

Poly(dimethylsiloxane)-Stabilized Polymer Particles from Radical Dispersion Polymerization in Nonpolar Solvent: Influence of Stabilizer Properties and Monomer Type

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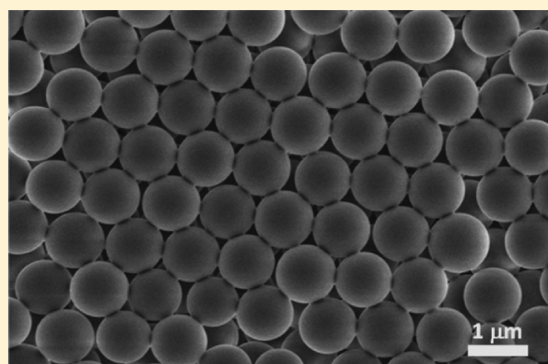
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S Supporting Information

ABSTRACT: Particles used in electrophoretic display applications (EPD) must possess a number of specific properties ranging from stability in a nonaqueous solvent, high reflectivity, low polydispersity, and high charge density to name but a few. The manufacture of such particles is best carried out in the solvent of choice for the EPD. This opens up new interests in the study of nonaqueous dispersion polymerization methods, which deliver polymer particles suspended in low dielectric constant solvents. We explore in this article the use of a poly(dimethylsiloxane) macromonomer for the stabilization of poly(methyl methacrylate) polymer particles in dodecane, a typical solvent of choice for EPDs. The use of this stabilizer is significant for this method as it is directly soluble in the reaction medium as opposed to traditionally used poly(12-hydroxystearic acid)-based stabilizers. Additionally, the present study serves as a baseline for subsequent work, where nonaqueous dispersion polymerization will be used to create polymer particles encapsulating liquid droplets and solid pigment particles. In this article, the influence of the macromonomer molecular weight and concentration on the properties of the synthesized particles is studied. In addition, we investigate the possibility of synthesizing polymer particles from other monomers both as a comonomer for methyl methacrylate and as the only monomer in the process. The influence of macromonomer concentration is also studied throughout all experiments.



1. INTRODUCTION

Recently, there has been renewed interest in the preparation of well-controlled functional polymer particles in nonpolar solvents due to their emergent application in electrophoretic displays (EPD).¹ Aside from an efficient steric stabilization, other requirements for the design of particles for applications in EPD include: well-controlled particle diameters with low polydispersity; density match with the continuous phase to minimize sedimentation; ability to produce the particles in a nonpolar solvent; strong charge density to drive rapid switching between electrodes; and strong reflectivity/color depending on the purpose of the particles within the EPD (i.e., particles providing background reflection in the first case or displaying color within a pixel in the second case). A successful production of suitable polymer particles for EPD is thus likely to result in complex particulate structures within which, for example, organic dyes, particle pigments or/and oleophilic salts are encapsulated.^{2,3}

Dispersion polymerization has commonly been used for the preparation of well-controlled polymer particles in nonpolar

solvents.^{4–8} This is of importance for EPD applications as the particles are dispersed in low dielectric media within the display. Thus, using dispersion polymerization to manufacture particles suitable for EPD applications has the potential to eliminate issues associated with solvent transfer, as may arise if using emulsion polymerization routes for example, as the particles can be synthesized directly in the same low dielectric constant solvent as that used in the displays.

The dispersion polymerization process involves several steps as follows. (1) Initially, it requires the preparation of a homogeneous mixture containing a monomer, a polymerization initiator and a stabilizer (with potential cross-linkers and chain transfer agents). (2) The polymerization process is initiated and the reaction starts propagating, thus forming short chain oligomers that are still soluble in the continuous phase. (3) Next the polymer chains precipitate upon reaching a critical

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length; they consequently form particle nuclei. (4) Coagulation of these oligomers occurs until there is enough adsorbed stabilizer on the growing particle surface to stop this process. (5) The stable particle nuclei continue growing without further coagulation until (most of) the monomer is consumed.⁴

The use of this method was initially driven by the coatings industry to enable a significant increase in the polymer content of paint and surface coating applications. Subsequently, the academic community used this technique to produce very monodisperse “model” polymer particles to study the fundamental mechanisms of steric stabilization. The use of dispersion polymerization was also found to be successful for incorporating organic dyes, both as physically trapped or covalently bound to the polymer particle cores.^{9–12}

We have recently explored the use of dispersion polymerization to give a simple, one-pot method for the preparation of EPD polymer particles in dodecane. We have particularly focused our attention on incorporating titanium dioxide pigments to the particle core to provide strong reflectivity in the suspensions. This article is the first in a series where we will be reporting the different approaches we have used to achieve the successful incorporation of TiO₂ pigments, including surface modification of the pigments with reactive groups and use of surfactant molecules for more efficiently dispersing the pigments in the dispersion polymerization medium.

