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Octadecyl acrylate based block and random copolymers prepared by ATRP as comb-like stabilizers for colloidal micro-particle one-step synthesis in organic solvents

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Abstract

Three random and three block copolymers of methyl methacrylate (MMA) and octadecyl acrylate (ODA) were synthesised by atom transfer radical polymerisation. These copolymers were assessed for their application as stabilizers in the one-step non-aqueous dispersion polymerisation of MMA 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 400–2730 nm. Uniform monodisperse 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.

Keywords: Octadecyl acrylate (ODA); Atom transfer radical polymerisation (ATRP); Dispersion polymerisation

1. Introduction

The synthesis of colloidal polymer particles (sub-micron and micron) dispersed in organic media via dispersion polymerisation (non-aqueous dispersion – NAD) whilst not as developed as colloid synthesis in aqueous media [1,2], has been known since the early sixties [3,4], and has been developed largely as a consequence of applications within the coating industries [5]. In a typical radical NAD polymerisation the monomer and initiator are soluble in the organic solvent. After polymerisation 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 polymerisation 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 polymerisations and readily commercially available, are not efficient as stabilizers for NAD systems. 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 stabilisation 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 [5,6]. Many were commercially available materials [7–9] and relatively few have been designed for the specific application as dispersion polymerisation stabilizers for example [10,11]. Following research and procedures developed by Antl et al. [12] and Campbell and Bartlett [13], Hu and Larson [14,15] recently reported the successful one-step synthesis of highly monodisperse micron size fluorescent poly(methyl methacrylate) (PMMA) particles (>2 μm) using a poly(hydroxystearic acid)-*g*-PMMA (PHSA-*g*-PMMA) stabilizer. This is a particularly attractive route to NAD polymerisation and our group has an interest in the synthesis of similar fluorescent particles by such fast and one-step processes.

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However, the reported synthesis of the PHSA-*g*-PMMA stabilizer [14] was far from trivial and it proved difficult to reproduce the synthesis of this graft copolymer readily.

Since its discovery atom transfer radical polymerisation (ATRP) has become an important laboratory synthetic route for a variety of copolymers [16–18]. 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 [19,20]. Our group has previously reported the synthesis of homo- and block-copolymers of octadecyl acrylate (ODA) by atom transfer radical polymerisation (ATRP) [21] by utilising an appropriate ligand for the copper(I) salt (*N*-(*n*-octyl)-2-pyridylmethanimine). Given that poly(octadecyl acrylate) (PODA) is soluble in non-polar solvents it was postulated that copolymers of MMA with ODA would act as efficient stabilizers in place of PHSA-*g*-PMMA in the dispersion polymerisation of MMA as reported by Hu and Larson. More generally they 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 principle copolymers of ODA synthesised by this approach can replace the poly(hydroxystearic acid) stabilizers widely utilised [5,12,14,24] for such colloid syntheses. In this paper we will report our preliminary results in utilising these block copolymers and random copolymers synthesised by ATRP (Scheme 1) as stabilizers (dispersants) in the synthesis of PMMA colloidal micro-particles.

2. Experimental

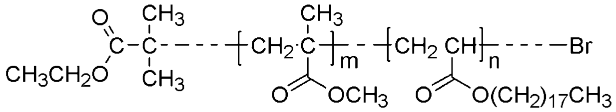
2.1. Materials

Toluene was pre-dried over magnesium sulphate followed by sodium wire and then distilled from sodium wire immediately prior to use. 2-Bromo-2-methylpropanoyl bromide (ethyl-2-*iso*-bromobutyrate, 98%, Aldrich), aluminium oxide (Acros Organics, activated, neutral, 50–200 μm), Cu(I)Br (Aldrich, 98%), octanethiol (Acros, 97%), benzoyl peroxide (recrystallised from diethyl ether), hexane (Aldrich, reagent grade), dodecane (Acros, 99%) 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 synthesised according to the previously reported procedures [21].

