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Effect of crosslinking agents on the dispersive behaviour of polymer particles in seed swelling polymerisation

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ABSTRACT

This study focused on the effect of crosslinker structure between PMMA on the dispersity of crosslinked particles in seed swelling polymerisation. We used five different crosslinking agents in an assessment of the dispersity of crosslinking monodisperse particles using PMMA seed particles in seed swelling polymerisation. These results show that the structure of the crosslinking agent affects the dispersity during the swelling stage. According to the solubility parameter theory of computation, the departure of similar solubility parameter causes the swollen particles to segregate into more dispersity.

Introduction

Highly crosslinked polymer particles have recently become popular materials in the field of electronics, such as for anisotropic conductive film or spacers for liquid crystal display assembly. Anisotropic conductive films comprise metal-coated polymer particles, epoxy, and latent hardener, in which the metal-coated polymer particles must be monodispersed and must have a narrow size distribution and smooth surfaces. This means that the polymer particles themselves also require these properties. Generally, these particles are prepared by emulsion, dispersion, or suspension polymerisations and in all these techniques the crosslinking polymer particles should be 1–10 μm with a broad particle size distribution and low crosslinking density [1–7]. Gong and Wang developed the technique of delayed addition of a cross-linker in soap-free emulsion polymerisation to prepare highly cross-linked monodisperse polystyrene (PS) [8]. Thomson et al. described how the morphology of crosslinked particle is important not only the degree of cross-linking, but also in the time when cross-linker is added [9]. Song and Winnik used a two-stage dispersion polymerisation to control particle growth until the end of the nucleation stage, growing particles by adding monomer during the particle growth stage to obtain a sample containing up to 6 wt.% cross-linker based on styrene [10].

In recent years, seeded polymerisation has been used to synthesise polymer beads. The popular materials were PS and PMMA. The method has often been used to synthesise crosslinking PS-based particles in the past, because it depends on the solubility of the monomer. Styrene is hydrophobic, so the associated formation of an oligomer and the extension of its length remain stable in water; however, methyl methacrylate is hydrophilic. This means that when the latter is used, it is difficult to control the particle size, dispersity, and size distribution.

Seed swelling polymerisation includes swelling stage and a polymerisation stage. The swelling stage starts from the addition of monomer and ends in the adequate absorption of the monomer and crosslinking agent into the swollen particle. Ideally, the monomer or crosslinking agent should be adequately absorbed by the seed particles after the swelling stage. The degree of absorption depends on the hydrophobicity and solubility of both the monomer and the crosslinking agent, and the molecular weight of the seed. Styrene has a super-hydrophobic character; it offers high absorptivity and dispersity in the seed swelling stage, even at low concentrations of dispersant [11–20]. In contrast, methyl methacrylate (MMA) is a more hydrophilic monomer; it exhibits less swelling than styrene.

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Kim et al. prepared crosslinked monodisperse spheres with four crosslinking agents by one-step seeded polymerisation in aqueous-alcoholic media in the absence of any swelling process; they observed that increasing concentrations of ethylene glycol dimethacrylate (EGDMA) from 10 to 90 mol% within PMMA/EGDMA created the phenomenon of localised heterogeneity [21]. In addition, Kim et al. prepared crosslinking-PMMA particles via one-step seeded polymerisation and determined the associated mechanical properties using a micro-compression test [22]. There have thus been a few reports of the synthesis of polymer spheres using PMMA monomer and acrylate-based crosslinking agent in seed swelling polymerisation; however, it has not previously been possible to reduce the roughness of the surface using highly disperse crosslinking particles.

In this study, according to the solubility parameter theory of computation, we report on crosslinking monodisperse PMMA microspheres with a smooth surface and high dispersity that were successfully synthesised by seed swelling polymerisation.

Experimental

Materials

Methyl methacrylate (MMA; 99%, ACROS Organics, Geel, Belgium), ethylene glycol dimethacrylate (EGDMA; ACROS Organics, Geel, Belgium), ethylene glycol diacrylate (EGDA; Sigma-Aldrich, St. Louis, MO, USA), trimethylolpropane triacrylate (TMPTA; Alfa Aesar, Heysham, Lancashire, UK), trimethylolpropane trimethacrylate (TMPTMA; Alfa Aesar, Heysham, Lancashire, UK), and divinylbenzene (DVB; Sigma-Aldrich, St. Louis, MO, USA)were purified through an activated aluminium oxide (Al_2O_3; Sigma-Aldrich, St. Louis, MO, USA) column to remove inhibitors and stored at 5 °C prior to use. Analytical-grade benzoyl peroxide (BPO; Alfa Aesar, Heysham, Lancashire, UK), 2,2′-azobis(2-methylpropionitrile) (AIBN; Showa Chemicals, Tokyo, JP), and potassium persulphate (KPS; Showa Chemicals, Tokyo, JP) as initiators, and poly(vinyl alcohol) (PVA; 80%/88% hydrolysed, Mw: 10,000/130,000, Sigma-Aldrich, St. Louis, MO, USA) as a stabiliser were used without purification. Sodium dodecyl sulphate (SDS; Tokyo Chemical Industry, Tokyo, JP) was used as a surfactant, 1-octanethiol (Alfa Aesar, Heysham, Lancashire, UK) as a chain transfer agent, and deionised water as polymerisation medium.

