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材料化学工程与纳米技术

伴有水解缩合反应的种子乳液聚合动力学(Ⅱ)参数求解和模型应用

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摘要 通过对伴有水解缩合反应的自由基种子乳液聚合动力学模型的求解，利用甲基丙烯酸-3-三甲氧基硅丙酯（MPS）和苯乙烯通过种子乳液聚合反应，仿真了不同反应条件下的反应动力学。并通过气相色谱（GC）和29Si固态核磁共振谱（NMR）测定了不同反应条件下的水解和缩合反应的动力学，并与动力学模型的仿真结果进行了比较。发现实验结果能与模型计算结果吻合，且水解和缩合反应的速率随体系中介质pH值、乳胶粒表面积和MPS在各相中分配的不同而变化。同时还总结出模型中参数f反映了乳胶粒中水解反应特点，与乳胶粒的表面积和功能基团扩散到乳胶粒表面的难易程度有关，并得出其半经验表达式。

关键词 种子乳液聚合 动力学 模拟 自由基聚合 水解缩合反应

分类号

Free radical seeded emulsion polymerization with participation of hydrolysis-condensation reaction（Ⅱ）Parameters and modeling application

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Abstract

The emulsion polymerization with the simultaneous hydrolysis-condensation reaction is an important method to synthesize the organic-inorganic hybrid nanoparticles.Its process modeling and simulation is really a challenge due to the complicated reaction mechanism.In the previous paper of the authors,a model was developed based on the analysis of the process mechanism.In this paper, the kinetic model of this process was calculated to simulate this complicated process.The model was used in the seeded emulsion copolymerization system of 3-trimethoxysilyl propyl methacrylate (MPS) and styrene.The kinetics simulated by the presented model was compared with the experimental data obtained by gas chromatography (GC) and solid-state 29Si NMR along with the emulsion copolymerization process.As predicted by the model and proved by experiments, the hydrolysis could be divided into two phases characterized by the different rates.At the beginning of the reaction,hydrolysis was more active because of the part of silicone groups existing in the water phase. A greater MPS addition amount would increase the MPS concentration in the water phase and then strengthen the hydrolysis and condensation reactions.A greater surface area of latex particles would increase the hydrolysis rate because more SiOR groups could contact with water in this case.The parameter f was directly related to the surface area and decreased with more MPS content in the shell polymer.A semi-empirical equation of the parameter f was derived.

Key words seeded emulsion polymerization kinetics simulation free radical polymerization hydrolysis-condensation reaction

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