mmol/L for **9** and **11**. Under these conditions, the change in absorbance followed good first-order behaviour, and the pseudo first-order rate constants, $k_{\mathrm{obs}}$, were evaluated by fitting the Abs. vs. time curves to a standard exponential model. The apparent second-order rate constants were evaluated as $k_{\mathrm{obs}}$/[bound $M^{2+}$] and are given in Table 3 for material with **7a**/$M^{2+}$ and in Table 2 for **8**/$Zn^{2+}$. Control experiments showed that in all but one case the rate constant obtained did not depend upon the frequency of shaking the mixture. This suggests that for these cases the overall catalytic process is not limited by transport through solution, although it might be limited by transport through the polymer or across the phase boundaries. On the other hand, we do have one case where there is a dependence of the reaction rate on the frequency of shaking for methanolysis of **9** in the presence of a relatively large amount (0.32 g) of Macro-PL-(II) **8**/$Zn^{2+}$. The kinetic results for the rate of disappearance of **9** and appearance of *p*-nitrophenol at $^{s}_{s}\mathrm{pH} = 8.52$ (6.5 mmol/L *N-iso*propyl morpholine) shown in Table 4 indicate that the rate constants for each process increase with the frequency of shaking, although in all cases the rate for liberation of product is slower by roughly a factor of two than the rate of disappearance of **9**. This is consistent with a process where the reaction rate is partially limited by the diffusion of the substrate into the polymer and more so by the chemical step of methanolysis to form *p*-nitrophenol and (or) its diffusion out of the polymer.

To demonstrate that the polymers are truly catalytically active, an experiment with an excess of substrate was done with 5.2 mg of Macro-PL-(II) **7a**/$Cu^{2+}$ in 2.5 mL of methanol solution buffered by *N-iso*-propylmorpholine (6.8 mmol/L) at $^{s}_{s}\mathrm{pH} = 8.8$ in presence of **9** at 1 mmol/L. In that case, the pseudo concentration of copper was 0.48 mmol/L and the Abs vs. time curve showed a complete loss of starting material with a $k_{\mathrm{obs}}$ value of 0.0083 $\mathrm{min}^{-1}$, which corresponds to a second order rate constant of 0.28 $(\mathrm{mol/L})^{-1}\mathrm{s}^{-1}$.

**Table 4.** Dependence of the pseudo first-order rate constants for the disappearance of **9** (0.03 mmol/L) and appearance of *p*-nitrophenol mediated by 0.32 g of Macro-PL-(II) **8**/$Zn^{2+}$ on the frequency of

| Frequency of shaking | $k_{\mathrm{obs}}$ for the loss of **9** ($\mathrm{s}^{-1}$) | $k_{\mathrm{obs}}$ for the appearance of *p*-nitrophenol ($\mathrm{s}^{-1}$) |
|---|---|---|
| 30 s | 0.011 | 0.0045 |
| 60 s | 0.009 | 0.0038 |
| 120 s | 0.007 | 0.0032 |

In the cases of the commercial macroporous polymers, and most prominently with Macro-Ald functionalized with **7a**/$Cu^{2+}$ and **7a**/$Zn^{2+}$, a less than expected amount of product phenol was observed during the reaction of **9** and **11**, along with a complete disappearance of starting material, although analysis of the Abs vs. time curves for each gave the same value of $k_{\mathrm{obs}}$. This suggests that the starting material is at equilibrium with respect to partitioning into the polymer and the rate-limiting step is the chemical one of cleavage, but the product partitions between the solution and the polymer phase.

