Polyisobutylene Oligomers as Tools for Iron Oxide Nanoparticle Solubilization

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Supporting Information

ABSTRACT: A series of terminally functionalized polyisobutylene (PIB) derivatives were synthesized and tested as agents for magnetic nanoparticle solubilization. PIB-bound catechol was found to be the best functionalized polyolefin at effecting such solubilization based on UV–vis spectroscopic absorbance measurements and thermogravimetric analysis. The PIB-modified magnetic nanoparticles obtained from grafting reactions contain up to 32 wt % of MNPs. They easily disperse in nonpolar and moderately polar organic solvents. The high loading (>50 wt %) of the PIB-modified magnetic nanoparticles even in alkane solvents makes the resulting solutions magnetically susceptible. This was illustrated by preliminary work where PIB-modified MNPs formed solutions with heptane that could be magnetically separated from water. These PIB-modified magnetic nanoparticles were also shown to be highly soluble in low melting polyethylene waxes and in liquid poly(α-olefin).

INTRODUCTION

The development of reliable synthetic routes to nanomaterials and their use continues to be an area of interest because of the usefulness of nanoparticles in widely different areas of chemistry.1−7 Developing ways to stabilize, disperse, and solubilize nanoparticles also remains an important goal. The most progress in this latter effort has been in developing methodology to form solutions or dispersions of nanoparticles for use in polar milieu by modifying the nanoparticle/solution interface.8 Often this has been accomplished using polymers that are either grafted to or grafted from the nanoparticle surface.9−11 This chemistry can be used to prepare dispersions of magnetic nanoparticles (MNPs) that are reasonably stable. However, in most cases, an external magnetic field or centrifugation can be used to separate the modified MNPs. Methods to make nanoparticles including MNPs dissolve or form stable dispersions in very nonpolar solvents or materials have also received attention. While in most cases these efforts form dispersions where the concentration of nanoparticles is <10 wt %,12−14 ferrofluids can have 15% or greater concentrations of modified nanoparticles.15 In this paper, we explore the use of functionalized polyisobutylene (PIB) oligomers to make solutions of modified magnetic nanoparticles in saturated hydrocarbon solvents. These PIB-modified MNPs effectively form solutions in weakly polar solvents like toluene and THF. These PIB-modified MNPs do not dissolve or form stable dispersions in polar solvents where PIB is insoluble. In the experiments below, we show that this ability to modify magnetic nanoparticle solubility is dependent on the nature of the terminal functional group on the polyisobutylene oligomer and show that catechol terminal groups are especially effective in forming these stable dispersions.

We have a long history of using polymers to manipulate solubility of homogeneous catalysts and metal complexes.16−18 While this work has mainly been focused on developing greener ways to effect catalysis, we have also shown that the same ligands that are used to make catalysts soluble and recyclable in nonpolar solvents like heptane can be used to make other typically insoluble materials highly heptane soluble. This is most evident in our studies of PIB-modified metallophthalocyanines.19 In that case, we found that we could prepare phthalocyanines with PIB substituents and that the resulting materials were viscous blue-green oils. These metallophthalocyanines with covalently attached PIB ligands were miscible with heptane at all concentrations and soluble at ca. 20 wt % even at −20 °C. Those results suggested to us that terminally functionalized PIB oligomers could similarly be used to disperse nanoparticles in nonpolar or weakly polar solvents.

Iron oxide magnetic nanoparticles (MNPs) are common types of nanoparticles with applications in medicine,20,21 as tracking agents,22,23 as reinforcement agents in plastics,24,25 and as tools for separations.26 There are numerous methods available to synthesize MNPs using as examples hydrothermal, thermal decomposition, coprecipitation, and polyl synthesis methods.1,5 These various methods result in MNPs with different shapes and sizes. It is also known that MNPs have a strong tendency to aggregate and that groups like surface...
modification can stabilize MNPs by introducing either electrostatic or steric repulsion to their surface. Hydrophobic surfactants can also impart varying stability and some organic solvent solubility to MNPs. For example, oleic acid-functionalyzed MNPs are more effective at stabilizing and solubilizing MNPs than stearic acid. Polyolefins containing succinic anhydride end groups have also been used to make stable colloidal suspensions or solutions of magnetite that contain up to 5 wt % magnetite. The work below explores the utility of modified polyisobutylene oligomers to modify MNP solubility by studying the effectiveness of various types terminal functional groups on PIB in solubilizing bare MNPs in alkanes. These results also compare PIB-bound functional groups to their saturated fatty acid derived alternatives. These comparisons show that using PIB-bound functional groups as ligands instead of stearic acid derivatives leads to PIB-grafted magnetic nanoparticles that have much higher solubility in weakly polar solvents. We show that by using appropriate PIB ligands we can prepare magnetic oils that contain up to 32 wt % MNPs and that such oils dissolve in alkanes or weakly polar organic solvents to form solutions of MNPs that are stable to centrifugation, magnetic separation, and external reagents.

