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Polymer-grafted Nanoparticles (PGN) and PGN Arrays with Tailored Canopy Interactions

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14. ABSTRACT

The research reported here focused on developing a new synthesis strategy to enable scaleup of polymer-grafted nanoparticles (PGNs) using an environmentally friendly 'grafting from' polymerization approach. This work described in this report was built on studies earlier in this program that developed new methods of emulation polymerization using living radical polymerization. Ludox is a family of commercially available silica (SiO2) nanoparticles with a narrow size distribution, making it an excellent model choice to develop a highly scalable synthesis process. The Ludox-TM 40 nanoparticles (26 nm) used in this work were first modified with an atom transfer radical polymerization initiator (ATRP). Subsequently, SiO2-polystyrene and SiO2-poly(methyl methacrylate) PGNs were synthesized in an aqueous mini-emulsion without the use of an organic solvent. Through the simultaneous addition of monomer and reducing agent, both the graft density and the molecular weight of the grafted polymer chains could be readily controlled. Furthermore, it was found that the directed localization of the polymerization in micelles can prevent the formation of unwanted side products, such as ungrafted polymer chains. The approach developed allows for the first time the efficient synthesis of PGNs of a broad variety of polymer compositions with a homogeneous polymer corona on a multigram scale.

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1. SUMMARY

The research reported here focused on developing a new synthesis strategy to enable scaleup of polymer-grafted nanoparticles (PGNs) using an environmentally friendly "grafting from" polymerization approach. Ludox® is a family of commercially available silica (SiO_2) nanoparticles with a narrow size distribution, making it an excellent model choice to develop a highly scalable synthesis process. The Ludox-TM 40 nanoparticles (26 nm) used in this work were first modified with an atom transfer radical polymerization initiator (ATRP). Subsequently, SiO_2-polystyrene and SiO_2-poly(methyl methacrylate) PGNs were synthesized in an aqueous mini-emulsion without the use of an organic solvent. Through the simultaneous addition of monomer and reducing agent, both the graft density and the molecular weight of the grafted polymer chains could be readily controlled. Furthermore, it was found that the directed localization of the polymerization in micelles can prevent the formation of unwanted side products, such as ungrafted polymer chains. The approach developed allows for the first time the efficient synthesis of PGNs of a broad variety of polymer compositions with a homogeneous polymer corona on a multigram scale.

2. INTRODUCTION

Polymer nanocomposites have been the focus of much research over the past few decades due to their ability to produce materials with a wide range of advanced properties. Polymer-grafted nanoparticles (PGNs), a building block of particular types of polymeric nanocomposites, possess unique properties due to their versatility and capacity to entangle with neighboring PGNS, giving them enhanced thermal, mechanical, optical and electrical properties compared to their micro and macroscale counterparts.[1,2] Nevertheless, several obstacles have remained, limiting the straightforward synthesis of PGNs on a multi-gram scale. Challenges include a complex purification procedure, control of the graft density and molar mass of grafted polymer chains, and particle aggregation.

Atom transfer radical polymerization (ATRP) is one of the most common and versatile methods for creating well-defined polymeric structures.[3] However, the use of organic solvents and large quantities of metal catalyst in traditional ATRP makes the purification procedure elaborate. To reduce the amount of copper catalyst used in ATRP, Matyjaszewski et al. introduced the Activators Regenerated by Electron Transfer – Atom Transfer Radical Polymerization (ARGET-ATRP) method by adding reducing agents to regenerate the active Cu(I) complex from the deactivated Cu(II) during polymerization. Applying this method, Matyjaszewski et al. demonstrated the synthesis of polystyrene (PS) with a low $Đ=1.17$ using parts-per-million concentrations of copper catalyst in environmentally friendly media (e.g., water).[4]

