Aqueous RAFT Synthesis

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RAFT Synthesis of Sterically Stabilized Methacrylic Nanolatexes and Vesicles by Aqueous Dispersion Polymerization**

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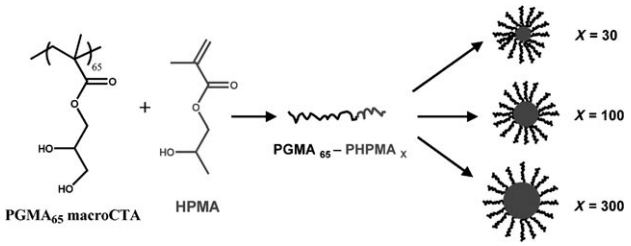
Emulsion polymerization is widely used for waterborne coatings.[1] Reducing the latex particle size is known to promote coalescence and hence enhance film formation. However, the synthesis of smaller latexes usually requires additional surfactant, which can compromise the quality of waterborne coatings (e.g. poor adhesion and reduced film quality due to migration of excess surfactant).[2] In principle, reactive surfactants offer a potentially decisive advantage over conventional surfactants in emulsion polymerization because they bind irreversibly to the latex and hence cannot migrate during film formation; this allows defect-free coatings to be produced with reduced moisture sensitivity.[3]

Over the last two decades, controlled/living radical polymerization techniques have become powerful tools in polymer synthesis.[4–8] There are many examples of latex syntheses based on these approaches.[9] For example, nitroxide-mediated living radical polymerization has been used by Charleux,[10–15] El-Aasser,[16] Okubo,[17] and Georges[18] to mediate the miniemulsion polymerization of *n*-butyl acrylate and styrene. ATRP has been optimized by Matyjaszewski[19–22] and Okubo[23–25] for the (mini)emulsion polymerization of (meth)acrylic and styrene monomers. Reversible addition–fragmentation chain transfer (RAFT) polymerization has been extensively exploited in the context of both emulsion and miniemulsion polymerization by Hawkett,[26–29] Charleux,[30–33] El-Aasser,[34] Cunningham,[35] and Zhu.[36] There are also a number of RAFT syntheses conducted under non-aqueous dispersion polymerization conditions.[37–39]

However, as far as we are aware, there are only three examples of the application of controlled/living radical polymerization techniques for latex syntheses by aqueous dispersion polymerization.[40] In each case, a relatively expensive speciality monomer was utilized for the latex core, namely *N*-isopropylacrylamide[40a] or *N*,*N*′-diethylacrylamide.[40b,c] This relative lack of research is perhaps surprising, because aqueous dispersion polymerization is conceptually much simpler than aqueous emulsion polymerization since the initial reaction solution is homogeneous in the former case. Presumably, the paucity of experimental data merely reflects the fact that there are relatively few vinyl monomers that are suitable for latex syntheses by aqueous dispersion polymerization.

Recently, we reported the use of conventional (non-living) free radical chemistry for the aqueous dispersion polymerization of a commodity methacrylic monomer, 2-hydroxypropyl methacrylate (HPMA).[41] The resulting PHPMA latexes were stabilized by poly(*N*-vinylpyrrolidone) and the mean particle diameter could be varied from approximately 100 to 1000 nm diameter, with good control over the particle size distribution being achieved in most cases. Herein we explore the RAFT synthesis of sterically stabilized PHPMA nanolatexes of 20 to 100 nm diameter by surfactant-free aqueous dispersion polymerization using a poly(glycerol monomethacrylate)-based chain transfer agent (CTA) as the reactive steric stabilizer. Thus both the latex cores and the steric stabilizer chains of the resulting nanolatexes are highly hydroxylated for this prototype formulation. Moreover, varying the length of the targeted PHPMA chains allows the final size of the sterically stabilized nanolatex particles to be controlled quite precisely (see Scheme 1, Table 1, and the Supporting Information).



Scheme 1. RAFT synthesis of sterically stabilized methacrylic nanolatexes by aqueous dispersion polymerization.