## RESULTS AND DISCUSSION

In the work below, we prepared MNPs by a literature procedure and then modified these MNPs with PIB groups, collecting modified MNPs using one of three procedures (Scheme 1). As depicted in Scheme 1, the magnetic decantation method A uses an external magnet to magnetically separate soluble PIB-modified MNPs from less soluble MNPs which were then repeatedly washed with solvent. Centrifugation is an alternative way to isolate highly soluble PIB-modified MNPs. A third method C was used for larger scale syntheses and combined a filtration step with a magnetic separation and is discussed below.

The starting iron oxide nanoparticles were prepared using a coprecipitation method. A 300 mL aqueous solution of 50 mmol of FeSO₄ and 100 mmol of FeCl₃ was added to 30 mL of a 30% aqueous ammonium hydroxide solution to form a black Fe₃O₄ nanoparticle precipitate. Figure 1 shows the X-ray diffraction pattern of the resulting product. Six peaks were identified and matched with characteristic peaks corresponding to (220), (311), (400), (422), (511), and (440) crystal planes of Fe₃O₄ nanoparticles in the literature. The Fe₃O₄ nanoparticles so formed have round shapes and an average 9 nm diameter as identified by a transmission electronic microscope (TEM) image (cf. Figure 3a; vide infra).

To study grafting of terminally functionalized PIBs onto MNPs, a series of PIB-bound ligands denoted as a PIB-X were prepared using known chemistry or variations on known chemistry as shown in Scheme 2. The syntheses of these functionalized PIB oligomers are described in detail in the Supporting Information. The PIB-X derivatives 1–11 were characterized by ¹H, ¹³C, and, where appropriate, ³¹P NMR spectroscopy and were prepared from commercially available alkene terminated PIB₁₀₀₀ (Mₙ = 1000 Da) and PIB₂₃₀₀ (Mₙ = 2300 Da). These PIB-bound ligands with different Mₙ values are denoted as PIB₁₀₀₀-X and PIB₂₃₀₀-X in the later discussion.

Our initial explorations of MNP modification using the PIB derivatives 1–11 involved reaction of 4.0 mg of the MNP with 0.04 mmol of a PIB-X derivative in an alkane solvent like hexane.
cyclohexane (Scheme 3). In these experiments, the MNPs were suspended in cyclohexane using sonication. Then 0.1 mL of 3% ammonium hydroxide was added. Initial studies showed this facilitated reactions of PIB-X derivatives with MNPs. We assessed the binding ability of terminally functionalized PIB oligomers 1–11 to MNPs by monitoring the extent of magnetic nanoparticles (MNP) solubilization by periodically measuring the optical density of the reaction solutions over a 4 h period of sonication. In this analysis, samples were taken from the reaction mixture and subjected to centrifugation at 3200 rpm for 15 min. This removed poorly soluble particles from the solution. We then measured the optical density of the supernatant phase at 380 nm.

Our experiments initially used PIB-X derivatives that our group had prepared previously. These PIB-X derivatives included the starting material PIB (1), PIB-2,6-dimethylaniline (2), PIB-OH (3), PIB-thioacetate (4), PIB-SH (5), PIB-carboxylic acid (PIB-CO2H) (6), PIB-phosphonic acid (7), PIB-hydroxamic acid (8), PIB-catechol (9), PIB-veratrol (10), and PIB-phenol (11).

In subsequent experiments, we prepared PIB oligomers with phosphonic acid (7), hydroxamic acid (8), catechol (9), veratrol (10), and phenol (11) end groups. These groups are all known to be good ligands for metals including iron. The results of these studies too are shown in Figure 2. These results show that catechol terminal groups are superior at effecting MNP solubilization in these experiments.

