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Inhibiting the Thermal Gelation of Copolymer Stabilized Nonaqueous Dispersions and the Synthesis of Full Color PMMA Particles

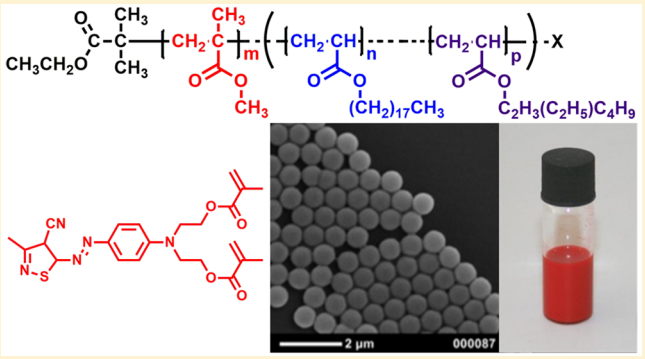
Kate E. Belsey,[†] Claire Topping,[‡] Louise D. Farrand,[‡] and Simon J. Holder*[,†]

[†]Functional Materials Group, School of Physical Sciences, University of Kent, Canterbury, Kent CT2 7NH, United Kingdom

[‡]Merck Chemicals Limited, Chilworth Technical Centre, University Parkway, Southampton SO16 7QD, United Kingdom

Supporting Information

ABSTRACT: Polymeric particle dispersions have numerous potential applications; currently one of the most relevant is their use as inks in electrophoretic displays. These colloidal particles are synthesized from the appropriate monomer using nonaqueous dispersion (NAD) polymerization in a nonpolar solvent, which requires a stabilizer to control particle size and morphology. We have previously reported the facile synthesis of poly(methyl methacrylate)-*block*-poly(octadecyl acrylate) (PMMA-*b*-PODA) by atom transfer radical polymerization (ATRP), and its use in the NAD polymerization of MMA in hexane/dodecane solvent mixtures. Here we report the synthesis of monodisperse PMMA particles in dodecane following a standard "industrial" procedure using these PMMA-*b*-PODA stabilizers. However, it was observed that the particle suspensions solidified when they were left at temperatures below ∼18 °C yet redispersed upon being heated. Differential scanning calorimetry, dynamic light scattering, and rheological studies demonstrated that this thermoresponsive behavior was due to a liquid−gel transition occurring at 17.5 °C as a consequence of the upper critical solution temperature of PODA in dodecane being traversed. Consequently, new copolymers were synthesized by ATRP with an ethylhexyl acrylate (EHA) co-monomer incorporated into the lyophilic (dodecane compatible) block. Dispersions stabilized by these PMMA-*b*-P(ODA-*co*-EHA) polymers with high EHA contents exhibited lower gelation temperatures because of the greater solvent compatibility with dodecane. The use of a $PMMA_{65}$-*b*-(ODA_{10}-*co*-EHA_{45}) copolymer stabilizer (with the highest EHA content) gave PMMA dispersions that showed no gelation down to 4 °C and monodisperse cross-linked PMMA particles containing organic dyes (cyan, magenta, red, and black) giving colored particles across the size range of approximately 100−1300 nm.



INTRODUCTION

In recent years, polymeric dispersions in nonaqueous media have received an increased degree of interest because of a wide range of emerging applications.[1−4] Historically, colloidal nonaqueous dispersions have found uses in paints, inks, cleaning products, binders, adhesives, and medical applications.[5,6] However, over the past few years, these dispersions have also found significant new uses, in particular in electrophoretic displays wherein the addition of charges to the particles or to the dispersions allows for the movement of the particles when a voltage is applied across electrodes within the display.[7,8] The use of a nonpolar solvent in these applications is necessary because they are inert and nonvolatile and have low dielectric constants.[9,10]

Nonaqueous dispersion (NAD) polymerization utilizes a lyophilic monomer and initiator. In the simplest scenario, the suspending medium is a nonsolvent for the polymer that forms, causing it to precipitate out of solution at a critical molecular weight. These precipitated polymer chains are unstable and begin to coagulate to form discrete particles. As the particles grow larger, the soluble polymeric stabilizer adsorbs to their surfaces providing steric stabilization. This behavior is due to the amphipathic nature of the dispersants, which feature a lyophobic block, having an affinity for the forming particles, and a solvated (lyophilic) portion that provides a steric barrier. The stabilizer thus plays a critical role in particle formation, prevents particle aggregation, and ensures long-term particle stability.[5,11] Dispersion polymerization is widely recognized as being a simple synthetic route to monodisperse particles from as small as 100 nm to more than 2 μm in size.[3,12] It has been shown that via variation of the reactant ratios (monomer, solvent, and stabilizer), accurate control over particle size can be achieved.[13−17] While considerable research has been directed at the design of stabilizers for NAD polymerization in polar

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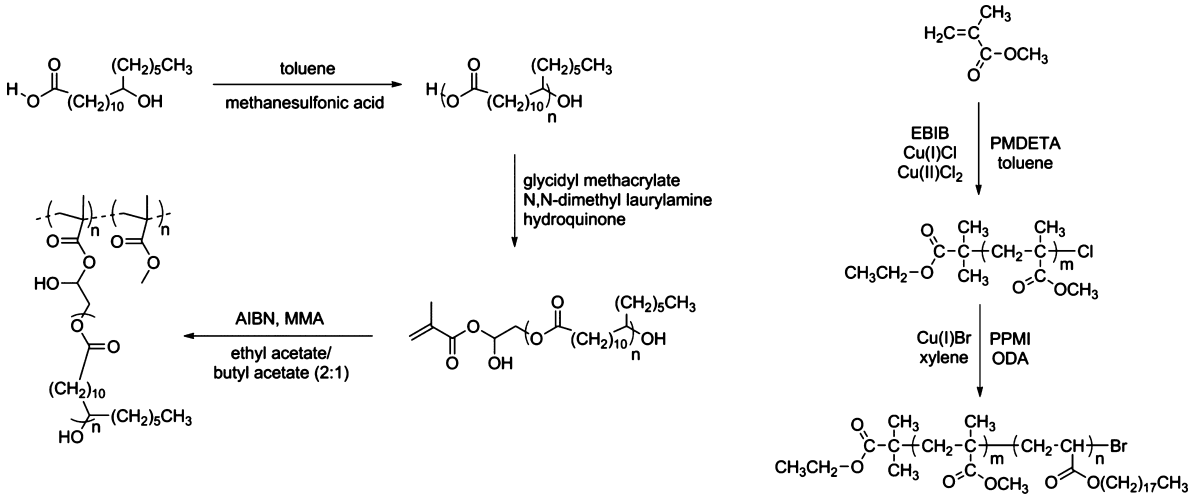
Scheme 1. Synthesis of PHSA-*g*-PMMA and PMMA-*b*-PODA



organic solvents,[18−20] there have been considerably fewer studies of the design of suitable stabilizers for NAD in nonpolar solvents.[3,21] Examples of stabilizers for nonpolar solvents include graft and random copolymers,[11,15,22] but some of the most interesting reports have involved block copolymers.[12,16,23]

