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Octadecyl acrylate – Methyl methacrylate block and gradient copolymers from ATRP: Comb-like stabilizers for the preparation of micro- and nano-particles of poly(methyl methacrylate) and poly(acrylonitrile) by non-aqueous dispersion polymerization

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ABSTRACT

Three random and three block copolymers of methyl methacrylate (MMA) and octadecyl acrylate (ODA) were synthesized by atom transfer radical polymerization. These copolymers were assessed for their application as stabilizers in the one-step non-aqueous dispersion (NAD) polymerization of MMA and of acrylonitrile (AN) in a non-polar solvent mixture of hexane and dodecane. In all cases stable spherical micro-particle colloidal dispersions were formed with particle diameters in the range of 62–2725 nm for PMMA. Uniform monodisperse PMMA particles with standard deviations in size distributions of less than 5% were obtained in two cases demonstrating the utility of ODA:MMA copolymers as replacement preformed stabilizers in the one-step synthesis of MMA micro-spheres. Overall the block copolymer PMMA$_{64}$-*block*-PODA$_{36}$ gave greater control over size when varying the solvent:monomer ration than a related gradient PMMA–PODA copolymer. These copolymers were further used as stabilizers in the one-step NAD polymerization of MMA with ethylene glycol dimethacrylate (EGDMA) under similar conditions allowing for the preparation of monodisperse cross-linked PMMA particles with diameters ranging from 110 to 1700 nm. The general utility of the copolymers as stabilizers was demonstrated by the NAD polymerization of acrylonitrile (AN) in non-polar solvent mixture of hexane and dodecane giving 'crumpled' latex dispersions with particle diameters in the range 85–483 nm.

1. Introduction

The synthesis of colloidal polymer particles (sub-micron and micron) dispersed in organic media via dispersion polymerization (non-aqueous dispersion – NAD) whilst not as developed as colloid synthesis in aqueous media [1–3] has been known since the early sixties [4,5], and has been developed largely as a consequence of applications within the coating industries [6]. In a typical radical NAD polymerization the monomer and initiator are soluble in the organic solvent. After polymerization commences the polymer chains precipitate forming primary particles which coagulate while the stabilizer present in solution segregates at the interface between the solvent and particles. This eventually generates a number of sites for the subsequent growth of the polymer by monomer polymerization within the particles. The stabilizers (or dispersants) provide a repulsive barrier at the surface of dispersed particles preventing aggregation.

Low-molecular-weight surfactants, especially ionic surfactants that are commonly used in aqueous emulsion polymerizations and readily commercially available, are not efficient as stabilizers for NAD systems [6]. The necessary essential features of an efficient stabilizer for such a synthesis in a non-polar organic solvent are a non-polar liquid soluble component capable of steric stabilization of the particles and an anchoring component compatible with the particle. A number of materials either preformed or prepared *in situ* have been employed as stabilizers [6,7]. Many were commercially available materials such as poly(vinylpyrrolidone) [8], Kraton G1701 polystyrene-*block*-(ethylene-*co*-propylene) [9] and methacryloxypropyl-terminated polydimethylsiloxane [10] and relatively few have been designed for the specific application as dispersion polymerization stabilizers for example poly(ϵ-caprolactone-*co*-octadecyl methacrylate-*co*-dimethylaminoethyl methacrylate) [11] and poly (2-(dimethylamino)ethyl methacrylate-*block*-alkyl methacrylate) [12]. Following research and procedures developed by Antl et al. [13] and Campbell and Bartlett [14], Hu and Larson [15,16] recently reported the successful one-step synthesis of highly monodisperse micron size fluorescent poly(methyl methacrylate)

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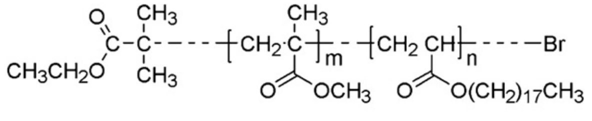
(PMMA) particles (>2 μm) using a poly(hydroxystearic acid)-*g*-PMMA (PHSA-*g*-PMMA) stabilizer. This is a particularly attractive route to NAD polymerization and our group has an interest in the synthesis of similar fluorescent particles by such fast and one-step processes. However, the reported synthesis of the PHSA-*g*-PMMA stabilizer [15] was far from trivial and it proved difficult to reproduce the synthesis of this graft copolymer readily. Since its discovery atom transfer radical polymerization (ATRP) has become an important laboratory synthetic route for a variety of copolymers [17–19]. The method permits the synthesis under mild conditions of a remarkable variety of vinyl polymers with a high degree of control over molecular weight, polydispersity and terminal group structure [20,21]. A number of copolymer structures have been synthesized by ATRP that were utilized as stabilizers for dispersion polymerizations in alcoholic, fluorinated, organic and supercritical CO_2 [22–26], and for the stabilization of inorganic nano-particles in organic solvents [27].

Our group has previously reported the synthesis of homo- and block copolymers of octadecyl acrylate (ODA) by atom transfer radical polymerization (ATRP) [28] by utilizing an appropriate ligand for the copper(I) salt namely (*N*-(*n*-octyl)-2-pyridylmethanimine). Poly(octadecyl acrylate) (PODA) is soluble in non-polar solvents and in a preliminary communication we have demonstrated that block and gradient copolymers of MMA with ODA act as efficient stabilizers in place of PHSA-*g*-PMMA in the non-aqueous dispersion polymerization of MMA [33].

Polyacrylonitrile (PAN) is not very soluble in its monomer acrylontitrile (AN) which makes the homo-polymerization of AN in dispersion or emulsion polymerizations much more difficult than PMMA [32]. Due to this low solubility there are not many examples in the literature of homo-PAN latexes by typical dispersion or emulsion polymerization [3,6,29] and co-polymerizations are more common [34–37]. Techniques like mini-emulsion polymerization [32] and precipitation in supercritical CO_2 [37,38] have been used in attempts to overcome the solubility issue. ABA block copolymers of polydimethylsiloxane–polystyrene–polydimethylsiloxane [33] as well as PHSA-*g*-PMMA [6] have been used to stabilise polyacrylonitrile (PAN) particles synthesized in hexane so it was postulated that the ODA/MMA stabilizers would be effective for PAN as well as PMMA. Generally the PMMA–ODA copolymers are far simpler to synthesise and ATRP offers a ready route to manipulate the architecture of the copolymers and keep the polydispersity indices of the copolymer samples to an acceptable level. In this paper we will report our results in utilizing these block copolymers and random copolymers synthesized by ATRP as stabilizers (dispersants) in the synthesis of PMMA colloidal micro- and nano-particles and PAN nano-particles. We also report a more detailed investigation noting effects of concentration of solvent and copolymer, copolymer composition, and the incorporation of a ethylene glycol dimethacrylate cross-linker.



1 = PMMA-*co*-PODA $_{(3.0:1)}$
2 = PMMA-*co*-PODA $_{(2.1:1)}$
3 = PMMA-*co*-PODA $_{(0.69:1)}$
4 = $PMMA_{80}$-*b*-$PODA_{45}$
5 = $PMMA_{80}$-*b*-$PODA_{65}$
6 = $PMMA_{80}$-*b*-$PODA_{125}$

Scheme 1. Octadecyl acrylate-methyl methacrylate block and gradient copolymer structures.

2. Experimental

2.1. Materials

Toluene was pre-dried over magnesium sulphate followed by sodium wire and then distilled from sodium wire immediately prior to use. Acryloyl chloride (96%) aluminium oxide (Acros Organics, activated, neutral, 50–200 μm), 2-bromo-2-methylpropanoyl bromide (ethyl-2-*iso*-bromobutyrate, 98%, Aldrich), Cu(I)Br (Aldrich, 98%), hydroquinone (≥99%, Fluka), methacryloyl chloride (97%, Lancaster), octanethiol (Acros, 97%), 1-pyrenemethanol (98%), 5,10,15,20-Tetrakis(4-hydroxyphenyl)-21H,23H-porphine (Aldrich, 95%), 2,2′-azobisisobutyronitrile (AIBN) (recrystallised from methanol), benzoyl peroxide (recrystallised from diethyl ether), palladium chloride anhydrous (Fluka, 60%Pd) hexane (Aldrich, reagent grade), dodecane (Acros, 99%), tetrahydrofuran (Fisher, reagent grade), petroleum ether (Fisher, reagent grade), methanol (Fisher, reagent grade), and dichloromethane (Fisher, reagent grade) were used as received. Octadecyl acrylate (97%) and methyl methacrylate (99%) were purchased from Aldrich and the inhibitors were removed by passing MMA directly through an alumina column and dissolving ODA in toluene and then passing through an alumina column. *N*-(*n*-octyl)-2-pyridyl(methanimine) and the PMMA–Br macroinitiator ($M_n = 8000$, $M_w/M_n = 1.13$) used in the block copolymer synthesis, were synthesized according to the previously reported procedures [28].