Where comparisons can be made, and using the pseudo $M^{2+}$ concentrations for the catalysts as described earlier, none of the functionalized polymers have second-order rate constants approaching those of the free **7a**/$M^{2+}$ catalysts in solution. This is a commonly observed phenomenon with polymeric catalysts and probably stems from a diminution of mobility in the solid catalytic systems, which impedes diffusion of substrate to the reactive sites. It is also possible that since the polymer supports described here require N-benzylated 1,5,9-triazacyclododecanes, that these are far more sterically hindered than **7a**/$M^{2+}$. Indeed, a recent report (23) indicates that the methanolysis of the carboxylate ester phenyl acetate promoted by **7c**/Zn(II):$^{-}OCH_3$ proceeds with a second-order rate constant of 0.046 $(mol/L)^{-1}s^{-1}$, which is fully 300 times slower than what is reported for the methanolysis of phenyl acetate by **7a**/Zn(II):$^{-}OCH_3$ (13.9 $(mol/L)^{-1}s^{-1}$ (24)). Our own repetition of the catalysis of methanolysis of phenyl acetate promoted by **7c**/Zn(II):$^{-}OCH_3$ indicates that the second-order rate constant is 4.0 ± 0.2 $(mol/L)^{-1}s^{-1}$, which is only a factor of three less than that reported for **7a**/Zn(II):$^{-}OCH_3$, which suggests that there is some anomalous error in the recently reported value (23). A similarly small steric effect of 2.5 fold is also evident in the second-order rate constant for the methanolysis of **9** exhibited by **7c**/Zn(II):$^{-}OCH_3$ (18.2 ± 0.2 $(mol/L)^{-1}s^{-1}$) relative to that of **7a**/Zn(II):$^{-}OCH_3$ (46.8 ± 0.5 $(mol/L)^{-1}s^{-1}$ (5*c*).

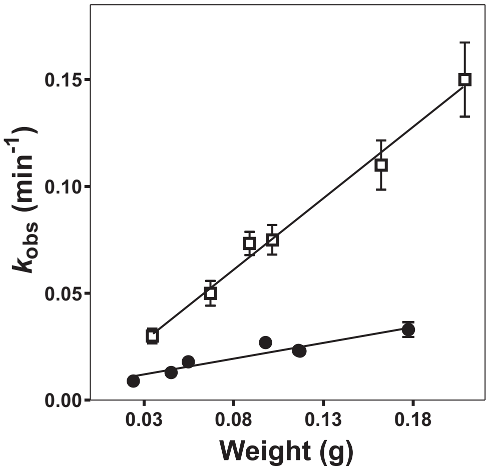
It therefore seems reasonable to ascribe the reduced activity of these functionalized polymers relative to the solution catalysts to surface effects with the polymers that impeded the mobility of the substrate in reaching the active sites. Nevertheless, the catalysts supported on these resins do accelerate appreciably the methanolysis of all the substrates compared with the background $^{-}OCH_3$-promoted reaction at the ${}^{s}_{s}pH$ where the catalyzed reactions are conducted. For example, the acceleration of the methanolysis of fenitrothion (**11**), mediated by the catalyst at an apparent concentration of 1 mmol/L (0.028 g of DVB50-(II) **7a**/$Cu^{2+}$ suspended in 2.5 mL of solution) is a factor of 2.9 × $10^6$ greater at ${}^{s}_{s}pH = 9$.

In the case of the polymers containing **8**/$Zn^{2+}$, the $k_2$ values are higher than those obtained with **7a**/$M^{2+}$ (see Tables 2 and 3). Previously we have found that the solution reactions of phenanthroline/$M^{2+}$ complexes are slower than with the triazamacrocycle/$M^{2+}$ complexes because of the fact that the former are inactivated by dimerization and must dissociate to the active monomeric forms (7, 25). However, the dimerization is minimized or precluded on the polymers so the phenanthroline grafted resins now become more active than their triazamacrocycle grafted comparisons (see Macro-PL-(II) **8**/$Zn^{2+}$ and Macro-PL-(II) **7a**/$Zn^{2+}$ entries in Tables 2 and 3).

As shown in Fig. 2, a plot of the pseudo first-order rate constant for the methanolysis of **9** at ${}^{s}_{s}pH = 8.7$ as a function of weight of added Macro-PL-(II)**7a**/$Cu^{2+}$ or **7a**/$Zn^{2+}$ polymer is linear, indicating there is no saturation phenomenon such as was observed with a previously reported (9) catalyst and the substrate diphenyl *p*-nitrophenyl phosphate in aqueous solution. The same linear dependence was observed with the **8**/$Zn^{2+}$-functionalized polymer except at high weight, where the reaction rate depends on the frequency of shaking.