As noted above, prior studies have used fatty acids and fatty acid derivatives to modify and solubilize MNPs in hydrocarbons. To show if PIB is more effective at solubilizing MNPs, we compared the extent of solubilization of MNP by excess PIB to the solubilization of MNPs by excess stearic acid. The result as shown in Figure 2 was that the PIB derivative was roughly twice as effective in these solubilization experiments that used excess hydrophobic ligands. We also prepared a low molecular weight catechol-terminated stearic acid derivative (12) and compared it to the catechol-terminated PIB derivative (9). Again, the PIB bound species afforded a ca. 2-fold greater MNP solubilization than a smaller hydrophobic group. We ascribe this increased solubilization with PIB derivatives to the larger alkyl group of PIB ligands versus the smaller alkyl groups of stearic acid and 12. Finally, we compared PIB1000 oligomers with PIB2300

![Scheme 3. Synthesis of Soluble Fe3O4 Nanoparticles Using Different Functionalized Polyisobutylene Ligands 1–11](image)

“X = 2,6-dimethylaniline (2), hydroxyl (3), thioacetate (4), thiol (5), carboxylic acid (6), phosphonic acid (7), hydroxamic acid (8), catechol (9), veratrol (10), and phenol (11).”}

![Figure 2. Comparison of UV–vis spectroscopic absorbance of the supernatant: (a) PIB1000-bound ligands and low molecular weight analogues; (b) PIB2300-bound ligands.](image)
oligomers. Those studies showed only modest differences in the extent of solubilization of MNPs with excess PIB-X. However, while PIB\textsubscript{1000} and PIB\textsubscript{2300} oligomers were comparable on a molar basis in solubilizing MNPs, subsequent work showed that PIB\textsubscript{2300}-catechol could produce higher concentrations of MNP nanoparticles in heptane than PIB\textsubscript{2300}-catechol.

Our original hypothesis was that the phase selective solubility of PIB derivatives could allow us to make MNPs highly soluble in alkanes and other weakly polar solvents. To see if we could achieve this goal, we quantitatively determined how much MNP we could dissolve in heptane using both PIB\textsubscript{1000} and PIB\textsubscript{2300}-catechol. These studies included optimizing the concentration of soluble modified MNPs using different PIB-catechol/MPN weight ratios as well as determining the polymer loading in the resulting materials as shown in Table 1.

Table 1. TGA Studies of the Effects of Changing the Weight Ratio of MNP/PIB-Catechol on the MNP Loading of a Heptane Soluble PIB-Grafted MNP

<table>
<thead>
<tr>
<th>entry</th>
<th>PIB-catechol (Mn)</th>
<th>MNP/PIB catechol (g/g)</th>
<th>separation method</th>
<th>starting solubilized MNP (%)</th>
<th>oil</th>
<th>solid</th>
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<td>1</td>
<td>1000</td>
<td>1.0:1.0 A</td>
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</tr>
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<td>1000</td>
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<td>83.1</td>
<td>8.0</td>
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<tr>
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<td>35</td>
<td>79.5</td>
<td>12.6</td>
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“Method A used a magnet and repeated washings to differentiate soluble vs insoluble PIB-modified MNPs. Method B used repeated centrifugations to differentiate soluble vs insoluble PIB-modified MNPs. The oil phase was the material isolated after removing cyclohexane from the combined cyclohexane supernatant phases isolated using either method A or B. The insoluble solid was residual material that never dissolved. While it did form a suspension in cyclohexane, the suspensions were not stable in the presence of a magnetic field or during centrifugation. The modiﬁed MNPs in the soluble magnetic oil have a much higher loading for PIB groups (typically >80 wt %) and are completely soluble in the alkane. This solubility leads to a weaker attraction of the supernatant solution to the magnet due to lower concentration of MNPs (cf. the discussion associated with Figure 6; vide infra). Thus, we were able to trap the lightly grafted MNPs using a magnet while pouring away the dilute solutions to successfully separate the insoluble particles with the lower ca. 10 wt % PIB loading from the highly soluble particles (ca. 80 wt % PIB loading).

This insoluble magnetic solid and the heptane soluble magnetic oil isolated from the combined supernatant phases visually had different appearances. The oil was dark brown, and the solid was black. Another difference was that while both materials can be dispersed in alkanes and other nonpolar solvents, the dispersions of the insoluble magnetic solid were not stable. Dispersions of the insoluble solids in alkanes were not stable to centrifugation or an external magnetic field. The dispersions formed from the magnetic oil however behave like solutions and are visually stable for extended time (vide infra) and stable to centrifugation and are stable to the application of an external magnet.