2.2. Instrumentation and analysis

^{1}H nuclear magnetic resonance (NMR) spectra were recorded at 30 °C using a JEOL GX-270 spectrometer from solutions in $CDCl_3$. The molecular weight parameters of the polymers were estimated relative to PMMA standards by gel permeation chromatography (GPC) using equipment supplied by Polymer Laboratories Ltd. All determinations were carried out at room temperature using a 600 mm × 5 mm mixed D PLgel column with THF as eluent at a flow rate of 1 mL min^{-1} with a refractive index detector. Transmission electron microscopy was carried out using a JEOL JEM (200-FX) operating at 120 kV. Drops of the colloidal solutions were deposited on carbon coated copper grids and excess solvent was removed after an appropriate amount of time (typically 10–40 s).

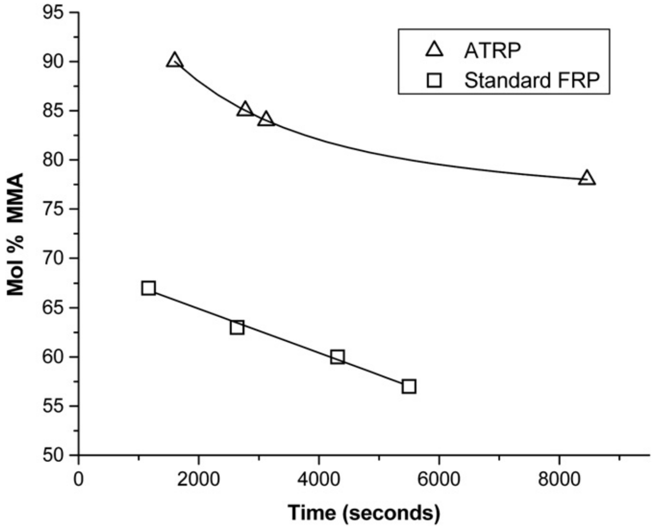


Fig. 1. Variation in methyl methacrylate content with time for isolated copolymer samples synthesized by free-radical polymerization (squares, stabilizer **7**) and by atom transfer radical polymerization (circles, stabilizer **1**).

Table 1
Molecular weight parameters and architectures of copolymer stabilizers employed in micro-particle synthesis.

Polymer	Tech.	Type	DP[a]	M_n[a]	M_w/M_n[a]	DP[b]	M_n[b]	MMA:ODA (%:%) by mol[c]	MMA:ODA (%:%) by weight[c]
1	ATRP	Gradient	169	29,000	1.4	–	–	68:32	40:60
2	ATRP	Gradient	163	25,500	1.42	–	–	75:25	48:52
3	ATRP	Gradient	60	14,000	1.33	–	–	41:59	18:82
4	ATRP	Block	105	19,000	1.29	125	22,500	64:36	35:65
5	ATRP	Block	65	13,000	1.3	145	29,000	55:45	28:72
6	ATRP	Block	114	27,000	1.58	205	48,500	39:61	16:84
7	FRP	Random				–	–	44:56	

[a] Measured by SEC, PMMA standard.
[b] Calculated from SEC for PMMA–Br macroinitiator ($M_n = 8000$) and ^{1}H NMR of copolymers.
[c] Calculated from ^{1}H NMR.

Dynamic light scattering measurements were carried out on the colloid solutions at 25 °C at a measurement angle of 90° using a Malvern Instruments 4700 system. The system consisted an Autosizer 4700 spectrometer, a pump/filter unit, a Model 2013 air-cooler argon ion laser (Ar laser 488 nm) and a computer with DLS software (PCS, version 3.15, Malvern) using the Multimodal intensity data analysis method.

2.3. Synthesis

2.3.1. Typical synthesis of a gradient copolymer of MMA and ODA by ATRP (copolymers **1–3**)

Nitrogen gas was bubbled through a mixture of ethyl-2-*iso*-bromobutyrate (0.02 mL, 0.234 mmol), Cu(I)Br (0.017 g, 0.254 mmol), *N*-(*n*-octyl)-2-pyridylmethanimine (0.111 g, 0.508 mmol), MMA (3.36 mL, 31.2 mmol), ODA (5.054 g, 15.6 mmol) and toluene (10 mL) for 30 min. The reaction mixture was then subjected to 4 freeze–thaw cycles and then stirred at 95 °C for 24 h. The mixture was thinned with DCM then run through an alumina column and the DCM was removed *in vacuo*. The polymer was dissolved in THF and precipitated into cold methanol twice to give an off-white (greenish-brown) powder (6.91 g, 84%, $M_n = 29{,}000$, $M_w/M_n = 1.41$).

2.3.2. Typical synthesis of a block copolymer of MMA and ODA by ATRP using PMMA macroinitiator (copolymers **4–6**)

Nitrogen gas was bubbled through a mixture of PMMA–Br (2 g, 0.245 mmol), ODA (7.938 g, 24.5 mmol), Cu(I)Br (0.0346 g, 0.245 mmol), *N*-(*n*-octyl)-2-pyridylmethanimine (0.1066 g, 0.49 mmol) and toluene (10 mL) for 30 min. The reaction mixture was then subjected to 4 freeze–thaw cycles and then heated at 95 °C for 6 days. The mixture was thinned with DCM then run through an alumina column and the DCM was removed *in vacuo*. The polymer was dissolved in THF and precipitated into cold methanol twice to give a light brown powder (6.12 g, 62%, $M_n = 19{,}000$, $M_w/M_n = 1.29$).

2.3.3. Typical synthesis of a random copolymer of MMA and ODA by free-radical polymerization (copolymer **7**)

Nitrogen gas was bubbled through a mixture of AIBN (0.019 g, 0.117 mmol), MMA (0.84 mL, 7.8 mmol), ODA (5.054 g, 15.6 mmol) and toluene (10 mL) for 30 min. The reaction mixture was then subjected to 4 freeze–thaw cycles and then heated at 95 °C for 24 h. The mixture was thinned with toluene then precipitated into cold methanol twice to give a white fluffy powder (4.61 g, 79%, $M_n = 20{,}000$, $M_w/M_n = 2.47$)

2.3.4. Typical dispersion polymerization of methyl methacrylate (reactions **A–H**, **D1–D8**, **E1–E8**)

MMA (4.3 mL, 39.95 mmol), octanethiol (0.244 mL, 0.021 g, 0.14 mmol), BPO (0.0494 g, 0.204 mmol), stabilizer (0.22 g), hexane (4.7 mL), and dodecane (2 mL) were stirred at room temperature.

