Emulsion polymerization of styrene under continuous microwave irradiation

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ABSTRACT

MW-assisted emulsion polymerization of styrene (M) is examined in this study. Six process variables namely, H_2O/M, SDS/M, KPS/M, temperature (T), reaction time (t) and MW power density (P) were investigated in comparison with the conventional heating (CH) method to assess their effects on the polymerization yield and the specific MW energy consumption. An experimental system was designed to keep both T and P continuous and constant during the polymerization. Based on a systematic study, it is found that MW power accelerates the polymerization rate, especially in the initiation step of the polymerization. While 95% conversion was achieved in 40 min under $P = 0.8$ kW dm^{-3}, 90 min was necessary for CH method to reach the same conversion level. Polymers obtained by MW and CH methods under the same process conditions were found to have the same structural and thermal characteristics.

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1. Introduction

The emulsion polymerization of styrene has been studied abundantly [1,2]. Different types of chemical activation methods have been reported. For example; visible light, ultraviolet (UV) light, ultrasound energy (US) and Microwave (MW) irradiation have produced different molecular-weight polystyrene polymers [1–8]. The use of MW irradiation to activate chemical reactions including polymerizations has gained importance in the last years. Higher product yields due to increased reaction rates using MW have been reported [9]. The literature on MW-assisted polymer synthesis by free-radical polymerizations (including emulsion) has recently been reviewed by the group of Schubert [10,11]. The use of MW in combination with potassium persulfate $K_2S_2O_8$ (KPS) to activate the emulsion polymerization of styrene has been studied by a few research groups [7,12–14]. They used a source of MW at a frequency of 2450 MHz and pulsed MW power. The results showed that MW irradiation has the advantages of a higher reaction rate (and so a greater yield of polymer within a given reaction time) when compared to CH method. But in all of the studies, intermittent MW energy was applied to achieve isothermal conditions in reaction medium. An important drawback of these studies is that MW power is no longer an independent variable controlled at constant level during the reaction, which impede the full assessment of MW irradiation on the reaction rate. However, there are some studies coming from our own group [15–17], reporting continuous (and constant) MW energy application under isothermal conditions. In addition that, compressed air-cooling methods with high air flow-rates has been used in single mode MW systems [18–21]. But, comparative tests showed that liquid-cooling method used in our experimental system outperformed air cooling method in terms of constant-continuous MW power supply and isothermal condition.

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Nomenclature

Symbols

T	reaction temperature (°C)
P	MW power density (kW dm^{-3})
P_{nom}	applied nominal power (W)
p	correction factor for MW power
t	reaction time (min)
ε''	dielectric loss factor
ε'	dielectric constant
$\tan\delta$	loss tangent ($\varepsilon''/\varepsilon'$)
c_p	specific heat capacity (J g^{-1} °C^{-1})
T_g	glass-transition temperature (°C)
T_m	melting point (°C)
M_v	viscosity-average molecular weight (g mol^{-1})
M_w	weight-average molecular weight (g mol^{-1})
M_n	number-average molecular weight (g mol^{-1})
M_z	z-average molecular weight (g mol^{-1})
D	dispersity
D_p	degree of polymerization

Abbreviations

SDS	sodium dodecyl sulfate
KPS	potassium persulfate
MW	microwave
CH	conventional
M	monomer (styrene)
PS	polystyrene
FO	fluoroptic sensor
IR	infrared sensor
GPC	gel permeation chromatography
DSC	differential scanning calorimeter

In recent years, the main subject under dispute has been whether the contribution of MW irradiation to a chemical reaction originates from a *specific MW effect* [22–26] or from a *dielectric heating effect* [27–31]. Although, evidences are found in modern MW reactors providing on-line temperature measurement that mechanisms in microwave-induced reactions do not differ from those observed in conventionally heated samples, while many publications also claim the existence of *specific MW effect* [32–35]. However, in many cases reaction rates are found to increase by up to 4 orders of magnitude. For polymerization reactions, it is important to have a polar solvent (or monomer) as a MW absorber to couple efficiently the MW energy supply into the system. This is why hetero-phase polymerization in water seems to be ideally suited for MW application.

As known, emulsion polymerization involves the propagation reaction of free radicals with monomer molecules in a very large number of discrete polymer particles dispersed in the continuous aqueous phase. So, emulsion polymerization proceeds via three consecutive basic reaction steps similar to free-radical polymerization. Initiation step (I) which continuously generates free radicals from an initiator to start the polymerization. Waterborne free radicals first polymerize with monomer molecules dissolved in the continuous aqueous phase. When a critical chain length is achieved, these oligomer radicals become so hydrophobic that they show a strong tendency to enter the monomer-swollen micelles and then continue to propagate by reacting with those monomer molecules therein. Propagation step (II) is responsible for the growth of polymer chains. When all the monomer droplets disappear, the reaction proceeds from step II to step III. The steady polymerization rate observed in step II cannot be maintained anymore and the polymerization rate decreases during step III. Although the step I is relatively short (proceeding up to about 10–20% monomer conversion), it controls the particle size and particle size distribution of latex products in the emulsion polymerization. The application properties of emulsion polymers such as rheology and film formation are strongly dependent on the particle size and particle size distribution. MW energy is predicted to be more effective in this step. Therefore, in our previous study, MW-assisted decomposition kinetics of KPS in water was investigated using an online experimental system allowing accurate measurements and controls of temperature and MW power [15]. The experiments conducted at constant temperature and constant MW power revealed that depending on the MW power, the first order rate constant was about 1.1–1.8 times higher than that of the conventional heating (CH) system at the same temperature.

On the other hand, one of the first industrial applications of ultrasound (US) energy was in the process of emulsification. When the interface of two immiscible liquids is ultrasonically irradiated, an emulsion is formed, tiny droplets of one liquid