



The performance of modified nanoclay using polymeric thiol surfactants assembled on gold nanoparticles in heterogeneous bulk polymerization of methyl methacrylate



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ABSTRACT

The performances of nanoclay, fabricated nanogold on nanoclay and modified nanoclay with assembled polymeric thiol surfactants on nanogold, were studied as heterogeneous catalysts in the bulk polymerization of methyl methacrylate (at 80 °C, for 5 h in inert (N₂) and in O₂ atmosphere). The polymeric thiol surfactants which assembled on gold nanoparticles are poly 6-(3-amino phenoxy) hexane-1-thiol, poly 8-(3-amino phenoxy) octane-1-thiol and poly 10-(3-amino phenoxy) decane-1-thiol. All catalyst samples were characterized using X-ray diffraction, transmission electron microscopy and fourier transform infrared spectroscopy techniques whereas the produced polymer was characterized by gel permeation chromatography and proton nuclear magnetic resonance spectroscopy. The results indicated that the assembled polymeric thiol surfactants on gold nanoparticles exfoliated and modified the activity of nanoclay. So, the performance of these modified samples increased by increasing the alkyl chain length of surfactant monomers (C_n = C₆, C₈ and C₁₀) due to the creation of new active sites and exposing those deep in clay. On the other hand, O₂ may give peroxides which decomposed thermally to free radicals, also activated the exposed active sites of clay. So, the conversion% of PMMA increased by 6, 9 and 14.7 times using C₆, C₈ and C₁₀ respectively relative to the conversion% in N₂ atmosphere. The most active sample (C₁₀) gave 5.3 and 78.11% PMMA in N₂ and in O₂ atmosphere respectively with better polydispersity index ($\bar{M}_w/\bar{M}_n = 1.46$ in O₂) mostly due to chain transfer.

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1. Introduction

Smectite clays have increasingly attracted research interests as hosts for preparation of nanoparticle/clay nanocomposites in the past decade due to the possibility to retain the small size and various shapes of the nanoparticles after intercalation and further industrial exploitation of the composite [1]. Clay minerals have a very strong swelling and adsorption capacity, which is particularly interesting for the impregnation of catalytically active noble metals in the interlamellar space of clay [2–5]. The catalytic activity of clay can be improved via modification with different organic and inorganic compounds [6]. So, several researchers studied the modification of clay with surfactants [7] to be used in the catalytic polymerization reaction. Ammonium or phosphonium cationic surfactants with long chains modified clay surface to be

organophilic and more compatible with organic polymers [6,8]. As an example, Doh and Cho [9] found that the structural affinity between the styrene monomer and the modified montmorillonite with tetra-alkyl ammonium cations, plays an important role in the final structure and properties of the nanocomposites. Also, immobilized metal complexes and metal oxides on bentonite improved the catalytic activity in aqueous and bulk polymerization of methyl methacrylate (MMA) via free radical mechanism [10–13]. The influence of the particle size and the surface nature of metal oxide nanoparticles (SiO₂, Al₂O₃, TiO₂ and CeO₂) in free radical MMA polymerization has been studied recently [14,15]. Previous publications proved that gold nanoparticles (AuNPs) supported on Fe, Ce and Al pillared bentonite and that intercalated in the walls of mesoporous silica improved their catalytic activity and thermal stability in different petrochemical reactions [16,17]. Also, AuNPs have attracted considerable attention due to their electronic, magnetic and optical properties, and their applications to catalysis and biology [18]. High affinity of organic functional groups like SH, –CN, –COOH, –NH₂ for metallic surfaces such as Au, Cu, Ag, Pd, Pt,

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Hg have motivated several research groups to focus on using this phenomena for industrial applications [19]. Self-assembled monolayers of organosulfur compounds like thiols, sulfides and disulfides on the surface of coinage metals like Cu, Ag and Au, have attracted much attention [20]. Self-assembled monolayers (SAMs) are typically formed from surfactant-like molecules which have a reactive head group that binds the molecules to the surface, and an organic tail of variable length and functionality. Currently most widely used and investigated model systems for self-assembly are thiols (R-SH, where R is an organic residue) on gold and silanes (R-Si-OH) on SiO₂ [21].

The effect of oxygen in bulk polymerization of MMA has a great attention. Solyman et al. confirmed that oxygen reduced to free radicals in presence of CuO/TiO₂ and enhanced MMA polymerization reaction via redox-initiated mechanism [22]. On the other hand, oxygen deactivated the polymerization reaction in presence of CuO/clay and completely stop the reaction in presence of CoPc/clay [11,12]. Other studies indicated that oxygen may produce peroxides with MMA with or without catalytic system and initiate its polymerization via free radical mechanism [23,24]. Also, Tunc et al. indicated that thioxanthone-anthracene possessing an octyl group form endoperoxide intermediate with oxygen which undergoes photochemical or thermal decomposition to generate radicals that are able to initiate free radical polymerization [25].

