

## Highly monodisperse, lanthanide-containing polystyrene nanoparticles as potential standard reference materials for environmental “nano” fate analysis

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**ABSTRACT:** For the safe commercialization of nanoparticle technology, there is a need for reference materials that can be used in studies related to the environmental fate of nanoparticles. This work produced metal-containing polystyrene nanoparticles with target parameters such as high monodispersity, tailorable size range (33–193 nm), and variable surface charge. In addition, the combination of organic and inorganic components made them detectable by all of the main analytical techniques routinely used in nanoparticle characterization, e.g., TEM, DCS, DLS, and ICP-MS (the latter when interfaced to chromatographic instrumentation). The lanthanides Gd, Dy, and Nd were investigated as the inorganic component because of their high response when analyzed by ICP-MS, and because of their low environmental abundance. Particles were prepared by emulsion polymerization using one of two stabilizers: the nonionic surfactant Pluronic F68 or the anionic surfactant sodium dodecyl sulfate © 2015 The Authors Journal of Applied Polymer Science Published by Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 2015, 132, 42061.

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### INTRODUCTION

The increasing use of nanoparticles in consumer products is likely to lead to their release into the environment. Uncertainty about their environmental fate hampers the development of coherent and meaningful legislation regarding the incorporation of nanotechnology into our everyday lives. Quoting Peter Hatto,<sup>1</sup> “If you can’t define it and you can’t measure it, you can’t regulate it.” This uncertainty stems from the poor comparability of data between the many physical characterization, environmental fate, and toxicological evaluation studies present in the literature. One way of reducing this uncertainty would be to include appropriate reference materials in study protocols and to use the resulting information to allow the normalisation and comparison of data.<sup>2,3</sup> However, for this approach to be truly effective, the reference materials would require the following characteristics:

a. Be tailorable in size, in particular to achieve particles with dimensions below 100 nm, in order to meet the European legal definition of “nano.”<sup>4</sup>

- b. Be detectable by the analytical techniques typically used in nano-based studies, i.e., dynamic light scattering (DLS), differential centrifugal sedimentation (DCS), nanoparticle tracking analysis (NTA), transmission electron microscopy (TEM), and inductively-coupled plasma–mass spectrometry (ICP–MS) hyphenated to various separation techniques such as asymmetric-flow field flow fractionation (AF4), hydrodynamic chromatography (HDC), and size exclusion chromatography (SEC).<sup>5</sup>
- c. Have a tailorable surface charge to allow the charge characteristics of target analyte particles to be closely mimicked.

While various polymer particles are commercially available, these tend to be larger than 100 nm, often in the micron size range, and they are rarely metal-containing. In this article, we present the synthesis and characterization of a range of polymeric particles designed for use as reference materials in size calibration and internal standardisation roles. The particle systems produced were:

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**Table I.** Literature Examples of the Use of Emulsion Polymerization Techniques for the Homogeneous Dispersion of Metal Complexes Within PNPs

Emulsion type	Particle type	Metals incorporated	Particle size range	Reference
Miniemulsion	PSt & PMMA	Pt, Fe, Eu	107–148 <sup>a</sup>	21
Macro- and miniemulsion	PSt	Pt, In, Fe, Cr, Zn	102–374 <sup>a</sup>	22
Miniemulsion	PSt, PBA, PLMA, & PMMA	Eu, Nd, Y, Pr, Sm, Nd	62–167 <sup>b</sup>	23
Inverse miniemulsion	PHEMA	Co	68–188 <sup>a</sup>	24
Inverse miniemulsion	PAA	Zn	149–333 <sup>a</sup>	25
Inverse miniemulsion	PHEMA & PMPC	Ag	132–161 <sup>a</sup>	26
Miniemulsion	PSt, PBA, PLMA	Gd, Al, Sm, Eu, La, Nd, Ho	164–363 <sup>a</sup>	27
Miniemulsion	P(St/DVB/LMA)	Ho, Tb, Eu, Pr	36–88 <sup>a</sup>	28
Miniemulsion	P(St/DVB)	Eu	19–97 <sup>a</sup>	29
Dispersion	PSt	Eu, Tb, Ho	162–1466 <sup>c</sup>	30
Miniemulsion	PBMA & P(BMA/PGMP)	ZrO <sub>2</sub>	114–207 <sup>a</sup>	31

<sup>a</sup>Sizing by dynamic light scattering (DLS).

<sup>b</sup>Sizing by photon cross-correlation spectroscopy.

<sup>c</sup>Sizing by scanning electron microscopy.

PSt, polystyrene; PMMA, poly(methyl methacrylate); PBA, poly(butyl acrylate); PLMA, poly(lauryl methacrylate); PHEMA, poly(2-hydroxyethyl methacrylate); PAA, poly(acrylamide); PMPC, poly(2-methacryloyloxyethyl phosphorylcholine); DVB, divinylbenzene; PBMA, poly butyl methacrylate; PGMP, polypropylene glycol methacrylate phosphate.

- Designed to cover a ~50 to 160 nm size range.
- Doped with complexes containing one of three lanthanides (rare earth elements): gadolinium (Gd), dysprosium (Dy), or neodymium (Nd).
- Prepared by emulsion polymerization using one of two stabilizers: nonionic Pluronic F68 (Plu) or anionic sodium dodecylsulfate (SDS).

