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Synthesis of Click Bile Acid Polymers and Their Application in Stabilization of Silver Nanoparticles Showing Iodide Sensing Property

Anjul Kumar, Rajesh K. Chhatra, and Pramod S. Pandey*

Department of Chemistry, Indian Institute of Technology Delhi, Hauz Khas,
New Delhi 110016, India

pramod@chemistry.iitd.ac.in

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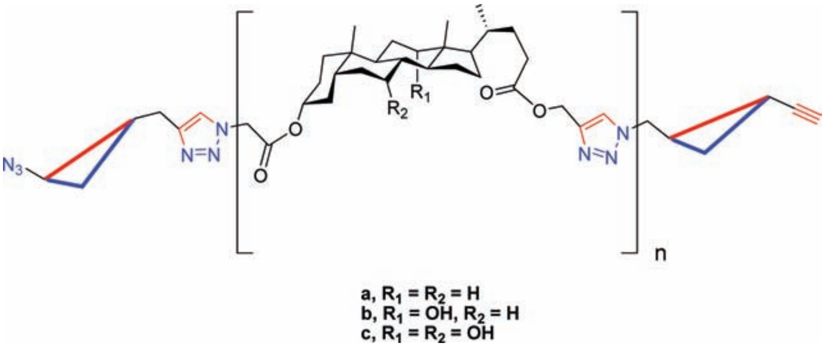
ABSTRACT



A novel method for the synthesis of bile-acid-based polymers has been developed using click chemistry. These 1,2,3-triazole-containing polymers have been found to stabilize silver nanoparticles that show selective colorimetric sensing for iodide ion.

Bile acids and their derivatives have received much attention in the recent past for their supramolecular and pharmacological applications.[1] The amphiphilicity, rigidity, and biocompatibility of bile acids make them potential building blocks for the design of polymeric materials for biomedical applications. Consequently, various kinds of bile-acid-based polymers with bile acids as pendent groups and as core or end groups have been synthesized via polycondensation, radical polymerization and atom transfer radical polymerization.[2] However, only a few reports are available describing the synthesis of main-chain bile-acid-based polymers.[3] Recently, Gautrot and Zhu have reported the synthesis of polyesters with bile acids in the main chain via entropy-driven ring-opening polymerization using Grubbs catalyst.[4]

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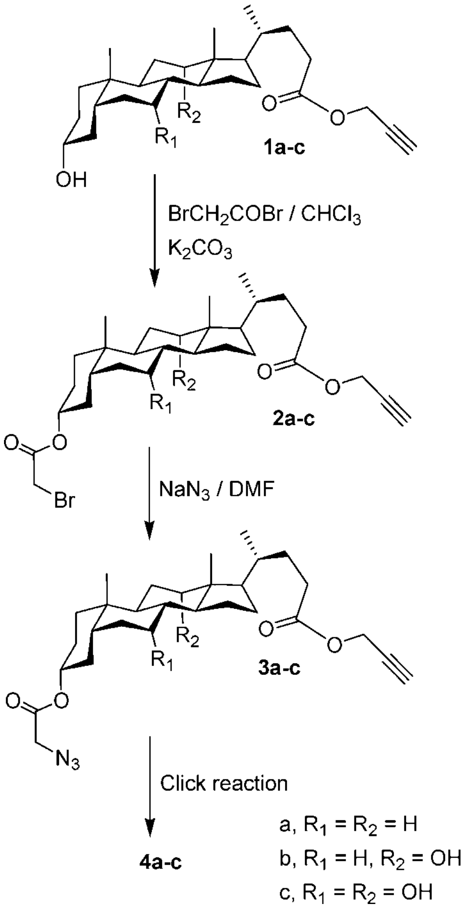
Scheme 1



The Cu(I)-catalyzed click reaction[5] involving 1,3-dipolar cycloaddition reaction between an azide and a terminal alkyne has been extensively used for the synthesis of linear, star-like, and hyperbranched polymers.[6] However, to our knowledge, no attempt has been made toward the synthesis of bile-acid-based polymers using click chemistry.

Herein, we report an efficient and economical synthesis of main-chain bile-acid-based polymers **4a−c** using Cu(I)-catalyzed 1,3-dipolar cycloaddition reactions of monomers having both azide and alkyne functionalities in the same molecule.

