Morphological features of PU/PMMA hybrid latex prepared by Miniemulsion Polymerization

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Abstract: PU/PMMA hybrid particles are synthesized by using the method of two-step miniemulsion polymerization. In the first step, PU prepolymer is synthesized by isophorone diisocyanates (IPDI) and poly(propylene glycol) (PPG) with methyl methacrylate (MMA) as a solvent. Then the oil phase, including the NCO-terminated prepolymer, MMA, hexadecane (HD), a chain extender as 1,4-butanediol (BD) or bisphenol A (BisA), a cross-linking agent trimethylol propane (TMP), and a catalyst dibutyltin dilaurate (SnDBL) is dispersed in the water phase containing SDS. Then the mixtures form miniemulsion by ultrasonication. Two kinds of initiators, BPO and KPS, are applied for the polymerization of MMA. The influences of chain extenders, initiators and PU/MMA weight ratios on the morphology of PU/PMMA latex particles are investigated. Conversion of MMA is measured and discussed. Particle sizes are analyzed by dynamic lighting scattering (DLS) and transmission electron microscopy (TEM). The cross section morphology of the hybrid particles is also characterized by TEM. For BD/BPO and BD/KPS systems, when increasing the load of PU component, PU-rich phase is moved to the outside of hybrid particles. A core-shell structure can be observed. However, for BisA/KPS system, while using hydrophobic bisphenol A as chain extender of PU, the boundary of PMMA and PU phases is not clear. A more homogeneous structure of hybrid particles is obtained.

Introduction

A new way to achieve dispersions of hydrophobic PU prepared by miniemulsion has appeared in some papers [1-3]. Miniemulsion [4-8] is created by ultrasonifying a system which usually consists of a hydrophobic monomer, a surfactant, a hydrophobe and water. A hydrophobe, such as hexadecane (HD), has low water solubility, which could generate osmotic pressure in monomer droplets and thus make the droplets stable. When the hydrophobe dissolves in the monomer droplets, it suppresses Ostwald ripening through osmotic pressure effect [9, 10]. According to the earlier studies from Tiarks et al. [1] and Barrere et al. [2], the molecular weight of PU prepared by miniemulsion in one step was always below 10,000. From our
previous research, high-molecular-weight PU could be synthesized successfully by two-step miniemulsion polymerization [11].

To obtain better mechanical property, a hybrid polymer through mixing of two polymers is desired. There has been some interest in the hybrid polymer of PU and PMMA, prepared by the polymerization of MMA in the presence of PU. Allen et al. [12-14] synthesized PMMA domains embedded in a PU matrix. Variations in domain size and mechanical properties were studied as a function of composition. Mishra et al. [15] has developed the metastable phase diagram of PU/PMMA system. The key events of interpenetrating network (IPN) synthesis were the time occurrence of gelation of polymers and phase separation. Frisch et al. [16] prepared an IPN composed of a polyacrylate and polyurethane. They showed that partial interpenetration occurred and thus led to enhancement in mechanical properties. Mohammed S. et al. [17] terpolymerized an isocyanate, MMA and BA together and varied the concentration of the isocyanate. They reported that the tensile properties of the resulting films were greatly influenced by the locus of isocyanate groups. Furthermore, there were various methods of preparing hybrid polymers, such as sequential polymerization of PU/PMMA that adding MMA monomer in the last stages of polymerization and then calculating the partition coefficient of MMA between two phases reported by Miahrah et al. [18, 19]. Or latex blending of linear PU and PMMA as prepared by Kim et al. [20], which showed the influence of different composition on the glass transition temperature of IPN. And simultaneous polymerization of PU/ cross-linked PMMA studied by Akay and Rollins [21]. They recorded unusually high elongations at failure in the simultaneous IPN due to improved homogeneity in the distribution of the component polymers.

In recent years, there have been some researches of preparing hybrid latex through miniemulsion polymerization. Gooch et al. [22] prepared the hybrid latex consisting of vinyl-modified PU resin, MMA and BA. The hybrid latexes showed excellent shelf-life stability (>5 months) and was free of coagulation. Films obtained from the latexes presented good adhesion properties and fair hardness properties. Li et al. [23] synthesized PU/PBMA hybrid latex (~50nm) via a redox-initiated miniemulsion. The amount of grafting agent (hydroxyethyl methacrylate; HEMA) had little influence on the particle size. Wang et al. [24] prepared a variety of hybrid latexes, combination of PU and acrylic copolymers of MMA and BA. The PU acted as a hydrophobe to stabilize the miniemulsion against Ostwald ripening. The PU was end capped with methanol or HEMA. Young’s modulus was sensitive to the amount of PU, being higher for lower amount of PU. They also showed the surface morphology and wetting properties of these films through TEM and contact angle measurement [25]. The better homogeneity of the hybrids led to improved mechanical properties.

