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SYNTHESIS AND CHARACTERIZATION OF A SERIES OF HYDROPHILIC POLYMER NANOPARTICLES PREPARED VIA EMULSION POLYMERIZATION TECHNIQUE

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Abstract: A series of hydrophilic polymer nanoparticles composed of methyl methacrylate (MMA), methacrylic acid (MAA) and 2-hydroxyethyl methacrylate (HEMA) monomers were successfully prepared via emulsion polymerization technique. The effects of different surfactant concentrations towards the particles size of polymer nanoparticles have been discussed. The hydrophilic polymer nanoparticles had mean diameters in the range of 100 – 270 nm depending on the reaction conditions and most of the polymer nanoparticles were obtained as spherical-like shape determined by scanning electron microscopy (SEM). The formation of hydrophilic polymer nanoparticles were confirmed by Fourier Transform Infrared (FTIR) spectroscopy and in turn, simple solubility test was conducted in order to confirm the hydrophilicity of polymer nanoparticles.

Keywords: Hydrophilic, biodegradable, poly(hydroxyethyl methacrylate), poly(methyl methacrylate), poly(methacrylic acid)

Introduction

During the past decades, the field of polymer nanoparticles (PNP) is quickly expanding and playing a pivotal role in wide spectrum of areas ranging from electronics to photonics, conducting materials to sensors, medicine to biotechnology, pollution control and environmental technology (Nagavarma *et al*., 2012; Yusoff *et al*., 2013).

The emergence of abundance synthetic polymers that mostly produced from petroleum sources which are non–biodegradable may lead to critical environmental issues. Therefore, researchers are now aware of the significant preservation that biodegradable materials would bring forth to fulfill the needs of "environmentally friendly" manufacturing process, where, the end products can be exploited in the most application fields for future sustainability (Avérous & Pollet, 2012). Hydrophilic polymer nanoparticles have attracted great attention because of their potential to be utilized especially in medical and biological applications (Ghosh, 2000).

When considering synthetic methods to prepare polymeric nanoparticles, variety of techniques can be performed including dispersion (Goa *et al*., 2008), suspension (Kassim *et al*., 2014), emulsion (Schmid *et al*., 2009) and microemulsion (Wang *et al*., 2008) polymerizations. For the highly water-soluble monomers, conventional emulsion polymerization is one of the most common techniques employed (Chu & Ou, 2003) because of initiation is taking place in aqueous solution where the homogenous mechanism dominates (Fitch & Tsai, 1973), but being convoyed with some coagulative nucleation mechanism (Lichti *et al*., 1983). The emulsion polymerization using high aqueous-soluble monomer was previously considered impossible to be polymerized in aqueous medium in order to obtain high solid latex particles (Chu & Ou, 2003). Previous works show that only monomers with low aqueous solubility were performed in emulsion polymerization and the latexes obtained can achieve quite high solid contents (Chu & Ou, 2000). However, a work performed by Chu and Ou (2003) have shown that the emulsion

polymerization of aqueous-soluble monomers of 2-hydroxyethyl methacrylate (HEMA) and hydroxypropyl methacrylate (HPMA) can be carried out successfully in the presence of surfactants. Poly(2-hydroxyethyl methacrylate) (PHEMA) latex with a solid content as high as 10 weight % was achieved throughout the synthesis.

In this study, a series of polymer nanoparticles was prepared using aqueous-soluble monomers of HEMA, MMA and MAA. The resulting polymer nanoparticles with improved hydrophilicity are expected to be more environmentally friendly, less toxic and having good biocompatibility. In this particular work, attention was drawn by the effects of different surfactant concentrations towards size and morphology of polymer nanoparticles. The development of polymer nanoparticles with improve hydrophilicity could impart huge contribution for future sustainability and may have potential to be further employed especially in biological and biomedical applications.

Methods

Materials

All chemicals were purchased from Sigma Aldrich and were used as received without further purification. Sodium dodecyl sulphate (SDS) and potassium persulfate (KPS) were used as surfactant and initiator respectively. Distilled water with no foreign ions was utilized in all experiments.

General procedure for emulsion polymerization

The emulsion polymerization of HEMA, MMA and MAA were conducted under nitrogen atmosphere. The polymerization reactor composed of three-necked round bottom flask, magnetic stirrer, reflux-condenser, nitrogen gas inlet and outlet, and thermometer. A mixture of monomers (7.5 g), distilled water (90 mL), and surfactant were added into the reactor and purged with N_2 for 15 min. The polymerization was performed at 60 ^{o}C with mechanical stirring rate of 300 rpm and initiated by addition of aqueous KPS solution (0.1 g). The polymerization was completed after 3 h and the reaction was terminated by cooling to room temperature. Throughout this study, the emulsion polymerization of HEMA, MMA and MAA were performed under different surfactant concentrations of below (5.0 mM), equivalence (8.2 mM) and above (9.0 mM) critical micelle concentration (CMC). The polymer nanoparticle samples were obtained by removing water from the polymer dispersion via rotary evaporator and freeze-drying. Polymer nanoparticles prepared at different surfactants concentration are displayed in Table 1.