There are other subtle differences observed between the phenanthroline and triazamacrocycle grafted complexes. In the case of **8**/$Zn^{2+}$ grafts on the Macro-PL polymer, stronger absorption of the phenol products is initially observed relative to the **7a**/$M^{2+}$ material. However, after several reactions with the same **8**/$Zn^{2+}$-grafted polymer, the appearance of phenol in the solution is more pronounced. Control experiments establish that the absorbance of a solution of *p*-nitrophenol decreases in the presence of fresh polymer functionalized with **8**/$Zn^{2+}$. These observations confirm that phenol does partition between the polymer and solution, but that after several reactions the polymer eventually becomes saturated with the product.

**Fig. 2.** Pseudo first-order rate constant, $k_{obs}$, for the methanolysis of **9** mediated by **7a**/$Cu^{2+}$ (□) and **7a**/$Zn^{2+}$ (●) functionalized Macro-PL-(II) vs. weight of the polymer at ${}^{s}_{s}pH = 8.7$, $T$ = 25 °C.



## Reuse of polymer catalysts

Except in the case of the methanolysis of substrate **10**, the activity of most of the polymeric catalysts showed good stability over several catalytic cycles. With substrate **9**, the second-order rate constant of 0.1 g of Macro-PL-(II) **7a**-$Cu^{2+}$ ($[Cu^{2+}]$ = 9.20 mmol/L) is stable 0.14 ± 0.02 $(mol/L)^{-1}s^{-1}$ over 10 consecutive experiments. Similar experiments conducted with Macro-PL(II) $Zn^{2+}$/**7a** polymers showed a large inconsistency in reactivity between cycles (a complete cycle comprises the reaction to completion, followed by filtration, washing of the recovered polymer with 50 mL of methanol, and drying in air overnight). However, it was observed that the Macro-PL(II) $Zn^{2+}$-loaded polymers do recover complete reactivity when they are allowed to stand in the *N-iso*-propylmorpholine buffer solution for more than 12 h after a cycle. This phenomenon is tentatively attributed to an interaction between $CO_2$ and $Zn^{2+}$/**7a** complex in the air, which reversibly inhibits the catalyst. This decrease of reactivity is not observed with material functionalized with **8**/$Zn^{2+}$.

As a further check to see that any loss in acitivty was not due to the loss of metal ion through subsequent reactions, we have reanalyzed the polymers for metal ion content following at least three cycles. For example, Macro-Ald 7a/$Cu^{2+}$ and Macro-Ald 7a/$Zn^{2+}$, after at least three cycles reacting with **9**, showed an analytical $Cu^{2+}$ loading of 0.17 and 0.15 mmol/g before and after use, while the $Zn^{2+}$ loading was 0.023 and 0.020 mmol/g before and after use. While the absolute numbers seem to show some decrease after use, the fact that the catalytic activity is unchanged with **9** over prolonged reuse suggests that the analytical numbers are the same within experimental uncertainty.

**Table 5.** Apparent second-order rate constants for different polymer resins functionalized with **7a**/$M^{2+}$ or **8**/$Zn^{2+}$, determined at ${}_{s}^{s}\mathrm{pH}$ = 8.9 in methanol buffered with *N*-*iso*-propylmorpholine, $T$ = 25 °C, [**10**] = 3 × $10^{-4}$ mol/L.

| Polymer | $k_2$ (**10**), 1st exp. ((mol/L)$^{-1}$s$^{-1}$) | $k_2$ (**10**), 2nd exp. ((mol/L)$^{-1}$s$^{-1}$) |
|---|---|---|
| DVB5**0** **7a**/$Cu^{2+}$ | 3.1 | 0.36 |
| Macro-Ald **7a**/$Cu^{2+}$ | 0.22 | No reaction |
| Meso-Ald **7a**/$Cu^{2+}$ | 0.17 | 0.011 |
| Macro-Ald **7a**/$Zn^{2+}$ | 0.20 | 0.18 |
| DVB50-hl **8**/$Zn^{2+}$ | 0.49 | 0.49 |