The synthesis of transition metal nanoparticles is a promising area because of their potential applications in catalysis, medicine, and supramolecular chemistry.[7] Recently, metal nanoparticle-based sensing of ions has received considerable attention, because it shows much enhanced sensitivity and provides their fast colorimetric detection even at low concentration.[8] Most of these studies have been focused on the detection of metal ions using gold nanoparticles. More recently, silver nanoparticles have gained attraction in regard to their application in detection of metal ions.[8l,m] However, colorimetric detection of anions through metal nanoparticles has not received much attention.[9] As there is growing interest in the design of sensors for the selective detection of anions because of their biological, medicinal, and environmental significance, it is important to develop efficient and selective colorimetric sensors for anions.

We have found that the 1,2,3-triazole-linked bile-acid-based polymers **4a−c** have excellent ability to stabilize silver nanoparticles. Astruc and co-workers have earlier used 1,2,3-triazole-based dendrimers to form Pd and Au nanoparticles.[10] Interestingly, these silver nanoparticles show a distinct colorimetric sensing of iodide ions. Very few reports are available on colorimetric sensing of this biologically important anion.[11]

Bile-acid-based polymers **4a−c** were synthesized as described in Scheme 1. For this, the propargyl esters of bile acids **1a−c** were synthesized by reactions of bile acids with propargyl alcohol in the presence of PTSA.[12] Then, their monobromoacetyl derivatives **2a−c** were prepared by the treatment of propargyl esters with 1 equiv of bromoacetyl bromide at 0 °C in the presence of K_2CO_3 in chloroform, in good yields. **2a−c** on treatment with sodium azide in DMF gave the corresponding monomer units **3a−c** containing both alkyne and azide functionalities. The click reaction of

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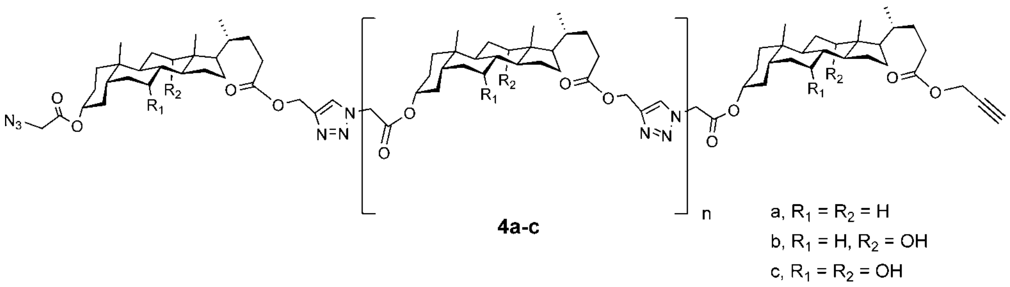

Figure 1. Bile acid polymers **4a**−**c**.

Table 1. Physical Properties of Polymers **4a**−**c**

polymer	M_w	M_n	PDI	T_g (°C)	n^a
4a	96688	74557	1.29	108	194
4b	69244	55026	1.25	117	134
4c	33580	26724	1.25	130	63

[a] Average number of monomers.

monomers **3a**−**c** in *t*-BuOH/H_2O (10:1) in the presence of $CuSO_4$ (10 mol %) and sodium ascorbate (20 mol %) gave polymers **4a**−**c** (Figure 1) with low polydispersity and high molecular weight (Table 1).[13]

We synthesized the silver nanoparticles by reduction of $AgNO_3$ by visible light[14] in the presence of bile acid polymers. To synthesize silver nanoparticles, 1 mL (100 μM) solution of $AgNO_3$ in $CHCl_3$/MeOH (7:3) was added to the 1 mL (100 μM, based on monomer unit) solution of the polymer in $CHCl_3$/MeOH (7:3) and the solution was exposed to visible light. The solution turned dark yellow within 15 min, which indicated the formation of silver nanoparticles. The presence of triazole-linked polymers is essential for the formation of Ag nanoparticles as without them there was no change in the color of the solution even after prolonged exposure to the visible light. The UV−vis spectrum showed a broadband at 415 nm for the polymer-stabilized AgNPs. The transmission electron microscopy (TEM) data confirmed the formation of the silver nanoparticles of 4.0−4.2 nm average size (Figure 2).

