Abstract

Nucleophilic substitutions of the reactive chlorine atoms in either cyanuric or phosphonitrilic chloride by the bridging 4,4'-bipyridine, 1,4-phenylenediamine or benzidine units lead to the formation of two- (2-D) or three-dimensional (3-D) covalent networks, according to the spatial arrangement of the chlorine atoms in each particular triazine core.\textsuperscript{1,2} The materials are electrochemically active and stable, and exhibit interesting optical properties. Due to the inherited ion exchange properties and variable interlayer spacing upon incorporation of various anions, the 2-D and 3-D ionic networks can be regarded as the organic analogues of conventional inorganic layered or zeolitic ion-exchangers respectively. Interestingly, the phosphonitrilic derivative assembles in hollow cornet-like structures as evidenced by both SEM and TEM analysis, notably without the use of extra hard or soft templates, and its surface, active, amine units can be employed for the one-step redox synthesis of silver cations towards the synthesis of ultra small silver nanoparticles (10-40 nm). The silver nanoparticles are attached and finely dispersed on the surface of the cornet-like polymer and inherit the composite with very high antimicrobial activity as tested in various bacterial strains and yeasts. The loading in silver nanoparticles is relatively high (~30 % wt) without the formation of agglomerates the later due to the mild conditions and the targeted synthetic route without the use any extra reducing agents.

1. POLYMER NANOCOMPOSITES WITH NOBLE METALS WITHOUT THE USE OF EXTRA REDUCING AGENTS

Many different approaches have been employed for the synthesis of silver/polymer nanocomposites and they may involve the one-step reduction of silver cations through functional sites of the polymer chains \textsuperscript{1a} instead of reduction with well known but harsh reducing agents, like NaBH\textsubscript{4}. In general these procedures can be divided in two different categories:

- Firstly, those that involve the use of silver cations as initiators of the polymerization
- Secondly, the polymer itself plays the role of the reduction agent.

The use of silver cations as oxidizing agents and initiators of polymerization in polymer chemistry is well known, particularly in the field of conductive polymers, such as pyrrole, aniline \textsuperscript{1} or even rhodanine. \textsuperscript{2} Herein silver cations acts as oxidizer and initiators and are simultaneously reduced to metallic nanoparticles.

The basic advantages of these reactions are the absence of extra reduction agents, the mild conditions of reaction and the targeted synthesis of nanoparticles that results in better dispersion of silver nanoparticles inside
the polymer matrix. Consequently the polymers play a multiple role; they act not only as reducing agents but also as stabilizers, templates, or protecting agents against agglomeration.

Polymers with functional groups may enable the reduction of cations and the simultaneous entrapment of the nanoparticles on the surface of the polymers. For example, pure and alkylated linear poly(ethyleneimine) (PEIs) have been reported to act as both reductants and stabilizers to prepare metallic nanoparticles. [3]

Among other polymer matrices that have been used for the synthesis of silver/polymer composites with antibacterial activity are common plastic or even hydrophilic tecophilic polymers [4-6], crosslinked poly(acrylamide)/poly(N-(hydroxymethyl)acrylamide) (PAAm-PHMAAm) or other hydrogel networks [7] as well as carboxymethylcellulose biopolymers or polysaccharides. [8-9]

2. TRIAZINE BASED POLYMERIC NETWORKS AND NOBLE METAL NANOCOMPOSITES

Triazine molecules appear to be of significant importance in the construction of supramolecular organic networks with widespread applications [10-11]. Recently, we have developed layered 2-D and porous 3-D polymeric networks based on a triazine central core, cyanuric chloride and phosphonitrilic chloride respectively, and bridging aromatic diamines that act as ligands after nucleophilic substitution of the reactive chlorine atoms. [12].

Different morphologies and orientations of the polymer chains are obtained according to the spatial arrangement of the substitution sites in the two different triazine core. The optical absorptions spectra are showing various absorptions in the visible region and they can be altered upon electrochemical or chemical oxidation.

Cyclotriphosphazenes are versatile tools for the construction of various complex structures upon substitution of the reactive chlorine atoms with organic molecules [13]. Herein the employed aromatic diamines are leading the network to expand in interesting hollow or cubic morphologies depending on the reaction conditions and the length of the aromatic reactant [14]. Interestingly the active amine units of the polymer can serve as reductant and matrix for the synthesis of silver nanoparticles without the use of any extra reducing agents [14].

LITERATURE REFERENCES