4-Cyanopentanoic acid dithiobenzoate (CTP) was used as a chain transfer agent for the RAFT synthesis of a near-monodisperse PGMA homopolymer. This chain transfer agent has previously been used to control the RAFT synthesis of both methacrylamide and methacrylate homopolymers.[42,43] In the present work, 1,4-dioxan was usually used as a co-solvent to improve the CTP solubility for the GMA polymerization, because a relatively large amount of CTP was required to target lower molecular weight polymers. However, it is also possible to conduct the RAFT polymerization of GMA in purely aqueous solution if the monomer concentration is increased to 50%, since the GMA can act as a co-solvent for the CTP under these conditions. Well-defined, low polydispersity PGMA homopolymers can be obtained under such conditions (see, for example, entry 1 in Table 1). This

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Table 1: Dynamic light scattering diameters and polydispersities obtained for various $PGMA_{65}$–$PHPMA_x$ nanolatexes synthesized by RAFT polymerization under aqueous dispersion polymerization conditions at 70 °C.

Entry	Targeted copolymer structure	Diameter (DLS) [nm]	PDI
1	$PGMA_{65}$ homopolymer	–	
2	$PGMA_{65}$–$PHPMA_{30}$	26	0.12
3	$PGMA_{65}$–$PHPMA_{50}$	29	0.12
4	$PGMA_{65}$–$PHPMA_{70}$	40	0.10
5	$PGMA_{65}$–$PHPMA_{100}$	58	0.10
6	$PGMA_{65}$–$PHPMA_{200}$	87	0.05
7	$PGMA_{65}$–$PHPMA_{300}$	105	0.003
8	$PGMA_{65}$–($PHPMA_{100}$/X_1)	86	0.12
9	$PGMA_{65}$–$PHPMA_{100}$ (20% solids)	73	0.11
10[a]	$PGMA_{55}$–$PHPMA_{100}$	20	0.12
11[a]	$PGMA_{55}$–($PHPMA_{100}$/X_1)	39	0.24
12[a]	$PGMA_{55}$–$PHPMA_{200}$	131	0.30
13[a]	$PGMA_{55}$–$PHPMA_{200}$ (15% solids)	324	0.16
14[a]	$PGMA_{55}$–$PHPMA_{300}$ (20% solids)	520	0.22
15	$PSEMA_{71}$–($PHPMA_{200}$-X_1)	129	0.03
16	$PKSPMA_{65}$–$PHPMA_{100}$	66	0.09
17	$PQDMA_{67}$–$PHPMA_{100}$	56	0.20

[a] One-pot syntheses conducted at the stated solids content; all other syntheses were conducted at a total solids content of 10%. X = EGDMA cross-linker; this was added at the start of the HPMA polymerization.

PGMA homopolymer was then used as a "macroCTA" for the second-stage RAFT polymerization of HPMA, which was conducted under aqueous dispersion polymerization conditions. In this case no organic co-solvent was needed, since both the PGMA homopolymer and HPMA monomer are fully soluble in aqueous solution under the initial reaction conditions (according to its manufacturer, the solubility of HPMA monomer in aqueous solution is around 13% w/w at 25 °C). HPMA is a relatively unusual monomer in that it is water-miscible, but the corresponding PHPMA is water-insoluble; this is an essential criterion for aqueous dispersion polymerization. Unlike our earlier synthesis of PHPMA latexes using conventional free radical polymerization,[41] we have utilized RAFT chemistry in the present work so the resulting PHPMA latexes actually comprise $PGMA_{65}$–$PHPMA_x$ block copolymers, since the PHPMA chains are grown from the $PGMA_{65}$ macroCTA. Initially, the growing $PGMA_{65}$–$PHPMA_x$ block copolymer remains water-soluble since the PHPMA block is still relatively short. However, as the PHPMA block becomes longer its hydrophobic character increases, which eventually drives in situ micellar self-assembly,[44,45] and ultimately a colloidally stable sterically stabilized PGMA-PHPMA nanolatex is formed. Using the same $PGMA_{65}$ macroCTA, a systematic increase in the mean target degree of polymerization (DP) of the PHPMA block from 30 to 300 leads to a monotonic increase in the mean nanolatex diameter, from 26 to 105 nm as judged by DLS (see Table 1 and Figure 1). Similar self-assembly behavior in aqueous solution has been reported for ABC triblock copolymers prepared by solution polymerization.[46]