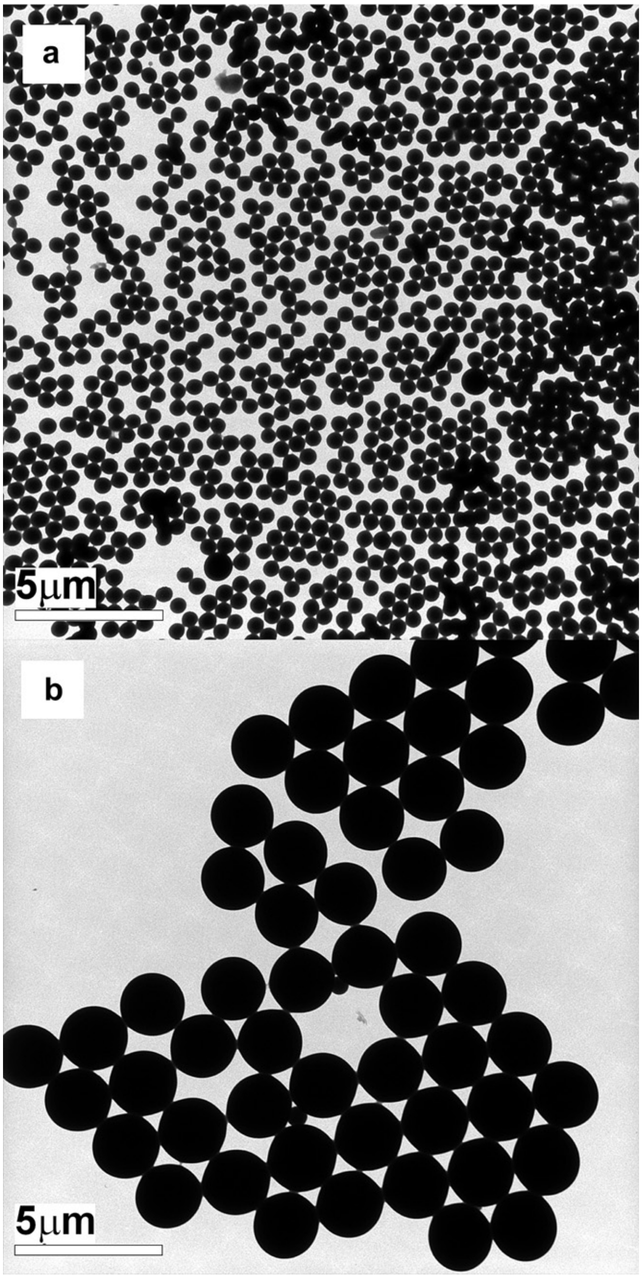


Fig. 2. TEM micrographs of PMMA particles: (a) sample **E** – stabilizer **4**; (b) sample **D** – stabilizer **3**.

Table 2
Component ratios and diameters and size distributions for PMMA particles synthesized using different PMMA–PODA stabilizers.

Sample	Stabilizer	Stabilizer:MMA (%:% by mass)	Solvent:MMA (%:% by volume)	D_{TEM} nm	σ_{TEM} nm	σ_{TEM} %	D_{DLS} nm
A	None	0:100	60:40	–	–	–	–
B	**1**	5.1:94.9	60:40	1240	280	22	1147
C	**2**	5.1:94.9	60:40	1020	260	25	1135
D	**3**	5.1:94.9	60:40	2700(450)[a]	105(160)[a]	4(36)[a]	1914
E	**4**	5.1:94.9	60:40	800	50	6	905
F	**5**	5.1:94.9	60:40	1650	200	12	1658
G	**6**	5.1:94.9	60:40	700	90	13	672
H	**7**	5.1:94.9	60:40	4270	975	23	3577

[a] A small fraction (<19% in number) of particles $D_{TEM} = 450$ nm were observed to be present - not detected by DLS.

The mixture was then rapidly heated to 80 °C and after a few minutes the reaction mixture became turbid. The reaction was then stirred for 2 h under nitrogen at 80 °C whereupon it was allowed to cool.

2.3.5. Typical dispersion polymerization of methyl methacrylate-co-ethylene glycol dimethacrylate (reactions ***XL1***–***XL6***)

MMA (4.25 mL, 39.45 mmol), ethyene glycol dimethacrylate (0.05 mL, 0.24 mmol), octanethiol (0.244 mL, 0.021 g, 0.14 mmol), BPO (0.0494 g, 0.204 mmol), stabilizer (0.22 g), hexane (4.7 mL), and dodecane (2 mL) were stirred at room temperature. The mixture was then rapidly heated to 80 °C and after a few minutes the reaction mixture became turbid. The reaction was then stirred for 2 h under nitrogen at 80 °C whereupon it was allowed to cool.

2.3.6. Typical dispersion polymerization of acrylonitrile (reactions ***I***–***R***)

AN (2.2 mL, 33.17 mmol), octanethiol (0.244 mL, 0.021 g, 0.14 mmol), AIBN (0.06 g, 0.366 mmol), stabilizer (0.25 g), hexane (10 mL), and dodecane (4 mL) were stirred at room temperature. The mixture was then rapidly heated to 60 °C and after a few hours the reaction mixture became turbid. The reaction was then stirred for 24 h under nitrogen at 60 °C whereupon it was allowed to cool.

Table 3
Component ratios and particle diameters (from TEM and DLS) for PMMA particles synthesized using different solvent and stabilizer concentrations.

Sample	Stabilizer	Stabilizer: MMA (%:% by mass)	Solvent: MMA (%:% by volume)	D_{TEM} nm	σ_{TEM} nm	σ_{TEM} %	D_{DLS}
E1	**4**	5.1:94.9	60:40	1190	159	13	1148
E2	**4**	5.1:94.9	65:35	630	44	7	620
E3	**4**	5.1:94.9	71:29	309	36	12	170
E4	**4**	5.1:94.9	76:24	140	16	11	63
E5	**4**	9.7:90.3	60:40	904	71	9	695
E6	**4**	9.7:90.3	65:35	561	68	12	261
E7	**4**	9.7:90.3	71:29	112	18	16	259
E8	**4**	9.7:90.3	76:24	62	19	31	56
D1	**3**	5.1:94.9	60:40	2725 (450)[a]	105 (162)[a]	4(36)[a]	1914
D2	**3**	5.1:94.9	65:35	1893	168	9	1741
D3	**3**	5.1:94.9	71:29	1174	145	12	630
D4	**3**	5.1:94.9	76:24	1272	90	7	778
D5	**3**	9.7:90.3	60:40	832	119	13	689
D6	**3**	9.7:90.3	65:35	900	101	11	606
D7	**3**	9.7:90.3	71:29	854 (1777)[b]	59(98)[b]	7(6)[b]	1919, 867
D8	**3**	9.7:90.3	76:24	447	53	12	339

[a] A small fraction (~9% in number) of particles $D_{TEM} = 450$ nm were observed to be present - not detected by DLS.

[b] A fraction (~14% in number) of particles $D_{TEM} = 1777$ nm were observed to be present - also detected by DLS.

3. Results and discussion

3.1. Synthesis of the octadecyl acrylate – methyl methacrylate copolymers by ATRP

The synthesis and characterization of the PODA–PMMA stabilizers employed in this study have previously been previously reported (Scheme 1) [33]. It is well known that copolymers formed by the simultaneous co-polymerization of two or more monomers leads to gradient copolymers from the ATRP technique where reactivity ratios for the monomer differ [43]. Previous studies that have determined the reactivity ratios of *n*-butyl acrylate polymerized with MMA by ATRP and standard free-radical polymerizations indicate significant differences between the reactivity ratios of MMA ($r_{MMA} = 1.79–3.15$) and BA ($r_{BA} = 0.11–0.37$) [31]. Similar magnitudes of difference in reactivity between MMA and ODA (potentially magnified by further differences in diffusion coefficients between ODA and BA) would inevitably lead to ODA rich domains towards the termini of the final copolymer products. To confirm this, samples were taken from an identical co-polymerization procedure used in the synthesis of stabilizer **1** and the composition of the precipitated copolymer monitored by ^{1}H NMR. Fig. 1 illustrates the variation in composition of the copolymer with time and a clear decrease in MMA content and consequent increase in ODA content is observed confirming a gradient structure. A further copolymer sample (**7**, Table 1) was prepared by a standard free-radical polymerization technique (AIBN, 80 °C, toluene, molar feed ratios of MMA:ODA = 1:2) to compare with the gradient

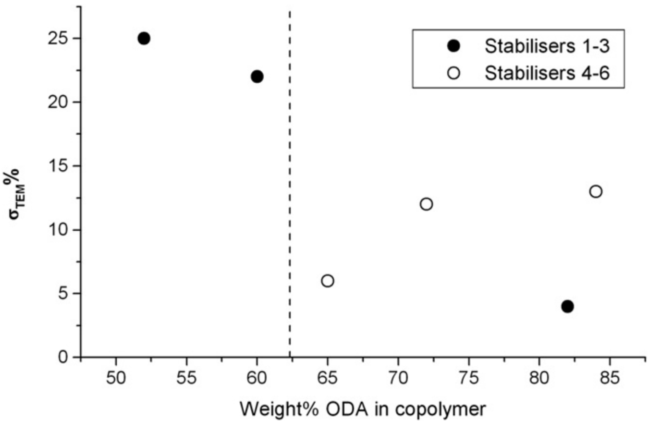


Fig. 3. Variation in standard deviation of PMMA particles relative to wt% ODA in stabilizer.