One of the first stabilizers to be synthesized specifically for nonaqueous dispersion polymerizations was poly(12-hydroxystearic acid)-*graft*-poly(methyl methacrylate) (PHSA-*g*-PMMA).[24] This stabilizer has repeatedly been shown to produce monodisperse particles, allow control over particle size via the variation of reaction conditions, and allow for the introduction of functionality into the particles such as fluorescent groups.[15,24−26] However, the synthesis is notoriously time-consuming and complex, with particular issues in reproducing the chemical and molecular weight characteristics of the resultant copolymers between batches.[1] While the original publication gave only a brief outline of the synthetic methodology to synthesize the PHSA-*g*-PMMA,[24] recent work has given a far more detailed synthesis.[1] The resulting stabilizer was used in the nonaqueous dispersion polymerization of MMA and produced particles between 330 nm and 2 μm in size, all with low dispersity (typically <0.15). However, although this work has suggested that the synthesis of the stabilizer is now reproducible, the method still describes a multistep reaction (Scheme 1), including complications due to impurities in starting compounds that require distillations and recrystallizations to resolve.[1]

Other copolymers have also received attention as potential stabilizers for nonpolar nonaqueous dispersions. Methacryloxypropyl-terminated poly(dimethylsiloxane) (PDMS) (with a functional group at each end of the chain) has been shown to be an effective stabilizer for the polymerization of PMMA in hexane, although the concentration of solids in the resulting dispersions for this particular system was typically below 30%. Above this concentration, nonspherical aggregates that were attributed to the rapid evaporation of solvent from the reaction mixture were seen to form.[17] Other work has shown an alternative explanation for an "upper limit" of solid content in dispersions;[27] it was suggested that a defined volume must be excluded around each particle to prevent aggregation, and that typically above 40% solids this volume is larger than the free space available, causing the agglomeration of particles. A particularly encouraging recent development investigated the previously reported use of monomethacryloxypropyl-terminated PDMS (PDMS-MA),[28] as opposed to using PDMS with functional groups at both ends. The PDMS-MA was used to synthesize particles from 530 nm to 1.6 μm in size, by varying the weight percentage of monomer or solvent.[4] However, varying the chain length of the stabilizer was not seen to produce discrete, stable particles; rather, large aggregates of smaller particles were observed. It was also shown that there was little control over particle composition when more than one monomer was included in the particle synthesis, with the proportion of MMA being included in the particles consistently lower than expected, implying incomplete monomer conversion.

We have previously reported the synthesis and application of new stabilizers of poly(methyl methacrylate)-*block*-poly(octadecyl acrylate) (PMMA-*b*-PODA) and poly(methyl methacrylate-*co*-octadecyl acrylate) (PMMA-*co*-PODA) for the synthesis of PMMA particles in nonaqueous nonpolar dispersions.[16] Our preliminary results demonstrated that these stabilizers could be used to synthesize particles between 700 nm and 1.7 μm in size with low polydispersities. While the random copolymers could be used successfully as stabilizers, particle sizes and polydispersities were typically higher for these dispersions compared to those for the block copolymers. Later studies of the PMMA-*b*-PODA block copolymer stabilizer demonstrated accurate size control of the particles upon variation of the concentration of the stabilizer and solvent, as well as their use in the synthesis of dispersions of poly(acrylonitrile), demonstrating general versatility.[23] In comparison with the PHSA-*g*-PMMA stabilizer, the principal advantage of the PMMA-*b*-PODA block copolymers is their simple, two-step synthesis (technically three steps if one includes the ligand synthesis, though this need be conducted only once giving high yields) through the use of atom transfer radical polymerization (ATRP) (Scheme 1), resulting in good control of molecular weight parameters and high reproducibility. Unfortunately, as we will discuss in this paper, gelation of the PMMA-*b*-PODA-stabilized particles is observed at just below room temperatures, precluding their use in commercial applications. Thus, in this paper, we demonstrate that changing the composition of the block copolymer by copolymerizing the ODA with 2-ethylhexyl acrylate (EHA) gives a poly(methyl methacrylate)-*block*-poly(octadecyl acrylate-*co*-ethylhexyl acrylate) [PMMA-*b*-

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Table 1. Composition and Molecular Weight Parameters of PMMA-*b*-PODA and PMMA-*b*-P(ODA-*co*-EHA) Stabilizers Synthesized by ATRP

stabilizer	type	DP_{MMA} [a]	DP_{ODA} [b,c]	DP_{EHA} [b,c]	Đ of PMMA block[a]	%MMA:ODA:EHA by mass	M_n [a,d]	Đ[a,d]
S1	block	50	80	–	1.19	15:85:0	31100	1.42
S2	block	65	13	18	1.22	47:29:23	14400	1.32
S3	block	65	12	33	1.22	40:23:36	16910	1.29
S4	block	65	10	45	1.24	37:18:45	18300	1.53

[a]Measured by SEC. [b]Calculated by SEC from the M_n of the PMMA macroinitiator. [c]Calculated from ^{1}H NMR. [d]Measured after back-precipitation (explained in the Supporting Information).

(PODA-*co*-EHA)] stabilizer suitable for the preparation of monomodal particle dispersions in a nonpolar medium. For the first time, we will (1) demonstrate the facile transfer of ATRP-synthesized block copolymer stabilizers into industrial PMMA particle production processes, (2) unequivocally demonstrate the correlation between polymer−solvent compatibility and the precipitation and gelation of stabilized particles, and (3) demonstrate the straightforward synthesis of colored colloidal particles by the incorporation of cross-linkable organic dyes at the start of the one-step polymerization process. Ultimately, these colored colloidal particles will be suitable for application as colored electronic inks.

EXPERIMENTAL SECTION

Materials. Copper(I) bromide (Aldrich, 98%), copper(I) chloride (Aldrich, 97%), copper(II) chloride (Aldrich, 97%), methacrylic acid (Aldrich, 99%), 2,2′-azobis(2-methylbutyronitrile) (V-59) (Wacko Chemicals, 99%), octanethiol (Aldrich, 98.5%), and dodecane (Aldrich, 99%) were used without further purification. Aluminum oxide (Acros Organics, activated, neutral, Brockmann 1, for chromatography, 50 μm), toluene, and tetrahydrofuran (all Fisher, analytical grade) were used as received. To remove inhibitors, ethylhexyl acrylate (EHA) (Alfa Aesar, 98%) was passed directly through an aluminum oxide column, and octadecyl acrylate (ODA) (Aldrich, 97%) was heated to 60 °C, stirred with alumina overnight, and hot filtered. *N*-(*n*-Propyl)-2-pyridyl (methanimine) (PPMI) was synthesized according to a literature procedure.[29] The polymerizable dyes B1, C1, M1, and R1 (98%, Merck Chemicals Ltd.) were used as received.

The synthesis of PMMA-Br macroinitiators and PMMA-*b*-PODA stabilizers followed procedures identical to those previously reported.[16,23] The molecular weight parameters of the copolymers discussed herein are listed in Table 1 and Table ESI1. Full details can be found in the Supporting Information. The PMMA-*b*-PODA samples were then used as stabilizers in the nonaqueous dispersion polymerization (NAD) of methyl methacrylate (full details of materials and syntheses and the resulting dispersions can be found in the Supporting Information and Table ESI2).

Characterization. ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded using a JEOL ECS-400 spectrometer at 30 °C from solutions in $CDCl_3$.