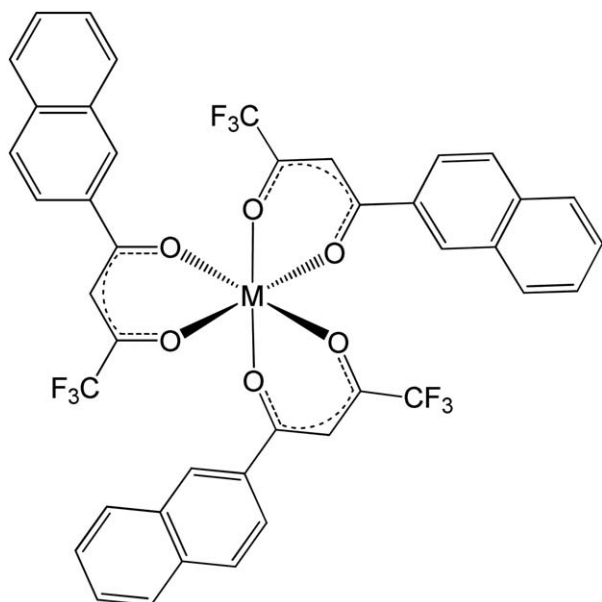
In order to construct a size calibration curve which would include the <100 nm legislative definition of “nano,” particles were produced with the following target dimensions; <60 nm, 70 to 100 nm, and 120 to 160 nm. The concentrations of surfactant and initiator required to produce particles over the desired size range were established in preliminary work.<sup>6</sup>

The specific lanthanides incorporated into the polystyrene particles were chosen because of their high response when analyzed by ICP-MS (i.e., the elements are easily ionized), as well as their relatively low environmental abundance. The assumption was that by combining these two factors only a small quantity of doped particles would be required when performing extraction efficiency and particle fate experiments. By varying the surfactant type and concentration, the size and the surface charge of the particles was controlled. A final expectation was that the combination of the polymeric and inorganic components would make the particles detectable by all of the major nanoparticle characterization techniques.

The use of emulsions to synthesise polymer particles of various types has been well documented in the literature over many years. As the number of articles is far too extensive to be covered here, reviews by Nagavarma *et al.*,<sup>7</sup> Rao and Geckeler,<sup>8</sup> Vauthier and Bouchemal,<sup>9</sup> and Allouche<sup>10</sup> are recommended. Three main oil-in-water emulsion types are used in the production of polymer particles, giving rise to macroemulsion polymerization (also referred to as conventional emulsion polymerization), miniemulsion polymerization, and microemulsion polymerization. In terms

of procedure and number of chemical constituents required for the synthesis, macroemulsion polymerization is the simplest method and usually produces particles with diameters >100 nm, although particle sizes down to 50 nm have been reported.<sup>10</sup> Miniemulsion polymerization requires an osmotic agent to be added to the oil (monomer) phase to stop monomer diffusion, as well as high energy mixing, such as high shear or ultrasonics. This allows the production of small emulsion droplets, which are polymerized as formed. Microemulsion polymerization is the most recently developed technique and can form smaller particles than macroemulsion polymerization, with particle diameters down to about 20 nm. However, microemulsions require very high surfactant concentrations, up to 30% w/w,<sup>11</sup> and often a co-surfactant (usually a medium chain alcohol) to facilitate greater interfacial curvature. Microemulsion polymerization can also be performed at much lower surfactant concentrations, in which case the monomer is added slowly during polymerization, in what is termed semi-continuous microemulsion polymerization.<sup>12,13</sup>

Within the literature there are many reported cases of encapsulation of molecules within polymer nanoparticles (PNPs).<sup>14,15</sup> The majority of these come from the pharmaceutical sciences, where encapsulation within hollow PNPs (or nanocapsules) is used in the delivery of drugs.<sup>16,17</sup> The encapsulation of metal-containing species, e.g. metal oxides<sup>18</sup> and metal complexes,<sup>19</sup> within nanocapsules has also been reported. Homogeneous encapsulation (or homogeneous dispersion) of metal complexes within the matrix of the PNPs is far less common than encapsulation within hollow particles, but has been achieved by the application of miniemulsion polymerization. The metal species being dispersed must be soluble in the monomer phase but insoluble in the continuous phase.<sup>20</sup> This and related techniques have been utilized to incorporate metal complexes in a variety of particle systems, examples of which are shown in Table I. Inverse microemulsions have been used to encapsulate metals within inorganic nanoparticles (NPs). Cerium, europium, manganese, and



**Figure 1.** Structure of the lanthanide complexes. M represents the lanthanide: Dy, Gd, or Nd.

neodymium were encapsulated within  $\text{BaMgF}_4$  NPs,<sup>32</sup> and neodymium has been encapsulated in barium fluoride NPs.<sup>33</sup>

## EXPERIMENTAL

### Particle Nomenclature

The particle systems are referred to here in terms of their composition and size by a code indicating the lanthanide (dysprosium = Dy; gadolinium = Gd; neodymium = Nd), the surfactant (sodium dodecyl sulfate = SDS; Pluronic F68 = Plu) and the particle size (large,  $\sim 150$  nm = 1; medium,  $\sim 80$  nm = 2; small,  $\sim 50$  nm = 3). For example, GdPlu-3 refers to a small, gadolinium-containing particle stabilized with Pluronic F68.