Kinetic studies (Figure S1 in Supporting Information) confirm that the RAFT polymerization of HPMA under aqueous dispersion conditions is relatively fast; for example, 80% conversion can be achieved within 2 h at 70 °C for a

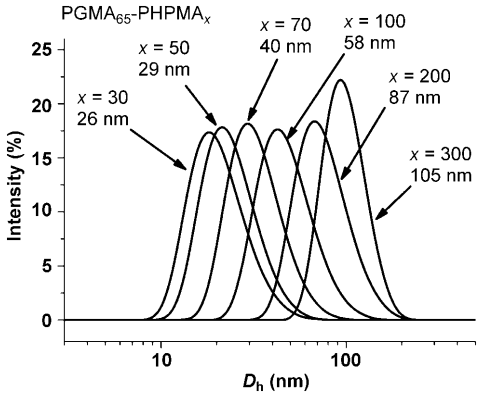

Figure 1. Dynamic light scattering particle size distributions obtained for a series of $PGMA_{65}$–$PHPMA_x$ nanolatexes in which the PGMA block length is fixed and the PHPMA block length is systematically varied.

targeted block composition of $PGMA_{65}$–$PHPMA_{200}$ at 10% solids. After 5 h, this same formulation leads to almost complete (> 99%) HPMA conversion and produces a final intensity-average latex diameter of around 78 nm.

^{1}H NMR spectra were recorded for the $PGMA_{65}$ macroCTA dissolved in D_2O, a RAFT-synthesized $PHPMA_{50}$ homopolymer control in CD_3OD, and four $PGMA_{65}$–$PHPMA_x$ latexes redispersed in D_2O (Figure S2). All the signals associated with the PGMA macroCTA are observed in each of the latex spectra. In contrast, none of the PHPMA signals are visible, regardless of the PHPMA block length. Thus these NMR observations are consistent with the $PGMA_{65}$ block acting as the solvated steric stabilizer, while the PHPMA block forms the non-solvated latex core.

HPMA monomer is known to undergo slow transesterification during storage at ambient temperature, generating a small amount of dimethacrylate species (< 0.2 mol%) with the elimination of a 1,2-propylene glycol by-product.[41] This dimethacrylate impurity can lead to a low level of cross-linking during the RAFT polymerization of HPMA. Thus the homopolymerization of HPMA in DMF by RAFT at 70 °C using CTP gave a polydispersity of 1.34 for a target degree of polymerization of 50, but a polydispersity of 1.92 for a target degree of polymerization of 300. These solution polymerization control experiments demonstrate that the dimethacrylate impurity leads to greater levels of cross-linking as higher target degrees of polymerization are targeted, as expected. A similar effect is anticipated for the polymerization of HPMA under aqueous dispersion polymerization conditions.

DMF GPC chromatograms obtained for the $PGMA_{65}$ macroCTA and selected $PGMA_{65}$–$PHPMA_x$ latexes are shown in Figure S3. Compared to that of the $PGMA_{65}$ macroCTA, the GPC traces obtained for the diblock copolymers are all shifted to higher molecular weight. Moreover, a high molecular weight shoulder gradually becomes more prominent as the target DP of the PHPMA block is increased. These results are quite similar to those reported for branched PHPMA syntheses involving statistical copolymerization of HPMA with a divinyl comonomer[47] and are also consistent with the results of our solution polymerization control experiments described above. In addition, there is also some evidence for a relatively low level of contamination (< 10–

15%) of these PGMA–PHPMA latexes by the original PGMA macroCTA, suggesting that the macroCTA efficiency during the second-stage HPMA polymerization is less than 100%. This is not unexpected given that RAFT chemistry has only pseudo-living (rather than genuinely living) character.

Although the PHPMA latex cores are cross-linked, this degree of cross-linking is still relatively low, since the copolymer chains can be fully dissolved for GPC analysis, as indicated above. To prevent such dissolution and hence obtain more robust latex particles, a bifunctional cross-linker such as ethylene glycol dimethacrylate (EGDMA) must be added to the reaction solution along with the HPMA monomer. Empirically, we find that 1 mol% EGDMA is sufficient to fully cross-link the latex particles (Table S2). Compared to a $PGMA_{65}$–$PHPMA_{100}$ latex prepared in the absence of any EGDMA (entry 5 in Table 1), the mean diameter of the corresponding cross-linked latex (entry 9 in Table 1) increased from 58 to 86 nm. The latex polydispersity also increases slightly from 0.10 to 0.12 as judged by DLS.

