



## Poly(propylene imine) dendrimer complexes as catalysts for oxidation of alkenes

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### ARTICLE INFO

#### Article history:

Received 17 November 2008

Received in revised form 21 April 2009

Accepted 7 May 2009

Available online 12 May 2009

#### Keywords:

Poly(propylene imine) dendrimers

Metal complexes

Organic hydroperoxides

Oxidation

### ABSTRACT

Complexes of poly(propylene imine) dendrimers D8[DAB-dendr-(NH<sub>2</sub>)<sub>8</sub>] and D32 [DAB-dendr-(NH<sub>2</sub>)<sub>32</sub>] were prepared by interaction of the dendrimers with transition metal salts such as FeCl<sub>2</sub>·6H<sub>2</sub>O; CoCl<sub>2</sub>·6H<sub>2</sub>O; CuCl<sub>2</sub>·2H<sub>2</sub>O; VOSO<sub>4</sub>·5H<sub>2</sub>O; Na<sub>2</sub>MoO<sub>4</sub>·2H<sub>2</sub>O and Na<sub>2</sub>WO<sub>4</sub>·2H<sub>2</sub>O at room temperature in aqueous solutions. The content of metal ions in the complexes was found to be from 8.2 to 69.6 mg metal ion/g polymer carrier. The complexes were characterized by using IR, UV–VIS, Moessbauer spectroscopy and EPR. The anticipated co-ordination structure of the compounds was suggested. It was found that the order of the catalytic activity of the complexes of poly(propylene imine) dendrimers D8 and D32 in the reaction of epoxidation of cyclohexene with organic hydroperoxides such as *tert*-butyl hydroperoxide (*t*-BHP), ethylbenzene hydroperoxide (EBHP) and cumene hydroperoxide (CHP) was as follows: D32-MoO<sub>4</sub><sup>2+</sup> > D32-VO<sub>2</sub><sup>2+</sup> > D32-WO<sub>4</sub><sup>2+</sup> > D32-Co<sup>2+</sup> > D32-Cu<sup>2+</sup> > D32-Fe<sup>3+</sup>. The order of reactivity of organic hydroperoxides in the reaction studied was: *t*-BHP > EBHP > CHP.

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## 1. Introduction

Dendrimers are a special class of polymers, and the studies of their synthesis and properties started in the last two decades. The interest towards this type of materials is continuously increasing and, until the past few years, the attention of the researchers was focused mainly on the synthesis of new generations of dendrimers with new structures. Recently, much effort has been devoted to the search of fields of possible application for these new materials. These interesting polymers were proved to be useful as participants in the preparation of homogeneous and heterogeneous catalysts. They are also expected to be useful in conducting some chemical and biological studies, as well as in gene therapy.

DAB poly(propylene imine) dendrimers were first synthesized by Meijer and de Brabander-Van den Berg back in 1993. The dendrimer box fragment of Meijer was used to demonstrate the possibility for selective encapsulation of small molecular units within the dendrimer space [1]. In a number of publications, the designers of DAB dendrimers such as Meijer and coauthors [2–5] studied the structure and properties of DAB, containing 2, 4, 8, 16, 32 and 64 end amino group functionalities. The preparation and electron paramagnetic parameters of a series of five generation nitroxyl-functionalized poly(propylene imino) dendrimers DAB-dendr (NH<sub>2</sub>)<sub>n</sub>, where *n* = 2, 4, 8, 16, 32 and 64 with 3-carboxy-2,2,5,5-tetramethyl-1-pyrrolidinyloxy radicals end groups, was described in other publications [2,3]. In further studies [4,5], Meijer and coauthors examined and analyzed in detail the nano-structural features of the first five generation of poly(propylene imine) dendrimers with 4–64 end groups. Carboxylate-type functionalized poly(propylene imine) dendrimers were synthesized and

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their behavior under the conditions of protonation, effected by potentiometric titration was studied [6].

General analysis of the structure, physical and chemical properties and the possible use of the dendrimers was published in the review of Meijer and co-authors [7].