We also used a second method—method B—to separate solubilized MNPs (the magnetic oil) from insoluble MNPs. This method used the same synthetic protocol used above but separated solubilized MNPs from less soluble MNPs by centrifugation. In this case, the modified MNPs were dispersed in 30 mL of heptane and centrifuged at 4000 rpm for 10 min. After decanting the supernatant, the mixture was dispersed in a second 30 mL portion of heptane and centrifuged again. This procedure was repeated until the supernatant layer was clear. Typically, this produced seven supernatant phases which were combined and concentrated to provide the highly soluble magnetic oil fraction. The insoluble solid fraction could be suspended in an alkane solvent with sonication like the insoluble fraction isolated using method A. The insoluble solids isolated in method B like those isolated in method A did not form stable suspensions and were always separable from solvent by centrifugation. The total amounts of PIB-modified nanoparticles isolated in methods A and B were generally comparable.

These experiments provided us with 22 samples of magnetic oil or insoluble solids. We analyzed each of these samples by thermal gravimetric analysis (TGA). Under these analysis conditions, the PIB catechol ligands quantitatively decompose. Thus, the residual solid in these analyses was iron oxide, and we could use these experiments to determine the loading of MNP in the soluble magnetic oil and in the insoluble magnetic solid.
The results of these TGA analyses are summarized in Table 1. While we did not carry out similar studies with all the other PIB-X derivatives, we did examine PIB$_{1000}$-phenol-modified MNPs by TGA. As expected based on the results in Figure 2, PIB$_{1000}$-phenol was a poorer ligand as solubilizing MNPs than PIB$_{1000}$-catechol. This TGA curve is provided in the Supporting Information (Figure S3). Mass balances showed that >90% of the amount of the original starting magnetic nanoparticle was typically accounted for in these TGA analyses of the highly soluble oil phase and the insoluble solid phase fractions.

When an equal mass of PIB$_{1000}$-catechol and MNP were used in the grafting reaction and method A was used for separation, the amount of polymer in the insoluble magnetic solids was ~11 wt % (Table 1, entry 1). When less PIB$_{1000}$-catechol was used in the reaction (Table 1, entries 2–4), the amount of polymer bound to the insoluble solids decreased slightly. The soluble magnetic oils generally had high loadings of the PIB graft. While there was some variation depending on the starting weight ratio of PIB-catechol/MNP and method used, the PIB loading on the soluble oil was always >70 wt %. By using roughly equivalent amounts of MNP and PIB-catechol (i.e., a 1:1 g/mmol ratio), 20–30% of the soluble magnetic oil was MNP. As much as 56% of the starting MNP nanoparticles could be solubilized with PIB-catechol by using more PIB-catechol. However, the concentration of MNP in the soluble material then dropped to ca. 10 wt % in these cases.

The size and the shape of the modified MNPs were analyzed by TEM. Particles size distribution of resolved particles in these images (Figure 3) were carried out using ImageJ software and are shown in histograms in the Supporting Information (Figure S4). The particle size analyses for ungrafted MNPs showed an average particle diameter of 10.7 ± 2.4 nm (after counting over 78 nanoparticles). However, most particles were agglomerated as is apparent in the micrograph of his material. In contrast, the PIB-catechol-modified magnetic solid that was partially modified with PIB groups appeared to have a better dispersion of MNPs (Figure 3b). In this case, analysis of 109 nanoparticles using the same ImageJ software led to an estimate for the average particle diameter of 10.7 ± 2.7 nm. We believe the agglomerated particles that were still observed result from the relatively low loading of PIB ligands on these poorly soluble modified particles. Figures 3c and 3d show that the nanoparticles of PIB$_{2300}$-catechol bound magnetic oil were better dispersed. In these cases, particle size analysis of 155 nanoparticles showed an average particle diameter of 10.3 ± 3.0 nm. While there is still some aggregation of MNPs in Figure 3d, we believe this aggregation reflects the sample preparation process. Indeed, an even better dispersion is seen in a TEM analysis of a solution of the soluble PIB-modified MNPs in a 1758 Da nonvolatile poly(α-olefin) oil (Figure 7a; vide infra).

While the magnetic separation and centrifugation methods used to prepare samples in Table 1 worked, these methods only afforded 0.5–1.0 g of the soluble magnetic oils. They were not very efficient for synthesis of larger amounts of PIB-modified MNPs. Thus, we modified these methods so as to carry out multigram syntheses of modified MNPs. These larger scale reactions used 10 g of starting MNPs and 10 g of PIB$_{1000}$-catechol or 5 g of starting MNPs and 11.5 g of PIB$_{2300}$-catechol in 250 mL of cyclohexane. Aliquots of these larger scale reactions were analyzed periodically over 48 h of sonication. As shown by the UV–vis spectroscopy data in Figure 4, these larger scale reactions were complete within 24 h. After the completion of the reaction (24 h), the reaction mixtures were allowed to stand for an additional 24 h. During this period, a small amount of solid settled out. This solid was separated by filtration through filter paper. While this process removed most of the insoluble solid, some additional sediment was seen after the second 24 h standing. That small amount of sediment that formed after this second 24 h period was trapped with a neodymium magnet (a 6.3 cm$^3$ cube; surface gauss: 4716 G). The solution that was decanted from this solid did not form any further precipitate after standing for 2 months. This solution of soluble MNPs was then concentrated under reduced pressure affording ca. 15 g of a viscous magnetic oil. This modified