Most of the previous researches about PU/PMMA hybrid polymers focused on the mechanical properties. How the components of reaction mixture influence the polymerization and the morphology of the hybrid latex particles is not fully understood. In this work, miniemulsion polymerization is applied to prepare hybrid latex particles of PU/PMMA. Different initiators and chain extenders are used in the preparation of hybrid latex. The morphology of the hybrid particles and the phase distribution in particles will be investigated and discussed.

Results and discussion

In this work, four systems of miniemulsion polymerization are studied by changing the reaction variables of PU/MMA weight ratio, NCO/OH ratio, initiators and chain
extenders of PU chains as shown in Tab. 1. The BD/BPO system is that PU is synthesized by using BD as the chain extender and PMMA is synthesized by using BPO as the initiator. The BD/KPS system, therefore, is that BD is used as the chain extender of PU and KPS as the initiator of PMMA. The BisA/KPS system indicates that bisphenol A is the chain extender of PU and KPS is the initiator of PMMA.

**Tab. 1.** Variables of PU/MMA hybrid latex.

<table>
<thead>
<tr>
<th>Reaction system</th>
<th>PU/MMA weight ratio</th>
<th>NCO/OH ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>20/80</td>
<td>1.7</td>
</tr>
<tr>
<td></td>
<td>20/80</td>
<td>1.0</td>
</tr>
<tr>
<td>BD/BPO</td>
<td>30/70</td>
<td>1.7</td>
</tr>
<tr>
<td></td>
<td>30/70</td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td>40/60</td>
<td>1.7</td>
</tr>
<tr>
<td></td>
<td>40/60</td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td>20/80</td>
<td>1.0</td>
</tr>
<tr>
<td>BD/KPS</td>
<td>30/70</td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td>40/60</td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td>20/80</td>
<td>1.0</td>
</tr>
<tr>
<td>BisA/KPS</td>
<td>30/70</td>
<td>1.0</td>
</tr>
<tr>
<td></td>
<td>40/60</td>
<td>1.0</td>
</tr>
</tbody>
</table>

Synthesis conditions: Ultrasonication time = 12 mins; [SDS] = 5 mM (per liter H₂O); [HD] = 35 mM (per liter H₂O); SnDBL = 0.1 wt% based on total weights of PU components; BPO = 1 wt% based on the weight of MMA; Reaction temp = 70°C; Reaction time = 3 hrs; Revolutions Per Minute = 200; Solid content = 19%.

**BD/BPO system**

- Influences of NCO/OH ratio and PU content on conversion of MMA and size of PU/PMMA hybrid particles

Fig. 1 shows the effect of NCO/OH ratio on the conversion of MMA. The results show that the increase of NCO/OH ratio decreases the polymerization rate and the limiting conversion of MMA. It is due to that NCO groups may trap radicals and reduce the initiation efficiency of BPO for MMA polymerization, so as to decrease the polymerization rate. As for the limiting conversion, it is also attributed to the “glassy
During the process of synthesis, the polymerization rate of MMA is faster than the PU condensation reaction within our experimental conditions. (See Fig. 1)

If phase separation occurs, and the $T_g$ of PMMA/MMA phase reaches the reaction temperature ($70^\circ C$), then the polymerization of MMA will be stopped. It is the “glassy effect” and the conversion of the system is limited. On the other hand, the increase of PU content increases the viscosity of minidroplets so as to retard the diffusion of reaction species and quench radicals, therefore, not only decreases the polymerization rate but also decreases the limiting conversion of MMA as shown in Fig. 2 and Fig. 3.

(See Fig. 2)
Fig. 3. Conversion of MMA for poly(IPDI-PPG1000-BD-TMP)/ PMMA latex system with different PU/MMA weight ratios; NCO/OH molar ratio=1.0 and BPO initiator.