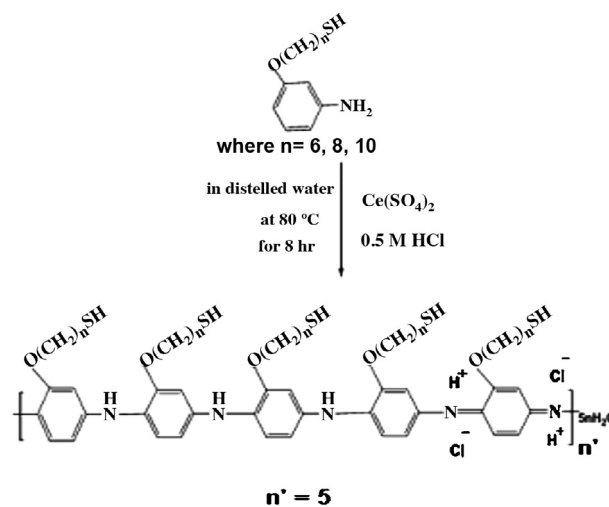
Bulk polymerizations of MMA are still the predominant method for producing high quality acrylic glass. Free radical mechanism is the major industrial mechanism to produce PMMA. The polymerization consists of four reactions: initiation, propagation, termination, and chain transfer. Initiators are decomposed to free radicals, these radicals propagate by reacting with surrounding monomers to form long chains, and the active site is shifted to the end of the chain when a new monomer is added to the chain. The reaction terminates when two radicals react. A new radical is yielded when an active site reacts with an active hydrogen atom from chain transfer agent, monomer, polymer or solvent. There are gel, glass, and cage effects in the MMA polymerization. These effects will cause the propagation and termination rate constants and initiator efficiency changes during the polymerization process, and make the kinetics and molecular weight more complex. Number- or weight- average molecular weight will increase with the free radical accumulation when the gel effect appears and decrease when the glass effect happens [26].

The combination between the effect of cationic surfactants and AuNPs on the performance of clay in MMA bulk polymerization in presence of oxygen is not examined before. So, in this study we investigated the effect of assembled polymeric thiol surfactants (with different alkyl side chain length C₆, C₈ and C₁₀) with gold nanoparticles (AuNPs) on both the characterization and the catalytic activity of nanoclay (NC) in the bulk polymerization of MMA in inert and oxygen atmosphere. All the catalyst samples were characterized through XRD, FTIR and TEM techniques and the produced polymethyl methacrylate samples (PMMA) were characterized through GPC and ¹H NMR techniques. The performance of all catalyst samples are correlated with their characterization.

2. Experimental

2.1. Catalyst preparation

The chemicals used in this work were supplied as follow: cerium (IV) sulfate (99.7%) Aldrich, 3-aminophenol (99%) Merck, thiourea (98%) Merck, 1,6-dibromohexane (98%) Merck, 1,8-dibromooctane (98%) Aldrich, 1,10-dibromodecane (97%) Aldrich, trisodium citrate



Scheme 1.

(99%) Aldrich, tetraauric acid (98%) Aldrich, clay (sodium montmorillonite) (98%) MI SWCO, hydrochloric acid (37%) Panreac and sulfuric acid (98%) Adwic. All chemicals were used as supplied.

The investigated catalyst samples in this study were prepared in several steps as shown in Schemes 1 and 2 and described as follow:

(1) The monomeric thiol surfactants and their polymers under investigation (poly 6-(3-amino phenoxy) hexane-1-thiol, poly 8-(3-amino phenoxy) octane-1-thiol and poly 10-(3-amino phenoxy) decane-1-thiol) in Scheme 1 were synthesized and their structure was confirmed as shown in the previous publication [27].

The polymeric thiol surfactants were denoted as C₆, C₈ and C₁₀ respectively according to the alkyl side chain length in the surfactant monomers (CH₂)_n. The synthesized surfactants were assembled onto the surface of gold nanoparticles (AuNPs) by mixing 20 ml of the prepared AuNPs solution with 5 ml of 1 × 10⁻⁵ M from surfactant solution and stirred at room temperature for 24 h until the solution became colorless [20] and they were denoted as NAuC₆, NAuC₈ and NAuC₁₀ (see Scheme 2).

(2) Gold nanoparticles (AuNPs) of ~25 nm size were prepared by the reduction of tetrachloroauric acid (HAuCl₄) using tri-sodium citrate (Na₃C₆H₅O₇): 2 ml of tetrachloroauric acid solution (1%) was heated to boiling temperature then 2.5 ml of tri-sodium citrate solution (1%) was added slowly and stirring until the color changed to winy red. All solutions were prepared using pure distilled water which obtained by passing twice-distilled water through a Milli-Q system. The formation of gold nanoparticles colloidal solution was characterized using the TEM and UV analysis and shown in previous publication [28].

(3) The clay nanopowder (denoted as NC) was prepared using RETSCH Planetary Ball Mills Type PM 400. The clay sample was milled using the ball mill at speed 150 rpm for 8 h [29].

(4) The fabrication of the nanoclay composites using the synthesized polymeric surfactant assembled on gold nanoparticles were carried as follow: A total of 1 g of (NC) was dispersed in 250 ml of water for swelling for 48 h, then separated by centrifugation and transferred into 50 ml solution of the assembled polymeric thiol surfactants NAuC_n (where n = 6, 8 and 10) in order to prepare the clay nanocomposite with the nanostructure of these assembled polymeric surfactants. The mixture was stirred for 24 h. The precipitate was separated by centrifugation, washed with water, and dried under vacuum overnight [5]. They denoted as NAuC₆/C, NAuC₈/C and NAuC₁₀/C. The fabrication of the nanoclay composites using AuNPs solution were carried out with the same method for comparison and were titled as NAu/C (see Scheme 2).

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