In all the subsequent articles from this work, we will use methyl methacrylate (MMA) as the monomer and a siloxane-based polymer stabilizer (monomethacryloylpropyl terminated polydimethylsiloxane (PDMS-MA)) for the dispersion polymerization. The present article focuses, therefore, on describing the properties of the polymer particles synthesized with this macromonomer and the influence of several reaction parameters on the particle properties. This study is required to allow us to control the properties of simple polymer particle systems when using PDMS-MA as a stabilizer. Indeed, PDMS-based stabilizers for nonpolar dispersions have so far only been the subject of a limited number of reports in the literature^{8,13–16} in contrast to the more commonly used stabilizers based on poly(12-hydroxystearic acid) (PHSA),^{4,5,7,12,17–20} despite offering several potential advantages. For example, most PHSA-based stabilizers require the use of additional solvents, such as ethyl and butyl acetate, to ensure full dissolution in common nonaqueous dispersion polymerization media such as alkanes. This is generally detrimental to obtaining a full understanding of the solvency of the medium for the growing polymer chains due to the overall complex solvent mixture forming the reaction continuous phase, which in turn is critical to the characteristics of the particles produced.²¹ The use of PDMS here ensures full solubility of the stabilizer in the nonpolar (generally alkane) reaction solvent at the start of the reaction. Previous work carried out with PDMS-MA stabilizers includes, for example, studies where the minimum amount of PDMS homopolymers functional at one or both ends (with methacryloylpropyl moieties) necessary for a stable particle suspension is characterized.¹⁴

The current investigation of the use of PDMS-MA as a stabilizer for MMA dispersion polymerization in a nonpolar solvent will act as a basis for controlling particle size and polydispersity before using this system for more complex particle systems. It complements the existing academic literature on the use of PDMS-MA as a stabilizer for nonaqueous dispersion polymerization.

The present article investigates the influence of several reaction parameters on the characteristics of the particles resulting from the radical dispersion polymerization in dodecane using PDMS-MA as stabilizer. Specifically, we study the effect of varying type and concentration of the monomer and concentration and molecular weight of the stabilizer as a basis for subsequent studies. In the past, MMA and styrene monomers have mostly been investigated as single monomers with few examples of comonomers being used in the process. Here we systematically investigate the possibility of incorporating a series of comonomers in a nonaqueous dispersion polymerization of MMA and characterize the final composition of the particles.

2. EXPERIMENTAL SECTION

2.1. Materials. Dodecane, methyl methacrylate (MMA), 2-vinyl pyridine (2-VP), 4-vinyl pyridine (4-VP), dimethylaminoethyl methacrylate (DMAEMA) and octanethiol (chain transfer agent) were purchased from Sigma-Aldrich. Monomethacryloylpropyl terminated polydimethylsiloxane (PDMS-MA) (5000 and 10000 g·mol⁻¹) was purchased from Fluorochem and 2,2'-azobis(2-methylpropionitrile) (AIBN) from Molekula.

MMA, 2-VP, 4-VP and DMAEMA were purified by passing through an alumina column to remove the polymerization inhibitors and subsequently stored at 2–3 °C for no more than 2 months before use. All other chemicals were used as received.

2.2. Dispersion Polymerization. Dispersion polymerization protocols were inspired by the initial work from Antl et al.⁷ (PHSA-based stabilizer) and Pelton et al.^{8,14} (PDMS-based stabilizer). A typical MMA dispersion polymerization in dodecane involves the following steps: 2.08 g (20 wt % vs MMA) PDMS-MA stabilizer macromonomer (5000 or 10000 g·mol⁻¹) was solubilized in 100 mL dodecane in a round-bottom flask. This stabilizer solution was then degassed by nitrogen bubbling for 30 min. After oxygen removal, the stabilizer solution was heated at 80 °C under magnetic stirring. A monomer solution was prepared by mixing 107 mg ([MMA]/[AIBN] = 159) of AIBN, 126 μL of octanethiol ([MMA]/[octanethiol] = 142) and 11 mL of MMA (10% v/v vs dodecane). The monomer solution was then degassed by nitrogen bubbling for 30 min in an ice bath. After degassing, the monomer solution was added in the stabilizer solution and the reaction was stirred at 300 rpm and at 80 °C under static nitrogen atmosphere for another 4 h. Once the reaction was complete, the particle dispersion was cooled down and purified by 3 cycles of centrifugation and redispersion in pure dodecane. The resulting polymer particles were then characterized.

2.3. Scanning Electron Microscopy (SEM). SEM analysis was performed using a LEO 1530 FEGSEM microscope. The samples were deposited on a silicon wafer and coated with palladium/platinum (with an approximate layer of 5 nm) before insertion in the SEM chamber. The analysis was run at 3 kV and room temperature. Particle size and polydispersity were estimated from this analysis by measuring the diameter of 100 particles.

2.4. Nuclear Magnetic Resonance (NMR) Spectroscopy. ¹H NMR analysis was performed using a 500 MHz Bruker spectrometer. The experiments were run at room temperature in deuterated chloroform (CDCl₃) (CHCl₃ reference peak taken at 7.26 ppm). ¹H NMR of the purified samples allowed calculation of the stabilizer grafting density by comparing the integration of the PMMA methoxy group and the integration of the methyl-Si groups. For this purpose, it is assumed that all silicone chains are located on the particle surface. Although this does not take into account the fact that some of these chains are physically entrapped within the particle cores, this assumption is commonly used in other studies and allows for comparison between samples using variations of the same particle formulation.¹⁴ ¹H NMR analysis also allowed determination of polymer composition (monomer ratio) when a mixture of monomers has been polymerized. On the other hand, ¹H NMR of nonpurified samples allowed estimation of monomer conversion for each reaction.

3. RESULTS AND DISCUSSION

We initially used MMA as the monomer of choice to study the influence of a number of variables associated with the macromonomer stabilizer. Subsequently, we explore the use of additional monomers, either as homopolymers or as copolymers with MMA, to demonstrate the possibility of producing a range of polymer particle cores.