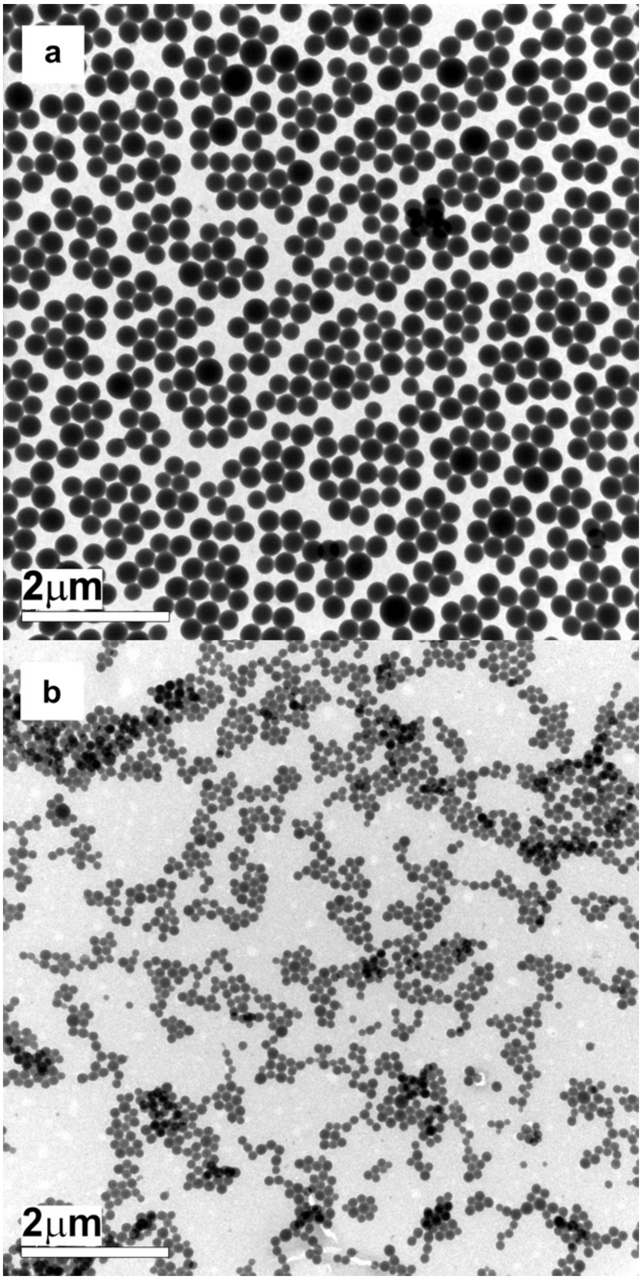


Fig. 4. TEM micrographs of PMMA particles: (a) sample **E3** – stabilizer **4**; (b) sample **D4** – stabilizer **3**.

copolymers synthesized by ATRP (copolymers **1**–**3**). Given the nature of thermally un-controlled free-radical polymerizations, differences in reactivity ratios between monomers leads to composition drift over the course of the polymerization and results in copolymer chains of profoundly different compositions at the start of the reaction from the end of the reaction. These materials are therefore complex mixtures of copolymer chains, low in ODA content and high in MMA content varying all the way to the converse situation with chains low in MMA but high in ODA. A sampling of the reaction used to synthesise this copolymer confirmed the decrease in MMA content and increase in ODA content with time as expected (Fig. 1). Table 1 shows the molecular weights and structural parameters of the copolymers employed in this study. However as previously noted comb-like polymers and copolymers show considerable inaccuracies in molecular weight parameters recorded by SEC as shown by our group [28,30] and others [24].

3.2. Dispersion polymerization of MMA in hexane/dodecane using PMMA–PODA copolymer stabilizers

All six of the copolymers (**1**–**6**) synthesized by ATRP acted as stabilizers in the NAD polymerization of MMA in hexane/dodecane (vol) mixtures (reactions **B**–**G**, Table 3) as previously reported. The reactions were carried out following the conditions outlined by Hu and Larson with an initial solvent to MMA volume ratio of 6:4 and a dodecane:hexane volume ratio of 7:3. These conditions were reported as optimum for the NAD polymerization of MMA using a PHSA-*g*-PMMA stabilizer and were not optimized for this stabilizers. However the fact that all copolymers enabled the synthesis of colloidal micro-particles and that at least two of these materials enabled the synthesis of particles with size distribution variations of less than 10% standard deviation justifies the approach to stabilizer synthesis and NAD polymerization (Fig. 2). The gradient copolymer stabilizers were synthesized for direct comparison with the block copolymers with the belief that they would not be effective stabilizers. However it was found that all the copolymers acted as stabilizers and the gradient copolymer stabilizer **3** gave the most uniform particles though stabilizers **1** and **2** gave high dispersity products. Stabilizer **3**, $PMMA_{25}$-*grad*-PODA35, enabled the synthesis of monodisperse PMMA particles (entry **D**) with very narrow particle size distribution ($\sigma < 4\%$) allowing hexagonal packing (Fig. 2b). As a control the copolymer of MMA and ODA prepared by a standard FRP (copolymer **7**) was employed as the stabilizer following the procedures and reaction conditions followed for the preparation of samples **A**–**G** (Table 2). The particle sizes of the MMA colloidal sample prepared (**H**, Table 2) were of a considerably larger dimensions (>4 μm) by TEM and DLS than any of the other samples and displayed a high standard deviation in size ($\sigma = 23\%$), similar to those produced by copolymer **1** and **2** ($\sigma = 22$ and 25% respectively) which possessed far lower ODA contents (52 and 60% by molar ratio) than copolymer **7**. The most likely explanation for the comparatively large size of the particles produced using stabilizer **7** is that a significant proportion of the copolymer chains are highly rich in MMA and do not contain sufficient ODA to act as steric stabilizers and consequently the relative ratio of stabilizer to monomer is greatly reduced leading to decreased surface coverage and increase volume:surface area ratios for the resultant particles.

Whilst a simple explanation for the better performance of stabilizer **3** compared to **1** and **2** might be it's significantly higher

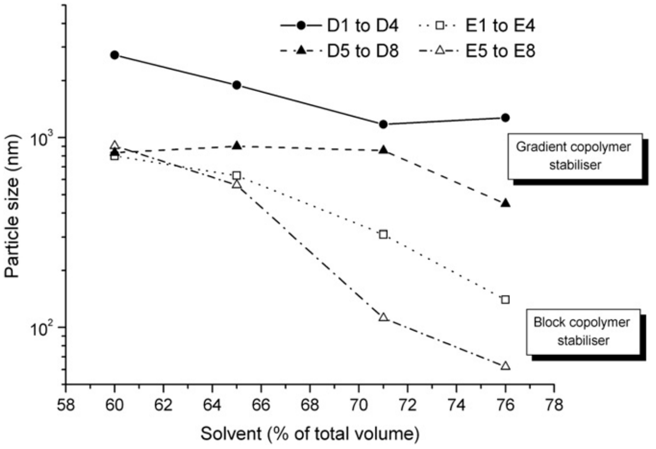
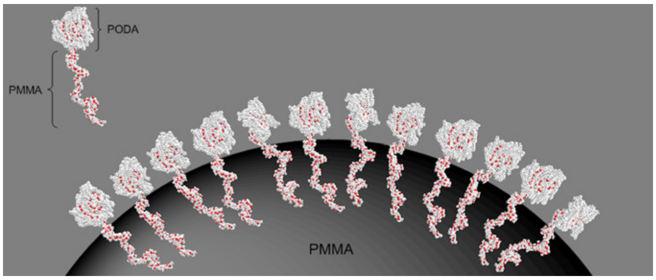


Fig. 5. Variation in particle size with solvent content and stabilizer concentration.

