

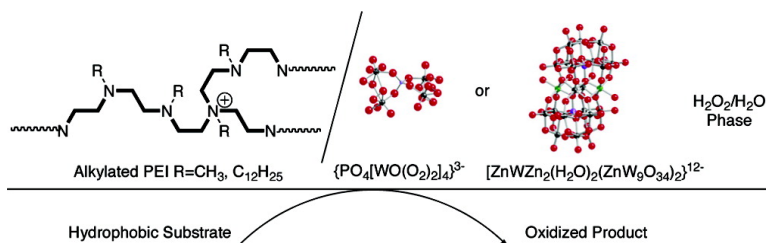
Communication

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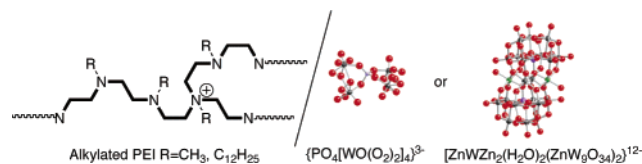
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Aqueous biphasic catalysis in the absence of organic solvent has potential for environmentally benign synthesis.¹ The technique, while attractive, has limitations such as reduced reaction rates because of slow mass transfer of the hydrophobic organic substrate to the aqueous catalyst phase and the requisite synthesis of water-soluble ligands for the organometallic catalysts. Mass transfer to the aqueous phase may be facilitated by addition of amphiphiles. Thus, reaction rates may be increased by formation of micelles,² (micro)emulsions,³ and other stabilized biphasic systems. The field of biomimetic catalysis using water-soluble catalysts also presents intriguing possibilities for aqueous biphasic catalysis. One example is the use of cyclodextrins as extracting agents for organic substrates into an aqueous phase.⁴ Recently, we have shown that certain water-soluble polyanionic polyoxometalates (POMs), with known catalytic properties in the activation of hydrogen peroxide,⁵ can be used in aqueous biphasic catalysis for oxidation of alcohols, diols, and amines.⁶ The systems were largely inactive for aqueous biphasic oxidation of hydrophobic substrates such as alkenes.⁷ In the context of this research, water-soluble randomly alkylated polyethylenimines have been shown to have properties that are enzyme-like (synzymes) for general acid–base catalytic reactions.⁸ Now, we show that POMs can be electrostatically bonded to quaternary ammonium sites of the alkylated polyethyleneimine (Alk-PEI). These new alkylated polyethyleneimine/polyoxometalate (Alk-PEI/POM) synzymes (Scheme 1) also have hydrophobic regions enabling the solubilization or binding of hydrophobic substrates and therefore are active catalysts for the selective oxidation of such substrates in water.

Scheme 1. Components of the Alk-PEI/POM Synzyme



Polyethyleneimine ($M_w \approx 10\,000$) was alkylated with a mixture of 1-iodododecane and iodomethane at a ratio $\text{CH}_2\text{CH}_2\text{NH}/\text{C}_{12}\text{H}_{25}\text{I}/\text{CH}_3\text{I} = 10.5:1:7.4$ in a literature-adapted procedure.^{8e,9} From the reaction yield and XPS measurements (see below), an $\sim 95\%$ efficiency in the alkylation reaction and $\sim 50\%$ formation of quaternary ammonium centers can be determined; Alk-PEI has an $M_w \approx 20\,000$. Under these random alkylation conditions, the purified Alk-PEI was first analyzed by a ^{15}N – ^1H HMBC experiment (Figure 1). One can see that for PEI (Figure 1, left) the methylene protons correlate with two different types of nitrogen atoms. Logically, primary amines are observed at 9–11 ppm (^{15}N),

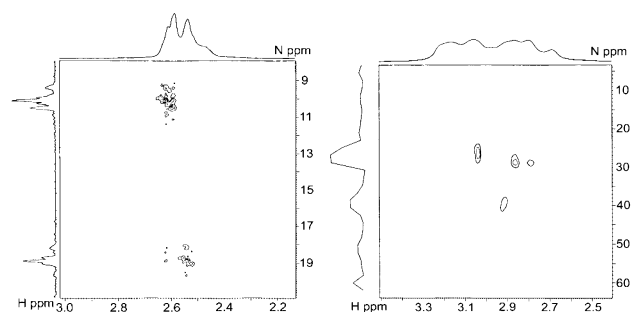


Figure 1. ^{15}N – ^1H HMBC NMR experiment for PEI (left) and Alk-PEI (right).