### Materials

Styrene (Sigma-Aldrich) was distilled under reduced pressure to remove inhibitors and was stored at  $-20^\circ\text{C}$  before use. Sodium dodecyl sulfate (SDS; Fisher) and potassium persulfate (KPS; Fisher) were re-crystallised from ethanol and water, respectively, before use. Neodymium chloride hexahydrate ( $\text{NdCl}_3 \cdot 6\text{H}_2\text{O}$ , 99.9%; Aldrich), dysprosium chloride hexahydrate ( $\text{DyCl}_3 \cdot 6\text{H}_2\text{O}$ , 99.9%; Alfa Aesar), gadolinium chloride hexahydrate ( $\text{GdCl}_3 \cdot 6\text{H}_2\text{O}$ , 99.9%; Aldrich), *n*-dodecane (Alfa Aesar), Pluronic F68 (poly(ethylene oxide)-block-poly(propylene oxide)-block-poly(ethylene oxide), average  $M_r \sim 8350$ ; Sigma), 1-(2-naphthoyl)-3,3,3-trifluoroacetone

(NTFA, 99%; Alfa Aesar), magnesium sulfate (Fisher), ammonia solution (35%; Fisher), dichloromethane (DCM; Sigma-Aldrich), 2-propanol (Sigma-Aldrich), hydrochloric acid (ARISTAR 37%; VWR) and nitric acid (ARISTAR 68%; VWR) were all used as received. De-ionized water was used for all polymerizations, characterizations and syntheses.

### Synthesis of the Lanthanide Complexes

The structure of the complexes is shown in Figure 1. As the preparation of lanthanide complexes is already documented in the literature,<sup>28,34</sup> only a brief description is provided here. The amounts of lanthanide chloride and 1-(2-naphthoyl)-3,3,3-trifluoroacetone (NTFA) used for each synthesis are listed in Table II. NTFA was dissolved by sonication (15 min) in a mixture of ethanol (50 mL) and ammonia solution (19 mL). The desired lanthanide chloride hexahydrate was dissolved in deionized water (10 mL) and then added, drop-wise with stirring, to the NTFA solution. The mixture was kept stirring for 24 h in a sealed vessel. The product was extracted into DCM (50 mL) and then washed with four aliquots (50 mL) of deionized water. The DCM layer was then dried with magnesium sulfate and Buchner filtered. DCM was removed using a rotary evaporator and the final product collected and dried overnight under vacuum at  $60^\circ\text{C}$ . The resulting yellow/green solids were insoluble in water, but soluble in DCM in styrene upon sonication or heating. Similar solubility behavior for similar complexes has been noted by Desbiens *et al.*<sup>29</sup>

The yields of each complex are reported in Table II. Elemental analysis was undertaken at the University of Manchester and was performed on all complexes.

Anal. calcd. for  $\text{DyC}_{42}\text{H}_{24}\text{F}_9\text{O}_6$ : Dy 16.96%, C 52.64%, H 2.52%; found: Dy 17.24%, C 50.94%, H 2.99%.

Anal. calcd. for  $\text{GdC}_{42}\text{H}_{24}\text{F}_9\text{O}_6$ : Gd 16.50%, C 52.93%, H 2.54%; found: Gd 14.64%, C 54.24%, H 2.60%.

Anal. calcd. for  $\text{NdC}_{42}\text{H}_{24}\text{F}_9\text{O}_6$ : Nd 15.35%, C 53.67%, H 2.57%; found: Nd 15.75%, C 54.45%, H 3.08%.

### Polymerization

A typical polymerization procedure (using DyPlu-2 as the example) was as follows: Pluronic F68 (0.5 g) was dissolved in de-ionized water (45 mL), in a four-neck round bottom flask. The flask was then fitted with an overhead stirrer (IKA R20.n) with a PTFE paddle through the central neck. A reflux condenser and an addition funnel were attached to two of the side necks of the flask and the remaining neck sealed with a Suba seal. The mixture was then heated to  $70^\circ\text{C}$ . Meanwhile, KPS (0.1 g) was dissolved in deionized water (5 mL) in a sealed vessel. *N*-dodecane (0.05 g) and  $\text{Dy}(\text{NTFA})_3$  (0.1 g) were dissolved in styrene (5 g) with sonication. The monomer phase was then placed in the addition funnel and sealed with a Suba seal. Once all solutions had been purged with nitrogen (30 min) and the surfactant solution had reached temperature, the monomer phase was introduced to the aqueous phase, drop-wise, via the addition funnel under mild stirring (60 rpm) forming a translucent mixture. Once addition was complete, the KPS initiator solution was introduced into the reaction through the Suba seal and polymerization was allowed to proceed for 3 h at  $70^\circ\text{C}$ . Once polymerization was complete the reaction mixture was allowed to cool to ambient temperature and then passed through

**Table II.** Amounts of Reagents and Yields of the Lanthanide 1-(2-naphthoyl)-3,3,3-trifluoroacetone Complexes

Lanthanide	Lanthanide chloride (g)	NTFA (g)	Yield (g)	Yield (%)
Gd	0.55	1.18	1.14	85
Nd	0.71	1.60	0.80 <sup>a</sup>	N/A <sup>a</sup>
Dy	0.75	1.60	1.76	92

<sup>a</sup>A significant amount of DCM phase was spilt during isolation of the product.

filter paper to remove any polymer grist. Latexes were stored at 3°C. A complete list of formulations can be found in Table S1 of the Supporting information.

