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Preparation and Characterization of Poly(glycidyl methacrylate)-grafted Magnetic Nanoparticles: Effects of the Precursor Concentration on Polyol Synthesis of Fe₃O₄ and [PMDETA]₀/[CuBr₂]₀ Ratios on SI-AGET ATRP

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Abstract: Polymer brushes based on poly (glycidyl methacrylate) (PGMA) have been successfully grafted from the surface of silica coated iron oxide (Fe₃O₄@SiO₂) nanoparticles via surface-initiated activators generated by electron transfer atom transfer radical polymerization (SI-AGET ATRP). The size of the nanoparticles could be adjusted from 7.3 to 9.6 nm by varying the precursor concentration of iron(III) acetylacetonate. The Fe₃O₄ nanoparticles possessed a highly crystalline structure, and the saturation magnetization of the as-prepared magnetite was strongly related to the particle size. Furthermore, the grafted PGMA content on the magnetic nanoparticles could be controlled by varying the ligand to transition metal ratio in a *N,N,N',N'',N''*-pentamethyldiethylenetriamine (PMDETA)/CuBr₂ catalyst system. The maximum grafted content was 23.1% at a ratio of [PMDETA]₀/[CuBr₂]₀ of =2:1.

Keywords: Fe₃O₄ nanoparticles; precursor concentration; poly(glycidyl methacrylate); surface-initiated AGET ATRP; [PMDETA]₀/[CuBr₂]₀ ratio

1. Introduction

Magnetite (Fe₃O₄) nanoparticles (NPs) have been developed for their fundamental scientific and technological interest including magnetic energy storage,¹ cell separation,² targeted drug delivery,³ selective enrichment,⁴ hyperthermia treatment,⁵ and magnetic resonance imaging (MRI).⁶ Control of the size and different morphologies (spherical, octahedral and cubic) of monodisperse Fe₃O₄ NPs is very important because these various structures generate distinct properties.⁷ To understand magnetic behavior and to improve applications, careful research related to synthetic strategies and growth mechanisms of Fe₃O₄ NPs are essential.

There are many reports on the synthesis of Fe₃O₄ NPs using different preparation methods including co-precipitation,⁸ hydrothermal reactions,⁹ thermal decomposition,¹⁰ flow injection syntheses,¹¹ and polyol process.¹² Of these, the polyol method is particularly attractive for the synthesis of hydrophilic nanoparticles. During preparation, the polyols often serve as reducing agents and high-boiling point solvents while also, stabilizing nanoparticle growth and preventing interparticle aggregation.¹³ The metal precursor becomes solubilized in the diol form and forms an intermediate, which is then reduced to form metal nuclei that will nucleate and form metal particles.

The classic oleic acid-oleylamine polyol system was developed by the Sun group.¹⁴⁻¹⁶ Oleic

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