It is noteworthy to mention that PMMA_1, PHEMA_2 and PMAA_3 were synthesized using SDS concentration at CMC (5.0 mM), PMMA_4, PHEMA_5 and PMAA_6 were obtained of surfactant concentration equivalence CMC (8.2 mM) and PMMA_7, PHEMA_8 and PMAA_9 were prepared using SDS concentration above CMC (9.0 mM).

Solubility test

Polymer nanoparticles (0.5 g) obtained from emulsion polymerization were dissolved in distilled water (5 mL) at room temperature. The ability of polymer nanoparticles to be dissolved in aqueous medium were observed.

Table 1: A series of polymer nanoparticles obtained at different surfactants concentration of below, equivalence and above CMC prepared via emulsion polymerization techniques.

Polymer Nanoparticles	SDS Concentration (mM)	CMC conditions
PMMA_1		
PHEMA_2	5.0	Below
PMAA_3		
PMMA_4		
PHEMA_5	8.2	Equivalence
PMAA_6		
PMMA_7		
PHEMA_8	9.0	Above
PMAA_9		

Characterizations

The formation of polymer nanoparticles were confirmed by Fourier transmission infra-red (FTIR) spectroscopy (Perkin Elmer of Spectrum 100). The morphology and particle size of polymer nanoparticles were determined using Scanning Electron Microscopy (SEM) (JSM-6360 LA Analytical SEM) performed under the magnification observation of 5,000x with acceleration rate of 15 kV.

Result and Discussion

Synthesis of hydrophilic polymer nanoparticles of PHEMA, PMAA and PMMA via emulsion polymerization

In this study, the development of polymer nanoparticles utilizing hydrophilic or highly soluble monomers was conducted under aqueous phase. Aqueous-soluble monomers of HEMA, MAA and MMA have been chosen on account of their good biocompatibility profile and intensively used in biomedical applications (Ghosh, 2000). PHEMA, PMAA and PMMA nanoparticles were successfully synthesized via emulsion polymerization technique in the presence of SDS as surfactant, KPS as initiator and water as dispersion medium. The effect of surfactant concentrations towards particle size and morphology of polymer nanoparticles were studied and the parameters involved were summarized in Table 1. After completely dried, PMMA and PMAA nanoparticles were obtained in the form of white powder, while PHEMA nanoparticles were attained in the form of hydrogels.

FTIR spectroscopy

The formation of PHEMA, PMAA and PMMA nanoparticles were confirmed by FTIR spectroscopy (Figure 1). Table 2 summarizes the absorption peaks of functional groups present in PMMA_1, PHEMA_2 and PMAA_3. The broad peak observed from PHEMA_2 and PMAA_3 in the range of 3440 – 3452 cm^{-1} are due to the polymeric associations of O-H stretching vibration mode. The peaks in the range of 2931 – 2996 cm^{-1} are referred to CH stretching of CH_3 and CH_2 groups. Strong absorption bands around 1707 – 1734 cm^{-1} belong to stretching of carbonyl group. IR peaks in the range of 1074 – 1193 cm^{-1} are on account of C-O-C for ether group of PMMA_1 and PHEMA_2. It worth to mention that all PHEMA, PMAA and PMMA nanoparticles obtained at different parameter conditions showed similar pattern in the FTIR spectra, hence, confirming the formation of polymer nanoparticles.

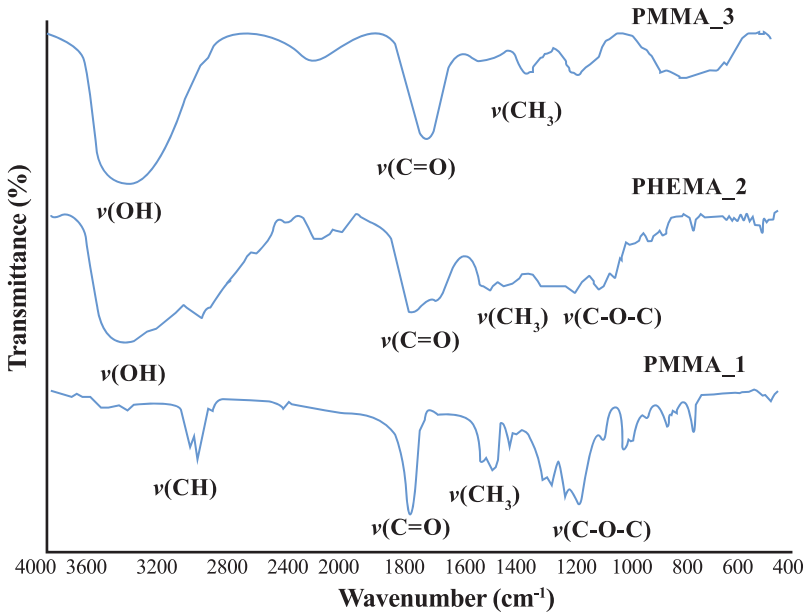


Figure 1: IR spectra of PMMA_1, PHEMA_2 and PMAA_3

Scanning electron microscopy (SEM)

