

Synthesis and Properties of Poly(styrene-co-butyl acrylate) Particles via Microwave-aided Emulsion Copolymerization

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Introduction

As a peculiar and powerful energy source, microwave has been widely applied to optimize and accelerate the chemical reaction since Gedye et al. first used microwave into organic synthesis[1,2]. As an alternative to conventional heating techniques, microwave irradiation provides an effective, selective, clean and fast synthetic method by heating the molecules directly through the interaction between the microwave energy and molecular dipole moments of the monomers[3]. This internal heating is thought to increase the efficiency of the reaction because the monomers, which have strong dipole moments, are the primary source of activation in the microwave electromagnetic field. For the monomers with high dipole moments that are strongly affected by microwave irradiation, their polymerizations including addition polymerization, condensation polymerization, graft polymerization and ring-opening polymerization have been dramatically accelerated by microwave irradiation.

In this study, a novel process for synthesizing polystyrene(PS), poly(butyl acrylate)(PBA) and their copolymers by microwave irradiation of the respective monomers, styrene(St) and butyl acrylate(BA), was described. The influences of the monomer contents, the initiator contents, the agitation speed and the reaction temperature on the monomer conversion, the particle size and its distribution were investigated. The composition drifts in copolymer were also evaluated according to the different heating sources.

Experimental

Materials

The St and BA monomers were purchased from Ducksan Chemical and

purified by washing several times with a 10wt.% aqueous sodium hydroxide solution to eliminate inhibitors and stored at -10°C before use. Potassium persulfate(KPS), sodium lauryl sulfate(SLS) and *t*-dodecyl mercaptan(TDM) were used as an initiator, a surfactant and a chain transfer agent, respectively.

Preparation of copolymer emulsion

Mixed monomers(70g) were emulsified with 210g aqueous solution of SLS(1 wt.% based on water) for about 10min. Prepared emulsion and initiator(0.1wt% based on monomer) were transferred into a self-made 500ml reaction flask for microwave irradiation or into a 500ml 3-necked round bottom flask for conventional heating. Emulsion polymerizations were carried out at 70°C for 3h; then, the latexes were heated to 80°C and this temperature was maintained for 1hr to remove the residual monomers and initiators. Emulsion copolymerization was performed in a microwave oven by the forward power being controlled to keep the reaction temperature, 70°C . Samples were withdrawn in appropriate intervals and the overall conversion of the reactions was evaluated using gravimetry.

Characterization

The compositions of the copolymers were determined by differential scanning calorimeter (DSC) and nuclear magnetic resonance spectrometer (NMR). Morphologies of the copolymer particles were investigated by scanning electron microscopy(SEM).

Results and Discussion

Polymerization rates in microwave oven are highly dependent on dipole moments of the reactants. Figure 1 shows the conversion-time curves for emulsion polymerization and copolymerization by microwave heating and conventional heating. BA(0.6 D) has relatively high dipole moment than St(0.36 D) and so is more sensitive to microwave energy fields. The results show that polymer and copolymer containing BA have the higher conversion in microwave oven. Moreover, it shows that chemical reaction such as emulsion polymerization in polar solvents can be carried out rapidly and conveniently using microwave heating.

The composition drifts of the resulting PS/PBA copolymer for

overall St/BA monomer compositions were found to be considerably different in microwave heating and conventional heating. Copolymerization rate by microwave irradiation was increased compared to conventional heating, and the reaction rates were affected by the values dipole moment of monomers. As shown in Figure 2, the composition drifts are relatively higher in microwave heating.

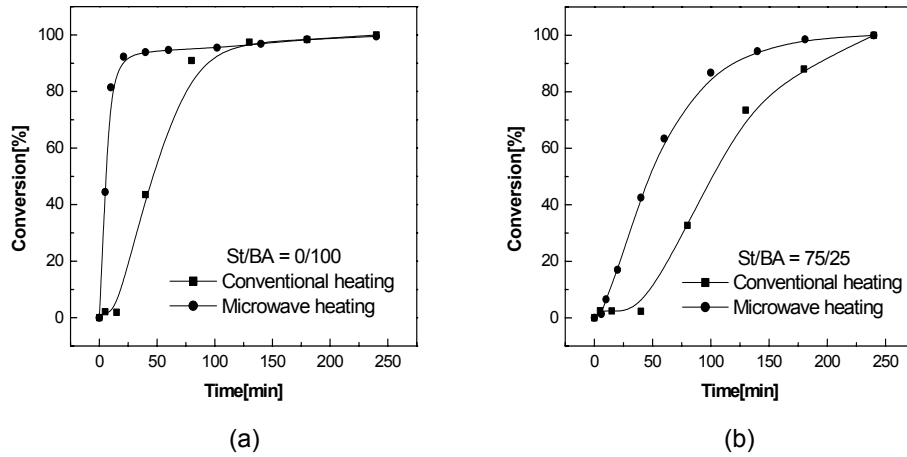


Figure 1. Conversion of copolymer latex prepared by microwave heating and conventional heating: (a) St/BA = 0/100; (b) St/BA = 75/25

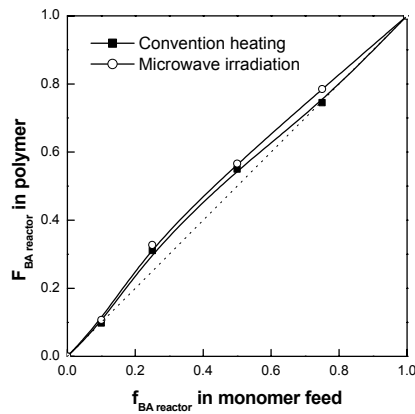


Figure 2. Composition drifts in PS/PBA copolymer by microwave aided emulsion copolymerization and conventional emulsion copolymerization

Figure 3 show SEM photographs of the particles prepared by different heating methods. It can be seen that the copolymer particles prepared by microwave heating show the more uniform particles size compared to the particles by conventional heating.

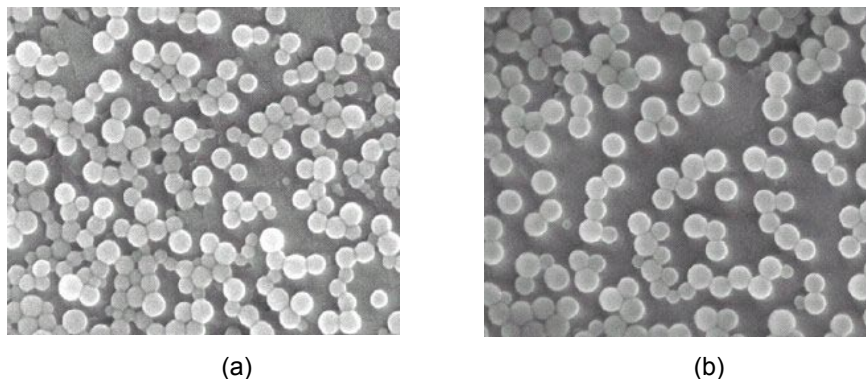


Figure 3. SEM photographs of PS/PBA copolymer particles prepared by (a) Conventional heating (b) Microwave heating

Conclusions

Emulsion copolymerization of St and BA was carried out successfully using microwave heating and conventional heating. Polymerization rates and the compositions of the resulting copolymer are highly influenced by monomer contents and its dipole moment. And copolymer particles prepared by microwave heating showed more uniform particle size than by conventional heating.

References

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