Water-based polymerization would be beneficial for the direct, green synthesis of PGNs. Previous efforts have used ARGET-ATRP in emulsion as a method for the synthesis of PGNs but successful large scale synthesis could not be accomplished.[5, 6] No prior existing methods could be shown to provide a simple and universal strategy for the aqueous synthesis of PGNs using a wide range of monomers. In particular, no existing techniques allow the precise control of both the graft density and molar mass of grafted polymer chains on a multi-gram scale for production of PGNs with homogeneous, size-tunable polymer coronas. Herein we report a scalable, universal, and robust water-based synthesis approach using ARGET-ATRP to synthesize well-defined PGNs with tunable graft density and corona thickness (Figure 1). The work we describe in this report has been carried out to make polystyrene or PMMA brushes on silica model PGNs and begun to investigate their mechanical properties with Dr. Vaia (AFRL) and his team. We have also carried out preliminary studies of the preparation of PGNs of Fe/Co based magnetic oxide nanoparticles. Because of the incomplete nature of this preliminary work these studies are not included in this report, but if invited to submit a proposal this summer, these new magnetic PGNs would form the basis of a proposed study of Faraday rotators made from self-assembled PGNs.

3. METHODS

The work reported here made use of surface modification of oxide nanoparticles and growth of polymer brushes on these modified nanoparticles. Typical procedures are profived here.

3.1. Synthesis of ATRP Initiators

Synthesis of 11-(ethoxydimethylsilyl)undecyl 2-bromo-2-methylpropanoate (EDMP)

10-undecen-1-ol (4.257g, 5 mL, 0.025 mol), pyridine (2.1 mL, 0.026 mol), and 30 mL tetrahydrofuran (THF) were added to a 100 mL round bottom flask, which was placed in an ice bath. BIBB (5.760g, 3.1 mL, 0.024 mol) was dissolved in 10 mL of THF and added dropwise over two hours under stirring. Afterward, the solution was stirred for 24 hours at room temperature. The precipitate was then filtered off and THF was removed under reduced pressure. The resulting crude product was obtained as a yellow oil. The crude product was then dissolved in dichloromethane (DCM) and extracted twice with a saturated Na_2CO_3 solution. The organic phase was dried using magnesium sulfate anhydrous, and excess DCM was removed under reduced pressure and purified using silica column chromatography using DCM as the mobile phase. A pale-yellow oil (yield= 95%) was obtained. The product (1.28 g, 4 mmol) was added to dimethylethoxysilane (8.9 g, 85.4 mmol), and Karstedt's catalyst (6 µL, 11µmol) was added to the mixture and stirred overnight at room temperature under argon. Excess solvent was removed under vacuum and the resulting liquid was stored at -20° C. The APTES-BIBB initiator synthesized according to the published work by Wang et al.[7]

3.2. Synthesis of Polymer-Grafted Nanoparticles

The following description details the synthesis of PGNs labeled as Sample 3 in Table 2. All other samples were prepared according to the following general synthesis procedure, while parameters such as monomer concentration, ascorbic acid feeding rate, reaction time, surfactant and initiator were varied. Initiator-functionalized Ludox-TM40 nanoparticles (200 mg) were mixed with 10 mL of a Pluronic F-127 (0.08 g/mL) solution in a 20 mL scintillation vial and vortexed and sonicated until a milky white suspension was formed. In parallel, TBAB (1.934g, 6 mmol), $CuBr_2$ (2 mg, 8.96 µmol), Tris(2-pyridylmethyl) amine (TPMA) (20.8 mg, 71.6 µmol), and water (40 mL, adjusted for each reaction to give a total reaction volume of 60 mL) were added in a 100 mL round-bottom flask equipped with a stirring bar. The particle dispersion was now added to the reaction flask and the dispersion was degassed for 20 minutes by bubbling with argon. Styrene (3.5 mL, 3.82 mmol/h) and an aqueous solution of ascorbic acid (2.27 mM, 4.8 mL, 5.6 µmol/h) were added to the reaction flask simultaneously over 8 hours using two syringe pumps. After 8 hours the polymerization was terminated by opening the reaction to air. The hairy nanoparticles were separated by centrifugation at 4400 rpm for 20 minutes, washed twice with THF and MilliQ water, dialyzed against water for two days, and afterward dried in a vacuum oven at 80 °C.

4. RESULTS AND DISCUSSION

A "green chemistry" synthesis approach was developed using an aqueous-based emulsion ARGET-ATRP, as shown in Figure 1. With the use of an uncharged surfactant, good control of the polymerization location could be achieved. A halide salt, tetrabutylammonium bromide (TBAB) in particular, was used to transport the catalytic complex into the non-polar monomer rich micelles, a process which has been extensively investigated in our previous work.[8]

The simultaneous addition of ascorbic acid (AA), which acted as the reducing agent, and monomer allowed both the graft density and the molecular weight of the grafted polymer chains to be controlled.