### Dialysis

Before final characterization, latex particles were “cleaned” of excess surfactant and KPS by dialysis. An aliquot of latex (10 mL) was placed in a regenerated cellulose membrane (Scientific Laboratory Supplies; molecular weight cut off 12,000–14,000 Da) and dialysed against deionized water for 50 h. Dialysis water (1000 mL) was changed seven times, with the first change being made after 2 h and the last at 48 h. An appropriate dialysis time was determined by ICP-MS analysis of the potassium content in the dialysis water. After six changes of water and a total dialysis time of 50 h, the potassium levels were the same as in deionized water.

### Particle Characterization

**Dynamic Light Scattering (DLS).** For all particle systems the *z*-average ( $D_z$ ), volume-average ( $D_v$ ), and number-average ( $D_n$ ) diameters were measured by DLS using a Zetasizer Nano ZS (Malvern Instruments, UK) with a 633 nm wavelength He-Ne laser at 25°C. Latex samples were diluted to 10% with deionized water before analysis. It was unknown what effect the presence of the lanthanide complex would have upon the final refractive index (RI) of the latex particles. While this would not affect the value of  $D_z$ , the values of  $D_v$  and  $D_n$  generated by DLS require knowledge of the material's RI. It was assumed that the low complex content of the particles (est. <2% w/w) would have a minimal effect upon the final particle RI, hence the RI of polystyrene (1.59) was used. The polydispersity index (PDI) was also determined by DLS and was expressed in two ways. Firstly, the PDI calculated by the Malvern software was defined as:

$$\text{PDI} = \sigma^2 / (D_z^2) \quad (1)$$

where  $\sigma$  is the standard deviation of  $D_z$ . PDI is dimensionless with values between 0 and 1, which is scaled such that values with 0.10 or less are considered highly monodisperse and values of 0.07 are rarely seen.<sup>35</sup>

Secondly, to allow comparison with the DCS data, dispersity was also expressed by the metric  $D_v/D_n$  ( $D_v = D_w$  assuming the particles have an equal density regardless of size)<sup>36</sup> where values close to 1 are highly monodisperse.

**Differential Centrifugal Sedimentation (DCS).** The DCS measurements were carried out at the Food and Environment Research Agency (Fera), York, using a CPS DC24000-UHR instrument (Analytik Ltd, UK). Instrument settings were as per the users' instruction manual, but with the following gradient: 8%–2%; 1.6 mL per gradient step; and 24,000 rpm spin speed. For latex particles <60 nm a lower thickness sedimentation path was created by injecting 1.4 mL per gradient step. The calibrant used was 522 nm latex particles with an injection volume of 100  $\mu\text{L}$ . The sample injection volume was 50  $\mu\text{L}$  with sample dilution between 0.5 and 5% v/v, dependent on individual sample opacity.

**Transmission Electron Microscopy (TEM).** TEM was performed at the Institute for Materials Research at the University of Leeds with a Tecnai TF20 field emission gun (FEG)-TEM

(TEI) operating at 200 kV. Samples were prepared by placing a drop of the latex onto copper grids coated with a holey carbon film (Agar Scientific, UK).

**Hydrodynamic Chromatography-Inductively Coupled Plasma-Mass Spectroscopy (HDC-ICP-MS).** Details for setting-up the HDC-ICP-MS for NP analysis is described elsewhere,<sup>37,38</sup> but in the work presented here the samples were diluted to 1% v/v in mobile phase. Injection volume was 20  $\mu\text{L}$ , with the ICP-MS monitoring 157, 158, 160, 161, 162, 163, 164, and 197 isotopes. Size calibration was performed using gold nanoparticle standards (BBI, UK) at 5, 20, 50 and 150 nm.

**Zeta Potential.** The zeta potentials ( $\zeta$ ) were measured with a Zetasizer Nano ZS (Malvern Instruments, UK) at 25°C. Latex (0.1 mL) was diluted in deionized water (0.9 mL) and injected into a disposable zeta cell. Analysis was repeated three times at constant voltage with the reported value being the average of these measurements.

**Solids Content.** Solid content of the latexes was determined by gravimetric analysis after dialysis, during which any residual initiator and surfactant were assumed to have been removed. A latex sample of known mass was dried. Once dry, the mass of the residue was measured and then expressed as a percentage of the original sample mass.

**Lanthanide Content of Latexes.** The lanthanide content of the latex particles was determined at Fera using the following method: 100  $\mu\text{L}$  of latex was mixed with 2 mL of 4 : 1 nitric:hydrochloric acid in a TFM<sup>TM</sup> Modified polytetrafluoroethylene tube, and microwave digested (20 min at 240°C and 80 bar) in an UltraWAVE microwave digester (Milestone). The sample was then diluted and analyzed using a 7700 series ICP-MS (Agilent, UK) in “no gas” mode.