![Figure 3. TEM images of as synthesized iron-oxide nanoparticles. (a) Unfunctionalized MNPs under 250K magnification. (b) PIB$_{2300}$-catechol bound magnetic solid under 250K magnification. (c) PIB$_{2300}$-catechol bound magnetic oil under 15K magnification. (d) PIB$_{2300}$-catechol bound magnetic oil under 200K magnification.](image-url)

![Figure 4. Plot of absorbance of the reaction mixture versus time when 10.0 g of PIB$_{1000}$-catechol with 10.0 g of MNPs and 11.5 g of PIB$_{2300}$-catechol and 5.0 g of MNPs were used for the grafting reaction.](image-url)
procedure simplified the procedure for obtaining larger amounts of the desired heptane-soluble magnetic oil.

The product of this larger scale synthesis was analyzed by TGA using the same procedures used to analyze the various samples in Table 1. The results are shown in Figure 5. Here we show TGA analyses of PIB2300-alkene, PIB2300-catechol, PIB1000-modified magnetic materials, and PIB3300-modified magnetic materials.

Figure 5. TGA comparison of PIB2300-alkene, PIB2300-catechol, PIB1000-modified magnetic materials, and PIB3300-modified magnetic materials.

The high solubility of the magnetic oil in heptane led us to explore the potential of these magnetic oils as agents for hydrocarbon sequestration. Studies with a series of solutions with different weight percentages of the magnetic oil in heptane were used to visually measure the attraction of each of these solutions toward an external magnet. With as little as 1 wt % of the PIB2300-catechol-modified MNP dissolved in heptane, the heptane phase in its entirety was very strongly attracted toward the magnet when the magnet was placed at the side of the vial containing a biphasic mixture of the MNP in heptane and water (Figure 6). The same effect was seen for heptane solutions containing higher loadings of the PIB2300-catechol-modified MNPs. Even when the PIB2300-catechol-modified MNP content was 0.5 wt %, the effect was still noticeable though the separation was no longer as effective in this latter case. Notably, the external magnet affected the entire solution—the magnet does not separate the PIB-catechol-modified MNPs from heptane over a 100-fold range of the concentration of the PIB2300-catechol-modified MNP in heptane. This process could be repeated multiple times over the course of several weeks. Other MNPs like the PIB-CO$_2$H-modified MNPs had a similar effect.

The high solubility of the magnetic oil in heptane led us to explore the potential of dissolving this viscous PIB-modified MNP magnetic oil in polyolefins. We found that a mixture of nonpolar and weakly polar solvents. Two other solvents—dichloromethane and 1,2-dichloroethane—initially dissolved the PIB1000-modified MNPs. However, in these cases, some precipitate did form upon standing. The PIB1000-modified MNPs were, as expected, insoluble in polar organic solvents. Similar results were obtained with the PIB2300-modified MNPs. These studies suggest that the solubility of the magnetic oil is determined mainly by the intrinsic solubility of PIB.

Our observation that the magnetic oils contained some heptane-soluble magnetic oil even after extended exposure to vacuum suggested that the PIB grafts on these MNPs tenaciously entrain hydrocarbons. This led us to briefly explore the potential of these magnetic oils as agents for hydrocarbon sequestration. Studies with a series of solutions with different weight percentages of the magnetic oil in heptane were used to visually measure the attraction of each of these solutions toward an external magnet. With as little as 1 wt % of the PIB2300-catechol-modified MNP dissolved in heptane, the heptane phase in its entirety was very strongly attracted toward the magnet when the magnet was placed at the side of the vial containing a biphasic mixture of the MNP in heptane and water (Figure 6). The same effect was seen for heptane solutions containing higher loadings of the PIB2300-catechol-modified MNPs. Even when the PIB2300-catechol-modified MNP content was 0.5 wt %, the effect was still noticeable though the separation was no longer as effective in this latter case. Notably, the external magnet affected the entire solution—the magnet does not separate the PIB-catechol-modified MNPs from heptane over a 100-fold range of the concentration of the PIB2300-catechol-modified MNP in heptane. This process could be repeated multiple times over the course of several weeks. Other MNPs like the PIB-CO$_2$H-modified MNPs had a similar effect.