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 $CDCl_3$.



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 copolymer structures.

The molecular weight characteristics 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).

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

The full experimental conditions and molecular weight characteristics for the copolymers synthesised are given in Table 2. Typical syntheses are given below.

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

Nitrogen gas was bubbled through a mixture of ethyl-2-isobromobutyrate (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 heated 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 a 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 (stabilizers ***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 brown powder (6.12 g, 62%, $M_n = 19{,}000$, $M_w/M_n = 1.29$).

2.3.3. Typical dispersion polymerisation of methyl methacrylate (reactions A–G, B1–B3)

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. 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.

3. Results and discussions

3.1. Synthesis of the octadecyl acrylate copolymers by ATRP

Our group has previously reported the synthesis of homo- and block-copolymers of ODA by atom transfer radical polymerisation (ATRP) [21] and these procedures were employed in the synthesis of PODA-*block*-PMMA (stabilizers **4–6**) with different molecular ratios of MMA to ODA. The PODA-*co*-PMMA samples (stabilizers **1–3**) were synthesised following similar procedures but including both the monomers at the start of the reaction. The molecular weight and structural parameters of the copolymers employed in this study are given in Table 1. As observed by our group [21,22] and others [23] comb-like polymers and copolymers show considerable inaccuracies in molecular weight parameters recorded by SEC. By combining the SEC data for the PMMA macroinitiators and the ^{1}H NMR spectral data for copolymers **4–6** the M_n values for the block copolymers could be calculated reasonably accurately. The molecular weight parameters recorded by SEC for the random copolymers and given in Table 1 are likely to be underestimates. The molar and weight ratios of the monomers in all copolymers are calculated from ^{1}H NMR and are accurate.

3.2. Dispersion polymerisation of MMA in hexane/dodecane using ODA copolymers

Copolymers **1–6** were assessed for their performance as stabilizers in the synthesis of PMMA particles. In performing this preliminary assessment, whilst our primary concern was to assess their ability to act as stabilizers in the synthesis of micro-particles in hexane/dodecane, we were also interested in (a) the stability of the colloidal suspensions produced, (b) the uniformity of the particles, and (c) the size of the PMMA particles.

The PMMA particles were synthesised following the procedure described by Hu and Larson [14]. A typical synthesis involved heating a mixture of MMA, octanethiol, benzoyl peroxide, the stabilizer, hexane and dodecane to 80 °C under nitrogen (MMA:hexane:dodecane 43:39:18 by volume). A few minutes after reaching 80 °C all reaction mixtures became turbid following precipitation and nucleation of the primary particles. The dispersions were then stirred at 80 °C for 2 h after which they were allowed to cool to room temperature. Samples of the solutions were then diluted for study by DLS and TEM.

As expected when no copolymer stabilizer was used (entry A), defined PMMA particles were not formed and a solid layer of polymer gradually formed and settled during the course of the reaction. All the copolymers (**1–6**) synthesised proved able to act as stabilizers in the syntheses of colloidal micro-particles of PMMA in hexane/dodecane. The particle sizes and uniformities were evaluated by transmission electron microscopy (TEM) and further investigated by dynamic light scattering. The average diameters (D_{TEM}) varied from 700 nm to 2800 nm and particle uniformities varied considerably. The particle diameters and σ-values recorded by DLS and TEM are given in Table 2 and representative TEM micrographs are given in Fig. 1. All the dispersions settled after a time but were easily reformed by rapid stirring for a few minutes; no permanent flocculation or aggregation took place.