## RESULTS AND DISCUSSION

Table III presents size and polydispersity data for the various particle systems produced (after having undergone dialysis clean-up) measured by a number of different analytical techniques. Table III also presents the basic compositional information for each system.

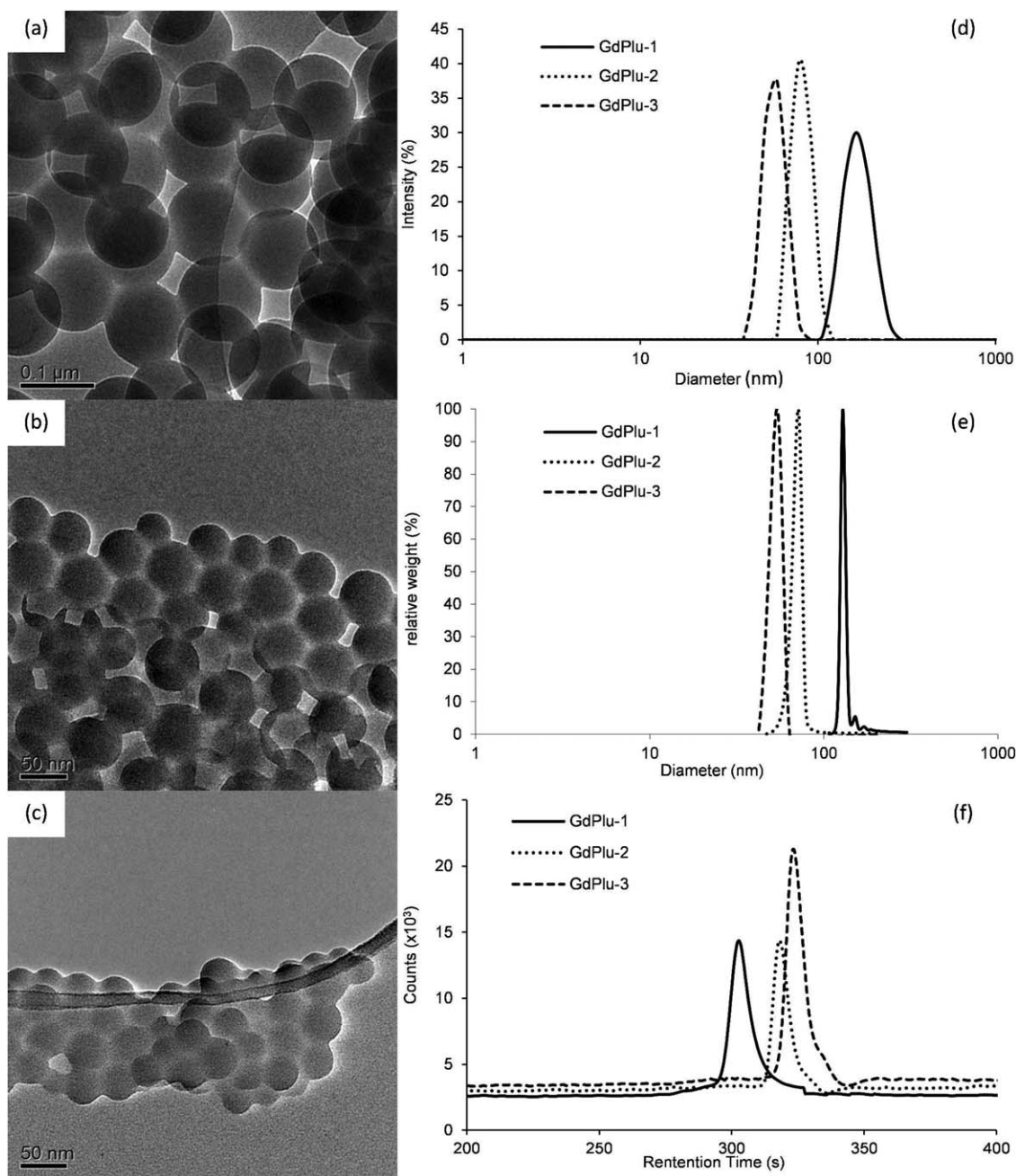
All the particles underwent an initial screening analysis by DLS, the data from which are presented in columns 5 to 8 of Table III. These data showed that the particles which used SDS as the stabilizing surfactant did not match the size requirements of the project i.e., did not cover the ~50 to 160 nm size range, whereas those stabilized with Pluronic F68 did. Therefore, only the Pluronic F68 stabilized particles were characterised further using the additional analytical techniques, i.e. DCS, TEM, and HDC-ICP-MS. Examples of the raw data outputs obtained from the various techniques are given for one particle system (GdPlu-x) in Figure 2. Comparable data for the other particle systems is provided in the Supporting information.

