

Photoinitiated Dispersion Polymerization of Crosslinked Polymer in Polar Solvents: Effect of Reaction Parameter on Morphology, Size and Size Distribution and Yield

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Abstract

Crosslinked polymer beads were prepared by photoinitiated dispersion polymerization in a mixture of ethanol and water. In this study, the effect of types of photoinitiator, types of monomer and reaction times on particles morphology, size and size distribution and yield were investigated. Better quality of poly(st-co-EGDMA-co-VBC) obtained compared to poly(methylmethacrylate-co-EGDMA-co-VBC). However, the yield of poly(st-co-EGDMA-co-VBC) lower than poly(methylmethacrylate-co-EGDMA-co-VBC). On this regard, poly(methylmethacrylate-co-EGDMA-co-VBC) was selected to investigate further. Changing the types of photoinitiator managed to increase the quality and size of poly(methylmethacrylate-co-EGDMA-co-VBC) particles but yield obtained was decreasing. Meanwhile, longer reaction time leading to high yield and bigger size of poly(methylmethacrylate-co-EGDMA-co-VBC) particles but with lower quality. For all cases, FTIR analysis proved all functional groups have successfully attached to the polymeric backbone.

Keywords: Crosslinked Polymer, Morphology, Photo Initiated Dispersion Polymerization, Size Distribution, Yield

1. Introduction

Polymer particles are widely used in various applications such as column packing materials, instrument calibration standard and biomedical and biochemical analysis. One of the common methods used to synthesize monodisperse polymeric microspheres with diameter ranging from 1 to 15 μm is dispersion polymerization¹⁻⁵. However, dispersion polymerization facing a big problem when co-monomer or 'problematic' particles are added the beginning of the reaction and resulting poor controlled on particle size, broader size distribution and caused coalescence⁶⁻⁸.

In recent years, photoinitiated dispersion polymerization has received a great revitalized due to its straightforward

one-stage polymerization^{9,10}. Photoinitiated dispersion polymerization compared to conventional dispersion polymerization composed several advantages such as short reaction times and higher energy efficiency. This is due to the reaction carried out within shorter time and at room temperature. Besides, in straightforward one-stage polymerization, co-monomer and cross-linker can be added at the beginning of the reaction resulting to uniform in particles size. Therefore, it can overcome the problem in terms of sensitivity during nucleation stage in conventional dispersion polymerization¹¹.

Commonly, styrene (St) and methyl methacrylate (MMA) have been used as monomers in the studies for both thermal initiator and photoinitiated dispersion polymerization¹². For photoinitiated dispersion polymerization, the

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used of cross-linker was limited to only dipropylene glycol diacrylate (DPGDA) or trimethylolpropane triacrylate (TMPTA)¹³. In addition, it is necessary to have co-monomer incorporated into the precursor polymeric backbone to explore further in post-polymerization such as in hyper crosslinking reaction^{14,15}.

For best of our knowledge, there is no study on polymerization of crosslinked polymer using VBC as co-monomer via photo initiated dispersion polymerization. Therefore, this paper focuses on producing crosslinked polymeric particles with styrene/MMA as monomer couple with VBC as co-monomer and EGDMA as a cross linker using photo initiated dispersion polymerization technique. In this study, several reaction parameters have been investigated including types of monomers types of photo initiator and reaction times to study their effect on formation of crosslinked polymer.

2. Materials and Methods

2.1 Chemicals

The chemicals used to synthesis polymer particles were styrene 99% and methyl methacrylate (MMA) 99% obtained from Sigma Aldrich. Ethylene glycol dimethacrylate (EGDMA) 98%, 4-vinylbenzyl chloride (VBC) 90%, poly vinyl pyrrolidone (PVP) Mw~55000, Triton X-305 70% in H₂O were purchased from Sigma Aldrich. Darocur 4265, Irgacure 819 and TPO supplied by BASF. Ethanol 98% obtained from HmbG. All chemicals were used as received.