and secondary amines are observed at 18–20 ppm (^{15}N). From the spectrum for Alk-PEI (Figure 1, right), it is clear that 1° and 2° amines in the original PEI have been alkylated. The peaks at 25–30 ppm (^{15}N) may be assigned to tertiary amines, and the peak at ~ 40 ppm (^{15}N) may be assigned to quaternary ammonium moieties.¹⁰

Further analysis of Alk-PEI by the XPS (Figure 2) showed a nitrogen 1s line for the tertiary amine moieties at a binding energy of 398.7 eV and nitrogen 1s lines for the quaternary ammonium moieties at 401.0 and 401.8 eV.^{9,11} Measurement of the peak areas reveals that approximately 50% of the nitrogen atoms are at quaternary ammonium centers.

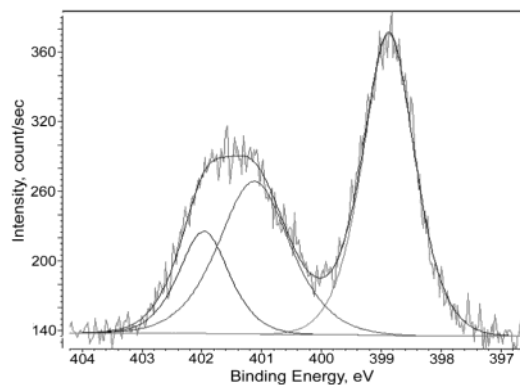


Figure 2. XPS N (1s) line for Alk-PEI. Solid lines are curve fits of data.

The hydrophobicity of Alk-PEI versus the unmodified PEI polymer was estimated by measuring the contact angle on a goniometer. For unmodified PEI, the contact angle was $11 \pm 4^\circ$, indicating a very hydrophilic compound. On the other hand, the contact angle for alkylated PEI was $30 \pm 5^\circ$, indicating a more hydrophobic material. Since Alk-PEI remained water-soluble, one may assume that there are indeed hydrophobic regions in the synzyme. This hypothesis was further tested by measurement of the fluorescence spectra of 3-aminopyrene, a hydrophobic probe,

[†] Department of Organic Chemistry.

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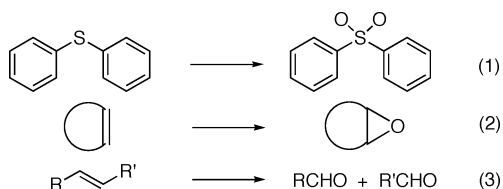
Table 1. Oxidation of Exemplary Substrates Catalyzed by Alk-PEI/POM^a

| substrate | catalyst | conversion mol % ^b | products ^c |
|----------------------------|-----------|----------------------------------|--|
| diphenylsulfide | Alk-PEI/A | 98 (8) | diphenylsulfoxide/sulfone ^d |
| cyclooctene | Alk-PEI/A | 99 (7) | cyclooctene oxide |
| cyclododecene | Alk-PEI/A | 99 (4) | cyclododecene oxide |
| styrene | Alk-PEI/B | 96 (0) | benzaldehyde ^e |
| methyl oleate ^f | Alk-PEI/B | 97 (0) | nonanal, methyl 9-oxononanoate |

^a Reaction conditions: (1) with Alk-PEI/A (A = Na₁₂[ZnWZn₂(H₂O)₂-(ZnW₉O₃₄)₂]); 6.1 mg of Alk-PEI, 1 μmol Na₁₂[ZnWZn₂(H₂O)₂(ZnW₉O₃₄)₂], 0.2 mL of H₂O, 0.5 mmol substrate, 2 mmol H₂O₂ (60% aq), 22 °C, 9 h. (2) with Alk-PEI/B (B = Na₃{PO₄[WO(O₂)₂]₄} formed in situ);¹⁴ 6.1 mg of Alk-PEI, 0.2 mmol substrate, 8.0 μmol Na₂WO₄, 10.0 μmol H₃PO₄, 2.0 mmol H₂O₂ (60% aq), 22 °C, 24 h. After the reaction, organic components were collected by phase separation; analysis was by GC and GC-MS using an external standard. ^b The results in parentheses are for reactions with PEI instead of Alk-PEI. With POM or Alk-PEI only there were no reactions. ^c The products given are the only ones obtained unless otherwise noted. ^d 72% Ph₂SO₂, 28% Ph₂SO. ^e 3% styrene oxide. ^f 70 °C.

