Polymerization Mechanism of Emulsifier-free P(MMA/BA/VAc/AM)/ nano-SiO_2 Composite Emulsion

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Abstract: P(MMA/BA/VAc/AM)/nano-SiO_2 composite emulsion was prepared via both emulsifier-free emulsion polymerization and sol-gel method in one step. The influence of the synthetic conditions such as the reaction temperature, the reaction time and the initiator concentration on the polymerization conversion was investigated in detail. Copolymer latex particles during the whole polymerization period were determined by Dynamic Laser scattering (DLS) and Transmission Electron Microscopy (TEM). The result showed that the reaction activity energy (E_a) was 44.154kJ/mol, the polymerization reaction rate was $R_p \propto [I]^{1.716}[m]^{0.33}$. DLS indicated that the average diameter and the particle disperse index of the latex particles increase with the increase of reaction time. TEM confirmed that the average diameter of the round amphiphilic P(BA/VAc/AM) was about 100nm and the strawberry-like P(MMA/BA/VAc/AM)/nano-SiO_2 composite particle was about 120-150nm. The polymerization mechanism of nanocomposite emulsion of the homogeneous nucleation was built up.

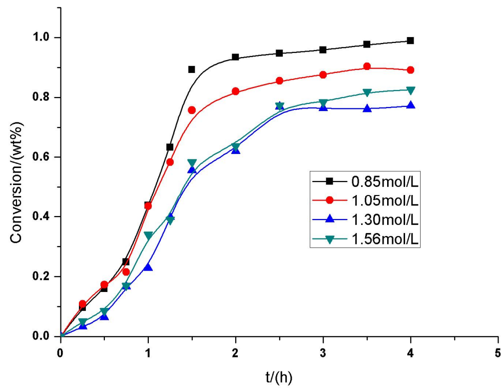

Fig.1 Effect of the reaction temperature on polymerization conversion

Figure 1 showed that the polymerization conversion and ratio of P(MMA/BA/VAc/AM)/nano-SiO_2 composite emulsion were improved with the increase of the reaction temperature. The polymerization ratio and conversion were biggest at 85℃. The relationship between $\ln R_p$ and T^{-1} was concluded according to Figure 1.The reaction activity energy (E_a) was 44.154kJ/mol.

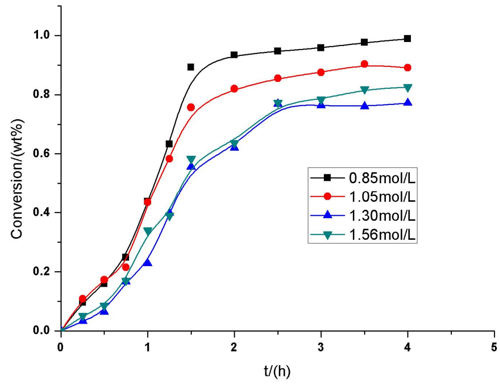

Fig.2 Effect of the monomer concentration on polymerization conversion

Figure 2 showed that the polymerization conversion and ratio of P(MMA/BA/VAc/AM)/nano-SiO_2 composite emulsion were decreased with the monomer concentration increased. When the monomer concentration was 1.30mol/L, the last polymerization conversion was about 70%. The relationship between $\ln R_p$ and ln[m] was concluded as $R_p \propto [m]^{0.33}$ on the basis of Figure 2.

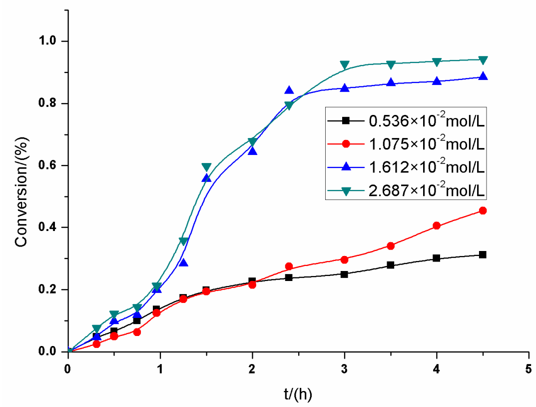

Fig.3 Effect of the use level of KPS on polymerization conversion

Figure 3 indicated that the polymerization ratio and conversion were improved with the use level of the initiators increasing during the preparation of P(MMA/BA/VAc/AM)/nano-SiO_2 composite emulsion. When the use level of KPS was 0.536×10^{-3} mol/L and 1.075×10^{-2} mol/L, the constant ratio period was inexistence during the polymerization process. The relationship between $\ln R_p$ and ln[I] was concluded as $R_p \propto [I]^{1.716}$ according to Figure 3.