3.1. Influence of Stabilizer Molecular Weight and Concentration. The PDMS-MA stabilizer (Figure 1) used in

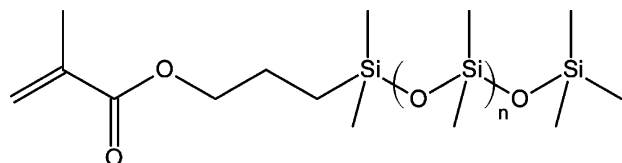


Figure 1. Structure of monomethacryloxypropyl terminated polydimethylsiloxane (PDMS-MA) used as steric stabilizer: $n = 64$ for PDMS-MA 5000 $\text{g}\cdot\text{mol}^{-1}$ and $n = 131$ for PDMS-MA 10000 $\text{g}\cdot\text{mol}^{-1}$.

this study is a commercial sample and is available in two different molecular weights, namely 5000 and 10000 $\text{g}\cdot\text{mol}^{-1}$ (synthesized via ionic polymerization, PDI < 1.10), both of which we investigated here. The data presented in Table 1 presents a comparison of the data obtained from equivalent procedures using both stabilizer molecular weights.

As PDMS-MA is a macromonomer, the stabilizer can take part in the polymerization reaction with MMA as a comonomer. This leads to the formation of a PMMA-*g*-PDMS graft copolymer. This block copolymer will preferentially position itself at the particle surface with the highly soluble PDMS block extending into the continuous phase, while the PMMA block anchors the polymer within the particle core. For both stabilizer molecular weights available, we found that the PDMS block (~ 64 units and 131 units, respectively) provides sufficient steric stabilization to enable colloidal stability of the final particle dispersions in dodecane. In most of the reaction conditions we studied, the particle suspensions we obtained were stable against aggregation over several months as verified separately by light scattering measurements.

Table 1. Polymerization Conditions and Resulting Particle Properties for 5 Experiment Series where Concentration of MMA Monomer and Stabilizer Molecular Weight Are Varied

entry	stabilizer	[stabilizer] (wt% vs MMA) ^a	[MMA] (v/v% vs dodecane)	average particle size (nm) ^b	Polydispersity Index (PDI)	stabilizer content (wt%) ^c	stabilizer density ^d /m ² $\times 10^{+17}$
1	PDMS-MA(5k)	2.5 [0.0936]	20	1380 \pm 140	0.05	0.69	2.26
2	PDMS-MA(5k)	5.0 [0.1872]	20	980 \pm 110	0.04	1.27	2.96
3	PDMS-MA(5k)	10.0 [0.3744]	20	875 \pm 65	0.03	2.16	4.46
4	PDMS-MA(5k)	20.0 [0.7488]	20	690 \pm 55	0.04	3.07	5.02
5	PDMS-MA(5k)	2.5 [0.1404]	30	1600 \pm 170	0.06	0.73	2.76
6	PDMS-MA(5k)	5.0 [0.2808]	30	1170 \pm 120	0.05	0.81	2.24
7	PDMS-MA(5k)	10.0 [0.5616]	30	1130 \pm 125	0.06	1.86	4.96
8	PDMS-MA(5k)	20.0 [1.1232]	30	765 \pm 110	0.10	1.79	3.24
9	PDMS-MA(10k)	2.5 [0.0468]	20	1250 \pm 70	0.02	0.73	1.08
10	PDMS-MA(10k)	5.0 [0.0936]	20	1040 \pm 70	0.03	1.29	1.59
11	PDMS-MA(10k)	10.0 [0.1872]	20	870 \pm 55	0.03	2.08	2.14
12	PDMS-MA(10k)	20.0 [0.3744]	20	620 \pm 35	0.02	3.21	2.36
13	PDMS-MA(10k)	2.5 [0.0702]	30	1410 \pm 80	0.02	0.59	0.98
14	PDMS-MA(10k)	5.0 [0.1404]	30	990 \pm 60	0.02	1.07	1.25
15	PDMS-MA(10k)	10.0 [0.2808]	30	805 \pm 45	0.02	1.76	1.68
16	PDMS-MA(10k)	20.0 [0.5616]	30	530 \pm 35	0.02	2.28	1.43
17	PDMS-MA(10k)	2.5 [0.0936]	40	1600 \pm 60	0.02	0.60	1.13
18	PDMS-MA(10k)	5.0 [0.1872]	40	1300 \pm 50	0.02	1.01	1.55
19	PDMS-MA(10k)	10.0 [0.3744]	40	920 \pm 40	0.02	2.83	3.08
20	PDMS-MA(10k)	20.0 [0.7488]	40	750 \pm 30	0.02	2.92	2.59

^aNumbers in brackets are $\text{mol}\cdot\text{L}^{-1} \times 10^{-3}$. ^bEstimated from SEM images over 100 particles. ^cEstimated using ¹H NMR. ^dAll PDMS assumed to be located on particle surface.