Molecular weight parameters of polymers were measured relative to PMMA standards by gel permeation chromatography (GPC) using a PL-GPC 50 instrument supplied by Polymer Laboratories Ltd., in conjunction with a refractive index detector. All determinations were conducted at 40 °C with tetrahydrofuran (THF) as a mobile phase at a flow rate of 1 mL min^{-1}, using a 50 mm × 7.8 mm 10 μm PLgel guard column and two 300 mm × 7.8 mm, 5 μm PLgel Mixed-C columns.

Scanning electron microscope (SEM) images were taken using a JCM-5000 Benchtop SEM (Neoscope), at a specimen height of 55 mm, at an acceleration voltage of 15 kV, and under high vacuum. Particles were sputtered with gold for 120 s at 18 mA before being assessed in the SEM chamber. Particle sizes were measured using ImageJ version 1.42q, with diameters of more than 100 particles for each dispersion measured from 8-bit, binary watershed images using a feret distribution.

Dynamic light scattering (DLS) measurements were taken on colloidal solutions over a range of temperatures using a Zeta-sizer Nano series (Nano-ZS) machine, supplied by Malvern Instruments. The *z*-average, number average, and dispersity were measured at temperatures between 10 and 45 °C with measurements taken over a period of 90 s with an automatically generated number of scans, ranging from 12 to 19. Samples were all in dodecane unless otherwise stated.

DSC measurements were taken using a Netzsch DSC 200 PC, with a protective and purge environment of nitrogen gas. Measurements were taken between −30 and 150 °C, at a heating or cooling rate of 10 °C min^{-1}, with cooling regulated by liquid nitrogen. An empty aluminum pan was used as a reference sample, and the machine was calibrated against five standards provided by Netzsch.

Rheology measurements were taken using a Bohlin Gemini rheometer with a Peltier plate temperature control unit installed. A 40 mm parallel plate geometry was used for oscillatory measurements, and a 25 mm cone and plate geometry with an angle of 2.5° was used for rotational measurements. Data were processed using Bohlin software.

Synthesis of PMMA-*b*-P(ODA-*co*-EHA). A typical procedure was as follows. Nitrogen gas was bubbled through a mixture of ODA (7.17 g, 0.0221 mol), EHA (4.074 g, 0.0221 mol), copper(I) bromide (0.106 g, 1.37 mmol), PPMI (0.219 g, 1.47 mmol), and toluene (15 mL) for 1 h. This mixture was then subjected to four freeze−pump−thaw cycles (heated to 35 °C in the thaw stages), before the mixture was heated to 95 °C. Nitrogen gas was bubbled through a separate flask of PMMA-Br (5.000 g, 0.737 mmol) in toluene (10 mL) simultaneously. The solution of PMMA-Br in toluene was then injected into the reaction mixture and the reaction mixture stirred at 95 °C under a nitrogen atmosphere for 6 days. The mixture was diluted with THF (∼30 mL) and run down an alumina column and the solvent removed under vacuum. The polymer was then redissolved in DCM and precipitated into cold stirring methanol twice to give an off-white (brownish) powder (77% yield): ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.1 to 3.8 (4H, -C**H**$_2$-O of ODA and EHA), 3.6 (3H, O-C**H**$_3$ of MMA), 2.2 (2H, -C**H**- in the backbone of ODA and EHA), 1.8 (7H, -C**H**$_2$-CH- in the backbone of MMA, ODA, and EHA and C**H** at the branch of EHA), 1.6 (2H, -CH-C**H**$_2$ in the branch of EHA), 1.2−1.4 [38H, -(CH$_2$)$_n$- of ODA and EHA], 1.0 [3H, O-CO-C(C**H**$_3$) of MMA], 0.9 (9H, C**H**$_3$-CH$_2$- of ODA and EHA).

Dispersion Polymerization of Methyl Methacrylate. A typical procedure was as follows. Methyl methacrylate (20.580 g, 0.205 mol), copolymer stabilizer 1 (1.050 g, 0.508 mmol), octanethiol (0.125 mL, 0.715 mmol), methacrylic acid (0.416 mL, 4.859 mmol), and dodecane (25.195 g, 0.146 mol) were added together and heated to 70 °C under nitrogen. V-59 initiator (0.200 g, 1.036 mmol) was then added, and the mixture was stirred under nitrogen for 2 h, before being allowed to cool to room temperature. The reaction mixture was then passed through 50 μm cloth (purchased from Sefar) to remove coagulum, washed in dodecane, centrifuged, and redispersed three times before analysis by SEM and DLS.

All other dispersion polymerizations were conducted as described above, but varying the ratios of monomer to solvent (to control the weight percent of solids) and stabilizer as required and utilizing different stabilizers.

Dispersion Polymerization of Methyl Methacrylate with Colored Dyes. The synthesis followed the method described above,

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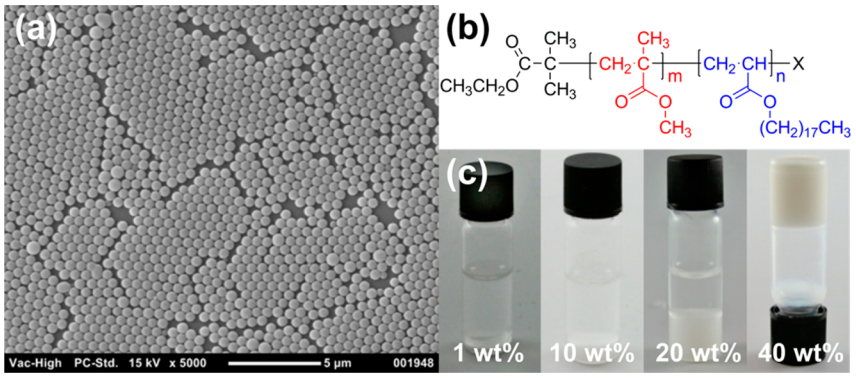

Figure 1. (a) SEM image of dispersion D1. (b) Structure of the PMMA-*b*-PODA stabilizer. (c) Dispersion D1 at room temperature, diluted to varying solid contents: 1, 10, 20, and 40 wt % from left to right, respectively.

Table 2. Characteristics of PMMA Particle Dispersions (42 wt % monomer) in Dodecane Incorporating Cross-Linked Color Dyes, Using PMMA-*b*-PODA and PMMA-*b*-P(ODA-*co*-EHA) Stabilizers (where M = magenta, R = red, C = cyan, and B = black)