However, in the case of *O*-ethyl-*S*-3,5-dichlorophenyl methylphosphonothioate (**10**) the results given in Table 5 with DVB20 and DVB50 show that the reactivity of the supported Cu((II) catalysts decreases with each cycle. For example, with [**10**] = 0.3 mmol/L, DVB5**0** **7a**/$Cu^{2+}$ exhibits a $k_2$ = 3.1 (mol/L)$^{-1}$s$^{-1}$ for its first cycle and 0.36 (mol/L)$^{-1}$s$^{-1}$ for the second cycle. This drop of reactivity is also accompanied by a change of the blue-green color of the solid to yellow, suggesting that the active Cu(II) form of the metal ion was reduced to Cu(I). Monitoring the reaction of 0.3 mmol/L **10** at 253 nm shows that the starting material disappears, but none of the thiolate product, which should absorb strongly at 270 nm, is observed to appear, Fig. 3). This observation, coupled with the loss of activity of the catalyst suggests that the thiolate product is absorbed by the catalyst and oxidized to the disulfide with concomitant reduction of the Cu(II) to Cu(I) and loss of activity. Although it seems counterintuitive that the small amount of S-containing substrate could inactivate all the Cu(II) through reduction, it is possible that there exists a variety of Cu-containing sites that have variable accessibility, with the most available and reactive ones being inactivated first.

For the $Zn^{2+}$ catalysts, a redox reaction between metal and thiolate cannot happen, and as shown in Table 5 there is no loss of reactivity observed for complex with **7a** and **8**.

## Influence of water

Experiments to determine the effect of 2% of added water on the reactivity of the polymers in methanol were conducted in the presence of *N*-*iso*-propylmorpholine buffer (6.8 mmol/L) at ${}_{s}^{s}\mathrm{pH}$ = 8.9. The results over 10 cycles (defined earlier) for the reaction of **9** mediated by 50 mg of Macro-PL-(II) **8**/$Zn^{2+}$ ([$Zn^{2+}$] = 1.96 mmol/L) are reported graphically in Fig. 4.

The first reaction is a reference one for the reaction using substrate **9** without water, after which the 2% water was added to the UV cell for all the subsequent reactions. As can be judged from the appearance of Fig. 4, water continually degrades the activity until it reaches a stable value of 0.03 min$^{-1}$ after the **9** runs, corresponding to a loss of 85% of the initial reactivity.

## General comments on activities

Comparison of the kinetic reactivities given in Table 3 suggests a general order of reactivity of Meso-Ald < Macro-Ald < Macro-PL < Macr-PL-hl ≈ synthesized polymers. The difference in reactivity between mesoporous and macroporous commercial polymers shows the importance of porosity in the activity of these supported catalysts. Since the polystyrene matrices used here as support materials do not swell in methanol solvent during the $M^{2+}$-complexation steps, the mesoporous polymers have the accessible catalytic sites present only on the surface of beads. It is known (21) that catalytically active polymers having an increased pore size allow an increased permeation of reagent and substrate into the beads, effectively increasing the local concentration of accessible catalyst. The activities of the synthetic resins made here are around 10 times better than the commercial polystyrenes, which is probably due, at least in part, to an increase in their pore size relative to the commercial macroporous polymers. However, the accessibility is not the only parameter that explains the difference of reactivity. The concentration of catalytic sites relative to the surface area is also important. The rather small bead size of the synthesized polymers and their higher loading gives a higher concentration of catalytic species on the surface. This is demonstrated by the difference in reactivity observed between Macro-PL

**Fig. 3.** UV spectra for the disappearance of **10** (at 0.3 mmol/L) catalyzed by DVB50-(II) **7a**/$Cu^{2+}$ ([$Cu^{2+}$] = 6.8 mmol/L) at ${}_{s}^{s}\mathrm{pH}$ = 9.1.

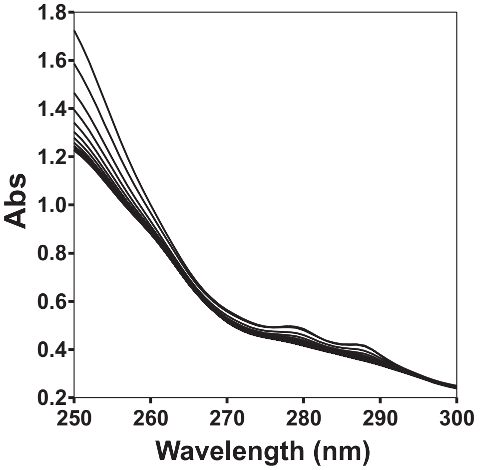


**Fig. 4.** Pseudo first-order rate constant, $k_{obs}$, for the methanolysis of **9** (10 cycles each with 0.03 mmol/L) with functionalized Macro-PL-(II) **8**/$Zn^{2+}$ (50 mg) at ${}_{s}^{s}\mathrm{pH}$ = 8.9 in presence of 2% *v*:*v* of water.