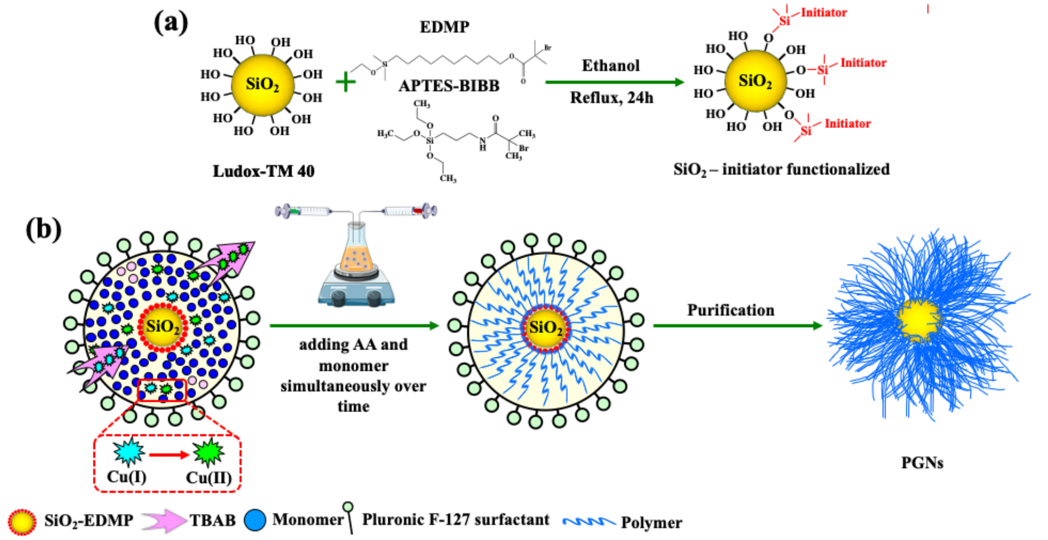

Figure 1. (a) Functionalization of Ludox-TM40; (b) Synthesis of PGNs in the aqueous phase.

To determine the graft density of polymer chains on PGNs according to the method provided by Pasetto et al., both the polymer weight content and the molecular weight of the grafted polymer chains were required.[9] The polymer content (wt%) of all PGN samples was determined using thermogravimetric analysis (TGA). Gel permeation chromatography (GPC) was used to determine the molar mass of grafted chains after the inorganic cores were removed via HF etching.
All SiO_2-PMMA and SiO_2-PMMA PGN samples synthesized, as well as the properties resulting from varying the reaction parameters, are discussed in the following sections.

4.1. SiO_2-PMMA PGNs

A series of experiments was performed by varying the feed rate of methyl methacrylate (MMA) monomer, leading to cumulative MMA concentrations in the reaction flask ranging from 0.67 mol/L to 1.34 mol/L (Table 1, Samples 1-4). Increasing the amount of MMA added over 6 hours led to an increase in the graft density and molar mass of the grafted PMMA chains, as seen in Table 1.

Table 1. Synthesized SiO_2-PMMA PGNs.

Sample	[MMA] (mol/L)	MMA feeding rate (mmol/h)	Polymer content (wt%)	Graft density (chains/Nm^2)	M_n (g/mol)	Corona thickness (nm)[a]
1	0.67	7.5	21	0.011	86400	2.5 ± 0.3
2	1.00	10.3	25	0.012	106200	7.0 ± 1.0
3	1.17	12.2	32	0.017	105800	11.0 ± 1.6
4[b]	0.67	N/A	32	0.0084	214300	---
5[b,c]	0.67	N/A	50	0.013	328700	---
6[b,c,d]	0.67	N/A	53	0.029	158600	---

[a] the corona thickness was measured by TEM and determined using ImageJ; [b] total MMA amount was added at the beginning of the reaction; [c] using acetone (20 vol%); [d] no TBAB.