For the small and medium-sized particles in each set there was reasonable conformity ( $\leq 9\%$ ) between the  $D_v$  measurements made using DLS, HDC-ICP-MS, and DCS. However, while there was still good agreement between the  $D_v$  of the large particle systems as measured by DCS and HDC-ICP-MS, the  $D_v$  measured by DLS was consistently 13% to 15% larger. The reason for this is currently unknown. TEM imaging of the particles

**Table III.** Particle Sizing and Polydispersity Data for the Particle Systems Produced, and the Associated Compositional Information

Sample	Lanthanide present	Surfactant type/mass (g)	KPS (g)	Diameter (nm)											
				DLS			DCS			TEM			HDC-ICP-MS		
				$D_z$	$D_v$	$D_n$	PDI	$D_w$	$D_n$	$D_w/D_n$	$D_n$	$D_w$		$D_n$	$D_w/D_n$
DyPlu-1	Dy	Plu F68/0.125	0.025	155	157	149	0.02	134	132	1.01	117	145			
DyPlu-2	Dy	Plu F68/0.50	0.10	78	75	71	0.05	69	68	1.02	54	68			
DyPlu-3	Dy	Plu F68/1.50	0.25	52	48	44	0.09	49	48	1.01	33	49			
GdPlu-1	Gd	Plu F68/0.125	0.025	144	145	138	0.02	126	122	1.03	107	138			
GdPlu-2	Gd	Plu F68/0.50	0.10	79	74	68	0.06	71	69	1.03	55	68			
GdPlu-3	Gd	Plu F68/1.50	0.25	58	55	50	0.06	53	52	1.02	35	53			
NdPlu-1	Nd	Plu F68/0.125	0.025	193	195	188	0.03	-	-	-	-	178			
NdPlu-2	Nd	Plu F68/0.50	0.10	69	66	57	0.09	-	-	-	-	58			
NdPlu-3	Nd	Plu F68/1.50	0.25	57	54	51	0.04	-	-	-	-	53			
Plu-1	None	Plu F68/0.125	0.025	148	149	143	0.01	126	125	1.01	113	-			
Plu-2	None	Plu F68/0.50	0.10	79	73	63	0.09	68	65	1.04	50	-			
Plu-3	None	Plu F68/1.50	0.25	49	41	35	0.10	42	-	-	26	-			
NdSDS-1	Nd	SDS/0.125	0.025	60	55	49	0.05	-	-	-	-	-			
NdSDS-2	Nd	SDS/0.50	0.10	48	45	42	0.04	-	-	-	-	-			
NdSDS-3	Nd	SDS/1.50	0.25	34	32	29	0.06	-	-	-	-	-			
GdSDS-1	Gd	SDS/0.125	0.025	78	69	54	0.08	-	-	-	-	-			
GdSDS-2	Gd	SDS/0.50	0.10	48	46	42	0.04	-	-	-	-	-			
GdSDS-3	Gd	SDS/1.50	0.25	35	32	28	0.06	-	-	-	-	-			
DySDS-1	Dy	SDS/0.125	0.025	68	63	57	0.05	-	-	-	-	-			
DySDS-2	Dy	SDS/0.50	0.10	49	46	42	0.05	-	-	-	-	-			
DySDS-3	Dy	SDS/1.50	0.25	33	30	26	0.06	-	-	-	-	-			





**Figure 2.** Left column: TEM images of (a) the large (PluGd-1), (b) the medium (PluGd-2), and (c) the small (PluGd-3) particles produced from emulsions stabilized by Pluronic F68. Right column (d): the intensity size distribution (measured by DLS), (e) the weight size distribution (measured by DCS) and (f) the HDC-ICP-MS chromatography of the Pluronic F68 stabilized gadolinium-containing particle set.

(Figure 2) showed that they were of a spherical morphology. The values of  $D_n$  obtained by TEM were consistently less than the values obtained by the other sizing methods. This difference can be attributed to the inability of TEM to visualize the surfactant sheath present at the particle surface. The two poly(ethylene oxide) hydrophilic tails of Pluronic F68 each contain 76 repeat units ( $M_r \approx 3340$  each, total  $M_r \approx 6680$ , approximately 80% of the total  $M_r$  of Pluronic F68)<sup>39</sup> and extend into the dispersion medium, thereby increasing the hydrodynamic diameter which is the parameter measured by DLS, DCS and HDC.

All the particle systems were highly monodisperse, with no PDI greater than 0.1 measured either before or after dialysis, although the neodymium doped particles increased in size during the dialysis process (see Supporting information). Similarly, no value of  $D_w/D_n$  measured by DCS was greater than 1.04, indicating high levels of monodispersity. Monodispersity appeared to be independent of the initial KPS/surfactant concentration, the type of surfactant, or the lanthanide complex employed.