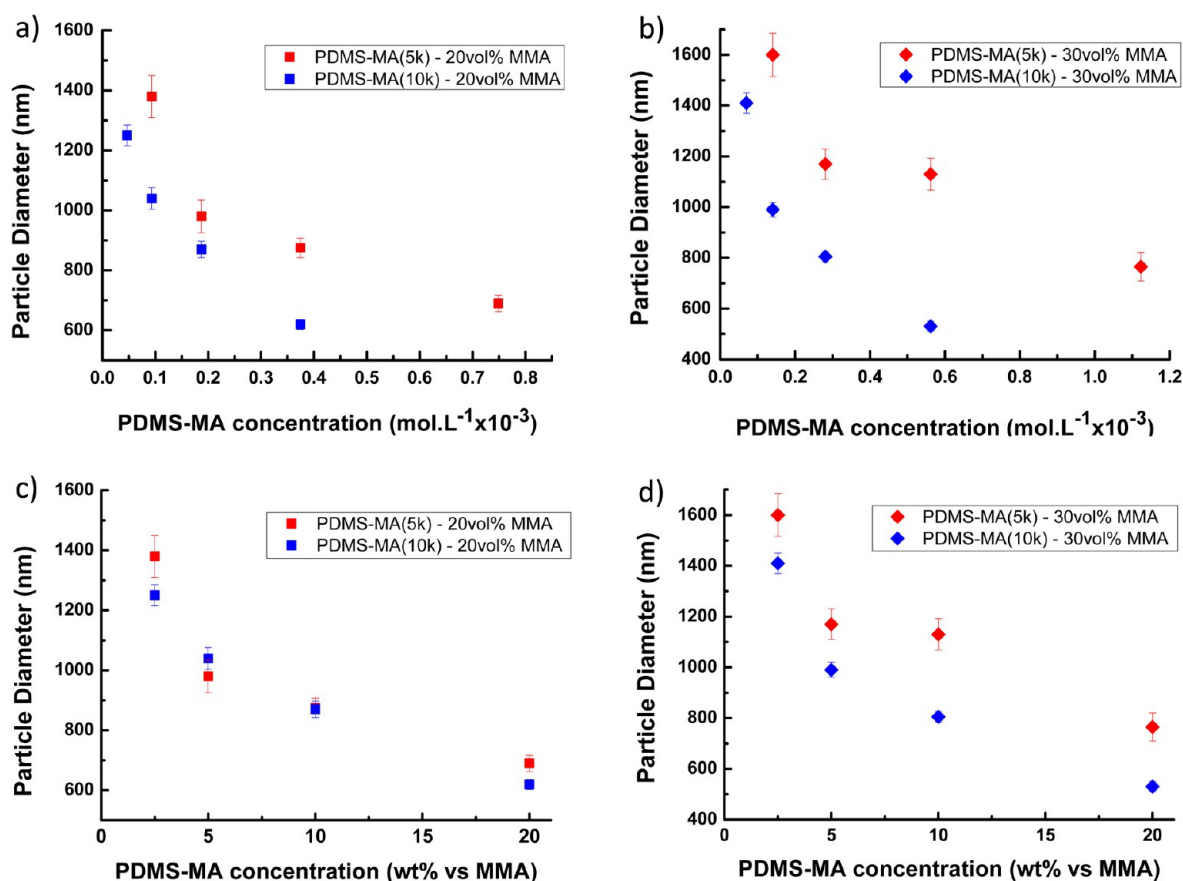


Figure 2. Comparison of the particle diameter obtained for dispersion polymerization of MMA in dodecane using two different stabilizer molecular weights, while varying concentration (expressed in $\text{mol}\cdot\text{L}^{-1}$ (a, b) or wt% (c, d)). All reactions were carried out at 80 °C and the monomer concentrations used were 20 vol% (a, c) and 30 vol% (b, d) with respect to the monomer.

However, the solubility of the stabilizer and the effective surface area it occupies is a function of its molecular weight and both these parameters influence the polymerization process. Thus, changes in polymeric stabilizer MW can influence the final particle size as demonstrated by literature reports for dispersion polymerization carried out in mixtures of water/alcohol^{22–24} and in nonpolar solvents.²⁵

Table 1 lists the particle diameter and associated polydispersity values obtained for several different experimental conditions for MMA dispersion polymerization. In this table, for each monomer concentration and stabilizer molecular weight, we have varied the stabilizer concentration from 2.5 wt % to 20 wt % (vs monomer concentration). This allows us to study the influence of multiple parameters in parallel, which we discuss below.

From Table 1, one can observe certain trends in the data that are well accepted for heterogeneous polymerization processes. For instance, in all experimental series (e.g., entries 1–4 or alternatively 9–12), the particle diameter is seen to decrease with increasing stabilizer concentration. This is simply due to the ability to stabilize an increased total particle surface area as stabilizer concentration increases. In practice, a larger concentration of stabilizer induces the precipitation of a larger number of seeds (with increased total surface area), which eventually leads to the growth of more particles of smaller diameter. This phenomenon is also clearly seen in Figure 2.

Figure 2 presents the influence of stabilizer molecular weight and concentration on particle size. Figure 2a and b demonstrate that increasing the molecular weight of the polymer stabilizer

while keeping the number of chains constant in the continuous phase, induces a reduction of the final particle size. This can be attributed to the fact that longer PDMS chains both create better barrier against particle aggregation and occupy a larger volume at the particle surface. Therefore more particle surface area can be stabilized with the larger polymer stabilizer, resulting in smaller particles.