With a MMA concentration of 0.67 mol/L, a polymer content of 21 wt% and a molar mass of M_n= 86400 were obtained, from which a graft density of 0.011 chains/nm^2 was calculated (sample 1, Table 1). Further increasing the MMA concentration to 1.00 mol/L, a polymer content of 25 wt%, molar mass of M_n= 106200, and graft density of 0.012 chains/nm^2 were achieved. When the monomer concentration reached a value of 1.17 mol/L, the polymer content increased to 32 wt% with a molar mass of M_n= 105800 and a graft density of 0.017 chains/nm^2. As expected, increasing the MMA concentration led to more homogeneous and thicker polymer corona (Figure 2) until the onset of particle aggregation at an MMA concentration of 1.34 mol/L.

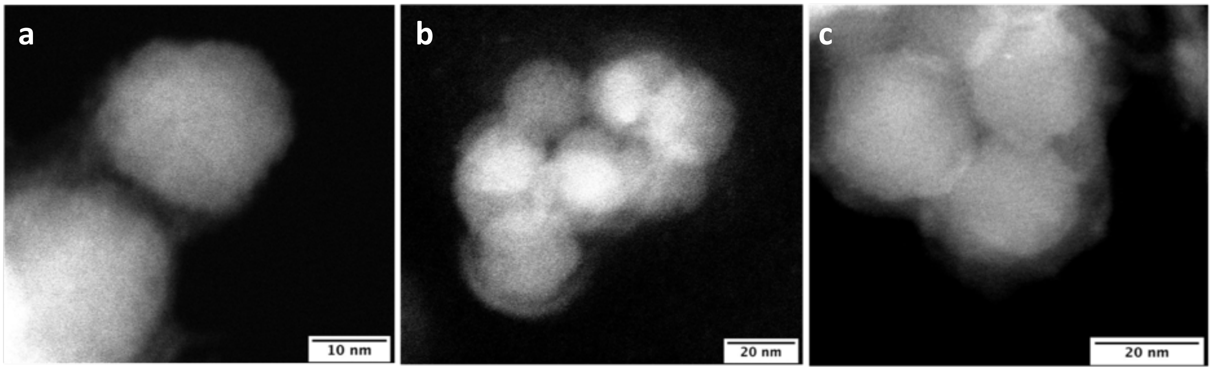

Figure 2. TEM pictures of SiO_2-PMMA PGNs with EDMP as initiator obtained via mini-emulsion ARGET-ATRP. (a) Sample 1, Table 1, graft density = 0.011 chains/nm^2; (b) Sample 2, Table 1, graft density = 0.011 chains/nm^2; (c) Sample 3, Table 1, graft density = 0.017 chains/nm^2.

The earlier trials for the PGN synthesis described above involved adding all monomer at once rather over the course of the reaction, in addition to using acetone as a cosolvent. Since the removal of all non-aqueous solvents was desired, the role of acetone in overall reaction control was determined through the series of experiments resulting in Samples 4-6 in Table 1. Drawing on the work of Ugelstad et al., earlier experiments introduced acetone into the reaction solution to increase the solubility of the monomer in the aqueous phase and to promote the diffusion of the monomer into transfer agent to support the diffusion of the monomer into the micelles due to the finite solubility the micelle, thereby localizing polymerization in the micelles. The roles of TBAB and acetone, both presumed to support the transport of monomer into the micelles, were investigated with a constant MMA concentration of 0.67 mol/L (Samples 4-6, Table 1). For these experiments, the total amount of monomer was added to the reaction flask at the beginning of the reaction, rather than using a syringe pump, to replicate the conditions of earlier experiments.[8]

The use of acetone led to the formation of a significant amount of ungrafted PMMA, which caused the aggregation of particles (Sample 4-6, Table 1). A possible explanation of this observation could be that acetone not only assists in the diffusion of MMA into the micelles but also increases the likelihood of chain transfer reactions and transport of MMA and oligomeric PMMA chains out of the micelles into the aqueous phase, where the reaction was terminated. On the other hand, we could demonstrate that TBAB is required to have a controlled and localized polymerization. In particular, if no TBAB (Sample 6, Table 1). is added to the reaction, the amount of obtained ungrafted PMMA is around 50wt%. This may be attributed to the TBAB-assisted transfer of monomer into micelles resulting in the localization of the polymerization inside the micelles.