2.2 Synthesis of Polymer Particles

Polymer particles prepared *via* photoinitiated dispersion polymerization¹¹. For the photoinitiated dispersion polymerization, reaction medium prepared by dissolving PVP (15 wt% based on monomer feed), PI (2 wt% based on monomer feed), Triton X-305 (5.5 wt% based on monomer feed), EGDMA (40 wt% based on monomer feed) and VBC (20% of total monomer) within 60:40 ratio of solvent (H₂O:Ethanol) and monomer in a flask (250 mL). The mixture purged with nitrogen gas for 15 minutes and stirred at 200 rpm throughout the reaction and flask irradiated by 3 W 365 nm LED lamp Figure 1. The particles formed were filtered using vacuum filtration on a 0.22 μm nylon membrane filter. Polymer particles dried in oven for 24 hours¹¹.

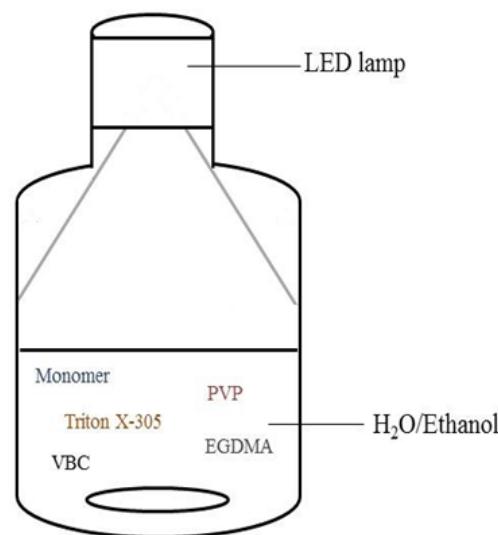


Figure 1. Schematic Set-up of Photo initiated dispersion polymerization.

Yield was calculated by determine the weight of particles after 24 hours dry in oven. The weight then divided by a weight total weight of monomers and crosslinker. The equation for yield calculation was showed below:

$$\frac{\text{weight particles after dry}}{\text{weight monomers}} \times 100 \quad (1)$$

2.3 Particles Characterization

The morphology of the polymer particles was captured by using CARL ZEISS Scanning Electron Microscopy (SEM). The analysis was carried out at a condition of 20X, 100X and 150X. The functional group presence in the polymer particles identified by Nicolet iS50 (Thermo Scientific) Fourier transforms infrared spectroscopy analysis (FTIR). Particles size distribution (PSD) of polymer particles were determined by using laser diffraction particle size analyser Mastersizer Scirocco 3000.

3. Results and Discussion

3.1 Effect of Types of Monomer on Polymer Particles

In dispersion polymerization of polymer particles, monomer(s) selection is important to form desirable particles in terms of morphology and mean size. In this study, styrene and MMA were used as a monomer to synthesis crosslinked

polymer (refer to supplementary data). Figure 2 shows the morphology of poly(st-co-EGDMA-co-VBC) (PSEV) and poly(methylmethacrylate-co-EGDMA-co-VBC) (PMEV) produced at 24 hours. From Figure 2, it showed that polydisperse particles for both PSEV and PMEV can be seen clearly. Polydispersity of the polymer particles showed poor control-ability during polymerization process. However, agglomeration of the particles was more apparent for PMEV compared to PSEV which some PSEV particles beads still can be observed. The polydispersity of the polymer particles might be due to nucleation stage disturbed by addition of co-monomer and crosslinker at the beginning of polymerization. Similar result also reported by other researcher⁸.

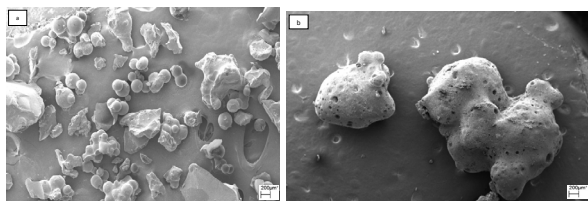


Figure 2. SEM images of a) PSEV and b) PMEV with at 24 hours by using Darocur 4265.

FTIR analysis showed that there are significant in intensity at 698 cm^{-1} band due to the presence of aromatic C-H bending which originated from aromatic ring in styrene and VBC in PSEV. For PMEV particles, 698 cm^{-1} band observed only originated from VBC. Referring to the Figure 3, FTIR spectra for both monomers have 1265 cm^{-1} band designated for chloromethyl group from VBC¹⁶. PMEV shows more significant in intensity at 1718 cm^{-1} compared to PSEV particles because of $-\text{COO}-$ group exist in both MMA and EGDMA. Meanwhile, $-\text{COO}-$ group in PSEV particles only originated from EGDMA¹⁶.