Preparation of cross-linked PMMA particles

Cross-linked PMMA particles were synthesised by emulsifier-free emulsion polymerisation and two-stage seed swelling polymerisation, as shown in Fig. S1.

Table 1
Molecular weight of the PMMA seed child particles

Sample	Mn ($\times 10^4$)	Mw ($\times 10^4$)	Mz ($\times 10^4$)	Mw/Mn
PMMA seed child	0.92	1.52	2.29	1.65

The detail of synthesis was written in supplementary data.

Characterisation

The molecular weight of the synthesised PMMA particles was measured using Waters gel permeation chromatography (GPC) equipped with a 2414 refractive index detector, a 1515 isocratic HPLC pump, and a 717 plus auto sampler. High resolution HR1-, HR3-, and HR4-Styragel packed columns were used. The calibration curve was obtained for 10 PS standard samples (Polymer Standards Service, USA) with molecular weights ranging from 580 to 299,400 g/mol. The flowrate of the PMMA particles dissolved in tetrahydrofuran (THF) was 1.0 mL/min. A JEOL (field emission scanning electron microscope (FESEM); JSM-6500F) was used to characterise the size and morphology of the particles. Mitani Winroof was used to calculate the particle size and coefficient of variation (Cv) from the FESEM images. Measurement of the FT-IR spectra was performed using a Spectrum One FT-IR Spectrometer (Perkin-Elmer) and all infrared spectra were recorded using eight scans for each specimen. The particle size distribution was also measured by a Zetasizer NANO ZS (Malvern Instruments; Malvern, UK). A Meiji optical microscope (ML-8530) was used to characterise the dispersity of the PMMA seed during the seed swelling stage.

Results and discussion

PMMA seed child particles

Fig. 1(a) shows an SEM micrograph of a PMMA seed child prepared by emulsifier-free emulsion polymerisation. The PMMA seed child particles displayed a clear surface and a spherical shape. A particle-size histogram for the PMMA seed child is shown in Fig. 1(b); an average particle diameter of 0.41 μm and a Cv of 2.01% were obtained. Table 1 shows the molecular weight of the PMMA seed child, which is 1.52×10^4. The emulsifier-free emulsion polymerisation led to excellent seed child quality in terms of surface, shape, and size homogeneity.

PMMA seed particles

The sub-micrometre PMMA seed particles had narrow size distributions, as shown by the micrographs in Fig. 2. The PMMA

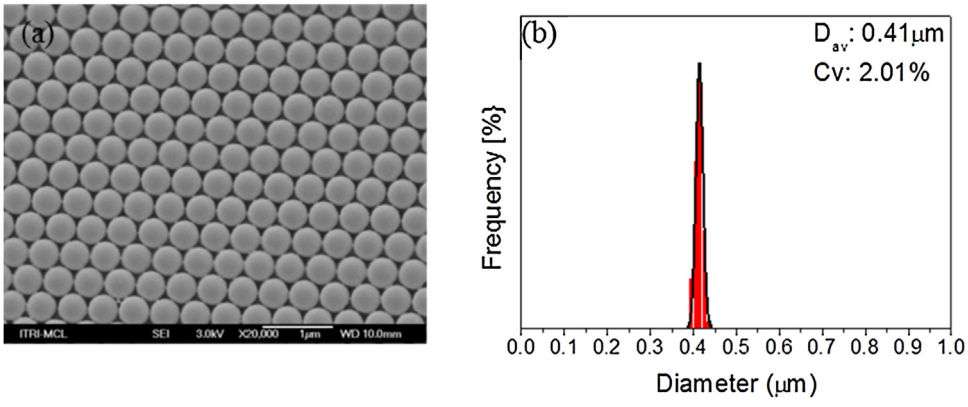

Fig. 1. (a) SEM micrograph and (b) a histogram of particle-size of PMMA seed child particles.

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