The particle systems stabilized by SDS were consistently smaller than the corresponding Pluronic F68 stabilized systems. This

**Table IV.** Comparison of the Zeta Potentials of the Two Sets of Particles Containing Gadolinium, One of Which was Stabilized by the Anionic Surfactant SDS and the Other by the Nonionic Surfactant Pluronic F68

Surfactant	Zeta potential (mV)		
	Large	Medium	Small
SDS	-37.8	-36.9	-38.8
Pluronic F68	-3.1	-4.1	-6.0

was the case even taking into account the different molar amounts of surfactant due to the difference in molecular weight. The difference in sizes can be rationalized by application of the hydrophilic-lipophilic balance (HLB) concept. Surfactants with higher HLB values produce interfaces with greater curvature<sup>40</sup> which would in turn allow the formation of smaller particles. Therefore, since SDS has a higher HLB number (HLB = 40) than Pluronic F68 (HLB >24), it would be expected to yield smaller particles.<sup>41</sup>

Moraes *et al.*<sup>42</sup> observed that the relationship between final particle size and surfactant concentration is inverse and nonlinear. They proposed that this nonlinear relationship resulted from limitations on surfactant packing. At high surfactant concentrations rod-like structures rather than spherical micelles are formed, thereby limiting the number and the surface area of micelles formed.<sup>43</sup>

As mentioned, particle size was controlled by variation of the initial surfactant and KPS concentration. As expected from the literature,<sup>36,44–51</sup> higher KPS and surfactant concentrations in the initial emulsions produced particles with a smaller final diameter. The common rationalization in the literature for the effect of the surfactant is that higher surfactant concentrations allow the stabilization of a greater interfacial area, meaning that

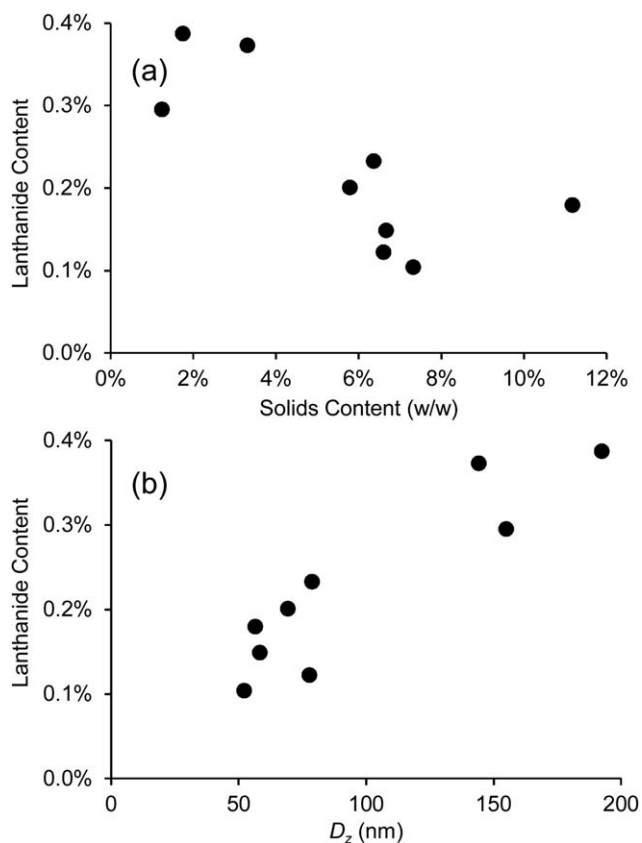
**Table V.** Solid Content and Lanthanide Content of Polystyrene Latex Particles Stabilized by Pluronic F68

Sample	Solid content postdialysis (%)		Lanthanide content (wt %)
	Measured	Max. estimated	
DyPlu-1	1.2	9.6	0.30 <sup>a</sup>
DyPlu-2	6.6	10.2	0.12 <sup>a</sup>
DyPlu-3	7.3	12.0	0.10 <sup>a</sup>
GdPlu-1	3.3	9.6	0.37 <sup>b</sup>
GdPlu-2	6.4	10.2	0.23 <sup>b</sup>
GdPlu-3	6.7	12.0	0.15 <sup>b</sup>
NdPlu-1	1.8	9.6	0.39 <sup>c</sup>
NdPlu-2	5.8	10.2	0.20 <sup>c</sup>
NdPlu-3	11.2	12.0	0.18 <sup>c</sup>
Plu-1	7.1	9.3	N/A
Plu-2	6.6	10.1	N/A
Plu-3	5.7	11.9	N/A

<sup>a</sup>Expected lanthanide content 0.34 wt %.

<sup>b</sup>Expected lanthanide content 0.29 wt %.

<sup>c</sup>Expected Lanthanide content 0.31 wt %.

**Figure 3.** Lanthanide content of the polystyrene particles as a function of (a) the solids content of the corresponding latex and (b) the particle size ( $D_2$ ) as measured by DLS.

increasing surfactant concentration allows stabilization of a greater number of smaller particles. The effect of the KPS is explained in the literature by formation of anionic sulfate-terminated styrene oligomers, which have a similar structure to a surfactant, and provide stability to the growing particles. The anionic sulfate of these species is assumed to locate at the interface, with the styrene chain extending into the monomer droplet/particle. Therefore, a greater amount of KPS would be expected to result in a greater amount of the stabilising oligomers and therefore smaller particles.<sup>45</sup>