In addition, one can see that if the mass of stabilizer (vs MMA concentration) is kept constant (Figure 2c and d), there is also an apparent decrease of particle size as the polymer MW is increased in the case of a higher monomer concentration (30 wt % vs MMA). The fact that no clear differences are seen for a 20 wt % (vs MMA) concentration of stabilizer is likely to be due to the increased solubility of the growing diblock stabilizer in a continuous phase containing more monomer. The changes seen in the case of the large monomer concentration here are consistent with the literature. This has been linked with various factors. For example, Shen et al. have attributed the variation of particle size as a function of polymer molecular weight to both a faster adsorption of the longer chain stabilizers and an increase in viscosity of the continuous phase as MW is increased.²⁴ It is also accepted that the high solubility of smaller MW stabilizers will prevent/slow down adsorption to the particle surfaces.^{8,23} Indeed, this has driven researchers to develop chemical anchoring mechanisms for the stabilizers to enable a more controlled process through an efficient particle seed stabilization.⁸ All phenomena mentioned above are linked to larger seeds being formed in the case of the smaller MW stabilizer, which eventually leads to fewer particles synthesized

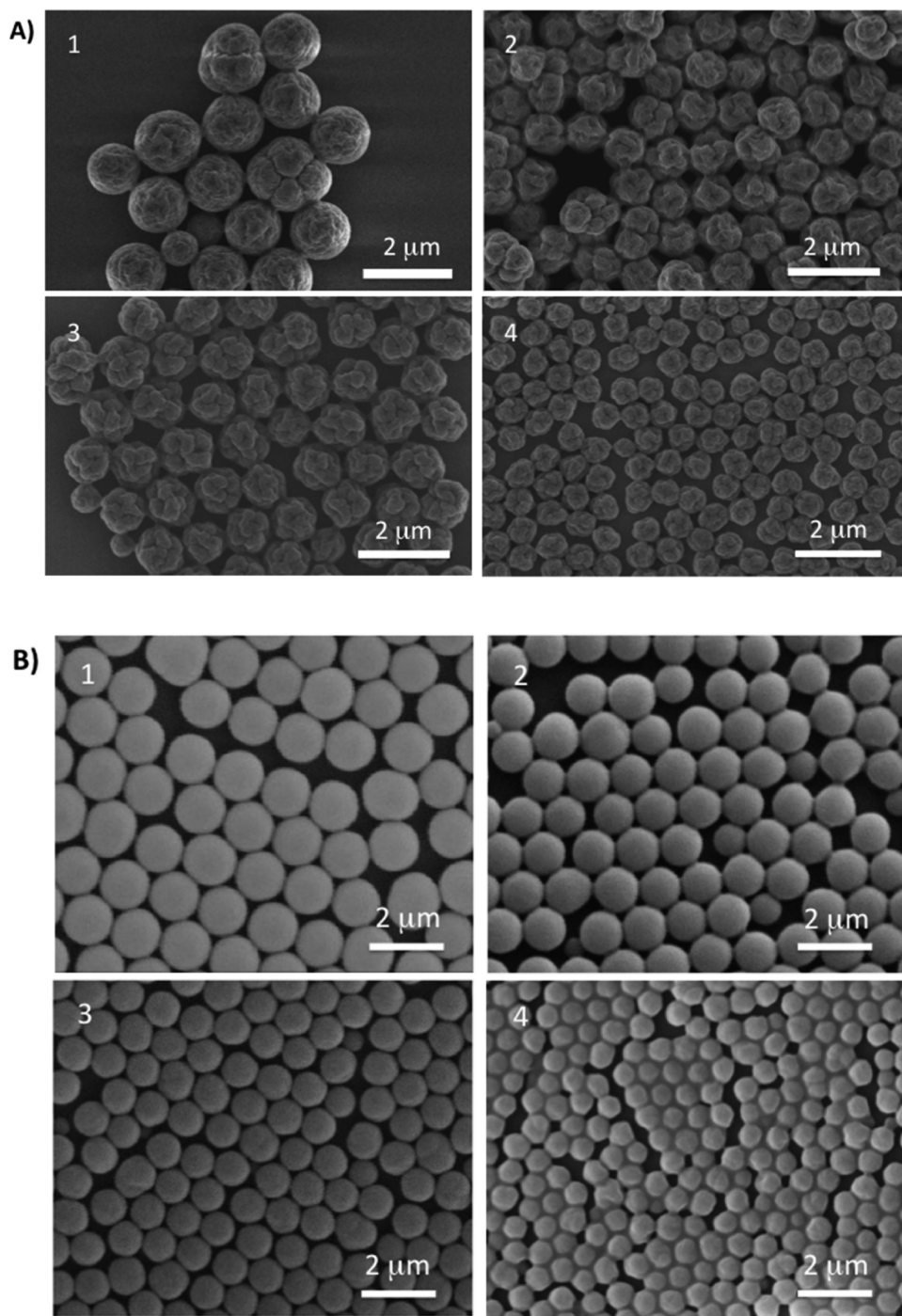


Figure 3. Scanning electron micrographs of PMMA particles polymerized with different stabilizer molecular weights (A) $5000 \text{ g}\cdot\text{mol}^{-1}$ or (B) $10000 \text{ g}\cdot\text{mol}^{-1}$ at different stabilizer concentrations (1) 2.5 wt %, (2) 5 wt %, (3) 10 wt % and (4) 20.0 wt % (vs MMA) for an initial monomer content of 20% (v/v Vs dodecane).

with a larger overall size. In our case, it is likely that this phenomenon is enhanced at higher monomer concentration (i.e., 30 wt %) due to the increased solubility of the stabilizer (when the second MMA block is growing) in the continuous phase as a result of the good solvency of MMA for its polymer.

Two further observations should be made on these samples. Firstly, the scanning electron micrographs presented in Figure 3 confirm the narrow particle size distribution for all samples shown. Particularly, one can notice hexagonal close packing, typical of monodisperse samples for the particles synthesized with the higher molecular weight stabilizer.