A selection of polymer nanoparticles were further analysed by SEM to provide further insight into their morphology and average particle sizes. SEM images obtained from PMMA_1, PMMA_4 and PMMA_7 indicate most of the polymer nanoparticles appeared as spherical-like shape. The SEM images for PMMA_1 and PMMA_4 (Figures 2a – b) showed the existence of aggregation, while, PMMA_7 (Figure 2c) which prepared at surfactant concentration above CMC displays less aggregation. When the amount of surfactant is higher, the area of the emulsion droplets will be covered by surfactants chains become significant, and hence droplets stabilised with surfactants repel each other due to the repulsive forces induced by surfactants, resulting in less aggregation of the polymer particles. This observation indicates different SDS concentrations could affect the distribution of polymer nanoparticles.

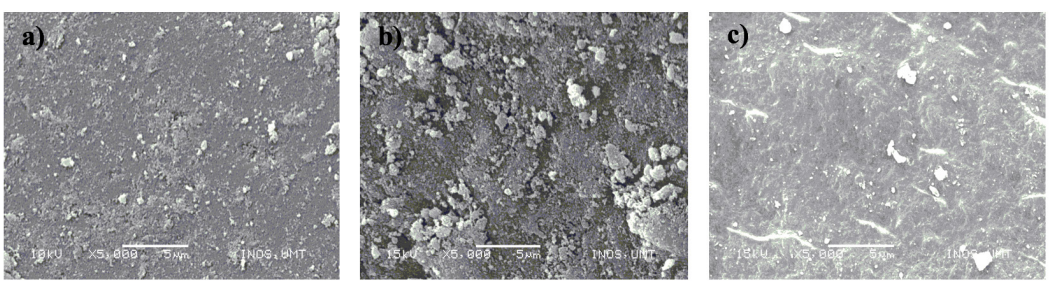


Figure 2: SEM images of (a) PMMA_1, (b) PMMA_4 and (c) PMMA_7 at different SDS concentrations (5000x magnification).

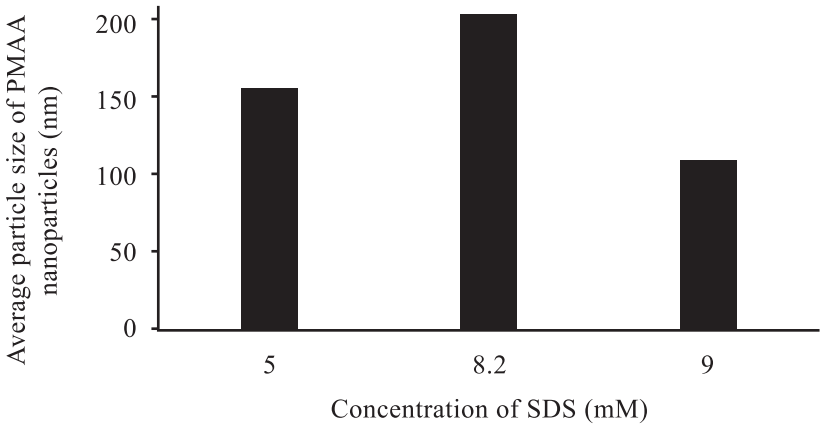


Figure 3: Average particles size of (a) PMMA_1, (b) PMMA_4 and (c) PMMA_7 at different SDS concentrations.

The average particle size of polymer nanoparticles were determined by randomly measured the particles obtained from SEM images. The average particles sizes of PMMA_1, PMMA_4 and PMMA_7 are 156 nm, 204 nm and 110 nm respectively (Figure 3). The average particle size of PMMA_4 was slightly bigger than PMMA_1 and PMMA_7. This is because the SDS concentration was at equivalence of CMC point which is the most stable condition to form micelle and for the emulsion droplets to be covered by surfactant chains (Langevin, 1992). Landfester *et al.* (1999) reported that the particle size of polystyrene nanoparticles can be controlled by the amount of surfactant.