The high solubility of the magnetic oil in heptane led us to explore the potential of dissolving this viscous PIB-modified MNP magnetic oil in polyolefins. We found that a mixture of

Table 2. Solubility Test of the Magnetic Oil in Common Organic Solvents

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<thead>
<tr>
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<th>solubility*</th>
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*A sample of 500 mg of PIB1000-catechol bound magnetic oil was stirred with 5 mL of solvent, and the resulting mixture’s solubility was visually assayed.
the magnetic oil in a polyethylene oligomer \(^{34}\) \((M_n = 400 \text{ Da})\) in a weight ratio 1 to 10 formed a homogeneous solution with gentle swirling at 90 °C. Cooling this solution led to a brownish wax. After cryogenic grinding, a magnetically susceptible dark brown polyethylene powder was obtained. Poly(\(\alpha\)-olefin) oligomers (PAOs) \(^{35,36}\) which are commercially available lubricants from ExxonMobile, have also been used as substitutes for heptane in other work in our group.\(^{37}\) They too are good solvents for this viscous PI-modified MNP magnetic oil. With heating and swirling, both PAO 10 \((M_n = 687 \text{ Da})\) and PAO 40 \((M_n = 1758 \text{ Da})\) formed dark brown viscous solutions. This was in contrast to efforts to mix either unmodified MNPs or the heptane insoluble magnetic solid with PAOs. In these cases, a similar mixture containing 1 g of MNP or the insoluble magnetic solid with MNPs that have ca. 10% PIB loading did not form a solution. A precipitate of the MNP was present in the mixture even after 1 h of heating and stirring at 100 °C.

This visually homogeneous viscous PI-modified MNP magnetic oil/PAO solution was further analyzed by TEM. In this case, a solution of the viscous PI-modified MNP magnetic oil in PAO 40 \((M_n = 1758 \text{ Da})\) was analyzed. As shown in Figure 7a, the MNPs were well dispersed. Using ImageJ software, the particles had an average diameter of 10.7 ± 3.3 nm (after counting over 115 nanoparticles) (Figure S5). The dispersion of MNPs in this case can also be compared to the dispersion of MNPs in heptane in Figure 3d. The more uniform dispersion of MNPs in this nonvolatile PAO 40 polymer solvent we believe results from PAO being a nonvolatile medium that minimizes aggregation of MNPs on the grid while the solvent evaporated during the preparation of TEM sample. We also examined the poorly soluble magnetic solid in PAO 40. This image shown in Figure 7b was also analyzed using ImageJ software and the particles had an average diameter of 10.9 ± 3.0 nm (after counting over 74 nanoparticles) (Figure S5). In this case, apparent aggregation was seen in the TEM image with the visually observed insolubility of MNPs with sufficient PI solubilizing groups in both heptane and this PAO solvent.

### CONCLUSIONS

We successfully synthesized a series of terminally functionalized PIB oligomers that chemically bind to and solubilize iron oxide magnetic nanoparticles. We found that, among the PIB ligands we tested, PIB oligomers functionalized with terminal catechol groups were the best ligands for solubilizing MNPs. Using this chemistry, we developed several methods to prepare solubilized MNPs. A method that uses a combination of magnetic separation and filtration was shown to yield soluble MNPs on a ca. 15 g scale. This separation method allowed us to solubilize as much as 56% of the starting MNPs as oils with 10–30 wt % MNP content. These oils were soluble at concentrations of >50 wt % in organic solvents including alkanes. We also showed that the viscous PI-modified MNP magnetic oil that is highly soluble in heptane dissolves in polyolefins. Poly(\(\alpha\)-olefin)s with \(M_n\) values of 687 and 1758 Da readily dissolve these modified MNPs. Similarly, a low melting point PE wax dissolved these same PI-modified MNPs at 90 °C leading to a magnetically susceptible PE powder on cooling and cryogenic grinding. Finally, other experiments showed that the PI-bound magnetic oil at loadings as low as 1 wt % magnetically separated an excess of an alkane solvent from water. Further work to explore PI oligomer modification of other types of nanoparticles and to study the uses of such modified nanoparticles is ongoing.

### METHODS

**Materials.** Vinyl-terminated PIB with \(M_n\) of 1000 and 2300 was provided by BASF and later by the TPC Group. All other reagents and solvents were purchased from commercial sources and used without further purification unless otherwise stated.