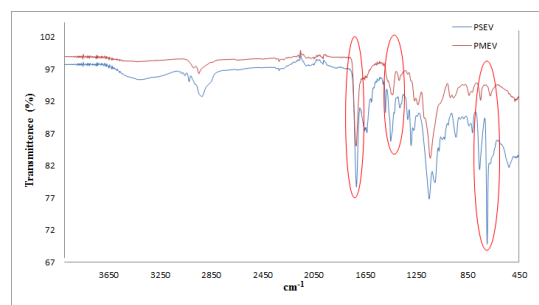


Figure 3. FTIR spectra for different types of monomer.

Based on Table 1, yield of PMEV higher than PSEV at 24 hours reaction due to more methyl methacrylate undergoes polymerization compared to styrene and contribute to the growth of primary particles instead of the increase of particle numbers¹⁷.

Figure 4 shows the particle size distribution (PSD) of PMEV and PSEV. It can be seen that PSD for PMEV broader than PSEV. It was due to the PMEV particles have odd shape compared to PSEV particles Figure 2 resulting the particles were varied in size.

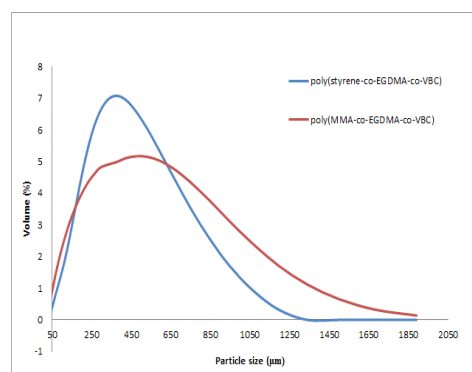


Figure 4. Particle size distribution of polymer particles for PSEV and PMEV.

Table 1. Data characterization for PSEV and PMEV

Sample	Type of monomer	Type of PIs	Reaction times (hours)	Mean size (μm) ^a	Yield (%)
RAM1	MMA	Darocur 4265	6	463.39	40.62
RAM2	MMA	Darocur 4265	12	721.04	66.48
RAM3	MMA	Darocur 4265	24	793.53	72.83
RAM4	MMA	Irgacure 819	24	595.79	61.16
RAM5	MMA	TPO	24	915.23	50.47
RAM6	Styrene	Darocur 4265	24	690.93	65.46

^a Based on mastersizer analysis.

^b Calculated using Eq.

3.2 Effect of Types of Photoinitiator on Polymer Particles

In this study, PMEV was chosen to investigate further since the particles can be produced in higher yield. Higher yield also important prior to explore in other application such as used as precursor in post-polymerization.

Figure 5 shows SEM images of PMEV particles produced using different photoinitiators (PIs). The best quality of PMEV was formed using Irgacure 819 as PI Figure 5a which individual beads can be seen clearly. This might be due to high photolysis rate under UV irradiation and had suitable solvent affinity¹⁸ and also was due to rapid decomposition compared -with other photoinitiators (Darocur 4265 and TPO). The nucleation occurred rapidly and caused stabilizer cannot be absorbed by nuclei immediately. Thus, the particles tend to coalesce with each other¹⁹. Meanwhile, the worst quality of particles obtained by using Darocur 4265 Figure 5b where spherical beads unidentified. This can be related to higher degree of aggregation at the early of the polymerization which leading in larger formation²⁰. For TPO, some beads still can be observed even though particle agglomerated and very poor quality Figure 5c.

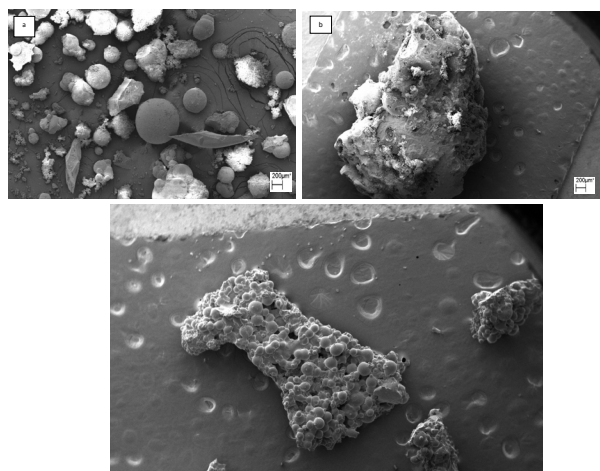


Figure 5. SEM images at different types of PIs a) Irgacure 819 b) Darocur 4265 and c) TPO.