dispersion	stabilizer	% stabilizer[a]	% dye[a]	D_{SEM} (nm)	SEM SD (%)	D_{DLS} (nm)	DLS (Đ)
D1	S1 $PMMA_{50}$-*b*-$PODA_{80}$	5.1	–	470	7.2	750	0.11
D2	S2 $PMMA_{65}$-*b*-P($ODA_{13}EHA_{18}$)	5.1	–	610	9	910	0.56
D3	S3 $PMMA_{65}$-*b*-P($ODA_{12}EHA_{33}$)	5.1	–	760	19.7	1460	0.28
D4	S4 $PMMA_{65}$-*b*-P($ODA_{10}EHA_{45}$)	5.1	–	620	12	740	0.20
D5	S3 $PMMA_{65}$-*b*-P($ODA_{12}EHA_{33}$)	5.1	2% EGDMA	960	8	–	–
D6	S2 $PMMA_{65}$-*b*-P($ODA_{13}EHA_{18}$)	5.1	3% EGDMA	590	15	–	–
D7	S1 $PMMA_{50}$-*b*-$PODA_{80}$	5.1	5% M1	700	9	–	–
D8	S1 $PMMA_{50}$-*b*-$PODA_{80}$	5.1	5% R1	780	9	–	–
D9	S3 $PMMA_{65}$-*b*-P($ODA_{12}EHA_{33}$)	5.1	10% M1	1070	5	1050	0.28
D10	S3 $PMMA_{65}$-*b*-P($ODA_{12}EHA_{33}$)	5.1	5% C1	1280	12	970	0.40
D11	S4 $PMMA_{65}$-*b*-P($ODA_{10}EHA_{45}$)	6.0	10% M1	830	12	920	0.17
D12	S4 $PMMA_{65}$-*b*-P($ODA_{10}EHA_{45}$)	7.5	10% M1	760	20	870	0.14
D13	S4 $PMMA_{65}$-*b*-P($ODA_{10}EHA_{45}$)	8.5	10% M1	660	7	800	0.22
D14	S4 $PMMA_{65}$-*b*-P($ODA_{10}EHA_{45}$)	25	10% B1	<150[b]	–[b]	230	0.37
D15	S4 $PMMA_{65}$-*b*-P($ODA_{10}EHA_{45}$)	15	10% B1	–[b]	–[b]	200	0.44

[a]By weight. [b]The synthesized particles were too small for the resolution of the SEM to allow accurate size analysis.

with the addition of colored dye (M1) (2.058 g, 4.73 mmol). The individual dye (M1, R1, C1, or B1) and the molar quantity of dye were varied between syntheses to give 5 or 10 wt % dye loadings.

RESULTS AND DISCUSSION

Synthesis of PMMA-PODA Stabilizers. ATRP is a common synthetic route for block copolymers, because of its versatile nature; mild conditions and a wide range of monomers, solvents, and catalysts can be used, while the mechanism of polymerization allows for accurate control of molecular weights, polydispersities, and end group functionality.[29−31] Two PMMA macroinitiators and both block and gradient copolymers with octadecyl acrylate (ODA) were synthesized following standard procedures. The molecular weight parameters for these samples are listed in Table 1 and the Supporting Information (Table ESI1). The mean copolymer compositions were calculated from the ^{1}H NMR spectra. The gradient nature of the copolymer of MMA and ODA has been previously demonstrated.[23]

Synthesis of PMMA Particles Using PMMA-*b*-PODA Stabilizers. We have previously reported on the synthesis of PMMA particles using PMMA-*b*-PODA stabilizers following well-documented and standard free radical procedures for nonaqueous dispersion polymerization.[16,23] This procedure (based on that reported by Antl et al.) involved MMA, octanethiol as a chain transfer agent, and benzoyl peroxide as the radical initiator in a solvent mixture of hexane and dodecane at 80 °C.[15] For this study, a larger scale commercial procedure was followed using MMA, octanethiol, methacrylic acid, and 2,2′-azobis(2-methylbutyronitrile) (V-59) in dodecane at 80 °C with various PMMA-*b*-PODA stabilizers and a PMMA-*grad*-PODA stabilizer. This procedure has previously been optimized for the industrial synthesis of PMMA particles using the PHSA-*g*-PMMA stabilizer. The 2,2′-azobis(2-methylbutyronitrile) was utilized in place of AIBN for the higher solvent compatibility with the dodecane solvent, and the slightly higher 10 h half-life temperature (68 °C in comparison to 65 °C). The octanethiol again acts a chain transfer agent, limiting PMMA chain length and controlling particle size distributions.[32] The methacrylic acid was incorporated as a "lock" for the PHSA-*g*-PMMA stabilizer (whereby in the latter stages of the dispersion polymerization process a covalent bond is formed between the acid function and epoxy groups in the stabilizer), and while this component was no longer necessary it was retained to allow a comparison between procedures utilizing different stabilizers. This procedure was followed for all the subsequent particle preparations in this study. The results of PMMA particle syntheses following this procedure using different PMMA-PODA stabilizers were largely in accord with our previously reported work (full details are given in the

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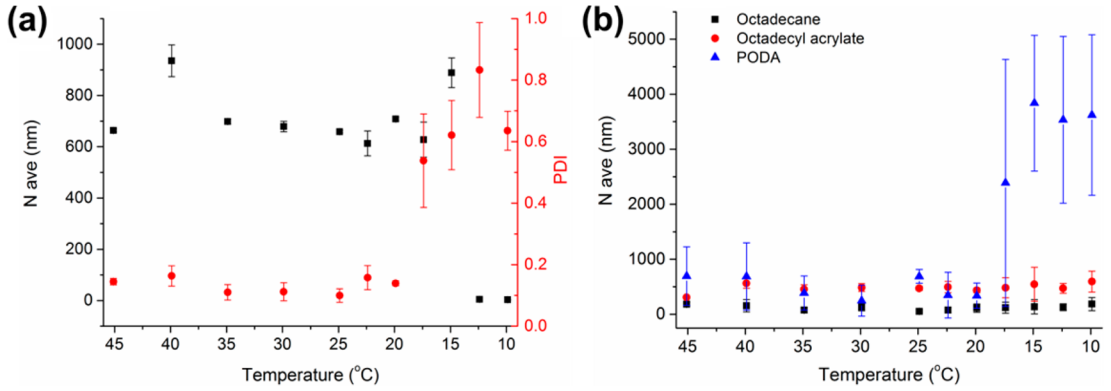

Figure 2. Results from DLS analyses. (a) *N* average size and dispersity data for dispersion D1. (b) Comparison of the *N* average sizes of octadecane, octadecyl acrylate, and poly(octadecyl acrylate).