**Synthesis of Fe\(_3\)O\(_4\) Nanoparticles.** 3.51 g of ferric chloride hexahydrate (FeCl\(_3\cdot6\)H\(_2\)O) and 1.81 g of ferrous sulfate heptahydrate (FeSO\(_4\cdot7\)H\(_2\)O) (molar ratio 2:1, respectively) were dissolved in 150 mL of deionized water and stirred vigorously under a N\(_2\) atmosphere at 70 °C. After 1 h, 15 mL of ammonium hydroxide (35%) was rapidly added to the mixture, and the reaction mixture was stirred for another 1 h and finally cooled to room temperature. The black precipitate that formed was trapped by a magnet, and the particles were washed five times with hot water and finally dried in an oven under vacuum at 50 °C overnight. Usually around 2 g of Fe\(_3\)O\(_4\) was obtained.

**Synthesis of Terminally Functionalized PIB Oligomers 2–11.** Detailed procedures of syntheses of terminally functionalized PIB oligomers and their characterization are reported in the Supporting Information.

Two representative examples of these procedures would be the synthesis of the PIB\(_{1000}\)-bound phosphonic acid \(\mathbf{7}\) and the PIB\(_{1000}\)-bound catechol \(\mathbf{9}\). The synthesis of PIB\(_{1000}\)-bound phosphonic acid \(\mathbf{7}\) began with a reported hydroboration of alkeno-terminated PIB \(\mathbf{1}\).\(^{31}\) The success of this reaction was evidenced by the disappearance of the multiplet signals for vinyl protons at 4.85 and 4.64 δ and the appearance of a pair of doublet of doublets for the diasterotopic –CH\(_2\)OH protons of \(\mathbf{3}\) at 3.48 and 3.31 δ. This hydroxyl-terminated PIB derivative \(\mathbf{3}\) was then converted into an iodide-terminated PIB derivative \(\mathbf{13}\). The iodide \(\mathbf{13}\) was then allowed to react with triethyl phosphate to afford the PIB\(_{1000}\)-bound diethylphosphonate \(\mathbf{7}\). The
success of this reaction was evidenced by the disappearance of the pair of doublet of doublets for the diastereotropic \( \text{CH}_3 \text{H} \) protons at 3.19 and 3.05 \( \delta \) and the appearance of multiplet signals for the diastereotropic \( \text{CH}_3 \text{P}(\text{O})(\text{OEt})_2 \) protons at 7a 4.12–4.06 \( \delta \). The diethylpolyisobutylphosphonate 7a was then allowed to react with bromotrimethylisilylene. A subsequent reaction in methanol and heptane afforded \( \text{PIB}_{1000} \)-bound phosphonic acid \(^7\). \( ^1H \) NMR (500 MHz, CDCl\(_3\)): \( \delta \) 1.7 (m, 2 H), 1.4–0.8 (m, 140 H), 1.36 (m, 40 H). \( ^13C \) NMR (125 MHz, CDCl\(_3\)) \( \delta \) multiple peaks at 60–58.2, 38.5–33.4, and 31.2–30.8. \( ^3P \) NMR (121 MHz, CDCl\(_3\)) 35.3. IR (neat, cm\(^{-1}\)): 2976, 2949, 2893, 1734, 1653, 1474, 1389, 1366, 1231, 908.

The synthesis of the \( \text{PIB}_{1000} \)-bound catechol 9 was representative of syntheses of other aromatically-terminated PIBs (cf. Supporting Information). In the synthesis of 9, 10 g (10 mmol) of \( \text{PIB}_{1000} \)-alkene in dichloromethane was allowed to react with 11 g (100 mmol) of catechol in the presence of sulfuric acid to afford 7a 7.3 g (67% yield) of \( \text{PIB}_{1000} \)-catechol 9 after purification. \( ^1H \) NMR (500 MHz, CDCl\(_3\)): \( \delta \) 6.88 (br, 1 H), 6.77 (br, 2 H), and 1.40–1.00 (m, 140 H). \( ^13C \) NMR (125 MHz, CDCl\(_3\)) \( \delta \) 143.5, 142.9, 140.7, 118.4, 114.9, 113.5, 44.7, 37.2, 31.9, 30.4, 29.7, 29.6, 29.4, 29.1, 24.7, 22.7, 14.1. IR (neat, cm\(^{-1}\)): 3374, 2951, 2893, 1707, 1605, 1468, 1389, 1366, 1228.

Synthesis of a Catechol Derivative of Stearic Acid 12. Detailed procedures for the synthesis of 12 from methyl stearate and the \( ^1H \) and \( ^13C \) NMR spectra of the intermediates and the final product are reported in the Supporting Information.

