ELSEVIER

Chemical Engineering Journal 135 (2008) 43–48

Chemical Engineering Journal

www.elsevier.com/locate/cej

Improvement of indirect ultrasonic irradiation method for intensification of emulsion polymerization process

Daisuke Kobayashi *, Hideyuki Matsumoto, Chiaki Kuroda

Department of Chemical Engineering, Tokyo Institute of Technology, 2-12-1-S1-42, O-okayama, Meguro-ku, Tokyo 152-8550, Japan

Received 15 August 2006; received in revised form 16 March 2007; accepted 10 May 2007

Abstract

Ultrasonic generators are used as emulsifiers and as alternative initiators in polymerization processes. Styrene was polymerized under indirect ultrasonic irradiation in this study. It was thought that the effect of ultrasound on the polymerization changed over the course of the polymerization. The polymerization process was improved by changing the irradiation conditions in a manner appropriate to each stage of the polymerization.

Keywords: Indirect ultrasonic irradiation; Polystyrene; Polymerization process; Processing; Position of a reactor; Frequency; Molecular weight; Radical generation; Degradation of a polymer; Emulsification

---

1. Introduction

There is at present increasing demand for functional particles in various fields such as drug delivery. In the manufacture of polymeric particles, it is important to control both molecular weight distribution and particle size distribution. In addition, polymerization processes have been investigated using novel equipment and alternative energy sources with a view to process intensification [1,2]. Boodhoo and Jachuck have investigated the polymerization of styrene using a spinning disk reactor [3], and Price has reported polymerization by ultrasound [4].

Ultrasound is used in various applications such as medical imaging; non-destructive testing of materials; underwater ranging; welding of thermoplastics. The effects of ultrasound on chemical and biological systems have been investigated for over 75 years [5]. The advantages of ultrasound in chemical processes are the possibility of lower reaction temperature; increased kinetic reaction rates; higher yields and selectivity. Ultrasonic cavitation is well known to be the origin of these chemical advantages.

In polymerizations, ultrasonic generators are used as emulsifiers and as efficient alternative initiators. Ultrasonic polymerization allows for low surfactant concentrations and obviates chemical initiators [6,7]. This technique is therefore advantageous from the viewpoint of green sustainable chemistry, because the use of chemical substances can be reduced. Many researchers have investigated the effects of frequency, ultrasonic intensity, surfactant concentration, and temperature on polymerizations. In the polymerization of styrene, Ooi and Biggs have reported that the rate of polymerization increased as any of the abovementioned parameters increased, but the latex particle size was not affected [7]. In many such studies, an ultrasonic horn was immersed directly in the sample solution. There have been few investigations on the effects of the type of irradiation (direct/indirect) on polymerization and on the effects of reactor's position on polymerization under indirect ultrasonic irradiation.

Although Soudagar and Samant have investigated the pressure intensity distribution in an ultrasonic cleaner [8], there have been few investigations on the effect of pressure intensity distribution on chemical reactivity. It was therefore thought necessary to quantify the sonochemical effect with a view to understanding reactivity.

Koda et al. have proposed KI oxidation dosimetry using 1.0×10^{-4} mol/m^3 KI solution as a standard method to calibrate the sonochemical effects in a specific reaction system [9]. Therefore, it was thought that changes in radical generation with changing reactor's position could be qualitatively evaluated by this method.

In our previous study [10,11], we investigated the effects of steady-state ultrasonic irradiation on the polymerization of styrene and KI oxidation dosimetry. A dimensionless index incorporating the wavelength was found to be one of the

---

* Corresponding author. Tel.: +81 3 5734 2140; fax: +81 3 5734 2140.
E-mail address: dkobayas@chemeng.titech.ac.jp (D. Kobayashi).