In order to gain information regarding the particles' surface charge, zeta potential ( $\zeta$ ) measurements were made. While not identical to surface charge, zeta potential is a closely related parameter, with larger values for zeta potential corresponding to a greater surface charge. As can be seen from Table IV, the particle surface charge was significantly influenced by the surfactant used in its preparation. Particles stabilized by the anionic surfactant SDS (utilizing a charge stabilisation mechanism) gave high  $\zeta$  values ( $-37$  to  $-39$  mV), whereas particles stabilized by the nonionic surfactant Pluronic F68 (utilising a steric stabilisation mechanism) gave low  $\zeta$  values ( $-3$  to  $-6$  mV). The residual surface charge present on the particles stabilized by Pluronic F68 can likely be attributed to sulfate anions attached to the end of the polymer chains. These sulfate anions are an artefact of initiation produced when the KPS decomposes to form a sulfate radical anion, which then initiates polymerization. It is reasonable to

assume that these ionic chain-ends would have located at the particle/water interface during polymerization and would, therefore, not be removed by dialysis. As can be seen from Table IV, the zeta potential for the Pluronic F68-stabilized particles is greater the smaller the particle. This change, whilst small, is consistent with the synthetic procedure in which larger amounts of KPS were used to produce the smaller particles. A larger amount of KPS will result in a larger number of sulfate-terminated polymer chains, leading to a higher surface charge on the particles and therefore a higher zeta potential. As reference/internal standards should mimic as closely as possible the analytes that are under investigation, the ability to tailor the surface charge on a particle would potentially allow researchers to produce bespoke materials optimized for specific uses.

With the exception of NdPlu-3, the solids content of the latexes was significantly lower than expected (Table V), with the lowest solids content being observed in the large particles of the set. Under the conditions of the polymerization, only minimal amounts of unreacted monomer are expected, so the discrepancy between the expected solids mass and that measured can be attributed to formation of a mass of bulk-phase polymer, which was observed to aggregate on the nitrogen purge needle and stirrer paddle during polymerization. This mass appeared larger for the synthesis of the large particles, which were probably more prone to aggregation due to the low surfactant content of the emulsions. NdPlu-3 was the exception, with a solids content of 11.2% (close to the 12.0% maximum expected).

The lanthanide content of the particles was found to increase with particle size (Table V and Figure 3), with the large particles in a set having either a similar amount to what was expected (DyPlu-1), or significantly more (GdPlu-1 and NdPlu-2). As the final location of the complex within the particles is unknown (energy-dispersive X-ray spectroscopy was not able to visualize it), little speculation can be made regarding this observation and will require further investigation. However, other authors<sup>28</sup> have noticed discrepancies between the expected metal content of polymer particles and the final measured amount when using miniemulsion polymerization and also could not rationalize the discrepancy.

There is uncertainty concerning the polymerization process and the mechanism by which the lanthanide complexes become encapsulated by the polymer particles. In macroemulsion polymerization there are initially three phases: (i) aqueous phase, containing the initiator and traces of molecularly dissolved surfactant and monomer, (ii) large monomer droplets, and (iii) monomer-swollen micelles. The large droplets serve only as a reservoir of monomer feeding the polymerization. In such a system the lanthanide complexes would most likely reside in the monomer droplets and, due to the insolubility of the complex in water, would not necessarily diffuse into the polymer particles. While there are cases in the literature of metal-doped polymer particles being produced by macroemulsion polymerization,<sup>22</sup> ethanol was added to the aqueous phase to allow diffusion of metal complex from the droplets. In the present work, the HDC-ICP-MS data show that the lanthanide complexes are indeed associated with the polymer particles. We can speculate

that there was in practice some diffusion through the aqueous phase of lanthanide complexes, perhaps in combination with surfactant and/or monomer, but further research is required to confirm this. In a miniemulsion polymerization there are many small droplets and particle nucleation occurs within these droplets. The droplets also contain any monomer-soluble species, which provides a way to encapsulate metal species within the resulting polymer particles (see Table I). However, it is unlikely that a miniemulsion formed in the present work, as miniemulsion polymerization generally requires an osmotic agent and high energy mixing. Microemulsion polymerization, on the other hand, requires minimal mixing and produces a thermodynamically stable and transparent/translucent system. While the emulsion described here did appear translucent, becoming turbid as the reaction progressed, the levels of surfactant were not as high as is usual for formation of a microemulsion, and while *n*-dodecane has been reported as a co-surfactant in microemulsion polymerization,<sup>36</sup> the co-surfactant traditionally is a medium-chain alcohol. Microemulsion polymerization also takes place with diffusion of monomer, as discussed above.<sup>11</sup>

## CONCLUSIONS

This work has demonstrated the production of polystyrene nanoparticles doped with complexes of dysprosium, gadolinium, or neodymium. Particles were produced which covered a range of sizes from 33 to 193 nm ( $D_w$ , measured by DLS) by tailoring the surfactant (Pluronic F68 or SDS) and initiator (KPS) content of the emulsion formulations. By altering the surfactant type and initiator amount, the surface charge on the particles was also able to be adjusted.

A number of different analytical techniques gave particle sizes in good agreement (given the different parameters reported by the individual techniques). Furthermore, they are highly monodisperse. This demonstrates the potential for these particles to be used as standardization materials in future multitechnique studies. This is currently under investigation at FERA using the particles as internal standards in a fate-and-behavior study of TiO<sub>2</sub> particles in sewage sludge and soils. The particles have also been used as standards to assess the separation performance of a polyHIPE-ICP-MS chromatography system.<sup>52</sup>

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