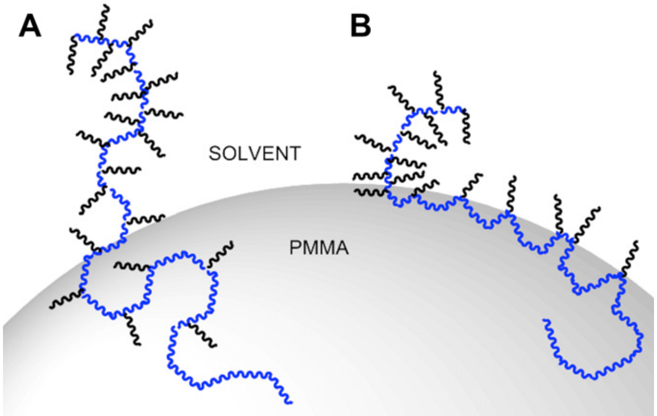


Scheme 2. Schematic of likely arrangement of stabilizer **4** at PMMA/solvent interface.

ODA content, this is certainly not true for the block copolymers where, whilst stabilizer **4** gave a better performance in controlling dispersity, all three stabilizers were relatively effective in producing particles with relatively narrow polydispersities. The role of the stabilizer in these polymerizations is two fold: firstly they act to sterically stabilise particles during formation and after, and thereby prevent agglomeration and flocculation; secondly they act to maintain a uniform particle size by covering the surface of the nuclei formed from precipitating MMA oligomers, and prevent further diffusion of oligomers into these nuclei, but still allow the entrance of monomer and initiator. It is obvious that easy conclusions with regard to stabilizer performance relative to macromolecular architecture cannot be easily rationalised given the limited number of samples here, however it is probably not too misleading to suggest that a minimum weight percentage of ODA (and hence chain length of PODA in the solvent) in the copolymer of greater that 60% is required (Fig. 3) for relatively low particle size dispersities. The absolute molecular weight parameters and polydispersities of the stabilizers will also play a role in particle size and uniformity but given the spread of structures studied understanding this relationship will require further study.

3.3. *Control of PMMA particle size through variation in monomer: solvent ratio and stabilizer concentration*

There are a number of key variables that can be altered in NAD polymerizations including the structure and concentration of the monomer, stabilizer, solvent, initiator and the reaction temperature [10,39]. In many cases fine control of particle size in aqueous and non-aqueous polymerizations can be obtained by varying the monomer to solvent ratio and the monomer to stabilizer ratio [10,39]. It has been noted that changes in concentration of initiator, stabilizer and chain transfer agent are not as important as the ratio of solvent to monomer [15]. Typically an increase in the solvent: monomer ratio leads to a decrease in particle sizes and conversely a decrease in sovent:monomer ratios leads to an increase in particle sizes. As a result of the low standard deviations in size for the particles synthesized in the preliminary study, copolymer **3**, $PMMA_{41}$-*grad*-$PODA_{59}$, and copolymer **4**, $PMMA_{64}$-*block*-$PODA_{36}$, were chosen for further study firstly into the effects of monomer: solvent ratio and secondly into that of stabilizer concentrations on PMMA colloid formation. Using polymer **3** as the stabilizer at a constant ratio of stabilizer:monomer of 5.1:94.9 by % mass and decreasing the monomer:solvent ratio led to a drop in particle size from 2725 nm to ~1100–1200 nm with variable standard deviations in size from 4 to 12% (**D1**–**D4**, Table 3). An increase in the stabilizer concentration relative to monomer at a similar monomer:



Scheme 3. Schematic illustrating two possible arrangements of gradient copolymers at PMMA/solvent interface.

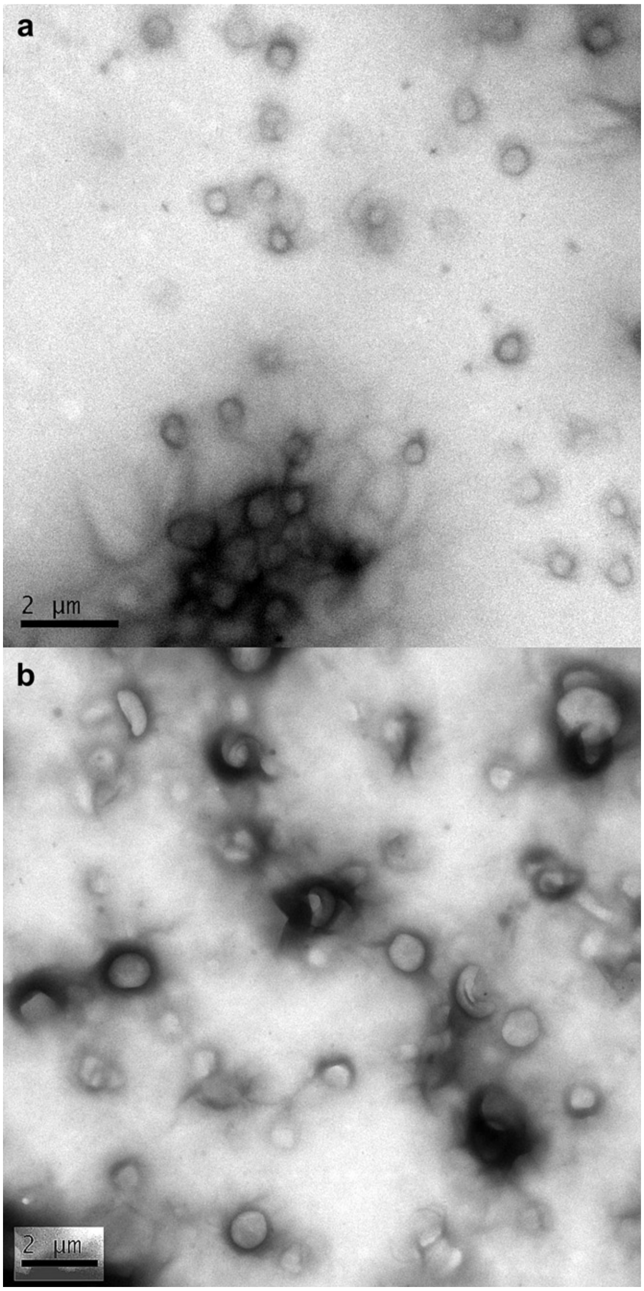


Fig. 6. TEM micrographs of aggregates in hexane/dodecane/MMA solutions for: (a) stabilizer **3**; (b) stabilizer **4**.

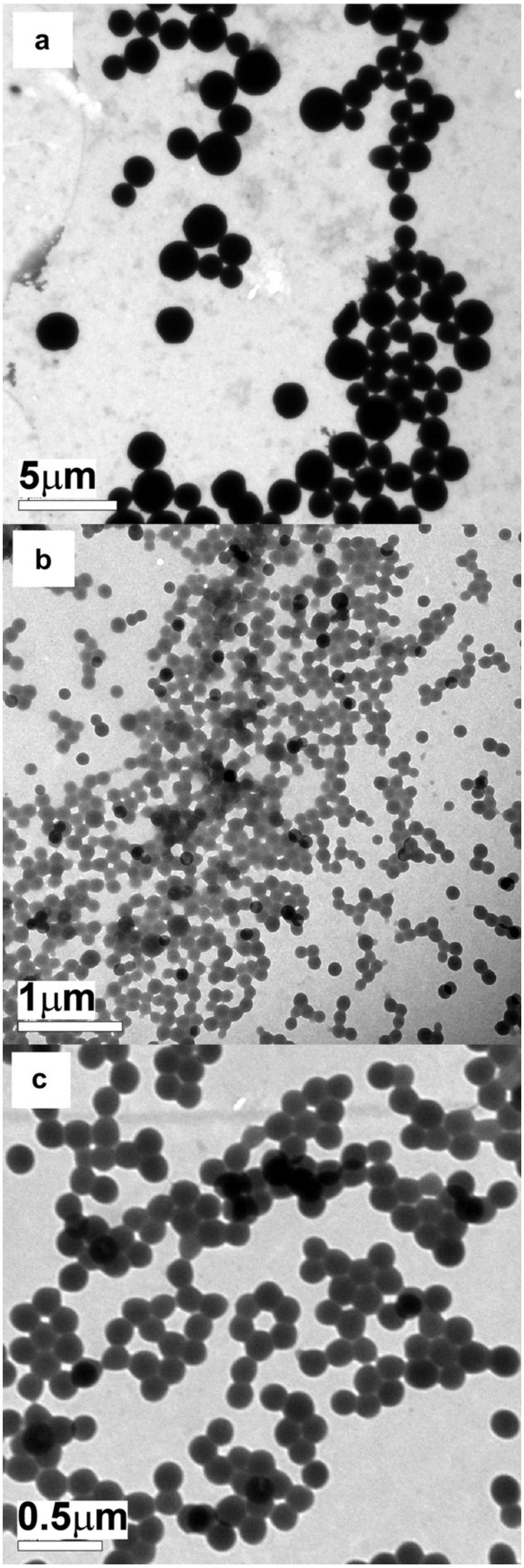


Fig. 7. TEM micrographs of cross-linked PMMA particles: (a) sample **XL4** – stabilizer **4**, 20% EGDMA; (b) sample **XL5** – stabilizer **3**, 1.1% EGDMA; (c) **XL6** – stabilizer **3**, 5.4% EGDMA.