1385-8947/$ – see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.cej.2007.05.015

Nomenclature

C_m	initial concentration of styrene monomer (wt%)
C_s	concentration of SDS (wt%)
d	distance between the transducer and the bottom of the reactor (mm)
$d+h$	distance between the transducer and the level of the sample solution (mm)
f	ultrasonic frequency (kHz)
M_n	number-average molecular weight (g/mol)
M_w	weight-average molecular weight (g/mol)
t	time interval of irradiation (min)
T	temperature in the water bath (°C)
V	sample volume (m^3)
W	output power of the ultrasonic generator (W)
x	polymer yield (%)

important factors governing chemical efficiency. Regions of low OH radical generation were seen to overlap with regions of low polymerization rate. It was deemed fruitful to investigate quantitatively the improvements that could be made in the efficiency of the polymerization by changing reactor's position. It has been considered difficult to control the molecular weight distribution, because Price has reported that ultrasound energy in ultrasonic polymerizations is expended not only in polymerization but also in polymer degradation [12].

Styrene was polymerized under indirect ultrasonic irradiation in this study. It was thought that polymer yield and molecular weight were influenced by the irradiation conditions, and that the effect of the ultrasonic energy changed over the course of the polymerization. Here, we focused on the effects of the geometric relation between reactor and ultrasonic transducer, and the dynamic process operational method, on the polymerization. At first, we investigated the effects of irradiation conditions (frequency and position of the reactor) on polymer yield and molecular weight under steady-state irradiation. Next, in order to improve polymer yield and to control molecular weight, the frequency and position of the reactor were changed with irradiation time. The purpose of this study was to examine an operational method involving variable indirect ultrasonic irradiation, by taking into account the progress of polymerization.

2. Experimental

2.1. Emulsion polymerization of styrene

Styrene monomer (99%) was washed with 10% NaOH solution to remove an inhibitor. Sodium dodecyl sulfate (SDS) and nitrogen gas were used for emulsification and deoxygenation, respectively.

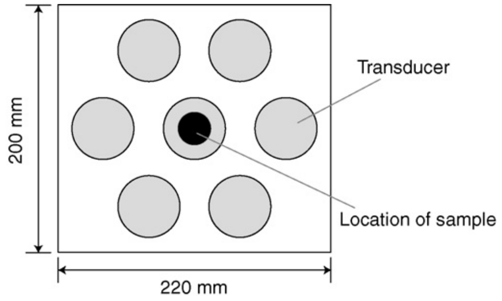

Fig. 1. The arrangement of the seven transducers in the ultrasonic generator.

Indirect ultrasonic irradiation was carried out with an ultrasonic cleaner (W-115, SMT). The frequency of the ultrasound was changed by 28, 45 and 100 kHz. In this equipment, seven ultrasonic transducers were set as shown in Fig. 1. The box with these transducers was installed in a water bath. It was thought that the reaction field was distributed in the water bath, because it has been reported that a distribution of pressure intensities existed in an ultrasonic cleaner [8]. We ourselves have noted a vertical variation in the sonochemical effects of a transducer. Next, the glass reactor was located in the center of the transducers with a variable vertical distance d of irradiation. The diameter of the ultrasonic transducer was 50 mm, and the diameter of the glass reactor was 30 mm. Glass reactor's volume was 50 mL. This whole experimental setup is illustrated schematically in Fig. 2. The temperature of the water bath was kept at 30 °C by a thermostatic flow of water. The reaction was conducted under a constant flow of nitrogen, because it has been reported that a nitrogen gas purge was necessary for the ultrasonically initiated emulsion polymerization of MMA [13].

Process variables were defined as follows: ultrasonic frequency, f; distance between the transducer and the bottom of the reactor, d; distance between the transducer and level of the sample solution, $d+h$; time interval of irradiation, t. Output power of the ultrasonic generator, W; sample volume, V; temperature of the water bath, T; concentration of SDS, C_s; initial concentration of styrene monomer, C_m, were kept constant as shown in Table 1. The ultrasonic energy in the reactor ranged from 0 to 0.71 W/cm^2 based on calorimetric measurements.