4.2. SiO_2-PS PGNs

The SiO_2-PS PGNs synthesized using a variety of initiators and surfactants are listed in Table 2. For Sample 1-4, EDMP was used as the initiator and Pluronic F-127 was used as the surfactant, whereas Samples 5-7 were synthesized using APTES-BIBB as the initiator and SDS as the surfactant.

Table 2. SiO_2-PS PGNs Synthesized using Mini-emulsion ARGET-ATRP.

Sample	[Styrene] (mol/L)	Styrene feeding rate (mmol/h)	Polymer content (wt%)	Graft density (chains/nm^2)	M_n (g/mol)	Corona thickness (nm)[a]
1	0.40	2.0	7	0.006	86000	2.4 +/- 0.5
2	2.00	10.0	23	0.019	106000	3.6 +/- 0.9
3	2.52	12.6	40	0.036	123000	8.4 +/- 1.9
4[c,d]	5.76	28.8	45	0.070	74000	4.0 +/- 1.0
5[c,d]	5.76	28.8	20	0.168	64000	2.2 +/- 0.4
6[c,d]	5.76	28.8	42	0.045	85000	4.5 +/- 1.3

[a] the corona thickness was measured by TEM and determined using ImageJ; [b] Samples 1-4 were synthesized with initiator EDMP. [c] Sample 4-6 were synthesized with initiator APTES-BIBB.[d] samples 4-6 were synthesized using SDS as the surfactant.

PGNs synthesized using EDMP as initiator showed a trend of increasing polymer content as the styrene concentration increased. As the concentration of styrene was increased from 0.40 mol/L to 2.52 mol/L, the polymer content of the PGNs rose from 7 wt% to 40 wt%. Additionally, the molar mass was observed to increase from 86000 g/mol to 123000 g/mol, while the graft density increased from 0.006 chains/nm^2 up to 0.036 chains/nm^2. Confirming these results, the corona thickness observed via TEM increased with increasing monomer concentration (Figure 3).

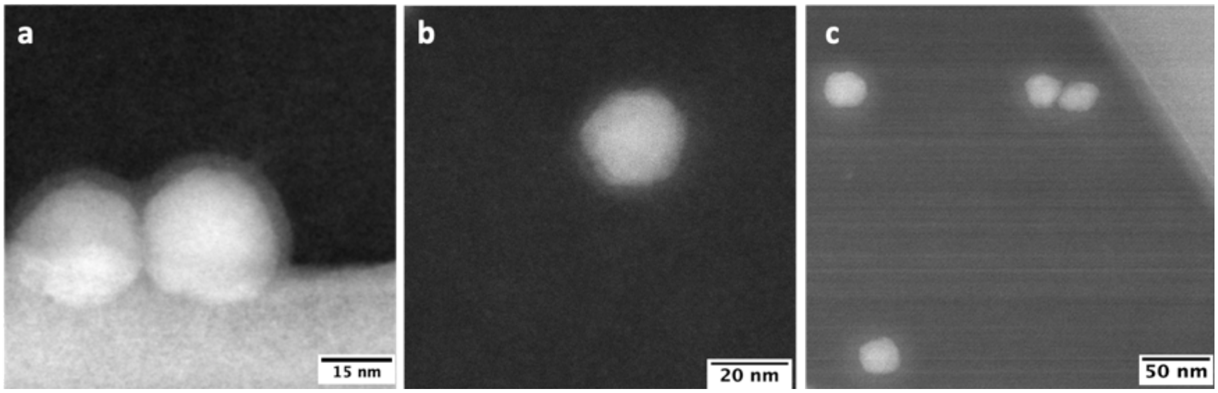

Figure 3. TEM pictures of SiO_2-PS PGNs with EDMP as initiator obtained via mini-emulsion ARGET-ATRP. (a) Sample 1, Table 2, graft density = 0.006 chains/nm^2; (b) Sample 3, Table 2, graft density = 0.019 chains/nm^2; (c) Sample 4, Table 2, graft density = 0.036 chains/nm^2.

