

Emulsion Polymerization of Styrene Under Pulsed Microwave Irradiation

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ABSTRACT: We performed the emulsion polymerization of styrene successfully with potassium persulfate (KPS) as an initiator and sodium dodecylsulfonate as an emulsifier under high-power pulsed microwave irradiation (PMI). We investigated the effects of the temperature, the concentration of initiator, and various parameters of PMI (i.e., irradiation power, duty cycle, irradiation energy, and pulse width) on the polymerization. The results indicated that PMI, compared to conventional heating (CH), caused a significant increase in the decomposition rate of KPS (2.4 times higher than that under CH at about 70°C) and in the amount of particles (5 times higher than that under CH); consequently,

the polymerization rate was effectively enhanced. For initiator concentrations of 0.10 and 0.20 wt %, the enhancement of the polymerization rate under PMI was 129 and 38% greater, respectively, than that under CH. The glass-transition temperature and the regularity composition of the polymers under PMI and CH showed no difference, which indicated that PMI had little effect on the physical properties and microstructure of the polymer. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 28–35, 2003

Key words: emulsion polymerization; irradiation; differential scanning calorimetry (DSC)

INTRODUCTION

As a peculiar source of energy, microwaves have been widely applied to enhance chemical reactions. The study of microwave irradiation has been focused much more on organic syntheses¹ and less on polymerization. The application of microwave irradiation to polymerization has included the bulk polymerization of styrene,² (methyl) methacrylate,³ and hydroxyethyl methacrylate;⁴ the bulk copolymerization between methyl methacrylate and hydroxyethyl methacrylate;⁵ and the seed emulsion polymerization of styrene.⁶ Our earlier work involved the polymerization of some monomers under microwave irradiation.^{7,8} The results showed that by comparison with conventional heating (CH), polymerization under microwave irradiation has the advantages of a higher reaction rate and a greater yield of polymer within a shorter period of time.

Recently, the main subject under dispute has been whether the contribution of microwave irradiation to a chemical reaction lies in a specific microwave effect^{9–13} or in a dielectric heating effect.^{14–18} Because domestic microwave ovens, which have been used

and reported as the main microwave irradiation apparatus, have the disadvantage of difficult temperature control and because the energy provided by a microwave oven is usually mixed up with a great deal of heat liberated by polymerization itself, it seems to be hard to distinguish clearly between the effects on polymerization by the thermal effect and by the non-thermal effect of the microwave.

In view of this situation, we designed a set of reaction apparatuses with high-power pulsed microwave irradiation (PMI) and studied the emulsion polymerization of styrene under PMI. In addition, the effect of microwave irradiation on the polymerization under a higher peak pulse power (P) but a much lower energy than domestic microwave ovens was explored. The results were compared to conventional emulsion polymerization.

EXPERIMENTAL

Apparatus

Our self-designed pulsed microwave reaction apparatus is schematically shown in Figure 1. The microwave frequency was 1250 MHz and the pulse width was 1.5 μ s and 3.5 μ s; the output P , the duty cycle (D), and the mean output power were all continuously adjustable within the range 20–350 kW, 0.1–0.01%, and 2.0–350 W, respectively. The end reactor was a rectangular waveguide (165 \times 82.5 mm), which formed a waveguide-type single model (TE₁₀) resonance cavity with an opening aperture in its wider side. A reaction