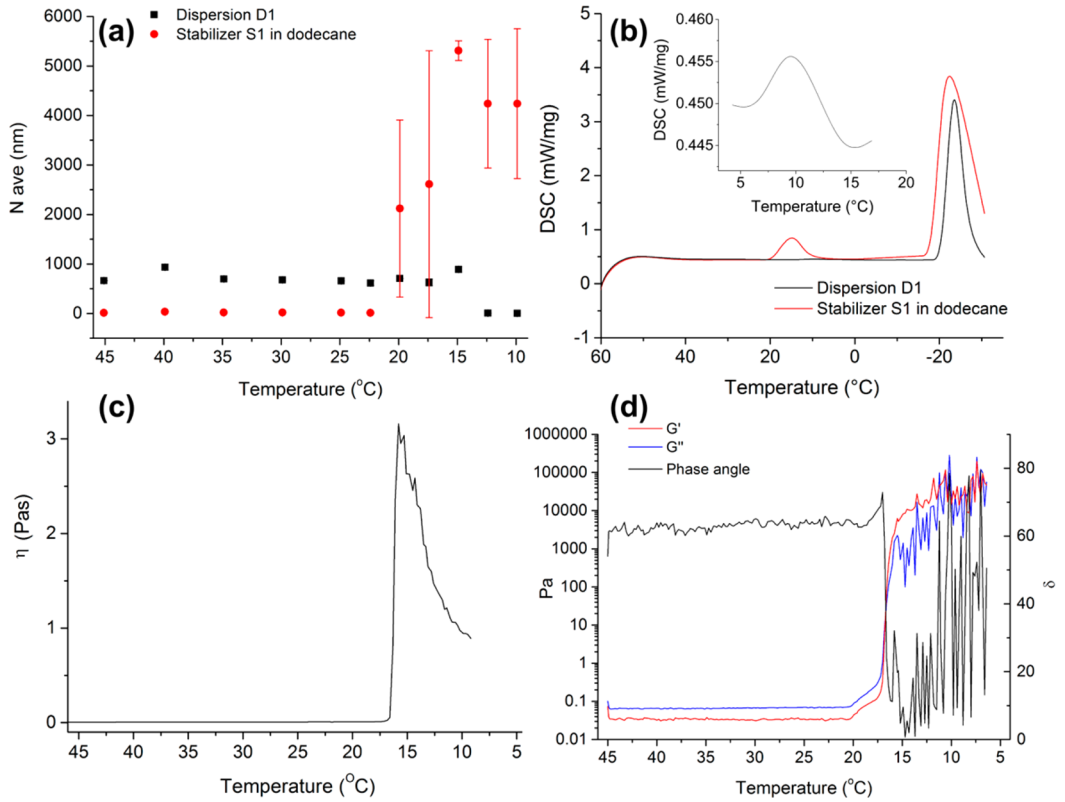

Figure 3. Data obtained for samples relating to PMMA-*b*-PODA stabilizers. (a) DLS *N* average sizes for 20 wt % stabilizer S1 in dodecane and dispersion D1. (b) DSC data for 20 wt % stabilizer S1 in dodecane and dispersion D1 (with the magnified transition of D1 between 5 and 15 °C). (c) Viscosity measurements of dispersion D1. (d) Viscoelastic measurements of D1.

Supporting Information).[16,23] No specific trend with respect to PMMA-PODA copolymer compositions and architectures was observed beyond poor control over particle size parameters with the gradient copolymer. Generally, block copolymers perform better as stabilizers than gradient copolymers.[16,33] Previous research has shown that shorter copolymers produced more uniform particles than longer, and also that the stabilizers that produced the most optimal particles typically contained >60 wt % ODA.[16] The results presented in the Supporting Information (specifically Table ESI2 and Figure ESI2) are consistent with these observations despite the slight changes in NAD polymerization conditions. Control over particle size could be achieved by varying the monomer content in the dodecane (thereby changing the stabilizer:monomer molar ratios), and an ethylene glycol methacrylate cross-linker could be incorporated at 1 wt % (relative to monomer) without coagulation of the dispersion.

Gelation of PMMA-*b*-PODA-Stabilized Particle Dispersions. While the majority of dispersions prepared by the route described above using the PMMA-*b*-PODA copolymer stabilizers consisted of monodisperse, spherical particles that exhibited close packing (see the Supporting Information and Figure 1a), it was observed that after a period of time the dispersions solidified and the particles could not be redispersed by simple agitation. However, it was noted that upon heating, the dispersion returned to its original fluid state.

To further investigate the gelation process for the PMMA-*b*-PODA-stabilized dispersions, one of the dispersions, D1 (Figure 1a and Table 2), stabilized by S1 [$PMMA_{50}$-*b*-$PODA_{80}$ (Figure 1b and Table 1)], was diluted with dodecane

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to obtain a number of different solid contents. When the temperature was decreased below ∼20 °C, the dispersions were seen to settle out at 1, 10, and 20 wt % solids, while an apparent gelation was observed for 40 wt % (Figure 1c). The gelation of the dispersion at 40 wt % solid content was confirmed by simple inversion of the sample vials (Figure 1c). Again, the gelation could be reversed by heating above 20 °C.

The thermoresponsive behavior of the dispersion was further studied using DLS. When dispersion D1 (42 wt %) was cooled from 45 to 10 °C, a considerable increase in the dispersity of the sample was observed between 20 and 17.5 °C (Figure 2a), though only a slight increase in the average particle size was observed in this temperature range. A dramatic decrease in size was, however, seen below 15 °C, presumably a consequence of the total gelation of the dispersion due to the cessation of Brownian motion. DLS analyses of octadecane, octadecyl acrylate, PODA homopolymer (M_n = 8500) (Figure 2b), and stabilizer S1 solutions were conducted to correlate this behavior with the components. Unusually, both the octadecane and octadecyl acrylate while visually fully soluble in dodecane, both showed discrete aggregate sizes by DLS across the temperature range from 45 to 10 °C. We hypothesized that these are due to local inhomogeneities within solution, i.e., some degree of microphase separation, and this is the purview of further research. However, no changes in size or dispersity were observed in the region observed for the D1 transition. PODA also displayed aggregation of some form in dodecane, but in contrast to the case with octadecane and octadecyl acrylate, when the temperature was reduced from 20 to 17.5 °C, the polymer aggregated, forming particles an order of magnitude larger. This was accompanied by the transparent solution becoming cloudy. This transition can be attributed to the upper critical solution temperature of the PODA in octadecane.

Stabilizer 1 also showed insolubility in dodecane below a certain temperature as demonstrated by a dramatic increase in aggregate size determined by DLS (Figure 3a) and precipitation from solution between 15 and 12.5 °C. DSC analysis of the solutions and dispersions was used to further investigate the transitions. The cooling thermogram (10 °C min^{-1}) for dispersion D1 (Figure 3b) showed a small transition with an onset of 12.1 °C and a peak at 10.6 °C (ΔH of 16.3 J/g based on the weight of S1 in the dispersion), and the thermogram for S1 in dodecane (20 wt %) showed a transition with an onset of 17.7 °C and a peak at 15.4 °C (ΔH of 70.1 J/g based on the weight of S1 in solution). The enthalpy for the stabilizer alone is close to the enthalpy of fusion measured for PODA homopolymer samples[34] (80.8−90.4 J/g), indicating that precipitation of S1 from solution is accompanied by crystallization of the side chains. It is uncertain whether the enthalpy recorded for the D1 transition is due to crystallization of the side chains; if so, the enthalpy that is lower than that of S1 suggests either significantly reduced crystallinity for S1 at the particle surface or other factors such as inclusion of dodecane molecules in the crystallites, as has been observed for octadecyl-stabilized silica particles.[35] However, the fact that D1 and S1 also showed crystallization peaks (onsets of −21.1 and −19.9 °C, respectively) for dodecane demonstrates that the solvent/dispersant is not crystallized in the gel.

Rheological measurements of polymeric stabilizers and dispersions were taken via both rotational and oscillatory modes of the rheometer, allowing data about the viscosity of the samples to be obtained, together with data on the viscoelastic properties of the materials.

Measurements of D1 were taken in rotational mode, while the temperature was steadily decreased from 45 to 5 °C. A constant low viscosity consistent with fluid behavior was observed until the temperature reached 16.3 °C (Figure 3c); at this point, a dramatic increase in viscosity was observed consistent with the observed gelation. Oscillatory measurements of D1 (Figure 3d) showed that at high temperatures, G'' was larger than G', giving a large phase angle (of ∼70°), which was consistent with a sample that could flow and was behaving as a liquid. Below 20 °C, a slight increase in both G' and G'' was observed, before a dramatic increase was seen at 17.0 °C with G' becoming larger than G'' at 16.7 °C. This led to a decrease in the phase angle, initially down to ∼10°, showing that the sample was behaving more as a solid. However, this phase angle was seen to fluctuate at lower temperatures, averaging closer to 45°. This was not entirely unexpected, as a phase angle of 45° is characteristic of a sample that has both solidlike and liquidlike behavior, also known as a gel. The temperature at which the increase in viscosity and decreased phase angle was observed for D1 fell within with the temperature range in which increased aggregate size was seen by DLS measurements.