There was no immediate and obvious correlation observable between the size and size distributions of the particles and the stabilizer structures. Though the much higher uniformities of the particles synthesised using copolymers **3** and **4** (entries D and E in Table 2) suggest that shorter chain copolymers are more efficient at ensuring particle uniformity. This may be a consequence of a higher solubility of these

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

Stabilizer	Structure	DP[a]	M_n[a]	M_w/M_n[a]	M_n[b]	DP[b]	MMA:ODA[c] % mol	MMA:ODA[c] % weight
1	MMA-*co*-ODA$_{(3.0:1)}$	163	25,500	1.42	–	–	75:25	48:52
2	MMA-*co*-ODA$_{(2.1:1)}$	169	29,000	1.40	–	–	68:32	40:60
3	MMA-*co*-ODA$_{(0.69:1)}$	60	14,000	1.33	–	–	41:59	18:82
4	MMA$_{80}$-*b*-ODA$_{45}$	105	19,000	1.29	22,500	125	64:36	35:65
5	MMA$_{80}$-*b*-ODA$_{65}$	65	13,000	1.30	29,000	145	55:45	28:72
6	MMA$_{80}$-*b*-ODA$_{125}$	114	27,000	1.58	48,500	205	39:61	16:84

[a] Measured by SEC, PMMA standards.

[b] Calculated from SEC for PMMA-Br macroinitiator ($M_n = 8000$) and ^{1}H NMR of copolymers.

[c] Calculated from ^{1}H NMR.

Table 2
Diameters and size distributions for particles using different dispersion polymerisation stabilizers and different stabilizer and solvent concentrations

Entry	Stabilizer	Stabilizer conc %[a]	Solvent conc %[b]	D_{TEM} (nm)	σ_{TEM}	D_{DLS} int. (nm)	M_n of PMMA[c]
A	None	N/A	58	–	–	–	28,000
B	**1**	5.11	58	1020	259 (25%)	1130	36,000
C	**2**	5.11	58	1240	278 (22%)	1150	27,000
C1	**2**	5.11	71	1280	257 (20%)	695	25,000
C2	**2**	9.73	58	1110	53 (4.7%)	1140	35,000
C3	**2**	9.73	71	400	64 (16%)	310	100,000
D	**3**	5.11	58	2730[d]	105 (3.8%)	1910	38,000
E	**4**	5.11	58	800	51 (6.4%)	900	35,000
F	**5**	5.11	58	1650	199 (12%)	1660	22,000
G	**6**	5.11	58	700	87 (12%)	670	19,000

[a] Stabilizer concentration relative to monomer (w:v).

[b] Solvent concentration relative to monomer (v:v).

[c] Measured by SEC, PMMA standards.

[d] A very small fraction (<3%) of particles $D_{\mathrm{TEM}} = 450$ nm were observed to be present – not detected by DLS.