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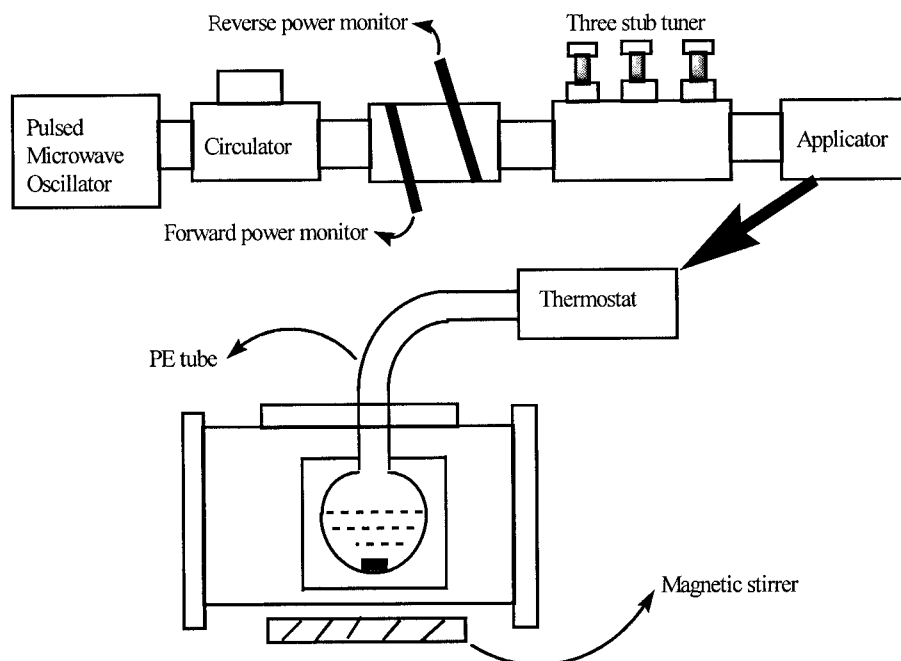


Figure 1 Apparatus for the pulsed microwave treatment of a single-mode cavity.

flask with a jacket was situated at the position of the highest electric field. A constant temperature was held by a thermostat with a thermostatic medium (tetrachlorethylene, dielectric constant = 2.3, with little absorption of microwave irradiation) provided through a polyethylene tube. There was a magnetic stirrer below the waveguide to stir the mixture during the reaction. When the reaction was run, microwave matching could be adjusted by a three-stub tuner to minimize the reflected power.

Materials

Chemically pure (CR)-grade styrene was purified by distillation under vacuum and stored in a freezer for

not more than 2 weeks before use; Analytical reagent (AR)-grade potassium persulfate (KPS) was recrystallized from water and stored in a desiccator for not more than 7 days; sodium dodecylsulfonate was CR grade, methanol was of technical purity, and hydroquinone was AR grade. All other reagents used in this study were analytical grade.

Determination of the decomposition rate constant (k_d) of KPS under PMI

KPS solution was prepared by dissolution of a certain amount of KPS in 25 mL of deionized water; another 50 mL of deionized water was added into a 100 mL self-made round-bottom flask with a thermostatic

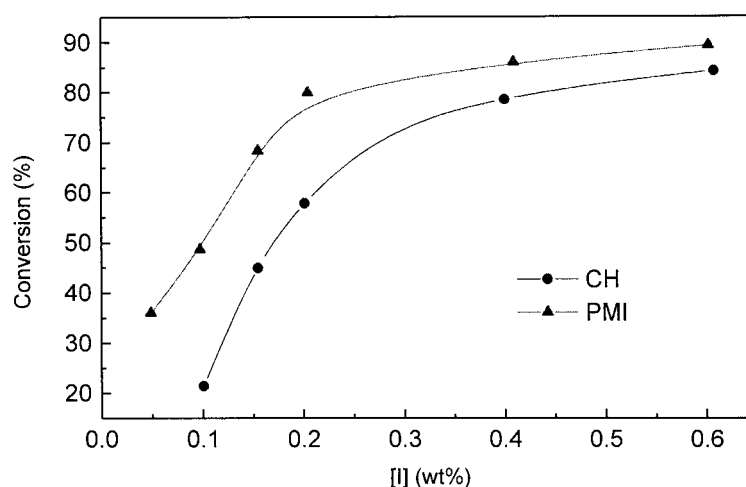


Figure 2 Conversion profile of PS with initiator concentration. For PMI, power = 120 kW, pulse width = $1.5 \mu\text{s}$, $D = 0.01\%$, $t = 40 \text{ min}$, and temperature = $72 \pm 3^\circ\text{C}$. For CH, reaction time = 40 min and temperature = $72 \pm 1^\circ\text{C}$.