Secondly, the SEM images appear to show a contrasting particle structure when using stabilizers of different MW. Indeed, the particles synthesized with the lower MW stabilizer appear to consist of smaller uniform particles aggregated into larger spheres. This observation has previously been made for PMMA particles synthesized in heptane using a relatively small triblock copolymer (isoprene-styrene-isoprene) stabilizer (MW $21000 \text{ g}\cdot\text{mol}^{-1}$ with each isoprene stabilizing block of $7400 \text{ g}\cdot\text{mol}^{-1}$).²⁵ This is likely a result of poorer stabilization of particle seeds at the start of the reaction when compared to particles obtained from a higher MW stabilizer. This eventually leads to

Table 2. Particle Size and Polydispersity Obtained using Various Monomers via Dispersion Polymerization in Dodecane ([MMA]/[CTA]: 142, [MMA]/[AIBN]: 164, 80 °C, N₂, 300 rpm, 4 h)

entry	[stabilizer] (wt% vs monomer mixture)	MMA/DMAEMA targeted molar ratio (actual ^a)	[monomer] (v/v% vs dodecane)	average particle size (nm) ^b	PdI	stabilizer content (wt%) ^a	stabilizer density ^a /m ² × 10 ⁺¹⁷
21	2.5	75/25 (52/48)	10	1130 ± 155	0.08	1.57	1.59
22	5.0	75/25 (52/48)	10	1250 ± 145	0.06	2.25	2.53
23	10.0	75/25 (53/47)	10	1010 ± 105	0.05	3.51	3.18
24	20.0	75/25 (53/47)	10	540 ± 60	0.06	5.85	2.84
entry	[stabilizer] (wt% vs monomer mixture)	MMA/2-VP targeted molar ratio (actual ^a)	[monomer] (v/v% vs dodecane)	average particle size (nm) ^b	PdI	stabilizer content (wt%) ^a	stabilizer density ^a /m ² × 10 ⁺¹⁷
25	2.5	75/25 (72/28)	10	1135 ± 95	0.04	4.49	2.52
26	5.0	75/25 (73/27)	10	960 ± 55	0.02	3.29	1.85
27	10.0	75/25(61/39)	10	800 ± 50	0.02	5.07	2.84
28	20.0	75/25(63/37)	10	615 ± 45	0.03	7.29	4.08
entry	[stabilizer] (wt% vs monomer)	[2-VP] (v/v% vs dodecane)	average particle size (nm) ^b	PdI	stabilizer content (wt%) ^a	stabilizer density ^a /m ² × 10 ⁺¹⁷	
29	2.5	10	1540 ± 115	0.03	0.46	0.61	
30	5.0	10	1120 ± 125	0.06	0.81	0.79	
31	10.0	10	930 ± 75	0.04	1.43	1.17	
32	20.0	10	675 ± 55	0.04	2.12	1.25	
entry	[stabilizer] (wt% vs monomer)	[4-VP] (v/v% vs dodecane)	average particle size (nm) ^b	PdI	stabilizer content (wt%) ^a	stabilizer density ^a /m ² × 10 ⁺¹⁷	
33	2.5	10	Polydisperse	N/A	1.89	N/A	
34	5.0	10	1100 ± 225	0.18	1.87	1.80	
35	10.0	10	890 ± 75	0.04	2.50	1.95	
36	20.0	10	690 ± 50	0.03	3.79	2.29	

^aEstimated using ¹H NMR. ^bEstimated from SEM images over 100 particles.

aggregation of the growing seeds and the larger particles obtained when the polymerization is complete are constituted of multiple smaller aggregated particles. In contrast, when using the larger 10k MW PDMS stabilizer, the produced polymer particles appear to consist of a single core, indicating the growth of stable single seeds into the larger final particles.

Additionally, there is a consistent trend in the data presented in Table 1 for a (slightly) lower grafting density in the case of the larger polymer molecular weight. For example, for particles designed with the same stabilizer and monomer concentrations, the use of different stabilizer molecular weight (5000 vs 10000 g·mol⁻¹) leads to ≥2× lower stabilizer grafting densities for the larger stabilizer (e.g., entries 1 to 4 compared to entries 9 to 12). This is also seen when contrasting the grafting densities for particles with approximately the same particle diameter obtained from synthesis with different stabilizer MW. For example, this is the case for entries 1 and 13 (both ~1400 nm), 2 and 14 (both ~980 nm), 3 and 11 (both ~780 nm), where the grafting density of PDMS 5 kDa is also ≥2× larger than that of PDMS 10 kDa. This is consistent with the fact that the higher MW stabilizer occupies a larger volume on the particle surface and should therefore less densely coat the surface of the particles.

Furthermore, we see that the degree of variation in grafting density across all samples is relatively low. This has also been observed by Pelton et al. who prepared PMMA particles in heptane.⁸ They found similar grafting density for their polymer particles, which included formulations varying the molecular weight and the concentration of PDMS-based stabilizers. Indeed, these authors used PDMS-MA and vinyltrimethylsilyl-terminated polydimethylsiloxane (PDMS-V) macromonomers.^{8,14} Independently of the stabilizer grafting mechanism, the resulting stabilizer grafting densities are comparable to those we obtain here: 1.7 × 10⁻¹⁷/m² using PDMS-MA (21500 g·mol⁻¹) or 8.6 × 10⁻¹⁶/m² using PDMS-V (28000 g·mol⁻¹).

Saam et al.¹⁶ have also used PDMS-based stabilizers for nonpolar dispersion stabilization. In this case, the stabilizers anchored onto the PMMA particle cores via H abstraction or via chain transfer using thiol groups. For example, Saam et al. reported a grafting density of 7.1 × 10⁻¹⁶/m² using a 21000 g·mol⁻¹ PDMS bearing thiol group, which is in the same range as the grafting densities we report here.