Structural and Optical Characterizations. Details on TEM, XRD measurements, and UV–vis spectroscopy measurements are presented in the Supporting Information.

Studies of Comparative Solubilization of MNPs with Ligands 1–12 and Stearic Acid. 4.0 mg of \( \text{Fe}_3\text{O}_4 \) nanoparticles was mixed with 4 mL of cyclohexane in a 50 mL two-necked round-bottomed flask. The test tube was sonicated at 40 °C for 75 min. Then 0.1 mL of 3% ammonium hydroxide aqueous solution and 0.1 mL of a \( \text{PIB}_{1000} \)-functionalized ligand, stearic acid, or 12 in 6 mL of cyclohexane was added to the test tube. The reaction mixture was then sonicated for 1 h at 40 °C. At this point, the sonication was stopped, and the reaction mixture was centrifuged at 3200 rpm for 15 min. A small portion (0.3 mL) of the supernatant was removed and diluted with 2.4 mL of cyclohexane. The diluted solution was analyzed by a UV–vis spectrometer to record the absorbance at 380 nm. The remainder of the reaction mixture was placed back in the sonication bath at 40 °C, and the sonication was continued for an additional 3 h. At this point, the sonication was stopped, and the reaction mixture was centrifuged at 3200 rpm for 15 min. A small portion (0.3 mL) of the supernatant was removed and diluted with 2.4 mL of cyclohexane. The diluted solution was analyzed by a UV–vis spectrometer to record the absorbance at 380 nm.

Optimization of the Concentration of Soluble Modified MNPs Using Different PIB-Catechol/MNP Weight Ratios with Either \( \text{PIB}_{1000} \) or \( \text{PIB}_{2300} \) Ligands. A sample of \( \text{Fe}_3\text{O}_4 \) nanoparticles (the weight of the \( \text{Fe}_3\text{O}_4 \) nanoparticles relative to the amount of PIB-catechol used is shown in Table S1) was mixed with 10 mL of cyclohexane in a 50 mL two-necked round-bottomed flask. The mixture was sonicated at 40 °C for 75 min, at which point 0.1 mL of a 30% ammonium hydroxide aqueous solution and \( \text{PIB}_{1000} \)-catechol or \( \text{PIB}_{2300} \)-catechol in 15 mL of cyclohexane were added to the flask. The reaction mixture was sonicated for another 75 min, at which point the flask was transferred to a heating bath and the reaction mixture was magnetically stirred at 40 °C for an additional 12 h. Then the solvent was removed at reduced pressure using a rotary evaporator, and the residue was suspended in 30 mL of heptane. The magnetic solid and the magnetic oil were separated from this suspension by two different methods: magnetic decantation (method A) and centrifugation (method B) as described in Scheme 1 and the text.

Multigram Scale Preparation of Plasma-Precipitation-Grafted MNPs. A 10 g portion of \( \text{Fe}_3\text{O}_4 \) nanoparticles was mixed with 100 mL of cyclohexane in a 500 mL two-necked round-bottomed flask. The mixture was sonicated at 40 °C for 75 min, at which point 1 mL of 3% ammonium hydroxide aqueous solution and 10 g of \( \text{PIB}_{2300} \)-catechol in 150 mL of cyclohexane were added. Sonication of the mixture was continued at 40 °C for 24 h. Then the magnetic solid and the magnetic oil were separated by method C as described in Scheme 1. During the reaction, the kinetics of the reactions were monitored by UV–vis spectrometer as described above by taking aliquots of the reaction mixture. Reactions with the \( \text{PIB}_{2300} \)-catechol used the same procedure except that reactions with \( \text{PIB}_{1500} \)-catechol used 5 g of the MNPs and 11.5 g of the \( \text{PIB}_{2300} \)-catechol.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.macromol.6b02407.

Experimental procedures, characterization data, and NMR spectra (PDF)

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

Support of this research by the NPRP award (NPRP 7-1263-1-230) from the Qatar National Research Fund is gratefully acknowledged as is the gift of samples of polyisobutylene originally from BASF and later from the TPC Group. N.R. also acknowledges support from the HEC Commission of Pakistan.

REFERENCES


(30) Alkene-terminated polyisobutenes were originally obtained from BASF and later functionally equivalent materials with the same M4 values were obtained from the TPC Group (http://www.performancechemicals.bASF.com/ev/internet/polyisobutene/en/content/EV3/polyisobutene/glossopal) (accessed Oct 10, 2016) and the TPC Group (http://www.tpcgrp.com/tpc-group/products/polyisobutylene-150.html?E%28%80%8B) (accessed Oct 10, 2016).