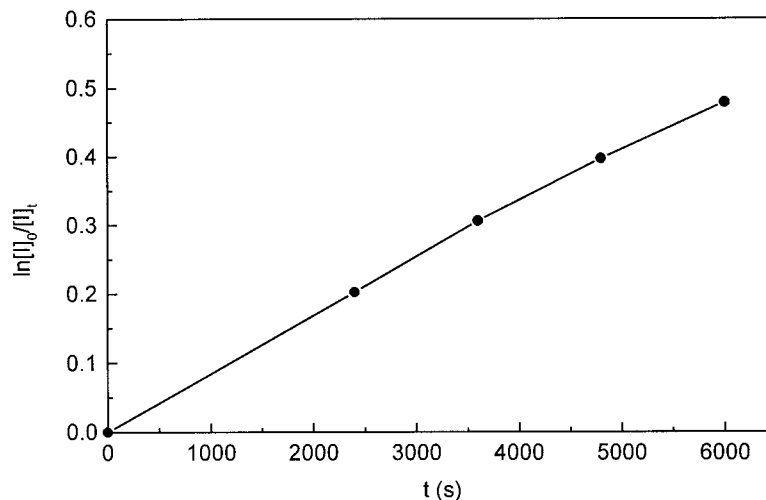


Figure 3 Decomposition of KPS at $68.5 \pm 1^\circ\text{C}$: power = 20 kW, pulse width = $1.5 \mu\text{s}$, and $D = 0.01\%$.

jacket, and it was stirred under nitrogen gas; when the temperature of the water remained at a constant temperature of 68°C , the KPS solution was added. The microwave power was adjusted to be 20 kW, and D was 0.01% ; the temperature was maintained at $68.5 \pm 1^\circ\text{C}$. Samples (10 mL) were taken out at 20 min intervals to determine the concentration of KPS remaining in the solution with iodometry. k_d was then calculated with eq. (1):

$$\ln([I]_0/[I]_t) = k_d t \quad (1)$$

where $[I]_0$ and $[I]_t$ are the concentrations of KPS at the beginning of the reaction and at time t , respectively.

Polymerization

Styrene monomer (10 mL), deionized water (20 mL), and sodium dodecylsulfonate (0.3 g) were transferred into a self-made reaction flask for PMI or into a 100-mL three-necked round-bottom flask for CH; the mixture was stirred under nitrogen gas and kept thermostated. When it reached a preset temperature (which was $1\text{--}3^\circ\text{C}$ lower than the polymerization temperature under PMI), 10 mL of KPS aqueous solution was added. The system was then exposed to PMI for a period of time under a given P (the practical irradiation power equaled the difference between the for-

ward and the reverse power) and D or was heated by water bath for CH. All polymerizations were conducted under protection by nitrogen gas. After the polymerization reaction was complete, we poured the product into a great deal of methanol to let the polymer separate out; it was then filtered, washed, and oven-dried until a constant weight was reached; the final weight was recorded to calculate the polymerization conversion (samples were dried directly in the oven in the instance of low conversion).

Characterization of the polymer

The molecular weight (MW) and MW distribution of the polymer were obtained with a Waters 1515 gel permeation chromatograph (Milford, MA) with tetrahydrofuran as the mobile phase and with a column temperature of 30°C . The glass-transition temperatures (T_g) were determined with a PE DSC-7 differential scanning calorimeter (New Jersey, USA) under protection by nitrogen gas at a heating rate of $20.0^\circ\text{C}/\text{min}$.¹³ C-NMR spectra were taken in an INOVA 400-MHz NMR instrument (Palo Alto, CA) with deuterated chloroform (CDCl_3) as the solvent. The Z -average mean (D_z) and polydispersity of the particles were determined with a Malvern 4700 auto sizer (Loc-Fc963) (Malvern, UK).

TABLE I
Particle Size and Latices Prepared by the Two Polymerization Processes

Initiator (wt %)	Conversion (%)		D_z (nm)		PDI		N ($10^{15}/\text{mL}$)	
	PMI	CH	PMI	CH	PMI	CH	PMI	CH
0.10	74.63	19.35	71.3	100.2	0.06	0.27	0.84	0.08
0.15	86.52	33.48	70.2	86.9	0.06	0.17	1.02	0.21

For PMI, power = 60 kW, pulse width = $1.5 \mu\text{s}$, $D = 0.02\%$, $t = 40$ min and temperature = $72 \pm 2^\circ\text{C}$. For CH, reaction time = 40 min and temperature = $72 \pm 1^\circ\text{C}$.