Effects of NCO/OH ratio and PU content on the particle size of PU/PMMA hybrid particles are shown in Tab. 2. On raising PU content, the viscosity of the reaction mixture increases, therefore, it reduces the emulsification efficiency and lead to larger size of mini droplet in the ultrasonication step; as a result, the size of final polymer particles increases significantly. It is worth mentioning that the size of final particles is always smaller than the size of initial droplets from DLS data. This discrepancy comes from the interaction between particles and colloidal stability.

Tab. 2 Limiting conversion of MMA and particle size for BD /BPO system.\textsuperscript{a}

<table>
<thead>
<tr>
<th>PU\textsuperscript{b}/MMA weight ratio</th>
<th>NCO/OH mole ratio</th>
<th>Conversion of MMA (%)</th>
<th>Initial</th>
<th>Final</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>$D_z$ (nm)\textsuperscript{c}</td>
<td>$D_n$ (nm)</td>
</tr>
<tr>
<td>20/80</td>
<td>1.7</td>
<td>89</td>
<td>179</td>
<td>173</td>
</tr>
<tr>
<td>20/80</td>
<td>1.0</td>
<td>99</td>
<td>185</td>
<td>178</td>
</tr>
<tr>
<td>30/70</td>
<td>1.7</td>
<td>85</td>
<td>184</td>
<td>179</td>
</tr>
<tr>
<td>30/70</td>
<td>1.0</td>
<td>96</td>
<td>215</td>
<td>208</td>
</tr>
<tr>
<td>40/60</td>
<td>1.7</td>
<td>80</td>
<td>239</td>
<td>230</td>
</tr>
<tr>
<td>40/60</td>
<td>1.0</td>
<td>85</td>
<td>235</td>
<td>228</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Synthesis conditions: Ultrasonication time =12mins; [SDS]=5mM (per liter H\textsubscript{2}O); [HD]=35mM (per liter H\textsubscript{2}O); SnDBL=0.1 wt% based on total weights of PU components; BPO=1wt% based on the weight of MMA; Rxn temp =70°C; Rxn time =3hrs; Rpm=200; Solid content=19%.

\textsuperscript{b}PU with 1,4-butandiol (BD) as chain extender.

\textsuperscript{c}$D_z$= Z-average particle size; $D_n$=number-average particle size.
The interaction between soft monomer droplets is stronger than that between final polymer particles due to the unreacted NCO and OH groups. The colloidal stability of droplets is lower. Hence, the hydrodynamic volume of monomer droplets measured from DLS experiment is always larger than their original size.

In the case of NCO/OH = 1.7, IPDI monomers may partially diffuse out of the droplets and form urea links from reacting with water, and partially react with PU prepolymer and chain extender and form crosslinked PU [11]. As shown in Fig. 4, particle size of hybrid latex becomes larger on increasing the PU content. In Fig. 4(a) and (b), their diameters are about 100~150 nm. When PU content is raised to 40%, the particle size becomes larger and ranges from 200~250 nm.

![Fig. 4](image)

**Fig. 4.** TEM analysis of poly(IPDI-PPG1000-BD-TMP)/PMMA with different PU/MMA weight ratios (a) 20/80 (b) 30/70 (c) 40/60; NCO/OH molar ratio=1.7, BPO initiator.

Fig. 5 shows the morphology of hybrid latex particles in which the NCO/OH ratio is 1.0. By raising PU content, particle size turns larger because of the increasing viscosity of reaction mixture as mentioned above. The TEM observation is consistent with the DLS results in Tab. 2. The size of particles ranges from 150~250 nm.
Fig. 5. TEM analysis of poly(IPDI-PPG1000-BD-TMP)/PMMA with different PU/MMA weight ratios (a) 20/80 (b) 30/70 (c) 40/60; NCO/OH molar ratio=1.0, BPO initiator.

BD/KPS system

Influences of PU content on conversion of MMA and particle size of PU/PMMA hybrid particles

In Fig. 6, using KPS as initiator, the polymerization rate and limiting conversion of MMA decrease seriously as increasing the PU content. In the reaction system with higher PU content, viscosity of reaction mixture increases so that the initiation efficiency of BPO and the diffusion of reaction species are largely reduced. Comparing Fig. 3 and Fig. 6, the limiting conversion of MMA is much lower for the system using KPS as initiator. In this system, KPS dissolves in the aqueous phase; radicals from KPS must diffuse from water into the phase of monomer droplets for polymerization. While radicals travelling to the monomer droplets before initiating MMA monomers, some of them can be quenched or trapped by high viscous PU components, especially as the content of PU is high. Therefore, in KPS system, radicals have lower opportunity of going into monomer droplets and lead to much lower conversion of MMA.
It appears from the results shown in Tab. 3 that particle size of hybrid latex also becomes larger with increasing the PU content, resulting from the higher viscosity of monomer droplets. In other words, as higher MMA is loaded, both initial and final particles are smaller because of the lower viscosity of reaction mixture in ultrasonication step.

