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Inkjet printable aqueous composite dye–polymer nanoparticles

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ABSTRACT

Here we report the synthesis of polymer stabilised anthraquinone dye-based aqueous nanoparticles using evaporative precipitation from dichloromethane into water and their use as novel aqueous inkjet colorants. Polymer stabilised dye nanoparticles in the 100 nm size range are demonstrated and the mechanism of formation of stable nanoparticles and the role of polymer stabiliser design is discussed. Formation of stable small particle size nanoparticles requires a fast dye crystal nucleation rate followed by a subsequent slow growth rate so as to avoid Ostwald ripening. Rapid nucleation can be achieved by metering small amounts of water-miscible organic solution of the dye to the non-solvent water under rapid mixing, referred to as quasi-emulsion solvent diffusion (QESD). These conditions result in high-supersaturation which causes spontaneous nucleation, followed by a rapid decrease in local supersaturation and hence slow crystal growth rate.

1. Introduction

Water insoluble crystalline disperse dyes have a broad colour gamut making them suitable for many high performance applications [1]. However their use in aqueous formulations requires either chemical modification, the use of energy intensive top-down dispersion methods using surfactants and/or polymeric dispersants, or appropriate polymer encapsulation [2–5]. Such processes usually involve mechanical force such as milling to achieve an appropriate particle size between 100 and 200 nm with no large particle size shoulder as required for robust inkjet printing.

In contrast bottom-up processing involves the formation of particles of the appropriate size from discrete molecules and as such a greater degree of control is possible [6,7]. Here we focus upon the use of evaporative precipitation which involves taking the dye of interest, dissolving it in a suitable solvent and on introduction to the aqueous continuous phase removal of the carrier solvent by evaporation leading to nanoparticle formation [8–12]. In synthesising nanoparticles based upon relatively hydrophobic crystalline disperse dyes two aspects need to be considered and controlled. Precipitation entails the creation of crystal nuclei, and their subsequent growth. Formation of stable small particle size nanoparticles requires a fast nucleation rate but slow growth rate so as to avoid Ostwald ripening [13]. Rapid nucleation can be achieved by metering small amounts of water-miscible organic solution of the dye to the non-solvent water under rapid mixing, referred to as quasi-emulsion solvent diffusion (QESD) [14]. These conditions result in high-supersaturation which causes spontaneous nucleation, followed by a rapid decrease in local supersaturation and hence slow crystal growth rate. In this paper we report the use of an evaporative precipitation technique involving the controlled metering of water-immiscible organic solvent containing dye and polymeric stabiliser into a temperature controlled aqueous solution with rapid solvent evaporation resulting in rapid and controlled dye-copolymer nanoparticle generation. Magenta H. 110300 (1-amino-4-hydroxy-2-[4-(1,1,3,3-tetramethyl-butyl)-phenoxy]-anthraquinone), Fig. 1) a hydrophobic crystalline dye ($T_m = 171.5$ °C) was chosen because of its low water solubility and good solubility in a range of organic water miscible and immiscible solvents including acetone and dichloromethane.

2. Experimental

2.1. Materials

1-Amino-2-bromo-4-hydroxyanthraquinone (C.I. Disperse Violet 17) (≥95%) was sourced from Advanced Technology and Industrial Company Ltd. and used without further purification. 2,2′-azobis(2-methylbutyronitrile) (Vazo 67) was kindly donated by Fujifilm Imaging Colorants Ltd. and was used as supplied.

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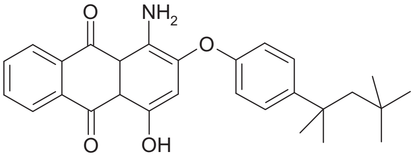

Fig. 1. Magenta H. 110300 (1-amino-4-hydroxy-2-[4-(1,1,3,3-tetramethyl-butyl)-phenoxy]-anthraquinone).

Methylmethacrylate (MMA), methacrylic acid (MAA) and 2-ethylhexylmethacrylate (EHMA) and all other reagents were obtained from Sigma Aldrich UK and used as received.

2.2. Characterisation

Molecular weights were measured using a Viscotek size exclusion chromatograph instrument equipped with 3 PLgel 10 μm Mixed-B columns and a differential refractive index detector. The eluent was tetrahydrofuran (THF) at a flow rate of 1 ml min^{-1} and the system was calibrated using polystyrene standards. ^{1}H NMR spectra were recorded using a 500 MHz Bruker. FT-IR spectra were obtained using a BioRad 'Excalibur' ATR-FT-IR spectrometer. Photocorrelation spectroscopy (PCS) particle sizing was performed in water using a Zetasizer-Nano from Malvern Instruments. Particle size (ps) and dispersity (PDi) were analysed assuming a monomodal distribution. For PDi > 0.2 particle diameter is quoted and for PDi < 0.2 'z-average' is quoted. Differential Scanning Calorimetry (DSC) was performed using a Perkin–Elmer Diamond DSC. Cryo Environmental Scanning Electron Microscopy (CESEM) was performed using a Philips ESEM XL30, 5–10 keV. Samples were prepared by adding a small amount to a sample tube, cooling rapidly in liquid nitrogen and cutting the tube in half. The cryogenically frozen surface is then coated with gold and viewed in a sample chamber held at around −130 °C. Powder diffraction was performed using a Philips Xpert station with a Cu K_α source at 1.5405980 nm. Ink-jet printing was carried out using a Dimatix DMP-2800 inkjet printer (Fujifilm Dimatix, Inc., Santa Clara, USA) fitted with a waveform editor and a drop-watch camera system which allows manipulation of the electronic pulses to the piezo jetting device for optimization of the drop characteristics as it is ejected from the nozzle. The nozzle plate consists of a single row of 16 nozzles of 23 μm diameter spaced 254 μm with typical drop size of 10 pl and drop diameter 27 μm. CIE colour space was measured on a Minolta CR-300 chroma meter colorimeter calibrated with a white card which had colour space of 0.3136 (x), 0.3194 (y) and 92.5 (Y).