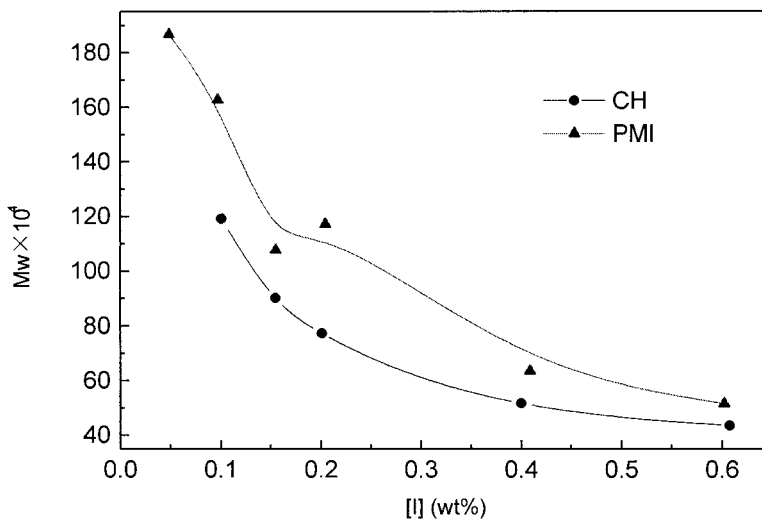


Figure 4 MW as a function of initiator concentration. For PMI, power = 120 kW, pulse width = 1.5 μ s, $D = 0.01\%$, $t = 40$ min, and temperature = $72 \pm 3^\circ\text{C}$. For CH, reaction time = 40 min and temperature = $72 \pm 1^\circ\text{C}$.

RESULTS AND DISCUSSION

Effect of initiator concentrations

The conversion profile of polystyrene (PS) with initiator concentration is shown in Figure 2. As shown, both of the conversions with the two methods, PMI and CH, increased with initiator concentration. A further observation revealed that the conversions rose steeply in the section of lower initiator concentration (≤ 0.2 wt %) and, thereafter, rose gradually; however, the percentage conversion under PMI at any initiator concentration was higher than that under CH, which was more obvious in the case of low initiator concentration. At an initiator concentration of 0.05 wt %, almost no polymer was found under CH, whereas a conversion of 36% was achieved under PMI. For a conversion to reach 75% under the experimental conditions shown in Figure 2, the initiator concentrations required for PMI and CH were 0.18 and 0.36 wt %, respectively, which suggested that the amount of initiator needed for PMI was only half that needed for CH.

Under comparable temperatures, the reaction rate enhancements (RE_c 's) for PMI and CH were calculated with the following equation:

$$RE_c = \text{PMI}_{\text{con}} / \text{CH}_{\text{con}} \quad (2)$$

where PMI_{con} and CH_{con} are the conversions achieved with PMI and CH, respectively, at the same initiator concentration and polymerization time. As shown in Figure 2, the RE_c 's at initiator concentrations of 0.10 and 0.20 wt % were found to be

$$RE_c \text{ at } 0.10\% = 49.2 / 21.5 = 2.29$$

$$RE_c \text{ at } 0.20\% = 80.0 / 57.8 = 1.38$$

These results demonstrated that the polymerization could be accelerated under PMI, and its rates were 129 and 38% greater than those for CH, respectively.

To further reveal the cause of the acceleration of the polymerization by PMI, we determined the k_d of KPS under PMI. As shown in Figure 3, at temperatures of $68.5 \pm 1^\circ\text{C}$, the k_d value calculated from the slope was $8.05 \times 10^{-5} \text{ s}^{-1}$, whereas at a similar temperature (70°C) and under CH, k_d was reported to be $3.35 \times 10^{-5} \text{ s}^{-1}$.¹⁹ A comparison of the two results showed that although the temperature under PMI was 1.5°C lower than that under CH, the k_d value with PMI increased 2.4 times. Because at a P of 20 kW and a D of 0.01%, the mean power of PMI was only 2 W and because the thermal effect of PMI should vary little, it seemed that the nonthermal effect of PMI played a main role in enhancing the initiator activity, raising its decomposition rate and further accelerating the polymerization process. As shown in Table I, the particle sizes (D_z 's) obtained under PMI were minor, and the particle numbers (N_s) were much more than those

TABLE II
 T_g values of PS prepared by Two Processes with Different Initiator Concentrations

Initiator (wt %)	T_g ($^\circ\text{C}$)	
	PMI	CH
0.60	109.3	107.5
0.40	107.9	110.6
0.20	108.9	109.3
0.15	105.1	106.8
0.10	105.1	105.7
0.05	108.6	—

For PMI, power = 120 kW, pulse width = 1.5 μ s, $D = 0.01\%$, $t = 40$ min, and temperature = $72 \pm 3^\circ\text{C}$. For CH, reaction time = 40 min and temperature = $72 \pm 1^\circ\text{C}$.