EDMP is a hydrophobic initiator with one ethoxy group, which results in a single covalent attachment point on the surface of the particles. To make a more robust linkage of the initiator on silica nanoparticle surface, the use of APTES-BIBB, which has three ethoxy groups, was examined. Although the use of APTES-BIBB as an initiator could potentially lead to the formation of multilayers on the surface of silica particles[CITE?], TEM images (Figure 4) showed PGNs with homogenous coronas and a low degree of aggregation.

In addition to changing the initiator, sodium dodecyl sulfate (SDS), a common ionic surfactant, was employed for the synthesis of Samples 4-6 in Table 2. The use of SDS results in inter-micellar repulsion, which was hypothesized to prevent PGNs from aggregating during synthesis. This was proven through STEM images of Sample 4 in Table 2, which showed PGNs without aggregation (Figure 4(a)). Additionally, we demonstrated the successful scale-up of PGNs with a multi-gram batch production for the experiment described as Sample 6 in Table 2.

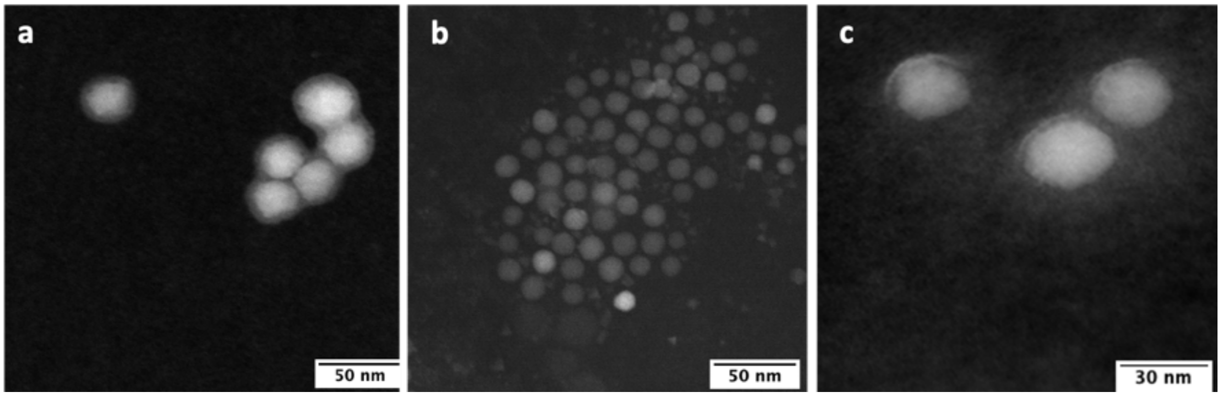

Figure 4. TEM and STEM pictures of SiO_2-PS PGNs with APTES-BIBB as initiator obtained via mini-emulsion ARGET-ATRP. (a) Sample 4, Table 2, graft density = 0.070 chains/nm^2; (b) Sample 5, Table 2, graft density = 0.026 chains/nm^2; (c) Sample 6, Table 2, graft density = 0.0145 chains/nm^2.

Mechanical properties are one of the key factors that must be considered for PGN particle arrays. It was observed that the mechanical properties of SiO_2-PS PGN films were significantly affected by corona uniformity and thickness. To quantify this dependence, the Young's modulus of arrays formed from Samples 5 and 6 (Table 2), which had relatively thick and homogeneous coronas, were determined by nanoindentation measurements, as shown in Figure 5.