Electron microscopy studies of these methacrylic latexes are rather challenging in view of their relatively small size, poor electron contrast, and marked propensity for chemical degradation under a focused electron beam. Nevertheless, field emission scanning electron microscopy allows good-quality images to be obtained for the largest nanolatexes (Figure 2). This particular $PGMA_{65}$–$PHPMA_{300}$ example has

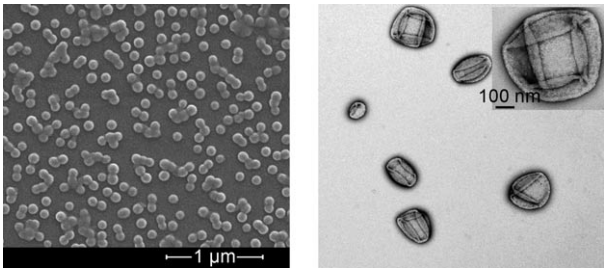

Figure 2. Electron microscopy images. Left) $PGMA_{65}$–$PHPMA_{300}$ latex prepared at 10% solids content by a two-stage synthesis (entry 7 in Table 1). Right) $PGMA_{65}$–$PHPMA_{300}$ latex prepared at 20% solids content by a one-pot synthesis (entry 14 in Table 1).

a near-monodisperse spherical morphology, with a mean number-average diameter of approximately 100 nm. However, less satisfactory images were generally obtained for the smaller nanolatexes prepared with shorter PHPMA blocks (Figure S4). Allowing for the effects of polydispersity and hydration, electron microscopy diameters are generally consistent with the corresponding DLS diameters. Intriguingly, a targeted $PGMA_{65}$–$PHPMA_{300}$ diblock copolymer prepared at 20% solids content (entry 14 in Table 1; right image in Figure 2) leads to a vesicular morphology, rather than a spherical morphology. Pan et al. reported similar findings for RAFT-synthesized diblock copolymers prepared by alcoholic dispersion polymerization,[39] while Charleux et al. used nitroxide-mediated polymerization under aqueous emulsion polymerization conditions to synthesize vesicles directly in water.[48] Block copolymer nanofibres through aqueous emulsion polymerization have also been recently reported by the same group.[49] However, vesicle self-assembly by aqueous dispersion polymerization appears to be unprecedented.

Dynamic light scattering size distributions of the cross-linked PHPMA latex $PGMA_{65}$–($PHPMA_{100}$–$EGDMA_1$) dispersed in water, methanol, and pyridine are shown in Figure S5. Both methanol and pyridine are good solvents for both PGMA and PHPMA homopolymers. Thus the cross-linked latex swells significantly in these latter two solvents. The intensity-average latex diameter increases from 86 nm (water) to 123 nm (methanol) to 166 nm (pyridine), as expected based on our earlier study of PHPMA latexes prepared by conventional free-radical chemistry.[41] ^{1}H NMR spectra recorded in [D_5]pyridine for $PGMA_{65}$ homopolymer, $PHPMA_{50}$ homopolymer, and the $PGMA_{65}$–($PHPMA_{100}$–$EGDMA_1$) latex are shown in Figure S6. In addition to the expected PGMA signals, two PHPMA signals are also observed at $\delta = 4.11$ and 4.50 ppm, which suggests significant solvation of the PHPMA latex cores in this solvent. However, our DLS studies confirm that this lightly cross-linked latex acquires microgel character in this solvent environment, rather than undergoing molecular dissolution.