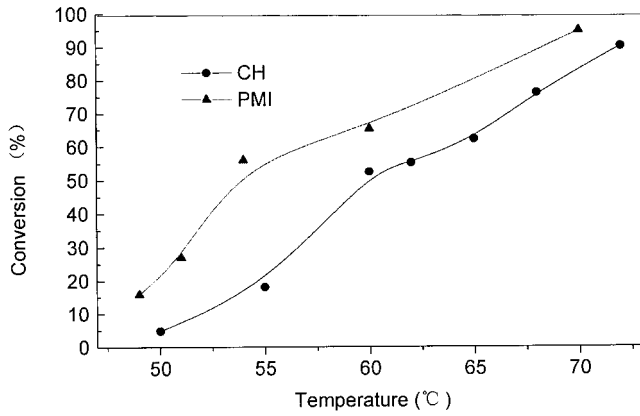


Figure 5 Conversion profile of PS with temperature. For PMI, power = 120 kW, pulse width = 1.5 μ s, $D = 0.01\%$, $t = 40$ min, and initiator concentration = 1.0 wt %. For CH, reaction time = 40 min and initiator concentration = 1.0 wt %.

under CH. As a result, the polymerization rate under PMI was obviously quicker than that under CH.

The MW of the polymer as a function of the initiator concentration is presented in Figure 4. As shown, at the same initiator concentration, the MW of the polymer obtained under PMI was 18.3–52.6% higher than that under CH. Under the usual conditions, an increase in the decomposition rate of KPS would result in a decrease of MW. However, according to polymerization kinetics, when N increases and the creation rate of the free radical (ρ) decreases, the degree of polymerization (\bar{X}_n) of the polymer would increase, which is shown here (in the second stage of emulsion polymerization):

$$\bar{X}_n = NK_p[M]/\rho \quad (3)$$

where K_p is the rate constant of propagation and $[M]$ is the monomer concentration. In the second stage of

emulsion polymerization, $[M]$ and K_p are constant. Then

$$\bar{X}_n \propto N/P$$

$$\begin{aligned} \bar{X}_{n(\text{PMI})}/\bar{X}_{n(\text{CH})} &\approx (N_{\text{PMI}}/N_{\text{CH}})(\rho_{\text{CH}}/\rho_{\text{PMI}}) \\ &\approx (N_{\text{PMI}}/N_{\text{CH}}) [K_{d(\text{CH})}/K_{d(\text{PMI})}] \geq 5/2.4 > 1 \end{aligned}$$

According to Figure 3 and Table I, $K_{d(\text{PMI})}$ was about 2.4 times as much as $K_{d(\text{CH})}$ (the mean decomposition rate was constant under PMI and CH). However, N_{PMI} increased 4 times more than N_{CH} . Therefore, under ρ and N working together, the MW of polymer obtained under PMI was higher than that under CH. Under the same conversion, the results were all the same, which is shown later, in Figure 7.

The T_g 's of polystyrene obtained with the two methods are listed in Table II. The T_g values under PMI and CH were very close. In addition, the results of ^{13}C -NMR spectroscopy measurement showed that the atacticity and isotacticity in the polystyrene obtained under PMI were 73.14 and 26.86%, respectively, whereas for the polystyrene under CH, they were 77.21 and 22.79%; also, the regularities of the polystyrene obtained with the two methods were also very similar. All of this proved that the physical properties and microstructure of polymer were not significantly modified by PMI.

