



New amphiphilic poly(quaternary ammonium) dendrimer catalyst for effective reduction of citronellal

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ABSTRACT

Three types of new amphiphilic poly(quaternary ammonium) dendrimer catalysts were prepared from poly(propylene imine) generation-2 (PPI-G2) dendrimer with 3 types of alkyl halides having varied chain length. The C–H stretching at 2922 and 2853 cm^{-1} and C–N⁺ stretching at 1108 cm^{-1} confirmed the attachment of alkyl chains and generation of poly(quaternary ammonium) ions at the dendrimer surface. Their ¹H and ¹³C NMR spectra also supported such confirmations. The hydrophobicity of these 3 poly(quaternary ammonium) based dendrimer catalysts was determined by the static water contact angle (θ). The catalyst derived from attachment of long alkyl chain viz., PPI-G2-(C₁₆H₃₃)₁₆ (CH₃)₈-N⁺Cl⁻ showed an increased contact angle (77.5°) thus proving high hydrophobicity. Their catalytic activity was evaluated through reduction of citronellal under pseudo-first order condition at ambient temperature. The rate constant (k_{obs}), of the catalyst containing medium length alkyl chain viz., PPI-G2-(C₁₂H₂₅)₁₆ (CH₃)₈-N⁺Cl⁻ was higher than those containing short and long alkyl chains due to its well-balanced amphiphilic character. It gave 100% selectivity/activity compared to commercial single-site phase transfer catalyst for citronellal reduction. The effect of [substrate], [catalyst], [NaOH], and [NaBH₄] on the rate of the reaction was studied and the results were discussed.

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1. Introduction

A significant and recurring problem in organic synthesis is caused by water-soluble reagents used for the chemical modification of water-insoluble organic substrates. For instance, if the synthesis was performed in two-phase heterogeneous process e.g., an organic-aqueous phase reaction, the rate of the reaction was usually very low due to (a) mass transfer limitations, (b) the concentration of the reactants at the interface and (c) where the reaction occurs [1]. So far, a number of methods have already been suggested to exclude this problem. These include rapid stirring, addition of co-solvents, surfactants and phase transfer catalysts. Of the various methods, phase transfer catalysis (PTC) is especially interesting because of the lower energy and downstream processing costs. Dendrimers are a new class of polymeric material that has generated much interest in diverse areas due to their unique structure and properties. Their unique structural features include highly branched and well-defined structure, globular shape, and controlled surface functionalities that make dendrimers as smart materials.

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Dendrimer by itself is an excellent catalyst for easy conversion of poly (electrolyte)/phase transfer catalyst to conduct the biphasic reaction [2,3]. Amphiphilic dendritic polymers can behave as unimolecular micelles that retain their colloidal structures regardless of concentration, ionic strength, and temperature of the solution. Polar end groups make them soluble in water, and their less polar cores and branching units can solvate hydrophobic molecules [4]. These unique properties may enable applications in the areas of molecular encapsulation, membrane transport, dispersibility of carbon nanotubes (CNT) via functionalization, and catalysis [5–7]. In addition, an increased yield for classical phase-transfer catalysis reactions could be obtained using quaternary ammonium dendrimers as catalysts. The ever increasing demand for speciality chemicals has raised the selective hydrogenation of α,β -unsaturated aldehydes to one of the current challenges to be tackled both from the fundamental and from the industrial standpoints [8]. Citronellal (3,7-dimethyl-6-octen-1-al) is a conjugated unsaturated aldehyde and its corresponding unsaturated alcohol is citronellol (3,7-dimethyl-6-octen-1-ol). They are essential components in many kinds of perfumes and the manufacture of them is profitable [9–11]. Due to the presence of C=C and C=O bonds, the chemo selective reduction of citronellal is a challenging task. A lot of work has been published on the hydrogenation of citronellal using mono/bimetallic nanoparticle supported catalysts [12–14]. However, these methods do not give 100% selectivity for