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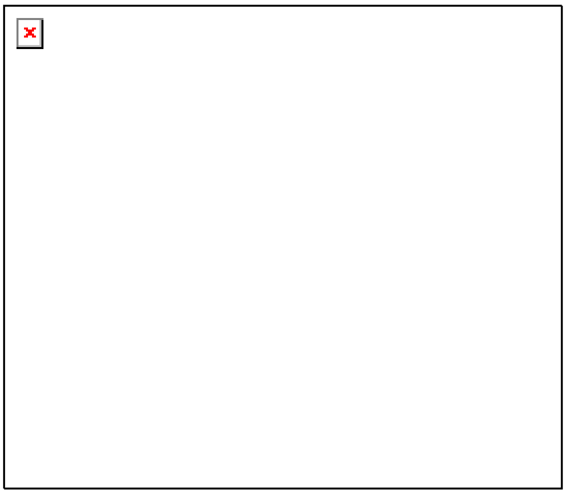

Fig.4 DLS analysis

Figure 4 showed that the dimension distributing curve of the latex was moved from left to right along the dimension axes, which explained the accretion of the average size of the latex particle with the polymerization reaction time processed.

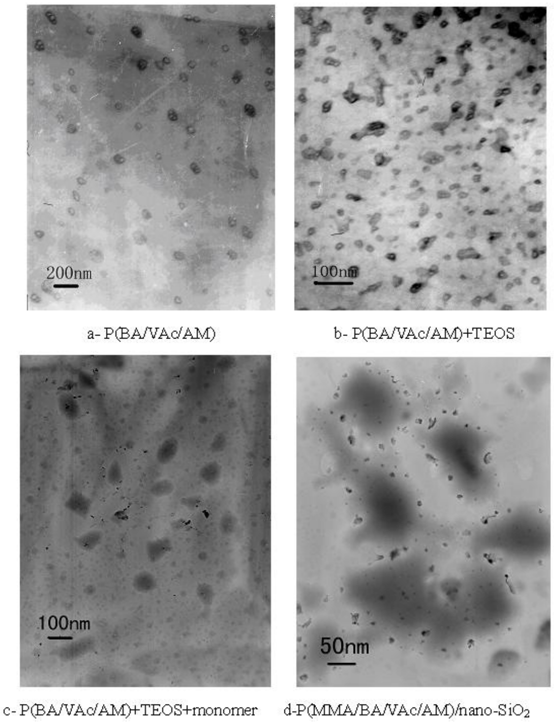

Fig.5 Result of TEM analysis

Figure 5 confirmed that the average size of the round amphiphilic P(BA/VAc/AM) was about 100nm. After the incorporation of tetraethoxysilane (TEOS) in P(BA/VAc/AM), the copolymer became adhesive between each other. At last, nano-SiO_2 obtained with TEOS functioned on the surface of polyacrylate particle by the organic silane coupling agent. The strawberry-like P(MMA/BA/VAc/AM)/nano-SiO_2 composite particle was about 120-150nm.

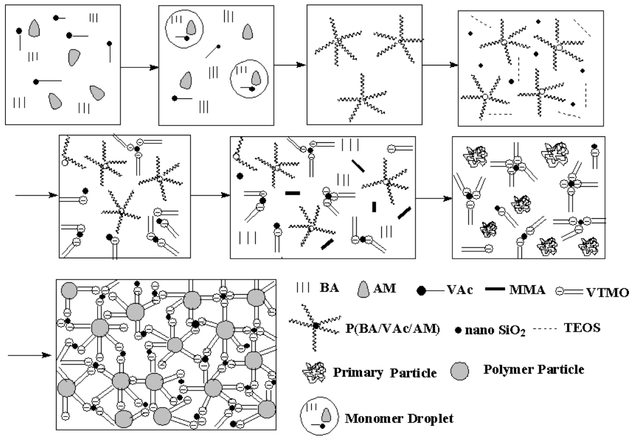

Fig.6 Polymerization mechanism of P(MMA/BA/VAc/AM)/nano-SiO_2 composite emulsion

Figure 6 explained that the main content of P(MMA/BA/VAc/AM)/nano-SiO_2 composite emulsion polymerization mechanism. P(BA/VAc/AM) was prepared by radical polymerization in aqueous solution. Then, the emulsifier-free emulsion polymerization was carried out with P(BA/VAc/AM) as the surfactants. The whole polymerization process obeyed the homogeneous nucleation

Conclusion

P(MMA/BA/VAc/AM)/nano-SiO_2 composite emulsion was successfully prepared via both emulsifier-free emulsion polymerization and sol-gel method in one step. The result showed that the reaction activity energy (E_a) was 44.154kJ/mol, the polymerization reaction rate was $R_p \propto [I]^{1.716}[m]^{0.33}$. TEM confirmed that the average diameter of the round amphiphilic P(BA/VAc/AM) was about 100nm and the strawberry-like P(MMA/BA/VAc/AM)/nano-SiO_2 composite particle was about 120-150nm. The polymerization mechanism of nanocomposite emulsion of the homogeneous nucleation was built up.

Acknowledgements

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References

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