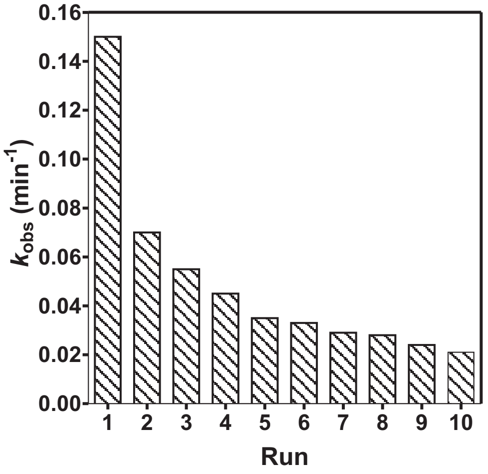


**Fig. 5.** Continuous flow system of total volume 1.5 mL, with polymer in the column represented as the shaded rectangle, a flow through UV cell, and a peristaltic pump to drive the solution at a flow rate of 1.17 mL/min.

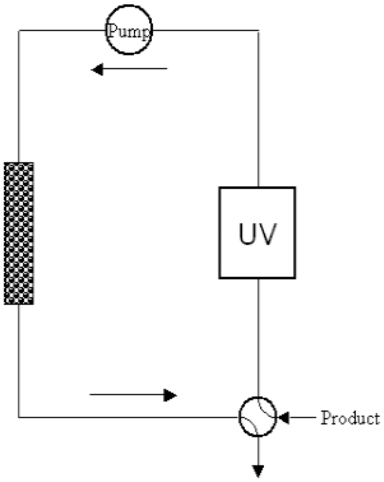


**Fig. 6.** Absorbance vs. time curves for the disappearance of **9** (0.03 mmol/L) (▲, absorbance at 275 nm) catalyzed by 0.113 g of functionalized Macro-PL **7a**/$Cu^{2+}$ and for the appearance of *p*-nitrophenol (■, absorbance at 310 nm) at $^{s}_{s}\mathrm{pH} = 8.8$.

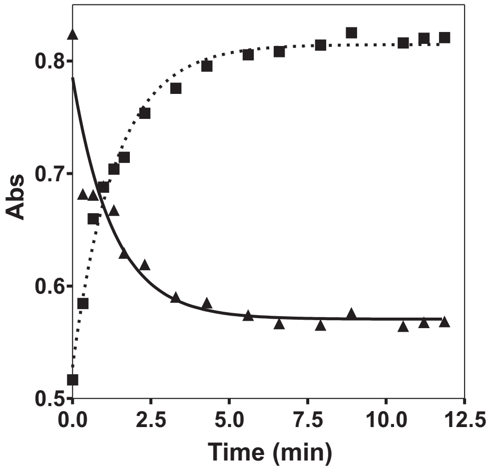
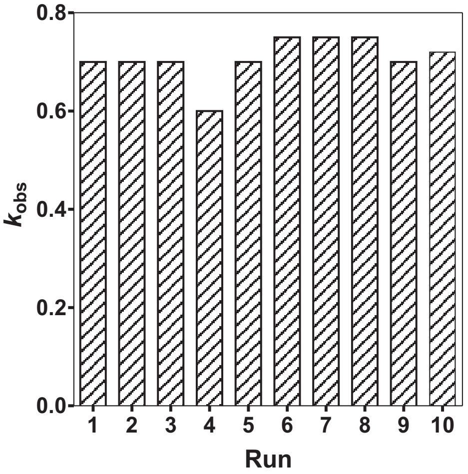


**Fig. 7.** Pseudo first-order rate constant, $k_{obs}$, for the methanolysis of **9** (at 0.03 mmol/L) with Macro-PL-(II) $Cu^{2+}$/**7a** (0.1130g) in a column at a flow rate of 1.17 mL/min at $^{s}_{s}\mathrm{pH} = 8.8$.



**7**/$Cu^{2+}$ and Macro-PL-(II) **7**/$Cu^{2+}$ for which the matrices are the same, but the loading of Macro-PL-(II) is higher by a factor 2 (see Table 1). The main difference between those materials is the surface concentration of $Cu^{2+}$, but the rate constant for the reaction with **9** and **11** vary by factors of 7 and 10 respectively. The increase of reactivity in the case of higher $Cu^{2+}$ concentration on the surface is consistent with a cooperative effect between two neighboring metal ions.