While using water-soluble KPS initiator, homogeneous or micelle nucleation of MMA is observed from TEM measurement. Both small and large particles existed in the reaction system as shown in Fig. 7. The larger ones are PU/PMMA hybrid particles whereas the smaller can be pure PMMA particles. The pure PMMA particles are from homogeneous or micelle nucleation of MMA in aqueous phase. As MMA content is reduced, the chance of forming pure PMMA particles decreases. It also means that homogeneous or micelle nucleation of MMA decreases. From TEM observation, as
shown in Fig. 7(c), the hybrid particles become larger as increasing the PU content and less pure PMMA particles are observed.

![Fig. 7. TEM analysis of poly(IPDI-PPG1000-BD-TMP)/PMMA with different PU/MMA weight ratios (a) 20/80 (b) 30/70 (c) 40/60; NCO/OH molar ratio=1.0, KPS initiator.](image)

**BisA/KPS system**

-Influences of PU content on conversion of MMA and particle size of PU/PMMA hybrid particles

As shown in Fig. 8, the limiting conversion of MMA is also influenced by PU content. The initiation efficiency of KPS is obviously affected by PU content. The higher the PU content, the lower limiting conversion of MMA is obtained. In Tab. 4, particle size also increases by increasing the PU content as in previous cases. Furthermore, considering the possibility of homogeneous or micelle nucleation of MMA in aqueous phase, TEM photographs of the BisA/KPS system show only a few small PMMA particles in Fig. 9. It means that less MMA monomers diffuse from monomer droplets into water phase and form PMMA particles in comparison with the BD/KPS system.
Fig. 8 Conversion of MMA for poly(IPDI-PPG1000-BisA-TMP)/ PMMA latex system with different PU/MMA weight ratios; NCO/OH molar ratio=1.0 and KPS initiator.

Tab. 4. Limiting conversion of MMA and particle size for BisA/KPS system.\(^a\)

<table>
<thead>
<tr>
<th>PU(^b)/MMA weight ratio</th>
<th>NCO/OH mole ratio</th>
<th>Conversion of MMA (%)</th>
<th>Initial (D_z) (nm)(^c)</th>
<th>(D_n) (nm)</th>
<th>Final (D_z) (nm)</th>
<th>(D_n) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20/80</td>
<td>1.0</td>
<td>91</td>
<td>179</td>
<td>175</td>
<td>131</td>
<td>125</td>
</tr>
<tr>
<td>30/70</td>
<td>1.0</td>
<td>84</td>
<td>206</td>
<td>203</td>
<td>210</td>
<td>195</td>
</tr>
<tr>
<td>40/60</td>
<td>1.0</td>
<td>77</td>
<td>241</td>
<td>235</td>
<td>246</td>
<td>222</td>
</tr>
</tbody>
</table>

\(^a\)Synthesis conditions: Ultrasonication time =12mins; [SDS]=5mM (per liter \(H_2O\)); [HD]=35mM (per liter \(H_2O\)); SnDBL=0.1 wt% based on total weights of PU components; KPS=1wt% based on the weight of MMA; Rxn temp =70\(^o\)C; Rxn time =3hrs; Rpm=200; Solid content=19%.

\(^b\)PU with bisphenol A (BisA) as chain extender.

\(^c\)\(D_z\)= Z-average particle size; \(D_n\)=number-average particle size.

Comparing Tab. 3 (BD/KPS) and Tab. 4 (BisA/KPS), the limiting conversion of MMA of BisA/KPS system is higher than that of BD/KPS system. When using hydrophilic BD as chain extender, it moves out to the surface of monomer droplets easily, so as to force MMA monomers moving into the inner zone. As a result, the surface MMA concentration reduces. The hydrophilic KPS is more difficult to diffuse into the inner zone of monomer droplets to initiate the polymerization of MMA so the much lower conversion of MMA is observed. On the contrary, in BisA/KPS system, bisphenol A mainly stays inside the droplets instead of moving out to the surface of monomer droplets. The concentration of MMA in droplets is more uniform than BD/KPS system and thus higher conversion of MMA is observed.
Fig. 9. TEM analysis of poly(IPDI-PPG1000-BisA-TMP)/ PMMA with different PU/MMA weight ratios (a) 20/80 (b) 30/70 (c) 40/60; NCO/OH molar ratio=1.0, KPS initiator.

