Preparation and Characterization of Stable Aqueous Ferrofluids Using Low Molecular Weight Sulfonated Polystyrene

Raquel Ledezma, Darío Bueno, Ronald F. Ziolo**

Summary: One of the most optically transparent magnetic materials known at room temperature consists of nanocrystalline γ-Fe_2O_3 dispersed in a DVB cross-linked sulfonated polystyrene (PS) matrix. When attrited dry or in water *without* surfactant and subsequently processed in water or water miscible liquids, the nanocomposite leads to a highly stable, low optical density ferrofluid with unique properties and uses in a variety of applications. We have heretofore identified the stabilizing agent in the ferrofluid as low molecular weight (~6000) sulfonated PS, which results from attrition of the cross linked polystyrene nanocomposite. We report on the synthesis of low molecular weight (LMW) PS by atom transfer radical polymerization (ATRP) followed by sulfonation with acetyl sulfate and on the one-step synthesis of a stable ferrofluid of nanocrystalline Fe_3O_4 using the newly synthesized LMW sulfonated PS. Physicochemical analyses and characterizations include GPC, GC-MS, GPC, NMR, FTIR, XRD, TEM and magnetic data.

Keywords: ATRP; ferrofluid; low molecular weight polystyrene; magnetic nanocomposite

Introduction

One of the most optically transparent magnetic materials known at room temperature consists of nanocrystalline γ-Fe_2O_3 dispersed in a DVB cross-linked sulfonated polystyrene (PS) matrix.[1] When attrited dry or in water, and subsequently processed, the nanocomposite leads to a highly stable, low optical density, aqueous ferrofluid without the addition of a surfactant.[2,3] This lack of surfactant in ferrofluid preparations is atypical. The same behavior is observed when the attrition is done in alcohols and other water miscible solvents. In several cases, the ferrofluids formed from the above nanocomposite have unique applications[4] or have lead to materials with unique properties, such as in the formation of free-rotor nanomagnets,[5,6] colored magnetic inks[7] and optically transparent ferrofluids for fluid dynamics studies.[8]

To date, the stabilizing component, which may be thought of as a surfactant or capping agent, in the aforementioned ferrofluids has not been identified, although it is recognized that the stabilization is of a steric rather than ionic nature, the two most common forms of aqueous ferrofluid stabilization.[9–11] Here, we report on the identification of the stabilizing component, its synthesis and characterization, and on the direct formation of a new ferrofluid with the component. An excellent review on stabilization of particles with small organic molecules is given by Pyun.[12]

Experimental Part

Analysis of Preexisting Sulfonated PS Ferrofluid

The aqueous ferrofluid for analysis was made earlier and supplied by one of the

Centro de Investigación en Química Aplicada. Blvd. Enrique Reyna No. 140, Saltillo, Coahuila 25253 México
E-mail: rziolo@cs.com

authors (RFZ). The iron oxide was removed by flocculation with a 0.5 M solution of NaCl and separated by ultracentrifugation. The supernatant was separated and analyzed by GPC, GC-MS, ^{1}H and ^{13}C NMR and FTIR.

Polymerization through Activator Generated by Electron Transfer (AGET) for ATRP of Styrene

Copper(II) bromide ($CuBr_2$, 7.46×10^{-4} mol) was added to a Schlenk flask that was first evacuated, purged and then filled with nitrogen. A solution of 1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA, 1.49×10^{-3} mol) in degassed 2-butanone (MEK) was added to the flask. Nitrogen-purged Styrene (9 g) was added via syringe. The mixture was stirred for 20 min to form the $CuBr_2$/HMTETA complex. Tin(II) 2-ethylhexanoate ($Sn(EH)_2$, 2.98×10^{-4} mol) and a purged solution of ethyl 2-bromoisobutyrate (EtBrIB, 7.46×10^{-4} mol) in MEK were added. Three "freeze-pump-thaw" cycles were performed to remove any oxygen from the polymerization solution. The flask was immersed in an oil bath at 100 °C. The product was purified by column chromatography using alumina and chloroform, and after, analyzed by ^{1}H NMR and GPC.