solvent ratio led to a more dramatic drop in size from 2715 to 832 nm (**D1** and **D5**, Table 3). However further decreasing the monomer:solvent ratio led to no significant drop in particle size except at 76% solvent volume (**D8**, Table 3).

In contrast, decreasing monomer concentration and/or increasing stabilizer concentration (**E1**–**E8**, Table 3) for particles prepared using polymer **4**, PMMA$_{64}$-*block*-PODA$_{36}$, as the stabilizer led to clear reductions in particle size in accordance with data obtained for related systems [10,39–41]. This allowed for the synthesis of monodisperse PMMA colloidal micro- and nanoparticles with diameters from 62 nm 1190 nm – with standard deviations in size in the range 7–16%; the only exception occurring in the preparation of sub-100 nm particles where a significant standard deviation in particle diameter was observed (31%). Typical micrographs illustrating PMMA sub-micron sized particles using polymer **4** as the stabilizer are shown in Fig. 4 and plots of solvent content versus particle size are illustrated in Fig. 5. These results suggest that the use of a block copolymer is advantageous over that of a gradient copolymer in obtaining fine control over colloidal particle diameters. The principal role of the stabilizer in NAD polymerizations is to block particle aggregation and flocculation. They furthermore help to regulate particle size by acting as a barrier to the further incorporation of PMMA oligomers formed in the dispersion medium [15]. It has been observed and is generally accepted that block copolymers segregate orthogonally at interfaces and the most likely arrangement of PMMA$_{64}$-*block*-PODA$_{36}$ at the solvent/PMMA interface is with the PODA segments protruding into the solvent medium and the PMMA segments ‘buried’ in the particle (illustrated in Scheme 2) [43]. There have been remarkably few studies on the interfacial properties of gradient copolymers but gradient copolymers have been predicted and shown to enrich at immiscible interfaces and lower interfacial tension but they form broader interfacial layers than the corresponding block copolymers [43–46]. Furthermore the exact arrangement of chains is unclear with some weaving in out of each component thought to be possible though to the best of our knowledge this has not been experimentally demonstrated [43]. Thus two extremes may be envisaged for the arrangement of stabilizer **3**, PMMA$_{41}$-*grad*-PODA$_{59}$ (Scheme 3); an orthogonal arrangement of the chains to the interface, with the ODMA rich segment in the solvent and the MMA rich segment in the particle. In contrast should some weaving of a copolymer chain between the solvent and PMMA occur, a significantly larger surface area would be occupied by each chain at the surface with less extension of the ODA rich segments into the solvent which consequently might have a poorer stabilising effect.

Another possible explanation for the difference in the stabilising behaviour of the two copolymers may lie in their different solubilities. It was observed that stabilizer **3** was soluble in hexane/dodecane (0.22 g in 4.7 mL hexane and 2 mL dodecane) giving a slightly cloudy but transparent solution, whereas stabilizer **4** appeared to be completely insoluble at the same concentration. Upon addition of the MMA the stabilizer **3** solution became completely transparent and stabilizer **4** gradually dissolved to give a very slightly cloudy transparent solution. DLS analysis was difficult at the concentrations employed here but TEM suggested that both stabilizers existed as vesicular structures in the MMA/hexane/dodecane solutions (Fig. 6) with diameters in the range 200–1000 nm. The difference in solubility of **3** and **4** in the hexane/dodecane mixture indicates a possible competition for the location of the stabilizer chains during polymerization. As the MMA is consumed block copolymer **4** becomes increasingly insoluble in the reaction mixture and preferentially segregates at the PMMA/solvent interface thereby efficiently controlling diffusion of oligo-PMMA chains into the PMMA particles. However gradient copolymer **3** retains solubility in the solvent mixture and an equilibrium

Table 4
Component ratios and particle diameters (from TEM and DLS) for cross-linked PMMA–EGDMA particles synthesized using different solvent and stabilizer concentrations.

Sample	Stabilizer	Stabilizer: MMA (%:% by mass)	Solvent:MMA: EGDMA (% by vol)	D_{TEM} nm	σ_{TEM} nm	σ_{TEM} %	MMA: EGDMA[c] (%:% by vol)
E	**4**	5.1:94.9	60/40/0	801	51	6	100:0
XL1	**4**	5.1:94.9	60/39.5/0.5	1658	94	6	98.9:1.1
XL2	**4**	5.1:94.9	59/38.8/2.2	1358	173	13	94.6:5.4
XL3	**4**	5.1:94.9	57.8/37.9/4.3	1698	205	12	89.8:10.2
XL4	**4**	5.1:94.9	54.9/36.1/9	1532	362	24	80:20
E4	**4**	5.1:94.9	76/24/0	140	16	11	100:0
XL5	**4**	5.1:94.9	75.9/23.8/0.3	110	17	15	98.9:1.1
XL6	**4**	5.1:94.9	75.1/23.6/1.3	150	12	8	94.6:5.4

Table 5
Component ratios and particle diameters (from TEM and DLS) for PAN particles synthesized using different solvent and stabilizer concentrations.

Sample	Stabilizer	Stabilizer:AN (%:% by mass)	Solvent:AN (%:% by vol)	D_{TEM} nm	σ_{TEM} nm	σ_{TEM} %	D_{DLS} nm
I	**3**	5.1:94.9	60:40	[a]	[a]—	[a]—	[a]—
J	**4**	5.1:94.9	60:40	[a]—	[a]—	[a]—	[a]—
K	**6**	5.1:94.9	71:29	[a]—	[a]—	[a]—	[a]—
L	**6**	5.1:94.9	86:14	[a]—	[a]—	[a]—	[a]—
M	**6**	9.7:90.3	86:14	120	15	13	58
R	**6**	10.9:89.1	86:14	85	7	8	95
N	**2**	10.9:89.1	86:14	353,68	29,11	8,16	92, 212
O	**3**	10.9:89.1	86:14	481	47	10	455
P	**4**	10.9:89.1	86:14	[a]—	[a]—	[a]—	[a]—
Q	**5**	10.9:89.1	86:14	[a]—	[a]—	[a]—	[a]—

[a] No particles formed just solid precipitate of PAN.

may be set up between segregation at the interface and solvation. In fact by increasing solvent concentration this equilibrium may be tipped towards solvation and hence particle size control is not obtained. This may go some way towards explaining the initial decrease in particle size by employing higher concentrations of stabilizer **3** (**D5** versus **D1**), but no further significant control of size through solvent volume manipulation. However we have no conclusive explanation for the difference in behaviour of the gradient (**3**) and block (**4**) stabilizers in controlling particle size and the subject area deserves further study with particular emphasis placed on the comparative solubility of the copolymers and their nature in solution.