### Column system

The most efficient materials made with polystyrene resin purchased from Polymer Laboratories (PL-CMS MP resin) were used in an improvised column system. This system, as illustrated in Fig. 5, consists of a variable-flow low-flow peristaltic pump connected to a column (i.d. 3.0 mm, length 50 mm, from Chrom Tech), which was filled with about ~0.1 g of the polymer support, and an injection valve (Chrom Tech, OM-1114) permitting the injection of a known volume of methanol containing the OP substrate.

Also included in the system is a UV–vis flow cell that allows monitoring of the absorbance vs. time profile of the circulating solution. The total volume of the circulating system is around 1.5 mL. A solution containing the OP substrate was introduced through the system and the valve was closed to permit continuous circulation. Shown in Fig. 6 is the kinetic curve of disappearance of **9** catalyzed by functionalized Macro-PL **7**/$Cu^{2+}$ (0.1130 g) with a rate flow of 1.17 mL $min^{-1}$.

Both absorbance vs. time curves can be fitted by NLLSQ fitting to a first-order kinetics model giving a pseudo first-order rate constant of 0.72 ± 0.05 $min^{-1}$. In general for this circulating system, the data do not exactly follow a first-order profile because of the fact that they have stairlike profile, where each step corresponds to one cycle of the system. In the case of the data in Fig. 6, the reaction appears to be done after three cycles through the polymeric support.

As shown in Fig. 7, the reaction of phosphonate **9** with Macro-PL-(II) **7a**/$Cu^{2+}$ has the same rate constant over 10 different injections of 0.03 mmol/L OP solution. The same stability was observed for **11** with Macro-PL-(II) **7a**/$Cu^{2+}$, and **9** and **10** with Macro-PL-(II) **7a**/$Zn^{2+}$.

To demonstrate turnover of the catalyst on the polymer, an experiment monitoring the decomposition of an excess of substrate was conducted wherein 25 mL of methanol solution containing $1.2 \times 10^{-2}$ mmol of **9** was circulated through a column (i.d. 3.0 mm, length 25 mm) containing 46.6 mg of Macro-PL-(II) **8**-$Zn^{2+}$ (total amount of $Zn^{2+}$ was $4.6 \times 10^{-3}$ mmol). The observed rate constant for the disappearance of the substrate was 0.002 ± 0.0007 $min^{-1}$, corresponding to a rather large half-time of 5.75 h. However, under these conditions the volume of the column containing the active polymer was only 0.175 mL, and since the flow rate was 0.29 mL/min, the great bulk of the substrate was not in contact with the polymer. These data indicate that the polymer is capable of destroying an excess of substrate, surviving prolonged contact with the reacting system and suggest that far greater efficacy would be possible with large columns in circulating systems, where the ratio of the column volume to total circulating volume is maximized.

## Conclusion

In this work we have shown that polymer-supported metal and (or) complex catalysts can be prepared by grafting a ligand (**7a** or **8**) onto a suitable chloromethylated polystyrene resin, which can then be loaded with $M^{2+}$ ($Cu^{2+}$ or $Zn^{2+}$). This catalytic matrix shows good activity for mediating the methanolysis of different kinds of OP esters like *O*-ethyl-*S*-3,5-dichlorophenyl methylphosphonothioate (**10**), *O*-ethyl-*O*-4-nitrophenyl methylphosphonate (**9**), and fenitrothion (**11**), which are simulants for V-agents, G-agents, and P=S pesticides. In the most favourable case, 28 mg of DVB50-(II) **7a**/$Cu^{2+}$ suspended in 2.5 mL of solution provides a factor of $2.9 \times 10^6$ in acceleration of the methanolysis of fenitrothion over the background reaction at ${}^{s}_{s}$pH = 9. The methanolysis reactivity is shown to be enhanced by a large porosity of the solids, which allows access of the OP ester substrates to the catalytic centers. This material can be used in column systems with a continuous flow and may show some promise for larger scale applications to cleanups of OP esters, where the contaminants can be dissolved in methanol that is passed through a column for decontamination.

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