solubilized in a water solution of Alk-PEI. 3-Aminopyrene (0.5 μM) has an emission peak at λ_{max} = 441 nm in water. Dissolution of 3-aminopyrene (0.5 μM) in aqueous PEI (3.8 mM) showed no shift in the fluorescence spectrum. On the other hand, dissolution of 3-aminopyrene (0.5 μM) in aqueous Alk-PEI (3.8 mM) resulted in a blue-shifted spectrum, λ_{max} = 433 nm. This hypsochromic shift, Δλ = 8 nm, shows that the probe is dissolved in a hydrophobic region of the Alk-PEI. The same hypsochromic shift was observed upon dissolution of 3-aminopyrene in cetyltrimethylammonium-based micelles,¹² lending credence to a hypothesis that Alk-PEI in water has a structure reminiscent of an enzyme with hydrophobic regions and a hydrophilic surface. It should be noted that in Alk-PEI there was no formation of micelles, as evidenced by the lack of light scattering, measured at 300–450 nm, at concentrations ranging from 0.1 to 250 mM Alk-PEI.¹³

The utility of Alk-PEI/POM synzymes for oxidation in water at room temperature with hydrogen peroxide was tested using several very hydrophobic, water-insoluble substrates. Reactions tested included (a) the oxidation of diphenylsulfide (eq 1) and the epoxidation of cyclooctene and cyclooctene (eq 2), both catalyzed by Alk-PEI/[ZnWZn₂(H₂O)₂(ZnW₉O₃₄)₂]¹², and (b) the selective oxidative carbon–carbon bond cleavage of styrene and methyl oleate to the corresponding aldehydes (eq 3) catalyzed by Alk-PEI/{PO₄[WO(O₂)₂]₄}³⁻.



The results show (Table 1) that reactions in the presence of Alk-PEI and the polyoxometalate catalyst were practically quantitative and highly selective to the products indicated, whereas in the presence of unmodified PEI the conversions were negligible, especially in the case of the alkene bond cleavage oxidation. Especially notable is the selective formation of aldehydes in the oxidative carbon–carbon bond cleavage reaction, since normally such bond cleavage with hydrogen peroxide requires more drastic reaction conditions that mostly lead to formation of carboxylic acids rather than aldehydes.¹⁵ In this case, possibly due to the intrinsic high acidity of Alk-PEI,⁸ there was carbon–carbon bond cleavage

with no significant formation of carboxylic acids by autoxidation reactions. Recycling of the Alk-PEI/POM catalysts is straightforward. After the completion of a reaction and removal of the products by liquid–liquid phase separation, a new amount of substrate and oxidant is added. In this way, cyclododecene was oxidized thrice by Alk-PEI/A without apparent loss of activity.

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- (9) PEI (*M_w* ≈ 10 000, 5.4 g, 0.126 mol CH₂CH₂NH) was reacted with C₁₂H₂₅I (3.1 mL, 0.0126 mol) in the presence of diisopropylethylamine (35 mL) and EtOH (130 mL) at reflux for 4 h. CH₃I (5.5 mL, 0.088 mol) was added dropwise and then refluxed for 17 h. Volatiles were removed by vacuum evaporation, and low molecular weight components were removed by dialysis (12 h): 50% EtOH in 50 mM HCl (×3), 20% EtOH in 50 mM HCl (×3), 10% EtOH in 50 mM HCl (×3), 50 mM HCl (×3), water (×3). The Alk-PEI obtained, 10.2 g, was dried by lyophilization.
- (10) The ¹⁵N-¹H HMBC and XPS experiments show several types of tertiary and quaternary amine species, respectively. This is probably due to primary formation of such moieties by alkylation with iododecane and iodomethane and some additional formation of such moieties during the purification process (dialysis in the presence of HCl).
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