Dendrimers are well-known as polymer materials with an application in the macromolecular chemistry, nano-science, biology and medicine [8]. The introduction of metal ions in the dendrimers is conducted for two principal purposes, namely, their application as structuring and non-structuring elements [9]. The metal–dendrimer complexes are known to catalyze various organic reactions. On the contrary, attempts for ionic bonding and its impact on the use of these materials have only been mentioned in the scientific literature. Some authors [10] have reported on new series of metal–dendrimer complexes based on ionic bonding between dendric polyammonium polycations and oxomethalates as well as their use as renewable catalysts in oxidation reactions. Typical vanadyl derivatives of poly(amido amine) dendrimers (PAMAM)-thiourea dendrimers were obtained, as reported in [11]. The authors studied the molecular dynamics of the vanadyl–chelate complexes covalently bound to the surface of cascade polymers–dendrimers. There are publications on Au complexes of dendrimers [12], as well as small organophosphine dendrimers containing palladium that participate in the electrochemical reduction of  $\text{CO}_2$  [13]. Other authors [14] have also obtained Au-containing dendrimer nano-composites by laser irradiation. The dendrimers were supposed to adsorb nano-particles in a monolayer. Metal complexes of the dendrimers were also used as catalysts for reduction of 4-nitrophenol [14]. Complexes of transition metal ions (Cu(II), Zn(II) or Ni(II)) of different generations of DAB, well defined as tridentant ligands were used to form nano-sized elements with certain structure and size, involving defined number of metal ions, more specifically from 2 to 32 end groups [15]. The relatively high local concentration of metal ions along the periphery did not hamper the formation of complexes until the full conversion was reached. This was an indication for the high degree of arrangement of these dendrimers at molecular level. The use of these metal-containing dendrimers as catalysts is currently subject of continuous scientific efforts. The use of dendrimers as carriers of active centers has also been discussed by Newcove [16] and Van Heerbeek [17]. The catalytically active centers attached to the dendrimers surface can be easily accessed by the substrate. The main shape of these highly branched structures is spherical and the atoms are confined within this space. The latest studies on dendrimers showed that many of the advantages cited above can be practically realized. Ford and coworkers [18–20] have published a number of papers, associated with their studies on poly(propylene imine) dendrimers and their derivatives. In one of these works [18], they investigated the polymerization of styrene in aqueous dispersion of dodecanamide derivatives and sodium dodecylsulphate, to observe the stabilization of the latex particles. The metal complexes of the DAB dendrimers with Cu (II), Zn (II) and Co (III) were prepared, studied and used as catalysts in the hydrolysis of *p*-nitrophenil diphenyl phosphate and bis-*p*-nitrophenyl diphenyl phosphate [19,20]. Other

researchers [21] have also reported on poly(propylene imine) dendrimers of different generation such as DAB-dendr-[ $\text{NH}_2$ ]<sub>4</sub> and DAB-dendr-[ $\text{NH}_2$ ]<sub>64</sub> and studied their behavior as polyelectrolytes by potentiometric titration with 0.1 N HCl. Studies on the catalytic activity of temperature-sensitive dendrite sets have been described [22].

Iron complexes of dendrimer-appended carboxylates for activating dioxygen and oxidizing hydrocarbons were prepared by Fréchet and coworkers [23]. This dendron compound, in the present in dioxygen, can oxidize external substrates such a bacterial monooxygenases. Fréchet and coworkers [24] described the immobilization of catalytic groups onto a dendritic support either at the core or at the periphery. In their review, the appearance of positive dendrimer effects from the literature will be highlighted as well as prospects for future work in the field [24].

Twyman et al. [25] were obtained a series of hyper-branched polymers when applied as epoxidation catalysts. These polymers were used as mimics for cytochrome P450, which is an enzyme responsible for a variety of biological oxidation reactions. Recently Crooks et al. have published the results about Pt dendrimer complexes on the base of poly(amidoamine) dendrimers. The authors were investigated the effect of particle size on the kinetics of the oxygen reduction reactions [26].

Therefore, poly(propylene imine) dendrimers are interesting materials for the polymer chemistry, due to the versatility of their properties, which determines their possible application in biomedical research, design of gene systems, vectors for controlled release of pharmaceutical substances and carriers of catalytically active centers.

The aim of the present work was to prepare new metal-immobilized complexes, based on dendrimers such as poly(propylene imine) D8 and D32, and to study their catalytic activity for the oxidation of alkenes with organic hydroperoxides.

## 2. Experimental

### 2.1. Materials and reagents

The poly(propylene imine) dendrimers D8 [DAB-dendr-( $\text{NH}_2$ )<sub>8</sub>] and D32 [DAB-dendr-( $\text{NH}_2$ )<sub>32</sub>] with 8 and 32 primary amine end groups were purchased from DSM (Netherlands) and were employed as starting polymeric materials. All other reagents such as  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ ,  $\text{VOSO}_4 \cdot 5\text{H}_2\text{O}$ ,  $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ ,  $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ ,  $\text{HNO}_3$ , alkenes (1-hexene, 1-heptene, 1-octene), cycloalkenes (cyclohexene, cyclopentene, cyclooctene), cumene hydroperoxide (CHP), and *tert*-butylhydroperoxide (*t*-BHP) from Fluka (Switzerland), glacial  $\text{CH}_3\text{COOH}$ , KI,  $\text{Na}_2\text{S}_2\text{O}_3$ , and starch from Chimsnab (Bulgaria) were of analytical grade and were used as received. *t*-BHP was purified prior to use by vacuum distillation at  $\sim 5$  mm Hg and  $\sim 296$  K under  $\text{N}_2$ .

Toluene and ethylbenzene were a products of Lukoil Neftochim, Burgas (Bulgaria) 2,4,4-trimethyl-2-pentene was purchased from Janssen Chimica, Beerse (Belgium). Toluene was purified through a method described in the literature [27]. Ethylbenzene hydroperoxide was obtained by oxidation of ethylbenzene, followed by isolation of the

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