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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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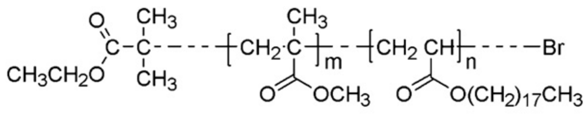
(PMMA) particles (>2 μm) using a poly(hydroxystearic acid)-*g*-PMMA (PHSA-*g*-PMMA) stabilizer. This is a particularly attractive route to NAD polymerization and our group has an interest in the synthesis of similar fluorescent particles by such fast and one-step processes. However, the reported synthesis 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).

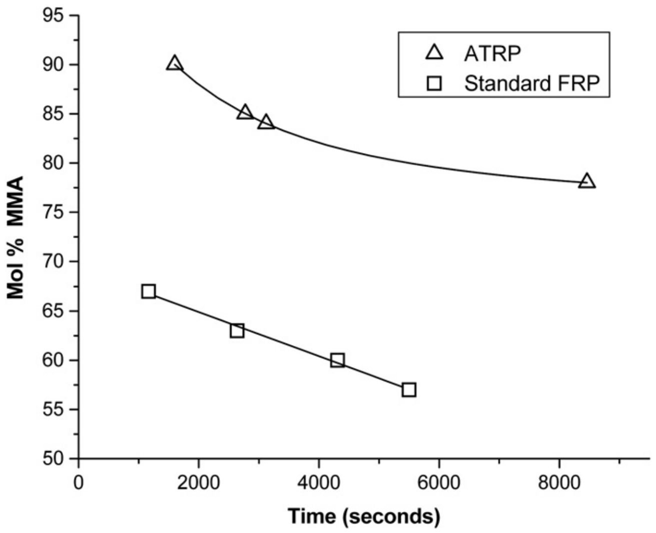


Fig. 1. Variation in methyl methacrylate content with time for isolated copolymer samples synthesized by free-radical polymerization (squares, stabilizer **7**) and by atom transfer radical polymerization (circles, stabilizer **1**).