Alkyl chains have been used to stabilize particle dispersions for decades, and gelation has been observed at well-defined temperatures as a result of solvent incompatibility with alkyl chains below a certain temperature, leading to crystallization of the chains.[35,36] This was in turn demonstrated to strengthen the particle−particle attraction due to van der Waals forces, resulting in aggregation and then gelation of the colloidal system (above a certain concentration of stabilizer chains). Flocculation of polymeric sterically stabilized colloidal particles in nonaqueous dispersions is also well-documented.[37,38] Flocculation occurs when the stabilizing soluble polymer chain becomes insoluble in the suspending solvent and for particle dispersions leads to precipitation from solution or, when the concentration of solids is typically greater than 40%, leads to the dynamic arrest of the solvent and gelation of the system. The correlation of theta temperature for a given polymer−solvent system was demonstrated to correspond with the flocculation temperature.[37] The results from the visual, DLS, DSC, and rheology studies strongly suggest that the PODA is displaying an upper critical solution temperature (theta temperature) in dodecane at ∼17 °C that leads to gelation of the system.[39] Unfortunately, in this case, this meant that the particle dispersions were limited in their practical use given that gelation was occurring not far below typical room temperatures.

Synthesis of PMMA-*b*-P(ODA-*co*-EHA) Stabilizers and Their Use in PMMA Dispersions. For this reason, a second set of stabilizers (S2−S4 in Table 1) were synthesized, incorporating ethylhexyl acrylate as a co-monomer in the ODA block. Ethylhexyl acrylate was chosen because of its low T_m (−50 °C in comparison to 35 °C for ODA), its branched structure (expected to disrupt any order of the C18 alkyl chains in the PODA), and the wealth of research regarding its viability as a monomer for ATRP.[40−42] The versatility of ATRP meant that this did not necessitate an additional step or a significant change in polymerization conditions; instead, the ratios of monomers added to the block copolymerization were just adapted to achieve the desired ODA:EHA ratio. These stabilizers were then used in the synthesis of PMMA particles (Table 2, D2−D6), following the same NAD polymerization procedure that was described previously. All stabilizers produced monodisperse particles (one peak in DLS), and 3%

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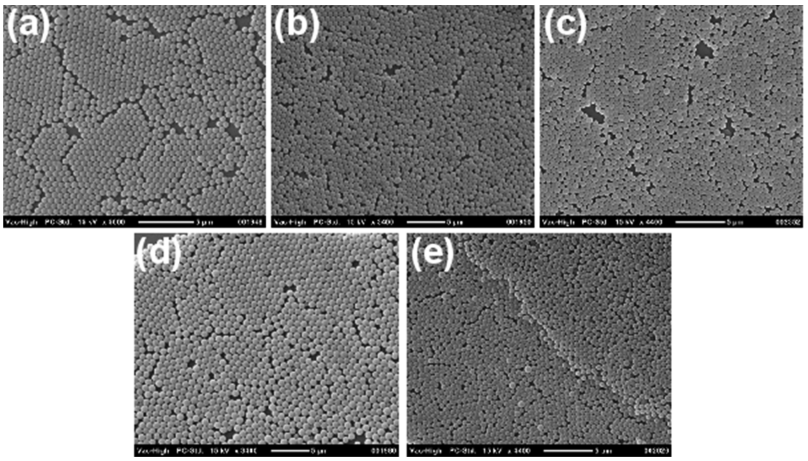

Figure 4. SEM images of PMMA particle dispersions with 42 wt % MMA using PMMA-*b*-P(ODA-EHA) stabilizers: (a) D2, $PMMA_{65}$-*b*-$P(ODA_{13}EHA_{18})$ (S2); (b) D3, $PMMA_{65}$-*b*-$P(ODA_{12}EHA_{33})$ (S3); (c) D4, $PMMA_{65}$-*b*-$P(ODA_{10}EHA_{45})$ (S4); (d) D5, $PMMA_{65}$-*b*-$P(ODA_{12}EHA_{33})$ (S3), 2 wt % EGDMA cross-linker; and (e) D6, $PMMA_{65}$-*b*-$P(ODA_{13}EHA_{18})$ (S2), 3 wt % EGDMA cross-linker.

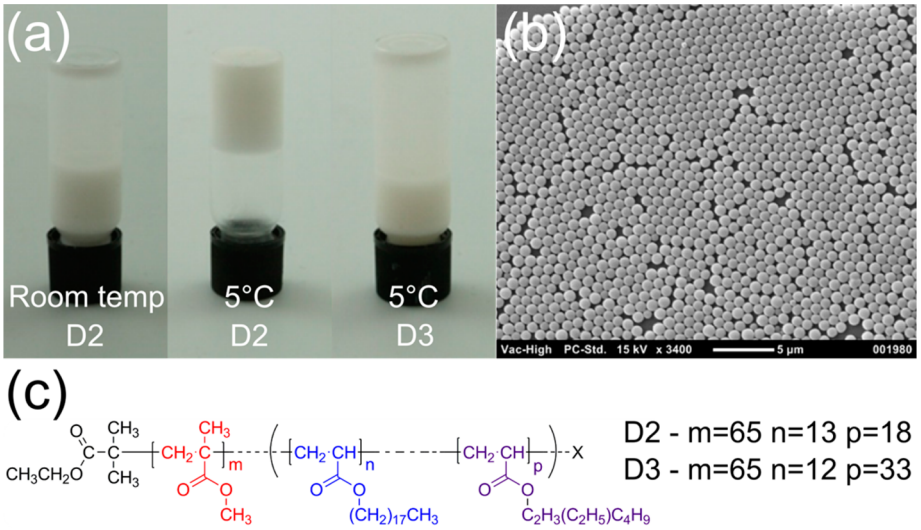

Figure 5. (a) Dispersions with varying EHA contents: D2 at room temperature, D2 after 5 min at 5 °C, and D3 after 24 h at 5 °C from left to right, respectively. (b) SEM image of dispersion D3. (c) Structure of PMMA-*b*-P(ODA-*co*-EHA), with values for *m*, *n*, and *p* of stabilizers used in each dispersion.

EGDMA was successfully incorporated without a dramatic increase in dispersity. Of note for these dispersions and the PMMA-*b*-PODA-stabilized dispersions (Table ESI2) is the difference between the DLS and the SEM particle diameters (Table 2) and dispersities. Generally, particle diameters recorded by DLS were larger than those recorded by the SEM (see Figure ESI3), and these particles possessed higher dispersities. The reason for this is not immediately apparent, and two possibilities present themselves. The first is that there is flocculation of particles in the dodecane dispersions, but the lack of bimodality or particularly large diameters from DLS suggests that if this is so, it is a weak and transient aggregation. The second is that the particles are partly swollen by the dodecane dispersant; while dodecane is regarded as a nonsolvent for PMMA, this need not preclude a degree of swelling or entrapment of solvent while the particles are in the dispersion. Regardless, as the SEM images demonstrate (Figure 4 and Supporting Information), good quality dispersions were achieved using the PMMA-*b*-P(ODA-*co*-EHA) stabilizers.