Sulfonation and Sulfonating Reagent

Concentrated sulfuric acid (0.016 mol) was slowly added with vigorous stirring to 10 mL of a 1, 2-dichloroethane solution containing 0.03 mol of acetic anhydride. After complete mixing, the concentrated reagent was equilibrated at room temperature and then diluted with 1, 2-trichloroethane (10 mL). *Sulfonation Reaction* - In a 100 mL round-bottom flask, 6.0 g of polystyrene (PS) was mixed with 20 mL of 1,2-dichloroethane (DCE) and heated (ca. 50 °C) until all the PS dissolved. With stirring, 10 mL of the sulfonating reagent in 1,2-dichloroethane was slowly added to the PS solution. The reaction was allowed to proceed for 2 hr at 60 °C. The reaction was quenched by placing the hot reaction vessel in a cold water bath at 10 °C. DCE was easily removed by decantation. Polystyrene sulfonated ($PSSO_3H$) was converted to $PSSO_3Na$ by slowly adding sodium hydroxide (NaOH) until the solution pH reached 10 in order to make sure that every sulfonate group was converted into the sodium salt form. The concentrated solution was loaded into a dialysis membrane bag and dialyzed with deionized water to remove the bulk of the ions (NaOH in excess, sulfates, acetates). Finally, the dialyzed solution was frozen prior to lyophilization. The final polymer was analyzed by ^{1}H NMR, FT-IR and GPC; the ion exchange capacity was determined by titration.

Current Ferrofluid Preparation

The resin (PSSNa) was exchanged with Fe (II) from an aqueous solution of iron chloride ($FeCl_2 \cdot 4H_2O$) in a relation 1:3 molar (SO_3Na:Fe^{2+}), the excess of ions was removed by dialysis with water. At pH 7, 1 mL of N_2H_4 is added slowly, followed by the dropwise addition of a 10 mL solution of 7M NaOH, The reaction mixture is stirred for 12 hr at room temperature (25 °C) then dialysed. An aqueous H_2O_2 solution is then added dropwise and the reaction mixture washed several times with water to neutral pH, resulting in the direct formation of a ferrofluid. The in situ preparation of particulate and ferrofluid in this case is similar to that using iron(II) cross-linked alginate gels.[13] The iron oxide particulate, which was separated by centrifugation and air dried, could easily be re-dispersed in water to form the ferrofluid.

Results and Discussion

One of the goals of the present study was to reverse engineer the highly stable, optically transparent aqueous ferrofluid that is formed by attrition of the DVB cross linked nanocomposite resin[1] to determine the stabilizing agent, which results from the breakdown of the cross linked resin. The three components of the ferrofluid, i.e., the particles, water and surfactant, were separated by physical and chemical means and the latter characterized by ^{1}H NMR, FT-IR and GPC. The surfactant or capping agent was found to be water soluble, sulfonated polystyrene with a molecular weight of ~ 6,000 g/mol. Thus, ball milling of the nanocrystalline maghemite nanocomposite used in the preparation of the original ferrofluid, results in a chemical and physical degradation of the DVB cross linked sulfonated polystyrene resin to form the unique fluid.

The next goal of this work was to demonstrate the feasibility of preparing a ferrofluid using a low molecular weight sulfonated polystyrene. To this end, it was necessary to synthesize low MW PSS since, to our knowledge, this is not available commercially. We chose a novel method to control the polymerization, an atom transfer radical polymerization combined with an activator generated by electron transfer (ATRP-AGET).[14] In our case we used the complex formed by $CuBr_2$/HMTETA and the reducing agent $Sn(EH)_2$; we obtained MWs of 6,000 to 10,000 g/mol for PSS, according to the concentrations used for each reaction. Homogeneous sulfonation of the PS was accomplished using acetyl sulfate. We note that the sulfonation reaction could also be accompanied by sulfone formation and concomitant cross-linking between the sulfonate groups. In this regard, it is important to control the concentration of acetyl sulfate. At high degrees of sulfonation, high water solubility was observed; the polymer was isolated after decanting the organic layer. The synthesized PSS was converted to the Na form with NaOH; the ion exchange capacity was determined to be ~ 1.18 meq/g polymer.