For the steady-state polymerization process, the sample solution and the rest of the reactor interior were deoxygenated by flowing nitrogen gas for 30 min at 30 °C. After deoxygenation,

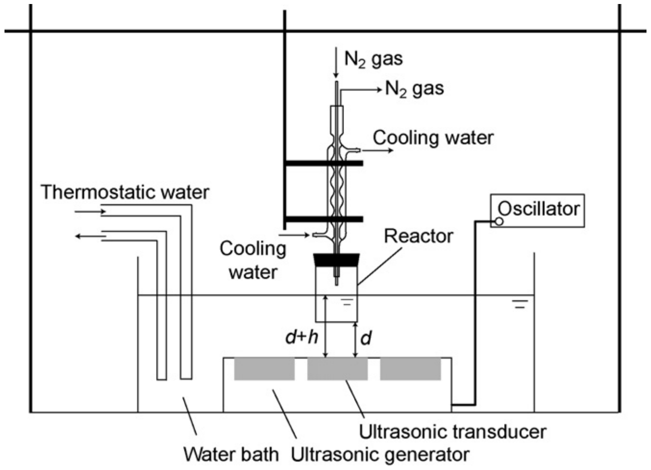

Fig. 2. Experimental setup.

Table 1
Experimental polymerization conditions

f (kHz)	28.45
W (W)	300
d (mm)	5.0–45
$d+h$ (mm)	20–60
V (m^3)	10×10^{-6}
t (min)	30–180
T (°C)	30
C_s (wt%)	1.0
C_m (wt%)	5.0

the sample was irradiated with ultrasound under a continuous flow of nitrogen gas.

2.2. Analysis

After ultrasonic irradiation, the number-average molecular weight, M_n; weight-average molecular weight, M_w; polydispersity, M_w/M_n; polymer yield, x, were analyzed using a gel permeation chromatograph (Shodex gel columns KF-806L) equipped with a UV detector (UV-1575, JASCO). THF was used as the eluent, and the flow rate was 1.0 mL/min. The instrument was calibrated with a series of polystyrene standards (SH-75, Shodex).

3. Results and discussion

3.1. Polymerization under steady-state indirect ultrasonic irradiation

Styrene monomer formed a separate layer from the water before ultrasonic irradiation, but was emulsified in the water upon irradiation, when the solution turned milky white and opaque. As the polymerization proceeded further, the solution became semi-transparent. In some cases, the monomer phase was separated from the aqueous phase, because polymerization did not progress sufficiently. In particular, polymerization did not proceed at 45 kHz, and therefore, polymerization was initially carried out at 28 kHz.

Based on the results of polymerization under steady-state irradiation conditions, two patterns of effects of reactor's position on polymer characteristics were found. One pattern corresponded to $d = 10$ and 45 mm, and the other was at $d = 20$ mm.

Fig. 3 shows the effect of t on x, and on M_w and M_n, for $d = 10$ and 45 mm. It was found that molecular weight increased with polymer yield, for $t < 120$ min. After 120 min irradiation, molecular weight decreased with t, and the polymer yield remained constant. Thus, it was thought that chain scission of the polymer by ultrasound increased after the progress of the polymerization stopped.

Fig. 4 shows the effect of t on x, M_w and M_n, for $d = 20$ mm. It was found that the molecular weight was independent of t. In addition, the molecular weight at 20 mm was greater than at $d = 10$ or 45 mm. Thus, it was thought that the fraction of ultrasound energy spent on degradation was small, and it was possible to obtain high molecular weight polymer (over 10^6 g/mol) under these conditions. However, the polymer yield at $d = 20$ mm was lower than at 10 and 45 mm.

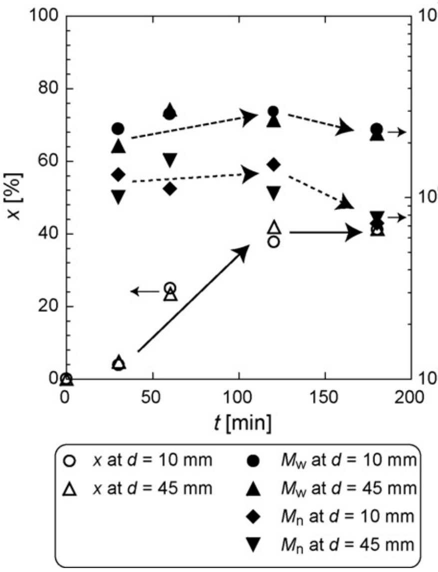

Fig. 3. The effect of t on x, M_w and M_n at $d = 10$ and 45 mm ($f = 28$ kHz).