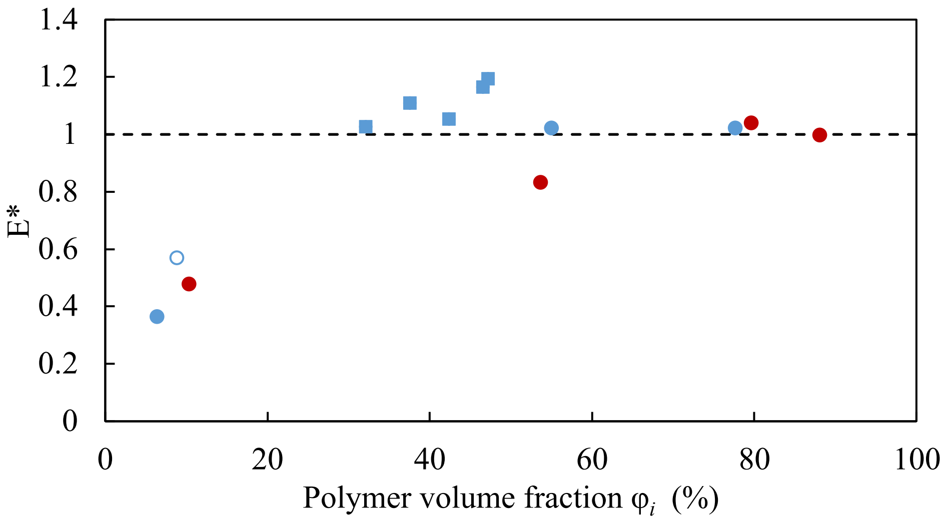

Figure 5. Normalized PGN modulus ($E^* = E_{PGN}/E_{polymer}$) depends strongly on polymer volume fraction (φ_i). Data obtained via nanoindentation are shown as circles, while those obtained using the wrinkling-crack method are shown as squares. Symbols in blue are for PGNs with a PS canopy, while those in red represent PGNs with a PMMA canopy. The data point obtained from Sample 6 is an open symbol, while those from literature[10, 11]are filled symbols. A dashed line at E* = 1 is added as a guide for the eye. PMMA has modulus 4.8 GPa [3], and this value was used to calculate E* for PMMA-based PGNs.

As shown in Figure 5, the value of E* for Sample 6 is consistent with results for other PGNs with low polymer volume fractions (< 30 %). This result suggests that the mechanical properties of PGNs synthesized via mini-emulsion polymerization via ARGET ATRP are similar to those of SiO_2-PS PGNs synthesized via a more traditional ARGET ATRP approach[3]. Thus, mini-emulsion ARGET ATRP allows us to produce PGNs of similar quality to those shown in literature, but in substantially larger batches.

We further note that the addition of the synthesized PGNs in bulk increases the modulus of elastomers, which are rubbery, low-modulus materials at room temperature, but does not substantially increase the modulus of glassy polymers such as PS and PMMA at room temperature. For example, PGNs containing a SiO_2 core and an elastomeric poly(butyl-acrylate)-grad-poly(methyl methacrylate) corona have moduli 5-8 times higher than that of the polymer at 32-65 volume % silica.[12]

5. CONCLUSIONS

SiO_2-PS and SiO_2-PMMA PGNs were synthesized with a “green chemistry” synthesis approach using an aqueous-based emulsion ARGET-ATRP. In particular, commercially-available Ludox-TM 40 silica nanoparticles with a diameter of 26 nm were functionalized with a hydrophobic ATRP initiator. Subsequently, we successfully demonstrated the synthesis of PGNs with homogeneous coronas consisting of either polystyrene or poly(methyl methacrylate), characterized in both cases by tunable corona thickness and graft density. Uniformity and control were achieved by the implementation of a polymerization process where the monomer and the reducing agent were added simultaneously over the entire reaction process. By this means, the formation of the ungrafted polymer could be avoided, which prevented the aggregation of PGNs during synthesis. Moreover, by optimizing the reaction conditions and the selection of the initiators and surfactants used, we were able to produce multi-gram scale batches of SiO2-PS PGNs with a stable corona and low degree of aggregation, characterized by good mechanical properties, as demonstrated by nanoindentation measurements. The approach developed herein for multi-gram scale PGNs synthesis opens up the possibility of producing PGNs with a wide variety of core and corona materials, which will be a main focus in future work.

At this time we have two manuscripts submitted/to be submitted in addition to the published paper in reference 8.

1. "Aqueous-phase based ARGET-ATRP for the synthesis of well-defined silica-poly(methyl methacrylate) hairy nanoparticles", Dung-Yi Wu, Florian Käfer, Nicholas Diaco and Christopher K. Ober, *Polymer Chemistry*, submitted.

2. "Multigram synthesis of polystyrene-grafted silica hairy nanoparticles for the formation of mechanically strong films", Florian Käfer, Yinglu Wang, Allen Schantz, Richard A. Vaia, Christopher K., to be submitted.

Roselynn Cordero has graduated and now works at 3M. Nick Diaco, an undergrad co-author of manuscript 1. above, will carry out an internship at AFRL this summer provided labs are open.

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