In summary, we have successfully demonstrated the potential for using PDMS-MA macromonomer as a stabilizer for the preparation of controlled size and low polydispersity MMA particles. In the following sections we explore the possibility of varying the composition of the particle core using the same stabilizer and different monomers.

3.2. Monomer Dependence. Within this study we also investigated the possibility of creating polymer particles of different core compositions by varying the monomer used. This is expected to dramatically influence the final particle properties. This can be attributed to known differences in: (1) the reactivity of the monomer and its solubility in the solvent; (2) the solubility of the polymer in the solvent and its own monomer; and (3) the anchoring efficiency of the stabilizer to the particle core. In the following sections, we investigate a range of monomers and monomer combinations using dispersion polymerization in dodecane.

In all subsequent experiments involving the polymerization of monomers other than MMA, the reaction conditions were kept the same as those for the reaction performed in Table 1 (80 °C under static nitrogen atmosphere). However, the reaction time was adjusted depending on the monomer polymerization kinetics (i.e., longer polymerization time allowed for vinyl pyridine monomers, which generally have a lower reactivity). In all cases, the monomer concentration was kept at 10 wt % with respect to the continuous phase and we varied the concentration of stabilizer in the same fashion as in Table 1.

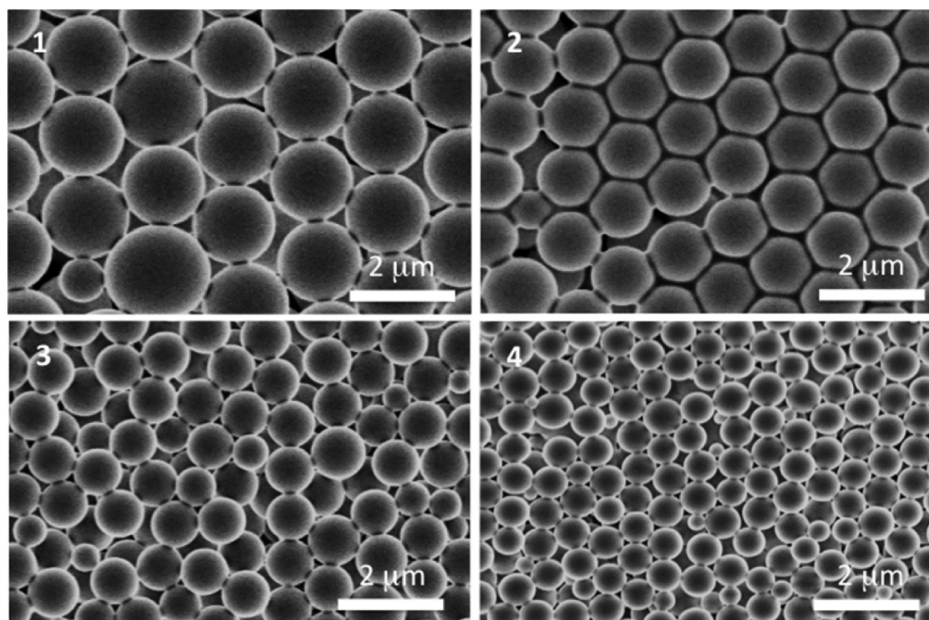


Figure 4. P2VP particles obtained from dispersion polymerization in dodecane at different stabilizer concentrations (1) 2.5 wt %, (2) 5 wt %, (3) 10 wt % and (4) 20.0 wt % (vs monomer) for an initial monomer content of 10% (v/v vs dodecane).

Initially we tested a range of monomers either on their own or copolymerized with MMA. The main purpose of changing the monomer used here is to show that dispersion polymerization in nonpolar solvents can be applied to various monomers, and to demonstrate the differences in particle properties seen when using monomers of varying structure, reactivity and solubility. It is expected that significant differences in size, polydispersity and stabilizer grafting density will be demonstrated.

3.2.1. Poly(MMA-co-DMAEMA) copolymer. Due to the relatively low glass transition temperature (T_g) of its polymer (around 19 °C), 2-(dimethylamino)ethyl methacrylate (DMAEMA) was copolymerized with MMA in order to enable characterization of the samples via electron microscopy techniques. Attempts to lower the MMA content in these particles proved successful but the resultant particles were difficult to characterize as a result of polymer swelling while focusing the electron beam on the dry samples. In this case, the dispersion polymerizations were carried out for a monomer molar ratio DMAEMA/MMA of 25/75 for 22 h. In all cases, monodisperse stable polymer particles were obtained.

As shown in Table 2 (entries 21–24), the particle size decreases as expected when increasing the stabilizer content. This observation is in accordance with what has been observed with the synthesis of PMMA homopolymer particles in Table 1. It is worth noting here that as a result of varying monomer reactivity between MMA and DMAEMA, the copolymer composition estimated by NMR from the produced samples (~1:1 molar ratio) varies significantly from the ratio of monomers used in the initial mixture (3:1 MMA/DMAEMA molar ratio).

Additionally, the PDMS stabilizer grafting density of the PMMA-co-PDMAEMA copolymer particles is in the same order of magnitude than for polymer particles of PMMA homopolymer. In all 4 samples the variation in grafting density is minimal as noted in the PMMA samples.

3.2.2. Poly(MMA-co-2-VP) Copolymer. In order to draw a comparison with particles of PDMAEMA/MMA copolymers,

we also performed a copolymerization of 2-vinyl pyridine (2-VP) and MMA in the same conditions. The particle size is seen to decrease as the polymer stabilizer concentration increases, as with previous examples. Additionally, the range of particle sizes obtained is comparable to that of the polymer particles from PDMAEMA/MMA copolymers.