Effect of polymerization temperature

In Figure 5, the profile of conversion with temperature is shown. In a certain polymerization time, the percentage conversions under both PMI and CH increased with the polymerization temperature. In the experimental temperature range, the conversion un-

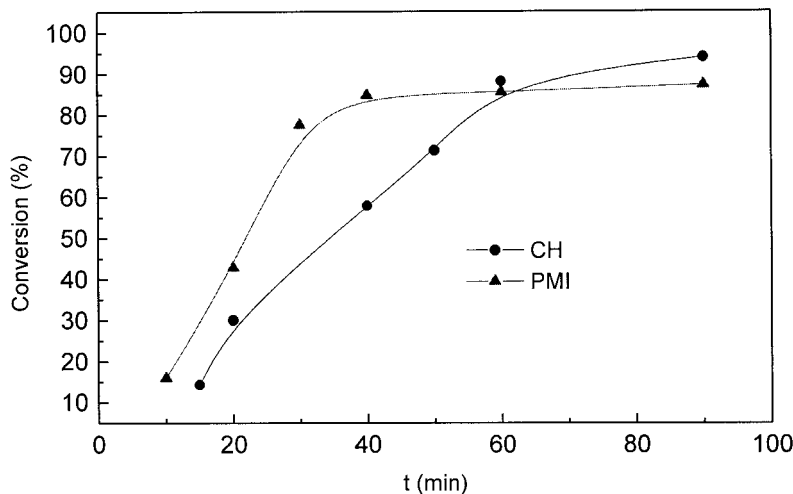


Figure 6 Conversion profile of PS with polymerization time. For PMI, power = 120 kW, pulse width = 1.5 μ s, $D = 0.01\%$, temperature = 71 \pm 2.5°C, and initiator concentration = 0.2 wt %. For CH, temperature = 72 \pm 1°C and initiator concentration = 0.2 wt %.

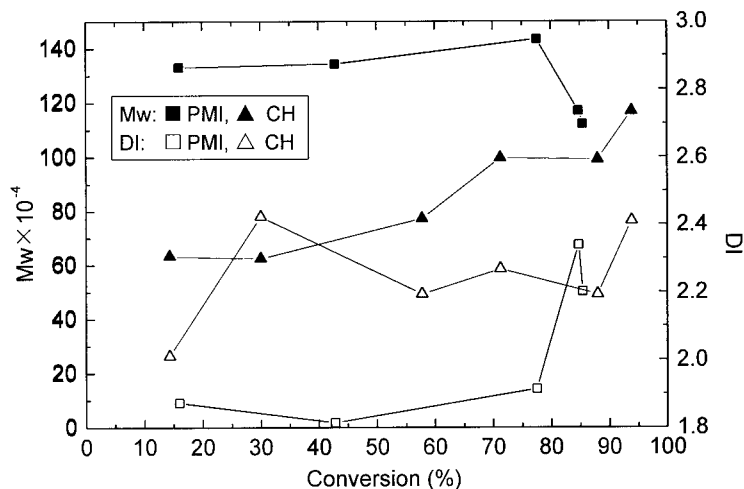


Figure 7 MW and PDI as a function of conversion. For PMI, power = 120 kW, pulse width = 1.5 μ s, $D = 0.01\%$, temperature = $71 \pm 2.5^\circ\text{C}$, and initiator concentration = 0.2 wt %. For CH, temperature = $72 \pm 1^\circ\text{C}$ and initiator concentration = 0.2 wt %.

der PMI was generally higher than that under CH. At a temperature of 60°C , the conversions under PMI and CH were 65.23 and 52.39%, respectively, whereas at a lower temperature of $50 \pm 3^\circ\text{C}$, the conversion under PMI was 17% was only 4.86% under CH. Obviously, the fact that at a lower temperature and under PMI of a mean power of 12 W for 40 min the polymerization system could reach 17% conversion proved that PMI had an evident nonthermal effect. This result was hard explain with the thermal effect of dielectric heating.

Effect of polymerization time

The conversion profiles with polymerization time are presented in Figure 6. The conversions with both of the different methods increased with polymerization

time. As shown in Figure 6, the conversion under the PMI process reached a high level in a very short time, and the curve exhibited an inflexion, indicating the occurrence of a gel effect. The MW and the molecular-weight polydispersity index (PDI) of the polymer under different conversions are shown in Figure 7. When the conversion was lower than 80%, the MW under PMI was higher than that under CH, whereas PDI under PMI was smaller. Both the MW and PDI under the two different polymerization processes were inclined to be the same along with a further increase in the conversion.