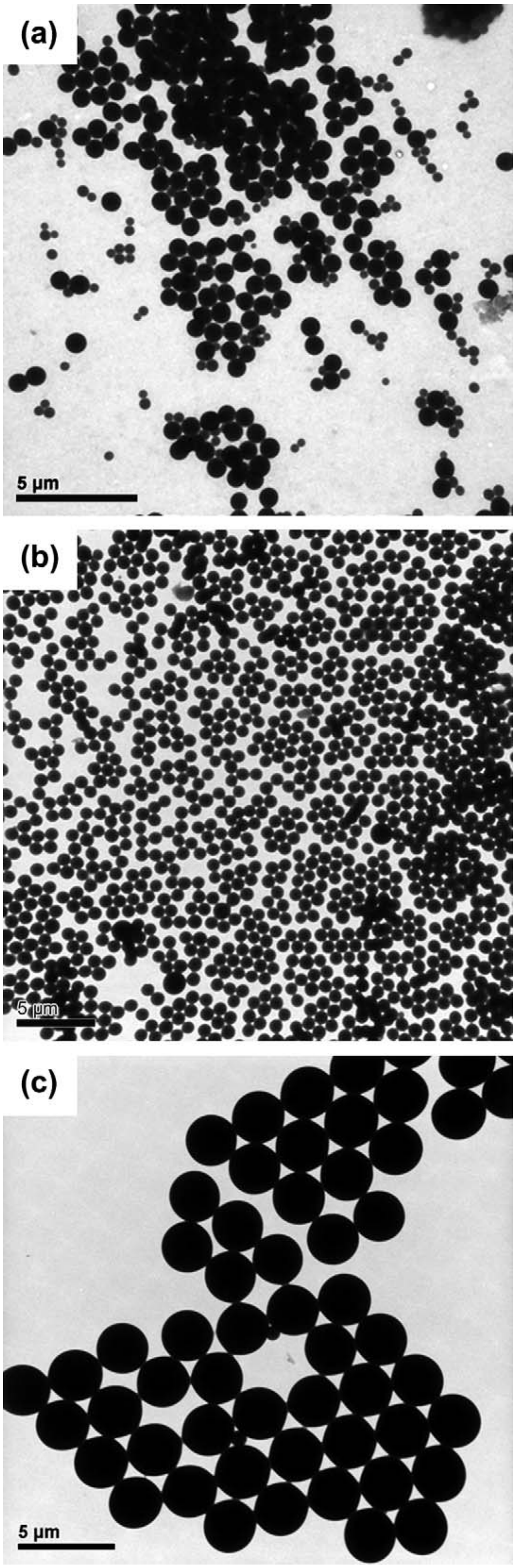


Fig. 1. TEM micrographs showing PMMA particles: (a) sample G – stabilizer **6**, (b) sample E – stabilizer **4**, and (c) sample D – stabilizer **3**.

copolymers in the solvent medium allowing faster equilibration of particle stabilisation in the nucleation and coagulation stages. The need for control of the absolute and relative lengths of the stabilizer components has been previously noted by Barrett [5] and Hu and Larson [14] for PHSA-*g*-PMMA.

However, the fact that all copolymers enabled the synthesis of micro-particles and that at least two of these materials enabled the synthesis of particles with size distribution variations of less than 10% (and a tendency to hexagonal packing, Fig. 1b,c) is reassuring in contemplating this approach to stabilizer synthesis. This is of particular note given that no optimisation of the reaction conditions or of the copolymer lengths was carried out at this stage. Of particular note also is the synthesis of monodisperse PMMA particles (entry D using PMMA$_{25}$-*co*-PODA$_{35}$) with very narrow particle size distribution ($\sigma < 4\%$) and a tendency to hexagonal packing (Fig. 1c) allowing the potential for the construction of colloidal crystals via this approach.

The original aim of this work was to synthesise block copolymers of ODA–MMA to study their efficacy as stabilizers in non-aqueous dispersion polymerisations. The random copolymers were synthesised for direct comparison with a belief that they would not be effective in the role of stabilizers (given the body of literature on the subject of the application of block copolymers in such dispersion polymerisations) [6]. Consequently the finding that both sets of materials can be used as stabilizers and that one of the random copolymers was the most efficient for preparing micro-particles of low polydispersity was initially surprising. Two options present themselves to explain the efficiency of the random copolymers: (i) the reactivity ratios of the monomers are sufficiently different that composition drift occurs during the polymerisation, leading to gradient copolymers with very long segments of ODA that are sufficient for steric stabilisation; (ii) that, despite the short length of the side-chains (octadecyl), the random copolymers are behaving as graft copolymers more closely than might be expected and that carbon chains of 18 atoms are sufficient for steric stabilisation in these systems. We are far more inclined to believe that the former explanation is more likely. Previous studies that have determined the reactivity ratios of *n*-butyl acrylate polymerised with MMA by ATRP and standard free radical polymerisations indicate significant