FTIR analysis Figure 6 showed there were significant in intensity at 1265 cm^{-1} band indicated C-O stretching for VBC which characteristic of CH_2Cl group. Strong band at 1718 cm^{-1} also can be seen which it showed the existence of COO^- in MMA and EGDMA for each PIs respectively¹⁹.

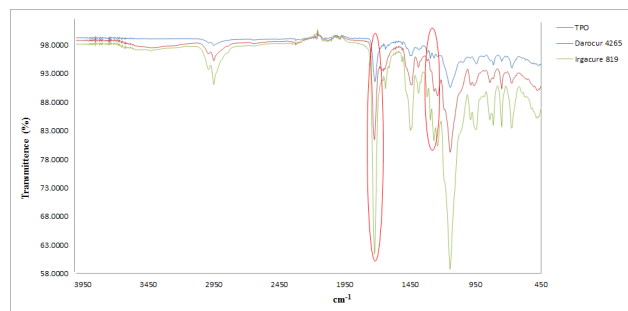


Figure 6. FTIR spectra of PMEV using different types of PIs.

According to the Table 1, even though all the PIs operated at the same wavelength (365 nm), the yield varied between each particles for respective PIs. The highest yield obtained by using Darocur 4265 and the lowest was obtained by TPO. This fact might be contributed by for Darocur 4265, it has high photolysis rate under UV irradiation and suitable with solvent affinity¹⁴. In addition, it also was due to rapid decomposition of Darocur 4265.

From Figure 7, the broadest particle size distribution obtained by Irgacure 819 followed by Darocur 4265 and TPO. Irgacure 819 produced good quality particles where individual's beads can be observed. Because of it, particles produced from Irgacure 819 have broadest PSD compared to the others (Darocur 4265 and TPO) due to individual beads varied in size.

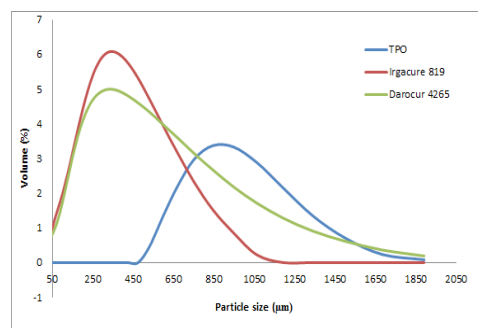


Figure 7. Particle size distribution of PMEV using different types of PIs.

3.3 Effect of Reaction Times on Polymer Particles

Figure 8 shows SEM images PMEV at different reaction times. According to Figure 8, high quality of PMEV was produced at 6 hours Figure 8(a) which individual beads can be observed due to sufficient amount of stabilizer absorbed on the growth particles during the reaction. This observation

was in agreement with finding¹⁸. It shows that high quality spherical beads can be formed at shorter reaction times. However, after reaction times increased to 12 hours and 24 hours Figure 8(b) and 8(c), the quality of beads decreased. Agglomerated particles and odd shaped particles tend to be formed as can be seen 24 hours reaction time Figure 8(c). This probably because of longer reaction times, the amount of stabilizer in the reaction medium decreased and at the same time new nuclei also formed after 12 hours results lacking stabilizer to be absorbed by new nuclei. Therefore, particles tend to coalesce between each other.