Cross-section morphology of the PU/PMMA latex particles

In BD/BPO system, on increasing the load of PU, PU phase moves to the surface of hybrid particles gradually. It shows somewhat a core-shell structure as shown in Fig. 10. Fig. 10(b) shows that the PU-rich phase is mostly located at the shell zone of the hybrid particles whereas PMMA-rich phase is located at the core zone. In this reaction system, the hydrophilic BD chain extender and excess IPDI molecules move to the shell zone of hybrid latex during synthesis. Therefore, the PU-rich phase is observed at the shell. With increasing PU content, this phenomenon is more obvious. From the above results, the hybrid PU/PMMA latex with core-shell morphology could be obtained by miniemulsion polymerization.

The morphology of the PU/PMMA latex with NCO/OH =1.0 in Fig. 11(a), indicates that PU-rich phase distributes randomly and shows not so obvious core-shell structure. As the PU content increases, the PU/PMMA latex shows more obvious core-shell structure as seen in Fig. 11(b). Compared with Fig. 10, the core-shell structure is not so clear when NCO/OH ratio is reduced to 1.0.
Fig. 10. TEM analysis of cross-section poly(IPDI-PPG1000-BD-TMP)/PMMA particles with different PU/MMA weight ratios (a) 30/70 (b) 40/60; NCO/OH molar ratio=1.7, BPO initiator.

Fig. 11. TEM analysis of cross-section poly(IPDI-PPG1000-BD-TMP)/PMMA particles with different PU/MMA weight ratios (a) 30/70 (b) 40/60; NCO/OH molar ratio=1.0, BPO initiator.

When using KPS as initiator, BD/KPS system shows clearer phase separation and core-shell structure. Fig. 12(b) indicates that higher PU content results in distinct phase boundary. In this system, the polymerization rate of MMA is much slower, which is favourable for the phase separation from thermodynamic consideration. On using hydrophobic bisphenol A as chain extender, the morphology of hybrid particle is extremely different. As shown in Fig. 13, the boundary of PMMA and PU phases is
not clear. Most of PU phase does not move to the shell of hybrid particles. PU and PMMA phases mix more homogeneously in hybrid particles even when PU content is increased. It is assumed that PMMA has higher compatibility with PU when bisphenol A is used as the chain extender.

**Fig. 12.** TEM analysis of cross-section poly(IPDI-PPG1000-BD-TMP)/PMMA particles with different PU/MMA weight ratios (a) 20/80 (b) 30/70; NCO/OH molar ratio=1.0, KPS initiator.

**Fig. 13.** TEM analysis of cross-section poly(IPDI-PPG1000-BisA-TMP)/PMMA particles with different PU/MMA weight ratios (a) 30/70 (b) 40/60; NCO/OH molar ratio=1.0, KPS initiator.
**Conclusions**

Four systems of PU/PMMA hybrid latex are prepared in this work. In BD/BPO system, NCO groups and high viscosity of PU prepolymer reduce the efficiency of BPO to initiate the polymerization of MMA. Some radicals from BPO can be trapped or quenched in droplets. The limiting conversion of MMA decreases.

As using KPS as initiator, the polymerization rate and limiting conversion of MMA both decrease seriously as increasing the PU content. In BD/KPS system, KPS radicals have lower opportunity of getting into monomer droplets to initiate the polymerization, which thus leads to much lower conversion of MMA.

The size distribution of latex particles in BisA/KPS system indicates that less homogeneous or micelle nucleation of MMA occurs than in BD/KPS system. On the other hand, in BD/KPS system, nucleation of pure PMMA particles occurs in aqueous phase more significantly especially when MMA content is high. The size of hybrid particles increases with increasing the PU content in four systems because of the increasing viscosity of reaction mixture in the ultrasonication step.

From the TEM observation of cross-section morphology of hybrid latex particles, for BD/BPO and BD/KPS systems, when increasing the load of PU component, PU-rich phase is moved to the outside of hybrid particles. A core-shell structure can be observed. However, for BisA/KPS system, while using hydrophobic bisphenol A as chain extender of PU, the boundary of PMMA and PU phases is not clear. A more homogeneous structure of hybrid particles can be obtained.