2.3. Synthesis of Magenta H 110300: (1-amino-4-hydroxy-2-[4-(1,1,3,3-tetramethyl-butyl)-phenoxy]-anthraquinone)

1-Amino-2-bromo-4-hydroxyanthracene-9,10-dione (C.I. Disperse Violet 17) (0.05 mol, 15.91 g), 4-tert-octyl phenol (0.5 mol, 103.17 g, 10 fold excess) and potassium carbonate (0.055 mol, 7.60 g) were combined and stirred at 150 °C for 15 h at which point all the C.I. Disperse Violet 17 had been consumed as analysed by TLC (hexane:diethyl ether; 3:1). The reaction mixture was cooled to 90 °C, and 180 ml of methanol slowly added causing the deep red product to precipitate. The reaction mixture was cooled to room temperature and the product filtered off. The product was washed four times with methanol and four times with deionised water, and dried under vacuum overnight yielding 1-amino-4-hydroxy-2-[4-(1,1,3,3-tetramethyl-butyl)-phenoxy]-anthraquinone as a deep red solid in 84% yield (18.70 g). Elemental analysis: Calculated (%) C 75.8, H 6.55, N 3.2; found C 74.72, H 6.55, N 3.07. ^{1}H NMR ($CDCl_3$) δ (ppm): 0.78 (br.s., 9H), 1.43 (br.s., 6H), 1.80 (br.s., 3H), 6.42 (br.s., 1H), 7.09 (br.s., 2H), 7.49 (br.s., 2H), 7.79 (s., 2H), 8.38 (br.s., 2H), 14.16 (br.s)., 1H. Melting point: 170.3 °C.

Calculated solubility parameters; $\delta_p = 4.5$ $\text{MPa}^{1/2}$, $\delta_d = 23.8$ $\text{MPa}^{1/2}$, $\delta_h = 10.6$ $\text{MPa}^{1/2}$ [15], log $P = 7.5 +/- 0.8$ at 25 °C and log $D = 7.5$, 7.4, 7.1, 6.3 and 5.4 at 25 °C and pH 5, 6, 7, 8, and 9 respectively [16].

2.4. Polymer synthesis

Statistical methacrylate copolymers were prepared using starve fed free-radical solution polymerisation. Each copolymer contained MAA, which when neutralised with 0.98 equivalents triethylamine provided the charge-based stabilisation required to maintain a finely divided dispersion. The main chain hydrophobic component, MMA and EHMA, was chosen so as to have differing affinities for the hydrophobic substituted anthraquinone dye based upon solubility parameter considerations. Compositions were chosen using established polymer dispersant and inkjet design principles [17–23], such that [MAA] = 17.5 wt-%, $M_n = 16–24$ kDa, PDi typically between 2–3, and overall hydrophobicity defined using a calculated Hansch Parameter, Log P in the range of 0.54–3.75 [21]. Calculated glass transition temperatures (Tg) were in the range 122 °C (**P1**) and 14 °C (**P9**).

The following synthetic methodology was used for all copolymers in the study. Polymer **P5**: Propan-2-ol (28.13 g) was added to the reaction flask, heated to reflux for 30 min and separate solutions of propan-2-ol (18.75 g) and Vazo 67 (0.0078 mol, 1.5 g) and propan-2-ol (28.13 g), MMA (0.358 mol, 38.85 g), EHMA (0.132 mol, 26.25 g) and MAA (0.150 mol, 12.90 g) fed into the reaction flask over 2 h while the temperature in the flask was held at 83 °C. Once addition was complete, the reaction was maintained at 83 °C for a further 4 h before being cooled to room temperature and a further amount of propan-2-ol (75 g) added and stirred until homogeneous. The polymer was isolated by precipitation into ice chilled water and collection by filtration. The polymer was dried under vacuum, yielding a fine white powder at 75.5% yield (65.3 g).

2.5. Dye–polymer dispersion

The following describes the final optimized process as assessed by small nanoparticle size and stability to sedimentation using dichloromethane (DCM) as volatile organic solvent. To 80 ml of distilled water, held at 80 °C stirred at a rate of 250 rpm using an overhead stirrer with a centrifugal impeller blade, 20 ml of an 80:5:15 DCM:dye:polymer (w/w) (polymer pre-neutralised with 0.98 equivalent triethylamine) was passed through a heated hot bath at 80 °C and injected at a flow rate of 2 ml min^{-1} using uncoated stainless steel GC tubing having an internal diameter of 0.01 inches with an end tip diameter of 1/16 inch placed 1 cm under the surface of the water. DCM was collected using a Dean and Stark condenser and upon complete removal the total solids content was adjusted to 5 wt-% by the addition of the appropriate amount of distilled water.

3. Results and discussion

3.1. Solvent evaporation method for the formation of dye–polymer nanoparticles

Particle size and resultant stability to sedimentation of dye–polymer nanoparticles prepared using evaporative precipitation were found to be highly process dependent. Nanoparticle dispersion quality was evaluated visually and by PCS particle size