After ion exchange of the as synthesized low MW PSS with iron(II) and the subsequent treatment outlined in the experimental section, a stable, dark ferrofluid was obtained. TEM images of the particulate show spherical to roughly cubic shaped particles ranging in size from 10 to 25 nm (Figure 1) and the absence of acicular particles. The XRD pattern along with the black color is consistent with magnetite and not maghemite.[15]

The field dependent magnetization data (M) at 75 K (Figure 2) were obtained for the dry powder using a Quantum Design PPMS instrument in the VSM mode. The saturation magnetization at 20 kOe (2T) (Figure 2A) is 59.04 emu/g. These data suggest about 80% particulate[16] and 20% polymer, consistent with TGA results for the dry powder. The coercive field of the particles is ~ 600 Oe consistent with the particle size range. The M vs H (applied field) curve for the dry powder suggests superparamagnetic behavior consistent

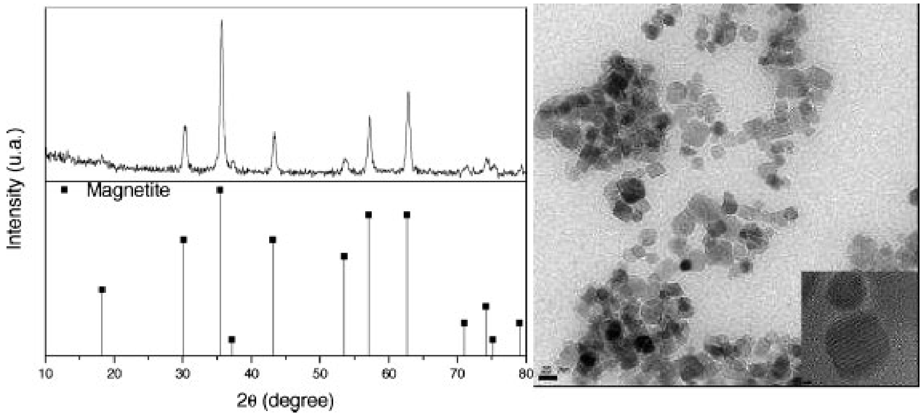

Figure 1.
X-ray diffraction pattern and transmission electron micrograph of the magnetic nanoparticles (TEM courtesy of Dr. A. Ponce).

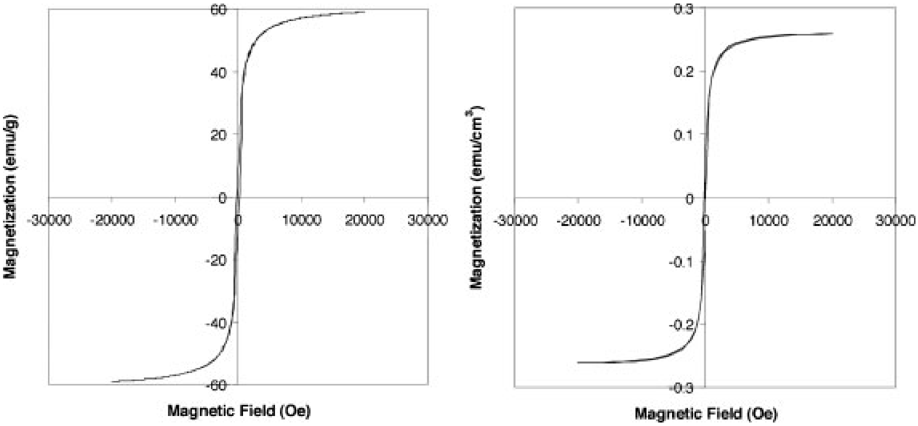

Figure 2.
Field dependent magnetization curve for the dry powder (left in emu/g) and the errofluid containing 0.5 wt-% powder (right in emu/cm^3).

with the particle size range of the samples and observed stability of the ferrofluid; M vs H for the latter is shown in Figure 2B.

Conclusions

The stabilizing agent in the optically transparent aqueous ferrofluid made by the attrition of the well known DVB cross-linked sulfonated PS nanocomposite was identified for the first time as being ~ 6000 MW sulfonated PS. Low MW sulfonated PS was synthesized with a molecular weight of ~ 8000 g/mol for the first time by ATRP-AGET and ion exchanged with iron(II), which resulted in the preparation of stable aqueous ferrofluids of magnetite. Upon drying, the LMW PSS coated particles were found to be easily *re-dispersible* in water and water compatible liquids to form stable ferrofluids. The phase of iron oxide was dependent, as expected, on the reaction conditions. The preparation and characterization of maghemite ferrofluids using the LMW surfactant will be reported elsewhere.

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