**Experimental**

**Materials**

Isophorone diisocyanates (IPDI; Lancaster), 1,4-butanediol (BD; TEDIA), bisphenol A (BisA; TCI), trimethylol propane (TMP; ACROS), dibutyltin dilaurate (SnDBL; TCI), sodium dodecyl sulfate (SDS; TCI), hexadecane (HD; TCI), benzoyl peroxide (BPO; ACROS), potassium persulfate (KPS; TCI) and hydroquinone (HQ; TCI) were used without further purification. Polypropylene glycol (PPG; Showa) with an average molecular weight of 1000 (g/mol), was dried under vacuum at 80 °C for 24 h before use. Methyl methacrylate (MMA; Showa) was distilled to remove impurities and then stored in refrigerator before use.

**Synthesis of PU prepolymer**

The synthesis of prepolymer was carried out in a 100mL round-bottom, three-necked flask with a magnetic stirrer, thermometer, condenser, nitrogen inlet and an outlet. Reaction temperature was set at 60 °C and was controlled by immersion in an isothermal oil bath. IPDI and PPG1000 dissolved in MMA were charged into the flask and then heated to the reaction temperature. Subsequently, SnDBL catalyst (0.1wt% based on the total monomer weight) was added into the solution. The equivalent ratio of IPDI and PPG 1000 was 2/1. The theoretical NCO value was determined by using a standard dibutylamine back titration method [26]. After achieving the theoretical NCO value, NCO-terminated prepolymers were cooled down to room temperature and then were stored in refrigerator before use.
Preparation of PU/PMMA hybrid latex

A typical procedure of miniemulsion polymerization is shown in Scheme 1. Two kinds of initiators were used: BPO and KPS. In an oil phase, NCO-terminated prepolymer, MMA, HD, chain extender (BD or BisA), SnDBL, TMP and BPO (if needed) were stirred together. SDS was dissolved in deionized water as a water phase. Then the oil and water phases were mixed and stirred.

**Scheme 1.** Procedure of miniemulsion polymerization to prepare PU/PMMA hybrid latex.

A miniemulsion was prepared by ultrasonifying the mixtures for 12 minutes. All the above steps were carried out in an ice bath in order to prevent the premature polymerization reaction. The miniemulsion was introduced to a 250mL round-bottom, four-necked separable flask with a mechanical stirrer, thermometer, condenser, nitrogen inlet and an outlet. After 5 mins, KPS (if needed) was added into reactor. Synthesis of PU/PMMA polymer was carried out at 70 °C for 3 hrs. The composition of materials and synthesis conditions were shown in Tab 1.

**Analysis**

-Conversion measurement

During polymerization, a given amount of hybrid latex was taken out of the reaction flask, weighed and introduced into a bottle containing 1 wt% hydroquinone-methanol solution. This latex was then cooled in an ice bath, poured into an aluminum plate, and dried under vacuum oven at 80 °C for 24 hrs. The conversion of MMA was calculated as the following equation:

\[
\text{Conversion\%} = \frac{(W_1 - W_2) - W_{latex} \times \frac{W_{unevap\,solid}}{W_{total}}}{W_{latex} \times \frac{W_{MMA}}{W_{total}}}
\]

Where \( W_1 \)=weight of aluminium plate and dry samples, \( W_2 \)=weight of aluminium plate and HQ, \( W_{latex} \)=weight of given latex, \( W_{unevap\,solid} \)=weight of PU, SDS, HD, SnDBL and
initiator in $W_{total}$, $W_{MMA}$=weight of MMA monomer in $W_{total}$, $W_{total}$= total weight of mixtures in polymerization.

**-Particle size measurement**

Hybrid latex was first diluted by SDS solution (8.6mM) and the size distribution of latex particles was measured by dynamic light scattering, using a Zetasizer 3000, Malvern.

**Latex morphology**

The morphology of particles of hybrid latex was characterized by TEM (JOEL JEM-1230 with Gatan DualVision CCD Camera). The latex sample was diluted first and then dropped on the 400-mesh Cu grid coated with carbon. To observe the phase distribution in particles, the ultrathin cross-section of the hybrid sample was stained by phosphotungstic acid (PTA) for 5 minutes. PTA can stain the PU phase but not the PMMA phase, so under the observation of TEM, the PU phase was dark whereas the PMMA phase was bright.

**References**