Figure 4 illustrates the morphology of PHEMA_2, PHEMA_5 and PHEMA_8 which were prepared at different surfactant concentrations. It can clearly be seen that all PHEMA samples show irregular shapes. The morphology of PHEMA_5 employs porous structure in comparison to other samples. The average particle size of PHEMA_2, PHEMA_5 and PHEMA_8 are 271 nm, 248 nm, and 219 nm respectively. The average particle size of PHEMA_8 that was prepared at SDS concentration above CMC is the lowest (219 nm). Landfester *et al.* (1999) reported that the particle size can be controlled by the amount of surfactant used, where, small particle size of polymer nanoparticles can be controlled by using high amount of surfactant.

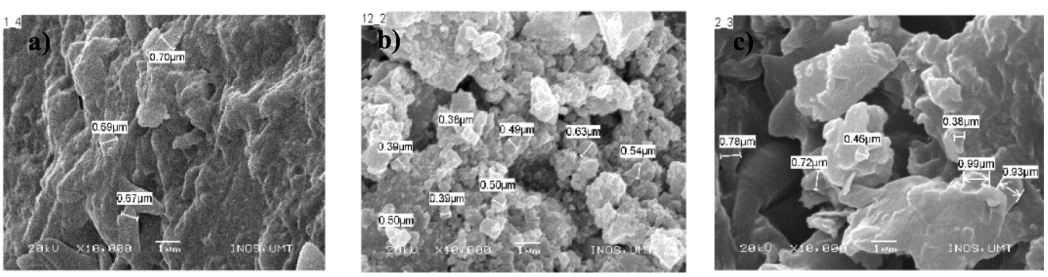


Figure 4: SEM images of (a) PHEMA_2 (b) PHEMA_5 and (c) PHEMA_8 at different SDS concentration (10 000x magnification).

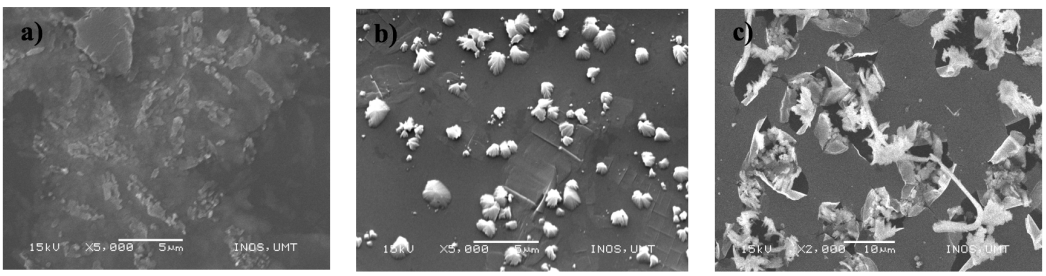


Figure 5: SEM images of (a) PMAA_3 (b) PMAA_6 and (c) PMAA_9 at different SDS concentrations (5000x magnification).

The SEM images of PMAA_3, PMAA_6 and PMAA_9 are depicted in Figure 5a – c. From the SEM images, only PMAA_6 which was prepared utilizing SDS concentration equivalence CMC shows the most similar morphology in the form of spherical-like shape as reported previously (Bai *et al*., 2007). In contrast, irregular morphologies were obtained from PMAA_3 and PMAA_9 which might be due to the incomplete of polymerization process. Thus, this observation suggests that different SDS concentrations can affect the morphology of PMAA nanoparticles. The average particles size of PMAA_6 is approximately 270 nm.

Solubility test

A simple solubility test was conducted to determine the hydrophilicity of PMMA, PHEMA and PMAA nanoparticles. It was observed that PMMA nanoparticles are partially soluble after dissolving with aqueous solution. This is on account that MMA monomer is partially soluble in water (Mittal, 2011), hence, some of the product remained in the aqueous solution. However, after prolong stirring, PMMA nanoparticles could be completely dissolved in aqueous solution. In addition, PMAA nanoparticles also show the ability to be dissolved in aqueous medium, hence, confirming the hydrophilicity of PMAA nanoparticles. On the other hand, PHEMA nanoparticles were not completely dissolved in water where the polymer tends to absorb and swollen in water producing hydrogels.

Conclusion

Emulsion polymerization of hydrophilic PMMA, PHEMA and PMAA nanoparticles has been successfully obtained and the formation of polymer nanoparticles were confirmed by FTIR spectroscopy. SEM images show that the morphology of PMMA and PMAA nanoparticles appeared as sphere-like shape, while PHEMA nanoparticles show irregularity in their morphology structures at different surfactant concentrations. The average particles size of PMAA, PHEMA and PMAA nanoparticles are in the range of 100 nm – 270 nm according to different surfactant concentrations. We expect that with engineered a series of polymer hydrophilic nanoparticles, a new potential biodegradable polymer for future "green" sustainability could be explored specifically in medical and biological applications.

Acknowledgments

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