Effect of irradiation power and D

Figure 8 presents the effect of the P on the conversion. At an irradiation time (t) of 40 min, nearly linear

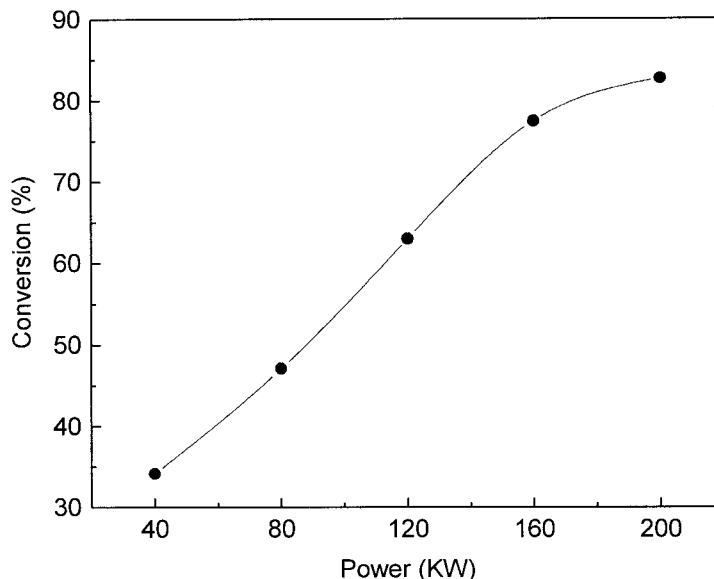


Figure 8 Conversion with pulse power: initiator concentration = 1.0 wt %, pulse width = 1.5 μ s, $D = 0.01\%$, $t = 40$ min, and temperature = $59 \pm 4^\circ\text{C}$.

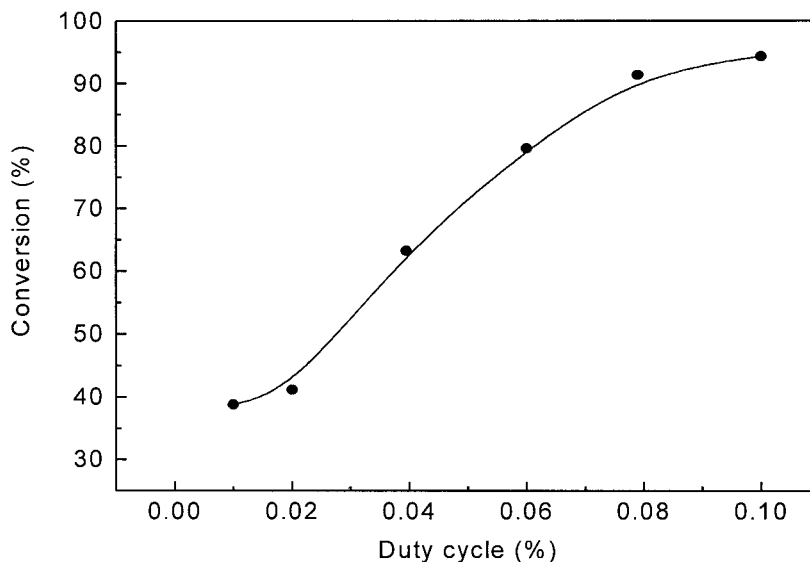


Figure 9 Conversion with D : power = 40 kW, pulse width = 1.5μ , temperature = $61 \pm 4^\circ\text{C}$, initiator concentration = 1.0 wt %, and $t = 40$ min.

behavior of the conversion versus the power was found. As P increased from 40 to 200 kW, the corresponding conversion increased from 40 to 80%; that is, when the former increased five times the latter was doubled.

The effect of D on the conversion is shown in Figure 9. The conversion at a t of 40 min also exhibited a nearly linear correlation with D . At a fixed P and pulse width, the lower pulse period was, the greater D was and the higher the energy provided by microwaves per unit time was. As D increased from 0.01 to 0.1% and the mean irradiation power increased from 4 to 40 W, the conversion increased by 1.43 times.