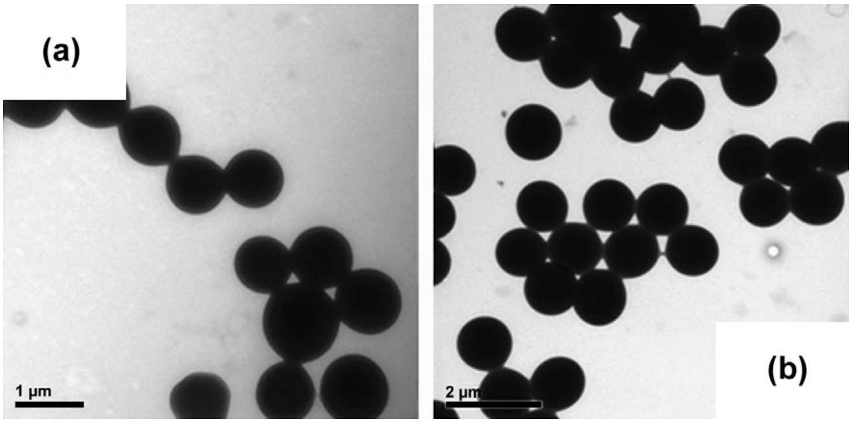


Fig. 2. TEM micrographs of PMMA particles: (a) sample C and (b) sample C2.

differences between the reactivity ratios of MMA ($r_{MMA} = 1.79-3.15$) and BMA ($r_{BA} = 0.11-0.37$) [25]. Similar magnitudes of difference in reactivity between MMA and ODA (potentially magnified by further differences in diffusion coefficients between ODA and BMA) would inevitably lead to ODA rich domains towards the termini of the final copolymer products. The effect would be more pronounced for copolymer **3** with a higher fraction of ODA. Studies of the composition of the random ODA–MMA copolymers with time during polymerisation are underway and will be reported in a future publication. Further work will also compare random copolymers of ODA–MMA prepared by classical free radical polymerisation techniques with those prepared by ATRP. In the former case composition drift will lead to inhomogenous copolymer mixtures in contrast to the gradient type copolymer synthesised via ATRP.

A preliminary investigation was made into the effect of stabilizer and solvent concentration on the particle sizes and size distributions. For our purposes, of particular interest is the one-step synthesis of PMMA particles with nanometer (sub-micron) dimensions and with uniform size distributions (standard deviations < 5%). To this end a single stabilizer ($PMMA_{115}$-*co*-$PODA_{54}$, copolymer **1**) was chosen and the solvent volume and stabilizer quantity varied in their application in the synthesis of PMMA particles (Table 2). Antl et al. [4] have reported that diluting the monomer (i.e. increasing solvent concentration) has the effect of decreasing particle size. Little effect was observed on increasing the quantity of solvent used (compare entry C to C1 in Table 2) whilst retaining the same stabilizer concentration for copolymer **3**. Upon increasing the quantity of stabilizer, however, but retaining the same solvent concentration, a dramatic increase in particle uniformity (the standard deviation in particle size decreased from circa 22% to 5%) was achieved (compare entry C to C2, Fig. 2). When both solvent and stabilizer quantities were increased (entry C3) the particle size decreased dramatically but the standard deviation remained high.

4. Conclusion

Both block and random PMMA–PODA copolymers synthesised by ATRP have been demonstrated to be successful stabilizers for producing PMMA colloidal dispersions in a hexane/dodecane non-polar organic solvent mixture. The average diameters of the micro-particles formed ranged from 400 to 2730 nm. Two of the preparations utilising these novel stabilizers resulted in very narrow size distributions (<5% standard deviation in size) of PMMA particles. Further optimisation of the chain lengths and relative molar ratios of the ODA:MMA in the copolymers is readily achievable by ATRP and is likely to lead to further control over particle size distributions. A further utility of this approach lies in the possibility of replacing the MMA component with other commercially available vinyl monomers for the one-step synthesis of colloidal particles of different chemical compositions. Studies of the monomer composition of the random ODA–MMA copolymer stabilizers with time during polymerisation are underway and will be reported in a future publication. Further work will also compare random copolymers of ODA–MMA prepared by classical free radical polymerisation techniques with those prepared by ATRP. We are currently studying block and random copolymers of ODA and acrylonitrile for the synthesis of polyacrylonitrile colloids in non-polar solvents.

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