The gelation temperature for the colloidal dispersions at 40 wt % was affected by the relative EHA content in stabilizers S2−S4. D2 [stabilizer S2, $PMMA_{65}$-*b*-$P(ODA_{13}EHA_{18})$] did not gelate near or around room temperature but did gelate at 5 °C (Figure 5a). In contrast, D3 [stabilizer S3, $PMMA_{65}$-$P(ODA_{12}EHA_{33})$] remained a fluid dispersion at this temperature even after 48 h. DLS analysis of S1−S3 demonstrated that the temperature of the onset of aggregation for S2 was ∼5 °C lower than that of S1 and no aggregation was observed for S3 down to 5 °C (Figure 6a). This behavior was largely mirrored by the dispersions formed from these stabilizers (D1−D3) (Figure 6b), with D2 showing evidence of gelation between 15 and 12.5 °C upon cooling but no evidence of gelation for D3 down to 10 °C.

Rheological analysis of dispersion D3 confirmed these observations with no dramatic increase in viscosity, consistent with a thermoresponsive gelation observed down to 5 °C (Figure 6c). The small increase in viscosity across the temperature range from 50 to 5 °C could be attributed to the reduced velocity of the particles at a reduced temperature.

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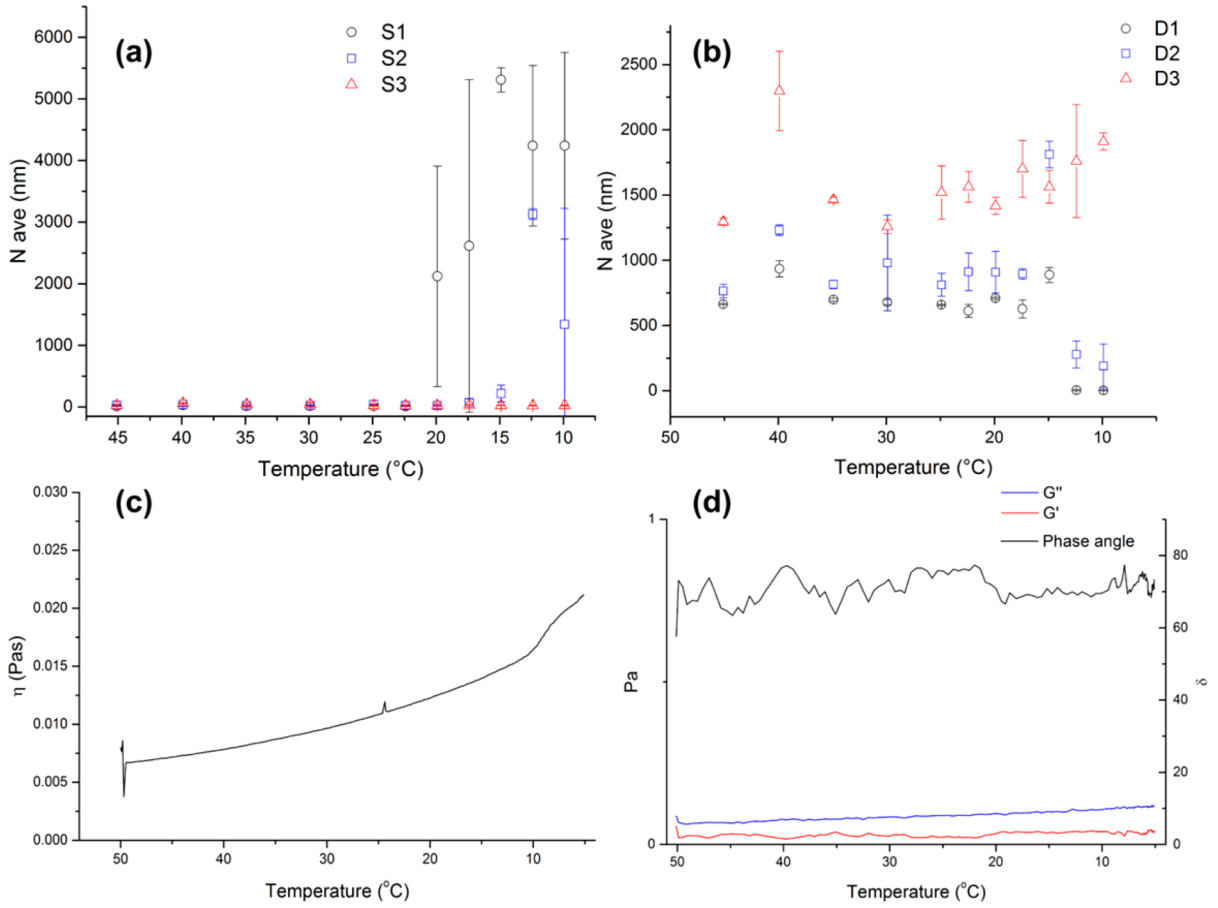

Figure 6. Data obtained for samples relating to PMMA-*b*-(PODA-*co*-PEHA) stabilizers. (a) DLS *N* average sizes for 20 wt % stabilizers S1 (no EHA), S2 (58% EHA), and S3 (73% EHA) in dodecane. (b) DLS *N* average sizes for dispersions D1−D3 (stabilized by S1−S3, respectively). (c) Viscosity measurements of dispersion D3. (d) Viscoelastic measurements of D3.

Furthermore, D3 did not exhibit the dramatic increase in G' and G'' over this temperature range, with the values for both of these moduli and the value of the phase angle remaining relatively constant down to a temperature of 5 °C (Figure 6d). The phase angle was consistently at ∼70 °C, indicating the sample was more "liquidlike" than "solidlike" at all temperatures measured.

Incorporation of Dyes. Polymerizable organic dyes (Figure 7)[43,44] were used in a series of dispersion polymerizations (Table 2). Dyes were added at 5 or 10 wt % relative to the weight of MMA used in the synthesis. The use of a polymerizable moiety in the structure of the dyes allows for the covalent incorporation of the dyes into the particles. This was particularly valuable in preventing the leaching of dyes into the dispersion medium, which has been observed in previous dyed colloidal systems.[45]

Colored dispersions stabilized by the PMMA-*b*-PODA stabilizers (D7 and D8) gelated just below room temperature, whereas all dispersions prepared using the PMMA-*b*-(PODA-*co*-EHA) stabilizers remained fluid down to 4 °C. The data in Table 2 demonstrate the versatility of the system with variation of stabilizer content, allowing for control over the range of particle sizes. For dispersions D11−D13 with 10 wt % magenta dye (M1), changing the weight percent of stabilizer from 6 to 8.5 wt % resulted in the reduction of particle size variation from 830 to 660 nm. With a further increase in the amount of stabilizer to 25%, monodisperse particles as small as 200 nm (by DLS) could be synthesized (dispersions D14 and D15). Interestingly, despite the dyes introducing cross-linking, they do not cause the coagulation during synthesis that was observed for 5 wt % EGDMA [dispersion D10 (Table ESI2)]. Figure 7 illustrates the range of colored dispersions that can be synthesized by NAD polymerizations, together with their corresponding SEM images and dye structures, demonstrating the monodisperse and spherical nature of these particles.