3.4. Cross-linked PMMA particles dispersed in hexane/dodocane

For widespread and practical use of PMMA micro- and nanoparticles in a variety of solvents, a means of maintaining structural integrity is required upon transfer from a medium in which the PMMA is insoluble (e.g. hexane/dodecane in this instance) into other solvents (e.g. butyl acetate). To ensure the particles maintain their coherence when dispersed in other solvents a cross-linker can be used. It is known that cross-linked particles are a challenge to make in dispersion polymerizations due to the polymer flocculating or coagulating and broad size distributions and irregular particles are often the result. Song and Winnik found that to minimize the problems of cross-linker addition it was best to add the cross-linker after nucleation had taken place [8]. With the delayed addition of EGDMA (1%) they were able to make polystyrene particles with the same size and polydispersity as uncross-linked particles prepared in the same way. We have been able to make monodisperse cross-linked PMMA particles with the cross-linker added at the start of the reaction (reactions **XL1**–**XL2**, **XL5**–**XL6**) (Table 4 and Fig. 7). Various concentrations of ethylene glycol dimethacrylate (EGDMA) were employed in NAD polymerizations of MMA using polymer **4** as the stabilizer and following the reaction conditions otherwise employed for the preparation of samples **E** and **E4**. Table 4 shows the TEM and DLS particle size data obtained for 4 concentrations of cross-linker. All the cross-linked samples with a solvent concentration of 58% (**XL1**–**XL4**) gave larger particle diameters ($D_{TEM} \sim 1350–1700$ nm) than the otherwise equivalent uncross-linked sample **E** with $D_{TEM} \sim 800$ nm (Table 4 and Fig. 8). For a higher solvent:monomer ratio (76:24 by volume, **XL5** and **XL6**) which yielded particles with $D_{TEM} = 140$ nm when the EGDMA was absent, the particle diameters (110 and 150 nm) were similar. The degree of uniformity of the particles for **XL1**–**XL4** decreases quite considerably with increasing EGDMA content ($\sigma = 6–24\%$) with the exception of **XL1** with the lowest EGDMA content.

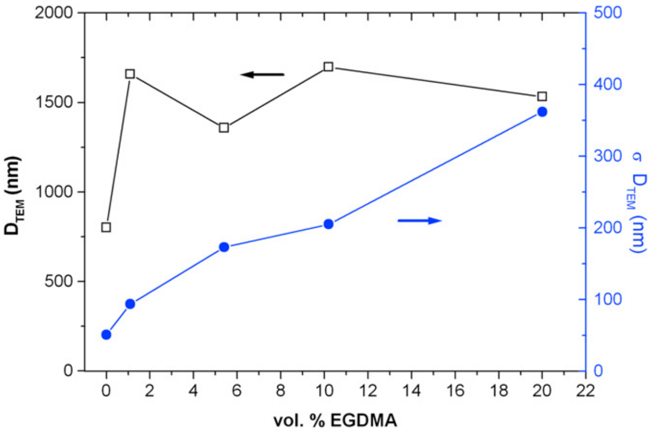


Fig. 8. Variation in particle diameter and standard deviation with EGDMA content (samples **E4**, **XL1**–**XL4**).

To confirm their structural integrity the cross-linked particles dispersed in hexane/dodecane were allowed to settle over a few days whereupon the supernatant was decanted off and the samples left to dry. Butyl acetate was then added and the mixture stirred rapidly to see if the particle would redisperse. The particles dispersed easily giving a dispersion that looked the same as the hexane/dodecane dispersion. The dispersion was stable but settled over the course of a few days though shaking or stirring resulted in re-dispersion of the particles.

3.5. Dispersion polymerization of AN in hexane/dodecane using PMMA–PODA copolymer stabilizers

For the purposes of our groups work on pressure sensitive paints PAN particles were synthesized to investigate the different effects of oxygen permeable particles (PMMA) and oxygen impermeable particles (PAN). It was hypothesized that the PMMA–PODA copolymers may also act as stabilizers in the synthesis of PAN particles. A number of the copolymer stabilizers were used in the NAD polymerization of AN in hexane/dodecane and Table 5 summarises the results obtained form analysis of the resulting samples. As is evident the successful use of PODA–PMMA copolymer stabilizers in the synthesis of PAN particles required a much higher concentration of stabilizer and solvent than for the equivalent PMMA particle syntheses. Where the volume percent ratio of solvent:AN was below 86:14 and the mass percent ratio of stabilizer:AN ratio was below 9.7:90.3 no PAN particle dispersions were formed and PAN simply precipitated from solution. Two of the gradient copolymers stabilizers (**2** and **3**) gave relatively large particles (D_{TEM}

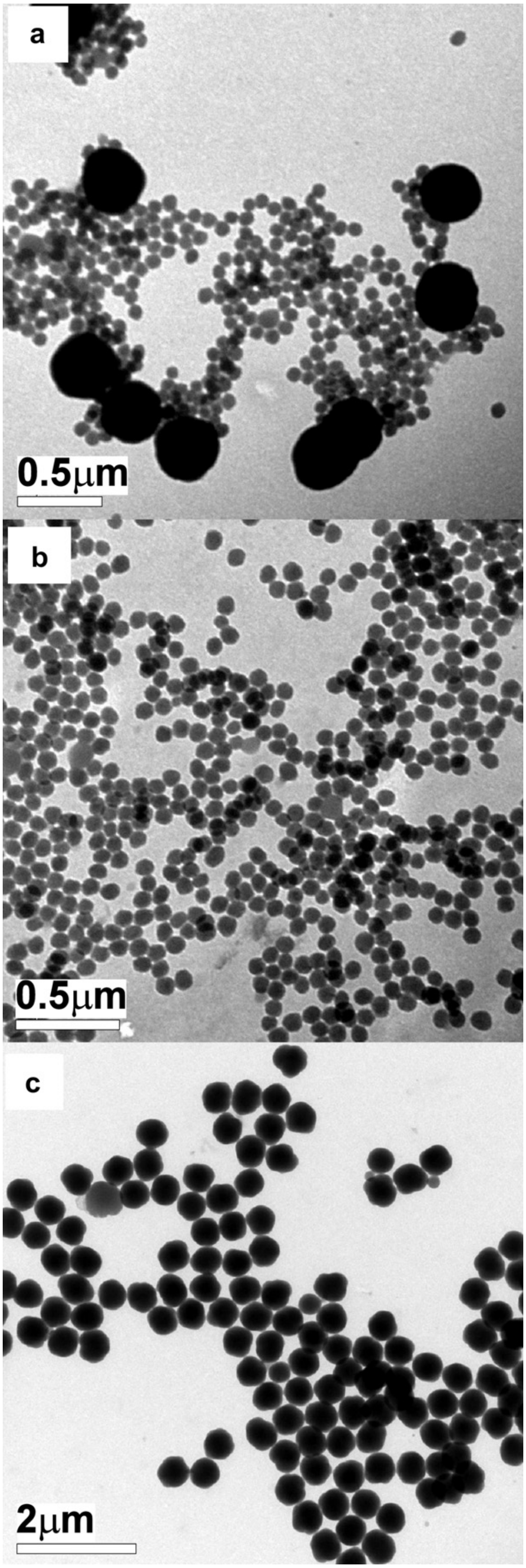


Fig. 9. TEM micrographs of PAN particles: (a) sample **N** – stabilizer **2**; (b) sample **R** – stabilizer **6**; (c) sample **O** – stabilizer **3**.

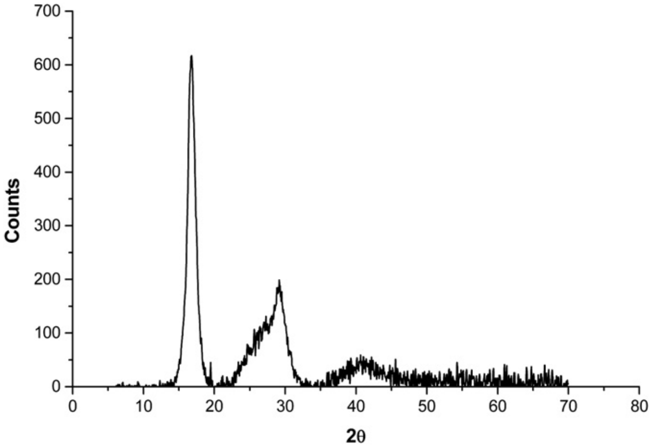


Fig. 10. X-Ray diffractogram of PAN nano-particles (sample **R**) prepared with stabilizer **6**.