3.2.3. Poly(2-vinyl Pyridine) and Poly(4-vinyl Pyridine) Homopolymers. 2-Vinyl pyridine (2-VP) and 4-vinyl pyridine (4-VP) were also polymerized in dodecane under the same reaction conditions as MMA (Figure 4).

2-VP (Table 2, entries 29–32) and 4-VP (Table 2, entries 33–36) dispersion polymerization in dodecane led to the formation of particles of very similar size and polydispersity for the same stabilizer concentration. Importantly, the lower stabilizer concentration appeared less effective at stabilizing the particles in these two cases, as large particles were obtained with a sample of significantly higher polydispersity for 4VP. This is likely to be a result of poorer/slower adsorption of the polymer stabilizer in these cases. However, upon increasing the stabilizer concentration, both P2VP and P4VP particles become comparable in size to those synthesized with the statistical copolymers discussed above (i.e., poly(DMAEMA/MMA) and poly(2VP/MMA)). In terms of stabilizer grafting density these samples show a relatively consistent value across all samples produced. However, this appears to be relatively smaller than in the previous cases of MMA and MMA copolymers. This phenomenon is also likely to originate from poor stabilizer adsorption onto the growing particles; it agrees with the noticeable issues in producing stable/well controlled polymer particles at lower stabilizer concentrations.

3.2.4. Varying Monomer Ratio in 2VP/MMA Copolymerization. Finally, we were interested in varying the monomer ratio of a successful copolymer polymer particle formulation. This dispersion polymerization was carried out for monomer molar ratios 2-VP/MMA from 90/10 to 25/75 for 4h and the PDMS-MA(10k) stabilizer concentration was kept at 20.0 wt % with respect to the monomer mixture. For all monomer mixture compositions, stable monodisperse polymer particles

Table 3. Particle Size and Polydispersity of P2VP/PMMA Particles Obtained by Dispersion Polymerization in Dodecane ([MMA]/[CTA]: 142, [MMA]/[AIBN]: 164, 80 °C, N₂, 300 rpm, 4 h)

entry	[stabilizer] (wt% vs monomer mixture)	MMA/2-VP targeted molar ratio (actual ^a)	[monomer] (v/v% vs dodecane)	average particle size (nm) ^b	PdI	stabilizer content (wt%) ^a	stabilizer molecules ^a /m ² × 10 ⁺¹⁷
37	20.0	10/90 (8/92)	10	660 ± 20	0.02	5.83	3.37
38	20.0	25/75 (6/94)	10	670 ± 30	0.03	8.01	4.71
39	20.0	50/50 (36/64)	10	650 ± 30	0.03	3.94	2.26
40	20.0	75/25 (60/40)	10	630 ± 30	0.03	11.49	6.43

^aEstimated using ¹H NMR. ^bEstimated from SEM images over 100 particles.

were successfully obtained (Table 3). Scanning electron micrographs of these 4 types of copolymer particles are available as Supporting Information in Figure S1.

Table 3 demonstrates that the final polymer particle size and polydispersity are not affected by the initial monomer composition. However, similarly to the case of particles from poly(MMA/DMAEMA) copolymers, a significant shift between targeted composition and final polymeric particle composition is observed via ¹H NMR. The final copolymer composition is always richer in 2VP than targeted. This is in accordance with values of copolymer reactivity ratios obtained from the literature where MMA was proven to have a lower reactivity ratio than 2VP in their copolymers.^{26–28} For example, Natanshon et al. reported ratios of $r_{2VP} = 1.1$ and $r_{MMA} = 0.27$, which correspond to the monomer ratios we characterize within our particles within a 10% margin. This is also in agreement with the values of monomer ratios recorded for entries 25–28. In addition, the same rationale can be applied to the copolymerization of DMAEMA and MMA in entries 21–24, where the monomer ratios found in the copolymers forming the particles also broadly agree with literature values for the monomer reactivity ratios.^{28,29}

As in the case for other mixtures of monomers used to synthesize the particles, the grafting densities recorded appear less reproducible than for pure MMA systems. However, they are generally of high values, demonstrating again the potential for using the PDMS-MA macromonomer for a successful synthesis of well-controlled polymer particles of a wide range of particle sizes and core composition.

4. CONCLUSIONS

We report here an initial study on the possibility of using a PDMS macromonomer for preparing a range of well-controlled polymer particles in a nonaqueous solvent via dispersion polymerization. Over a large range of reaction parameters, the prepared particles were observed to be both size monodisperse and colloidally stable. The use of this macromonomer stabilizer provides an important alternative to the commonly used PHSA-based polymer stabilizers, which requires the use of additional solvents in the continuous phase for an efficient solubilization.

When using MMA as the monomer in the system, we show how variations in particle size and the final particle structure can be controlled with changes in the stabilizer molecular weight and concentration. These results are consistent with previous observations from the literature. Additionally, we demonstrate that it is possible to obtain the same control over the particle properties when using other monomers, either on their own or when copolymerized with MMA. In the latter examples, we can accurately relate the monomer ratios of the

copolymers forming the final particles to literature values of the monomer reactivity ratios.

■ ASSOCIATED CONTENT

Supporting Information

Scanning Electron Micrographs of polymer particles obtained from dispersion polymerization of 2 monomers (MMA and 2VP) in dodecane with the following initial monomer ratios: 1:9, 1:3, 1:1 and 3:1 (MMA:2VP). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

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