One of the most significant advantages of nonaqueous dispersion is its versatility; with a simple variation in the monomer:solvent mass ratio, the percentage of stabilizer added, the structure of the stabilizer, or the reactants in the system, particles with mean diameters ranging from 200 nm to 1.3 μm can be synthesized. It has previously been shown that there is a strong correlation between the weight percentage of monomer added to the synthesis and the size of the polymeric particles synthesized; this control is demonstrated in Figure 8, where data from this work are combined with data from ref 15.

■ CONCLUSION

Despite the previous successful use of PMMA-*b*-PODA copolymers as stabilizers for the NAD polymerization of MMA in hexane/dodecane solvents, their industrial application for the synthesis and dispersion of PMMA particles has proven not to be possible because of solvent incompatibility and a surprisingly high UCST for the PODA block in dodecane. This results in the thermally reversible transition of the dispersions at a high solid content (>42%) from a liquid to gel at

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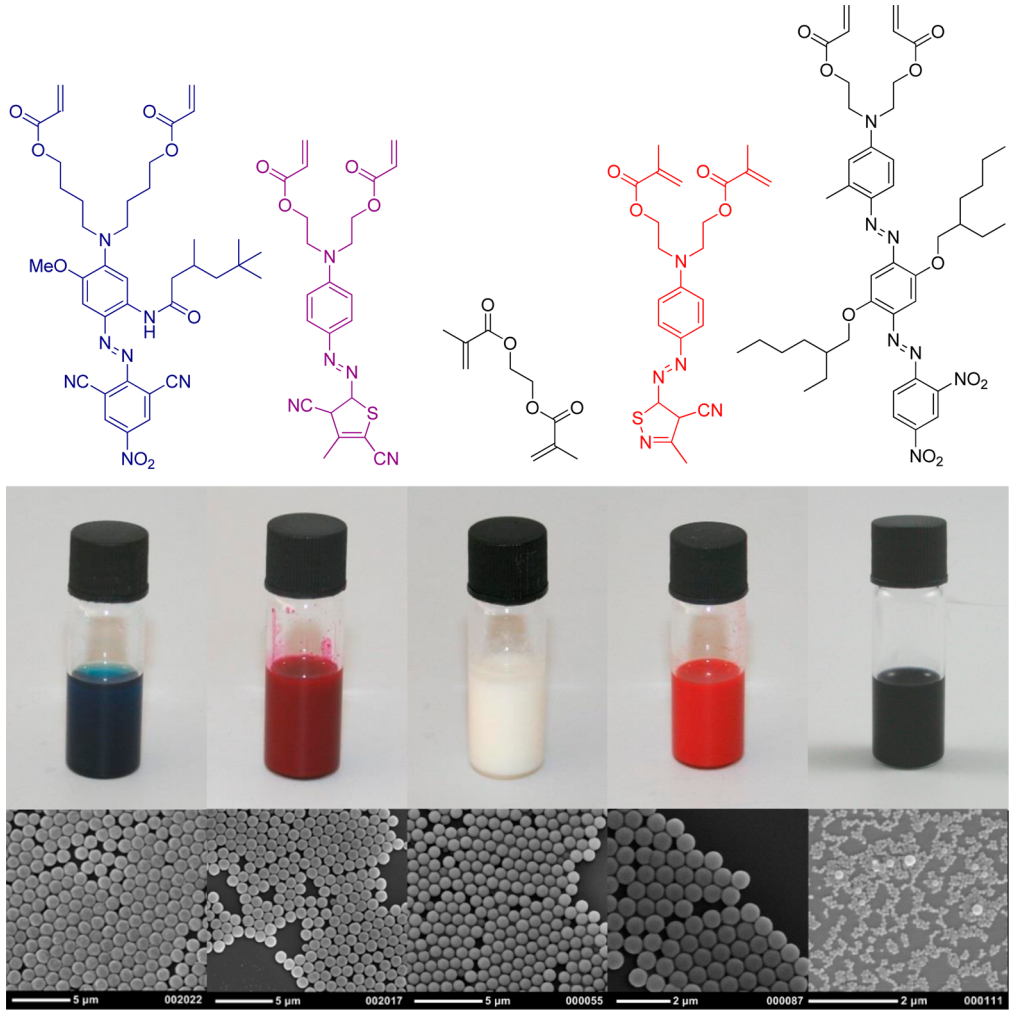

Figure 7. SEM images and photographs of dyed and cross-linked polymeric dispersions. Cyan dispersion D10, magenta dispersion D9, white dispersion D1, red dispersion D8, and black dispersion D15 from left to right, respectively.

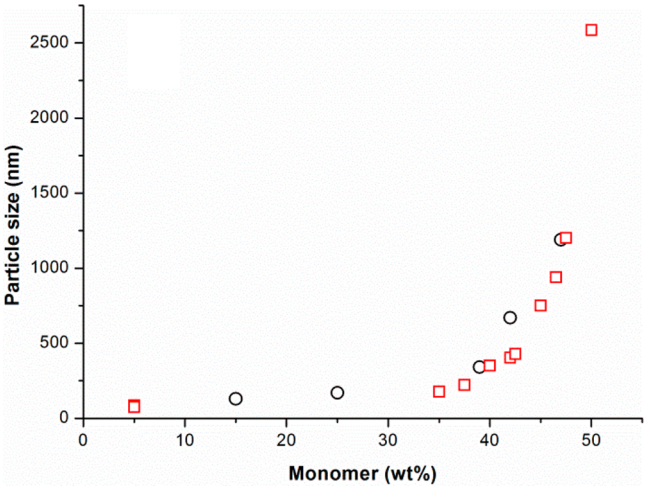

Figure 8. Plot illustrating the variation of particle size with monomer content compared to literature results (black circles represent data from this work, while red squares represent data from ref 15).

temperatures below 17.5 °C. While this transition is not readily observable at day to day indoor temperatures, it obviously precludes the use of PMMA dispersions as ink components in applications such as e-readers.

The ATRP synthesis of block copolymer stabilizers containing ethylhexyl acrylate (EHA) in addition to ODA led to PMMA-*b*-(ODA-*co*-EHA) copolymers that, when used as stabilizers, gave monodisperse PMMA particle suspensions that showed decreased gelation temperatures. The $PMMA_{65}$-*b*-(ODA_{10}-*co*-EHA_{45}) copolymer with the highest EHA content gave PMMA dispersions that showed no gelation down to 4 °C. By using these copolymers as stabilizers, the incorporation of cross-linkable colored dyes into the NAD polymerization of MMA in dodecane was demonstrated to give monodisperse spherical particles with no interparticle cross-linking or particle aggregation. These colored particles are currently being tested for application as colored inks in electrophoretic displays, and these results will be reported in a future publication.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.langmuir.6b00063.

Full details of materials used, the full stabilizer and dispersion syntheses, supplementary scanning electron micrographs of all polymeric dispersions, and typical NMR spectra (PDF)

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AUTHOR INFORMATION

Corresponding Author

*E-mail: S.J.Holder@kent.ac.uk.

Notes

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