~350–480 nm), one sample of which, **N**, was bimodal in distribution (Fig. 9a) and the other, **O**, monomodal (Fig. 9c). In contrast he block copolymer with the highest percentage of PODA (**6**) gave smaller particles ($D_{TEM} = 120$ nm) (Fig. 9b) and some evidence of size control was demonstrated when the stabilizer:AN % ratio by mass was increased from 9.7:90.3 to 10.9:89.1 whereupon PAN nano-particles with $D_{TEM} = 85$ nm and relatively low dispersity ($\sigma = 8\%$) were obtained [3,32]. Whilst further studies are needed it is apparent that relatively high stabilizer:monomer ratios (>9.7:90.3) and high solvent:monomer ratios (>86:14) are required for the successful syntheses of PAN particles.

PAN is a semi-crystalline polymer so the particles formed are irregular spheres and 'boulder-like' (Fig. 9); they have previously been described as crumpled latexes which is an appropriate term [32]. Powder X-ray diffraction analysis of the sample **R** when decanted and dried, demonstrated the crystallinity of the giving peaks at $2\theta = 16.8°$ and 29.4° which are identical to the database values for PAN [42] and those recorded by Boguslavsky for PAN nano-particles (Fig. 10) [3]. In contrast the average crystallite size calculated from the Scherrer equation is 6.23 nm which is half that recorded by Boguslavsky [3] and Landfester [32] for their samples prepared in aqueous media.

4. Conclusion

Three gradient and three block copolymers of octadecyl methacrylate and methyl methacrylate prepared by ATRP have been demonstrated to act as successful stabilizers for the non-aqueous dispersion polymerization of methyl methacrylate. In all cases stable monomdal colloidal dispersions of PMMA particles with diameters from ~62 to 2725 nm and standard deviations from 6 to 25%. Of these stabilizers one gradient and one block copolymer were used for NAD polymerizations of MMA varying the stabilizer: MMA and solvent:MMA ratios. The block copolymer PODMA–PMMA (**4**) was demonstrated to enable the fine control of particle size generating monomodal stable colloidal dispersions with PMMA nano- and micro-particles with diameters from 62 to 1190 nm. The gradient copolymer PODMA–PMMA (**3**) was ineffectual in controlling particle size predictably.

The PODMA–PMMA block copolymer **4** was also use as the stabilizer in NAD co-polymerization of ethylene glycol dimethacrylate and methyl methacrylate in various molar ratios of MMA to cross-linker to give cross-linked PMMA micro- ($D_{TEM} \sim 1300–1700$ nm) and nano-particles ($D_{TEM} \sim 110–150$ nm). Finally the successful application of three of the PODMA–PMMA block copolymers as stabilizers in the NAD polymerization of acrylonitrile to synthesise polyacrylonitrile nano-particles was demonstrated. Overall the results support the conclusion that the easily synthesized block copolymer of PODMA–PMMA with ODMA molar contents of >60% is a highly versatile stabilizer for non-aqueous dispersion polymerizations. The full range of variables have not been explored in this study but taking PODMA–PMMA block polymer as the most versatile of the copolymers studied, in terms of monomers polymerized, low dispersities and control over particle size, there is considerable scope for studies on effect of ODMA content and molecular weight (chain length) in addition to reaction conditions (e.g. temperature and stirring speed) for further optimization of the polymer colloid synthesis by this approach.

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References

[1] Bovey FA, Kolthoff IM, Medalia AI, Meehan EJ. Emulsion polymerization. Interscience Publishers; 1955.
[2] Kawaguchi H. Prog Polym Sci 2000;25:1171–210.
[3] Boguslavsky L, Baruch S, Margel S. J Colloid Interface Sci 2005;289:71–85.
[4] Imperial Chemical Industries, British Patent 893,429; 1962.
[5] Rohm and Hass, British Patent 934,038; 1963.
[6] Barrett KEJ. Dispersion polymerization in organic media. Wiley-Interscience; 1975.
[7] Riess G, Labbe C. Macromol Rapid Commun 2004;25:401–35.
[8] Song J-S, Winnik M. Macromolecules 2005;38:8300–7.
[9] Hirzinger B, Helmstedt M, Stejskal J. Polymer 2000;41:2883–91.
[10] Klein SM, Manoharan VN, Pine DJ, Lange FF. Colloid Polym Sci 2003;282:7–13.
[11] Jakubowski W, Lutz JF, Slomkowski S, Matyjaszewski K. J Polym Sci Part A Polym Chem 2005;43:1498–510.
[12] Baines FL, Dionisio S, Billingham NC, Armes SP. Macromolecules 1996;29: 3096–102.
[13] Antl L, Goodwin JW, Hill RD, Ottewill RH, Owens SM, Papworth S. Colloids Surf 1986;17:67–78.
[14] Campbell AI, Bartlett P. J Colloid Interface Sci 2002;256:325–30.
[15] Hu H, Larson RG. Langmuir 2004;20:7436–43.
[16] Hu H, Larson RG. J Am Chem Soc 2004;126:13894–5.
[17] Kato M, Kamigaito M, Sawamoto M, Higashimura T. Macromolecules 1995;28:1721–3.
[18] Wang JS, Matyjaszewski K. Macromolecules 1995;28:7901–10.
[19] Percec V, Barboiu B. Macromolecules 1995;28:7970–2.
[20] Davis KA, Matyjaszewski K. Adv Polym Sci 2002;159:1–169.
[21] Coessens V, Pintauer T, Matyjaszewski K. Prog Polym Sci 2001;26:337–77.
[22] Itoh T, Fukutani K, Hino M, Ihara E, Inoue K. J Colloid Interface Sci 2009;330:292–7.
[23] Zhu Y, Ford WT. Macromolecules 2008;41:6089–93.
[24] Butun V, Armes SP, Billingham NC. Macromolecules 2001;34:1148–59.
[25] Yang YJ, Wang Z, Gao Y, Liu T, Hu CP, Dong QZ. J Appl Polym Sci 2006;102: 1146–51.
[26] Woods HM, Nouvel C, Licence P, Irvine DJ, Howdle SM. Macromolecules 2005;38:3271–82.
[27] Datta H, Bhowmick AK, Singha NK. Polymer 2009;50:3259–68.
[28] Street G, Illsley D, Holder SJ. J Polym Sci Part A Polym Chem 2005;43:1129–43.
[29] Vincent B, Clarke J, Barnett KG. Colloids Surf 1986;17:51–65.
[30] Kurjata J, Chojnowski J, Yeoh C-T, Rossi NAA, Holder SJ. Polymer 2004;45:6111–21.
[31] Ziegler MJ, Matyjaszewski K. Macromolecules 2001;34:415–24. and references therein.
[32] Landfester K, Antonietti M. Macromol Rapid Commun 2000;21:820–4.
[33] Harris HV, Holder SJ. Polymer 2006;47:5701–6.
[34] Chen W, Zhu M, Song S, Sun B, Chen Y, Adler H-JP. Macromol Mater Eng 2005;290:669–74.
[35] Shi S, Kuroda S, Hosoi K, Kubota H. Polymer 2005;46:3567–70.
[36] Nunes DSS, Coutinho FMB. Eur Polym J 2002;38:1159–65.
[37] Shen Q, Gu Q-F, Hu J-F, Teng X-R, Zhu Y-F. J Colloid Interface Sci 2003;267:333–6.
[38] Wang Z, Yang YJ, Dong Q, Liu T, Hu CP. Polymer 2006;47:7670–9.
[39] Yang W, Hu J, Tao Z, Li L, Wang C, Fu S. Colloid Polym Sci 1999;277:446–51.
[40] Horák D. J Polym Sci Part A Polym Chem 1999;37:3785–92.
[41] Paine AJ, Luymes W, McNulty J. Macromolecules 1990;23:3104–9.
[42] Joint Committee of Powder Diffraction Standard—International Center for Diffraction Data (JCPDS-ICDD) 48–2119.
[43] Matyjaszewski K, Ziegler MJ, Arehart SV, Greszta D, Pakula T. J Phys Org Chem 2000;13:775–86.
[44] Beginn U. Colloid Polym Sci 2008;286:1465–74.
[45] Lefebvre MD, Dettmer CM, McSwain RL, Xu C, Davila JR, Composto RJ, et al. Macromolecules 2005;38:10494–502.
[46] Shull KR. Macromolecules 2002;35:8631–9.