The recognition property of these polymer-stabilized silver nanoparticles toward various anions such as HSO_4^-, $H_2PO_4^-$, OAc^-, I^-, Br^-, Cl^-, and F^- was studied by addition of their tetrabutylammoniun salts (2.5 mM) to the solution of polymer-stabilized AgNPs (1 mL). In only the case of iodide ion, the color of the solution became colorless within 1 min as a result of aggregation of AgNPs (see Supporting Information for the TEM image). The minimum concentra-

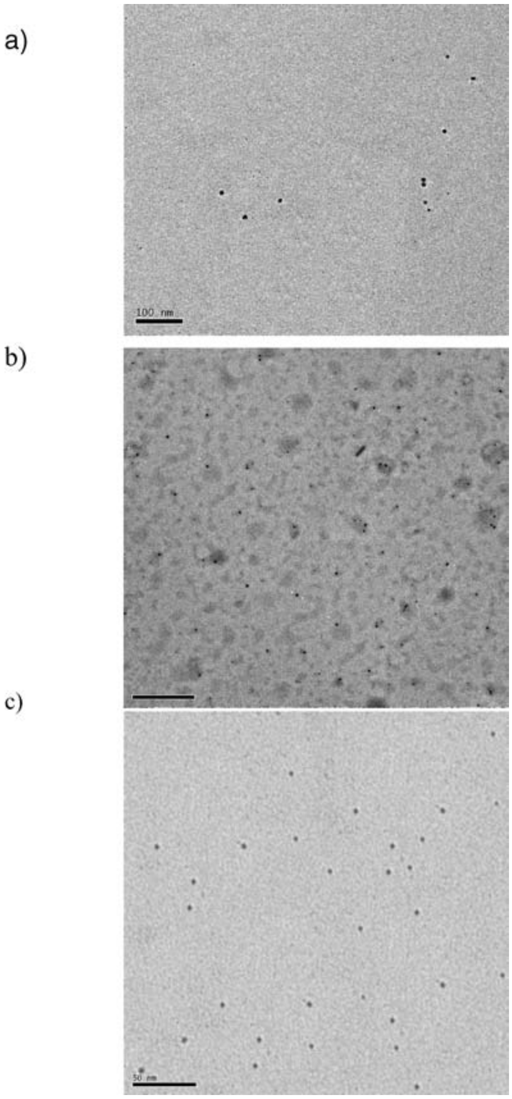

Figure 2. (a) TEM image of AgNPs (4.2 ± 1.5 nm) stabilized with polymer **4a**; scale bar, 100 nm. (b) TEM image of AgNPs (4.1 ± 1.2 nm) stabilized with polymer **4b**; scale bar, 100 nm. (c) TEM image of AgNPs (4.0 ± 0.9 nm) stabilized with polymer **4c**; scale bar, 50 nm.

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(13) **General Procedure for the Synthesis of Polymers 4a**−**c**. To a solution of **3a** or **3b** (0.1 mmol) or **3c** (0.7 mmol) in 35 mL of *t*-BuOH was added $CuSO_4{\cdot}5H_2O$ (10 mol %) and sodium ascorbate (20 mol %) in 3.0 mL of H_2O. The solution was stirred at 60 °C for 20 h. The solution was evaporated under vacuum. The residue was washed with ethyl acetate to remove the starting material and low molecular weight oligomers. The residue was then dissolved in $CHCl_3$ (20 mL) and passed through a silica gel column. The organic layer was dried over Na_2SO_4 and evaporated under vacuum to give **4a** (81%), **4b** (67%), or **4c** (55%).

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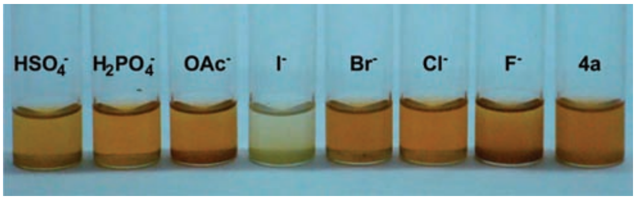

Figure 3. Photograph of the solutions containing the mixture of polymer **4a** stabilized AgNPs with different anions. Ion concentration of HSO_4^-, $H_2PO_4^-$, OAc^-, Br^-, Cl^-, and F^- is 2.5 mM; $[I^-] = 500\ \mu M$.

tion of iodide ions detectable by the color change was found to be 250 μM. Iodide ions induce the color change even in the presence of other anions. Thus, these polymer-AgNPs are highly selective for the colorimetric detection of the iodide ion.

In summary, we have synthesized main-chain bile-acid-based polymers using click chemistry involving Cu(I)-catalyzed azide−alkyne 1,3-dipolar cycloaddition. These polymers display remarkable ability to stabilize silver nanoparticles that show selective colorimetric sensing for the iodide ion.

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Supporting Information Available: Experimental details, characterization data, and GPC chromatograms for polymers. This material is available free of charge via the Internet at http://pubs.acs.org.

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