Effect of irradiation energy (E)

E can be expressed as

$$E = PDt \quad (4)$$

where P is peak pulse power, D is duty cycle, and t is irradiation time. Figure 10 presents the percentage conversion at different E s. It was very interesting that with the same E , the percentage conversion achieved with a lower pulse power was greater than that achieved with a higher pulse power. There seemed to be a factor of E efficiency; in other words, for the

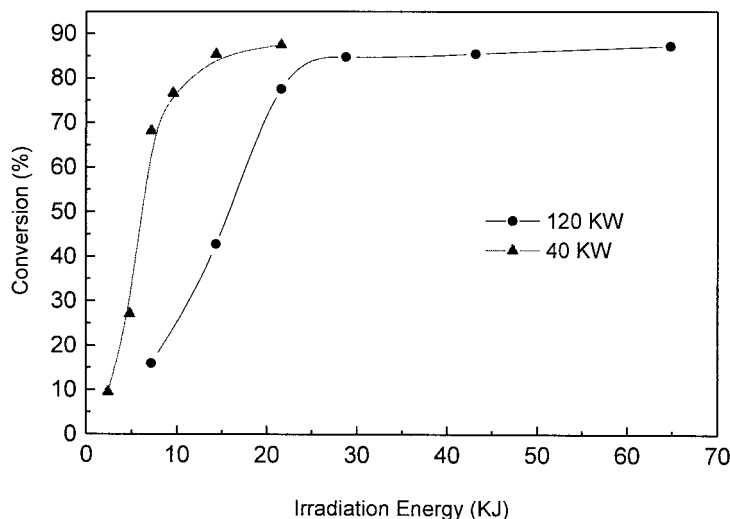


Figure 10 Conversion profile of PS with E at different powers: pulse width = 1.5μ , $D = 0.01\%$, temperature = $71 \pm 2.5^\circ\text{C}$, and initiator concentration = 0.2 wt %.

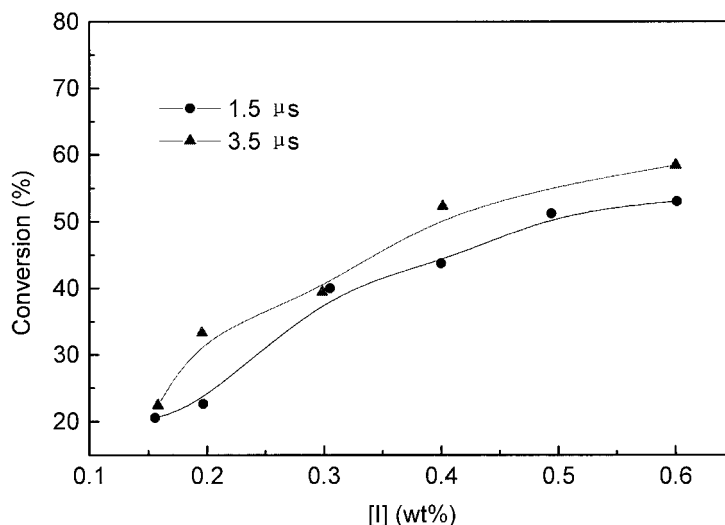


Figure 11 Conversion profile of PS with initiator concentration: power = 120 kW, $D = 0.01\%$, $t = 40$ min, and temperature = $59 \pm 4^\circ\text{C}$.

monomer conversion, E of low pulse power had a higher efficiency. As shown in Figure 10, both conversion profiles showed an inflexion, appearing at an E of 10 kJ for a power of 40 kW and at an E of 22 kJ for a power of 120 kW, respectively. After the inflexion, the conversions reached their maximum, and the polymerization was almost complete.

Effect of pulse width

At a fixed D and P , it was expected that in the same polymerization time, the energy supplied by microwave irradiation would be the same. However, in a single pulse, the duration time for which the reaction system is continuously exposed to the irradiation is different and is dependent on the pulse width: the greater the pulse width is, the longer the duration time is. This would, therefore, affect the movement state and reaction activity of the various molecules in the reaction system. In Figure 11, the effect of the initiator concentration on the conversion at two different pulse widths is shown. Under the same conditions of polymerization, the conversion at a pulse width of $3.5 \mu\text{s}$ was about 10% more than that at $1.5 \mu\text{s}$.

CONCLUSIONS

The emulsion polymerization of styrene was conducted successfully under high-power PMI. From the studies of the effects of the various parameters of PMI on the polymerization, the results indicated that PMI had a significant nonthermal effect on the emulsion polymerization, which increased the decomposition rate of KPS and the amount of particles. Consequently, the polymerization rate was effectively enhanced. The T_g and the regularity composition of the polymers

under PMI and under CH showed no difference, which indicated that PMI had little effect on the physical properties and microstructure of the polymer. In addition, irradiation power, D , E , and pulse width also had some effect on both the conversion and the MW of the polymer.

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