Selected nanolatexes were characterized by aqueous electrophoresis (Figure 3). As expected, the non-ionic PGMA steric stabilizer effectively shields any surface

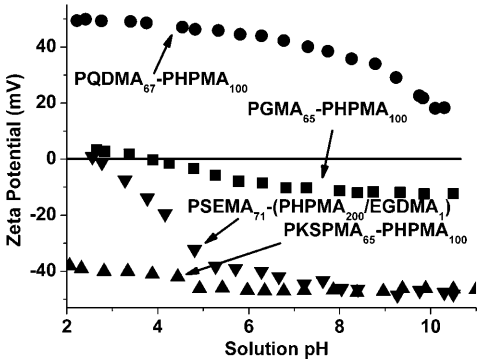

Figure 3. Zeta potential vs. pH curves obtained for non-ionic $PGMA_{65}$-$PHPMA_{100}$, cationic $PQDMA_{50}$-$PHPMA_{100}$, and anionic $PSEMA_{53}$-$PHPMA_{100}$ and $PKSPMA_{50}$-$HPMA_{100}$ nanolatexes. See main text for details.

charge, leading to a relatively flat zeta potential vs. pH curve, with zeta potentials only varying from +4 mV to −12 mV. In contrast, PHPMA particles prepared using polyelectrolyte-based macroCTAs exhibited markedly different electrophoretic behavior. Thus macroCTAs based on methyl chloride-quaternized poly(2-(dimethylamino)ethyl methacrylate) (PQDMA) and poly(potassium 3-sulfopropyl methacrylate) (PKSPMA) lead to strongly cationic and anionic particles, respectively, over a wide range of solution pH. On the other hand, using poly(2-(methacryloyloxy)ethyl succinate) (PSEMA) macroCTA led to highly anionic zeta potentials above the pK_a of this poly(carboxylic acid) (around pH 5), whereas much lower zeta potentials were observed at low pH. Freeze–thaw stability experiments were also conducted to examine the effectiveness of the steric stabilization mechanism. A $PGMA_{65}$–$PHPMA_{300}$ latex of 105 nm diameter

was frozen overnight at −20 °C and thawed at ambient temperature. DLS studies of the thawed aqueous dispersion indicated a mean particle diameter of 107 nm, which suggests that minimal aggregation had occurred. A similar DLS diameter was obtained for this latex in the presence of 1.0 M NaCl; thus the steric stabilization conferred by the $PGMA_{65}$ chains provides an effective barrier towards electrolyte-induced coagulation, as expected.

Although the water solubility of HPMA monomer is limited to only 13 % at room temperature, it is nevertheless possible to prepare PGMA–PHPMA nanolatexes at 20 % solids with little or no coagulum (Table 1, entry 9). In such a formulation, the PGMA macroCTA and azo initiator are fully dissolved at room temperature, but the HPMA monomer remains partially immiscible even on heating to 70 °C. However, the reaction solution becomes transparent after about 30 min at 70 °C due to partial consumption of the HPMA monomer. It is also possible to conduct convenient, wholly aqueous, "one-pot" syntheses of these PGMA–PHPMA latexes. In this case, GMA is polymerized by aqueous RAFT at 50 % w/w. Under these conditions, the monomer initially acts as a co-solvent to ensure complete dissolution of the CTP RAFT agent. The GMA conversion reaches 96 % after 3 h at 70 °C, then an aqueous degassed solution of HPMA monomer was added to this reaction solution and the total comonomer conversion reached 99 % after 24 h. The final sterically stabilized PGMA–PHPMA latex had an intensity-average diameter of 39 nm and a polydispersity of 0.24, as judged by DLS.

In summary, a wide range of sterically stabilized nanolatexes can be prepared by RAFT polymerization of 2-hydroxypropyl methacrylate under surfactant-free aqueous dispersion polymerization conditions. The electrophoretic behavior of these particles strongly depends on whether a non-ionic, cationic, or anionic macroCTA is selected as the steric stabilizer. Electron microscopy and DLS studies confirm relatively narrow particle size distributions in most cases, and the mean latex diameter can be conveniently controlled over the 20 to 105 nm range simply by adjusting the target block composition. Applications for these new nanolatexes are likely to be dictated by the functionality imparted by the steric stabilizer chains. For example, the well-known highly biocompatible nature of the poly(glycerol monomethacrylate) stabilizer[50] suggests potential biomedical applications. Finally, targeting longer core-forming blocks leads to the formation of circa 500 nm block copolymer vesicles, rather than sterically stabilized nanolatexes. This is a potentially very convenient route, since it enables vesicles to be prepared at relatively high solids.

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