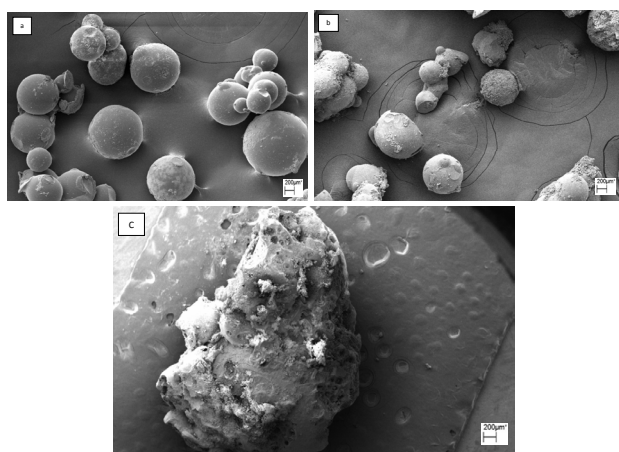


Figure 8. SEM images at different reaction times a) 6 hours b) 12 hours and c) 24 hours.

Figure 9 shows FTIR spectra for PMEV at different reaction times. For all cases, significant intensity at 1143 cm^{-1} can be seen clearly due to the presence of C-O stretching in MMA and EGDMA at the backbone of particles. Strong band at 1718 cm^{-1} assigned the existence of COO⁻ stretching in MMA and EGDMA. In all cases, FTIR spectra have significant peak at 1265 cm^{-1} band designated for chloromethyl group arise from VBC¹⁶.

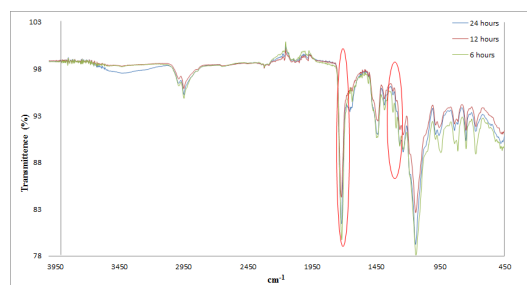


Figure 9. FTIR spectra of PMEV at different reaction times.

Based on Table 1, yield of PMEV increased with increasing reaction times up to ~73%. Even though complete conversion occurred at 24 hours reaction resulting more yield obtained, however, the quality of PMEV particles decreased with increasing times Figure 8(c). The mean size also increased with increasing reaction times. As the amount of stabilizer decreased over time, new PMEV particles formed tend to coalesce between each other and forming larger particles²¹. Figure 10 showed PSD of PMEV at 6 hours was the narrowest compared to the others. This is because of when stabilizer decreased with time, particles formed varied in diameter as stabilizer was fully utilized before 12 hours reaction. Insufficient stabilizer caused new nuclei formed after 12 hours reaction to agglomerate. Therefore, with increasing reaction time broader PSD curve obtained.

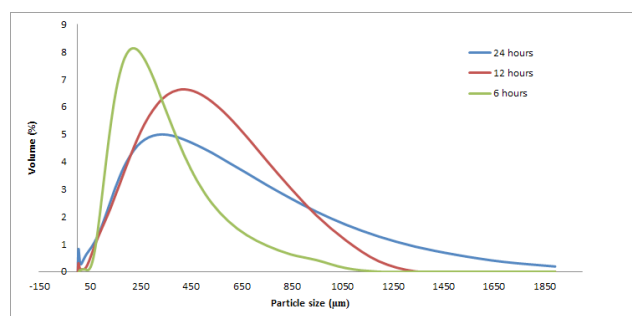


Figure 10. Particle size distribution of PMEV at different reaction times.

4. Conclusion

Crosslinked polymers successfully synthesized *via* photoinitiated dispersion polymerization. PSEV produced in better quality compared to PMEV. However PMEV produced higher yield compared to PSEV. On this regard, PMEV was chosen to investigate further.

Changing in PIs managed to improve the quality and size of PMEV particles, but slightly decreased in yield. Besides that, changing Darocur 4265 to Irgacure 819 only give small increment in terms of yield and quality of the final product due to the rapid decomposition of PI.

At 6 hours reaction, good quality, narrow particle size distribution and moderate yield of PMEV particles were obtained, however increasing reaction times

caused the quality of polymer particles decreased due to lack of stabilizer as the reaction continued. In addition, no significant increasing in particle size when the reaction was allowed at longer reaction time. In all cases, FTIR spectra showed all the functional groups have successfully attached to the polymeric backbone. However, in all cases, polydispersity of particles still observed. Hence, further study is recommended to increase the monodispersity of the particles produced *via* photoinitiated dispersion polymerization.

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