From these results of polymerization under steady-state irradiation, it was concluded that the polymerization process could be divided into three stages. The first stage was the formation of a stable emulsion, with very little polymerization. It was surmised that most of energy of the ultrasound went towards emulsification of the monomer in water. In the second stage, the ultrasound generated radicals, which initiated polymerization. In the final stage, there was no further progress in the polymerization reaction, because the polymer yield remained constant after 120 min irradiation. Rather, the molecular weight decreased with irradiation time in this last stage, and consequently it was concluded that the ultrasound energy was expended in polymer degradation. On the other hand, the second stage was seen to overlap with the final stage. Then, it is difficult to separate process operation in these two stages.

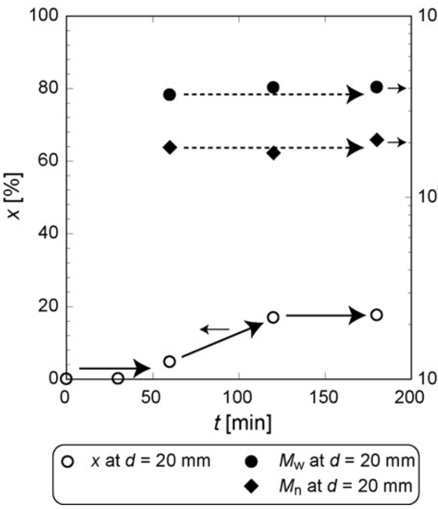

Fig. 4. The effect of t on x, M_w and M_n at $d = 20$ mm ($f = 28$ kHz).

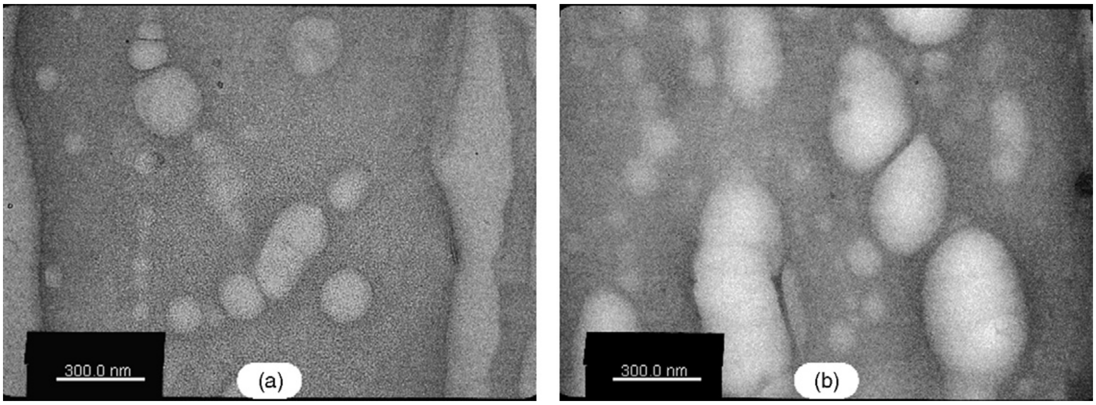

Fig. 5. Micrographs of the state of emulsification at (a) $f = 28$ kHz and (b) $f = 45$ kHz [11].

3.2. *Improvement of the indirect ultrasonic irradiation method*

It is clear from the foregoing analysis that the ultrasonic energy performed different functions over the course of the polymerization. In light of these results, variable operation of indirect ultrasonic irradiation was investigated for the purposes of intensifying the polymerization process. In order to control the ultrasonic reaction field over the course of the polymerization, the frequency and position of the reactor (d and $d + h$) were changed with irradiation time. In this study, styrene was polymerized with the division of the irradiation time into two stages, taking into account the emulsification and the effect of chain scission on the polymer, respectively.

In this study, polymerization did not take place when 45 kHz ultrasonic irradiation was used. The effects of two different frequencies, 28 and 45 kHz, on the polymerization were therefore examined. In our previous study, the effect of frequency on radical generation was investigated by KI oxidation dosimetry, and the effects of frequency on emulsification were observed using a transmission electron microscope (JEM-200CX, JEOL) [11]. The influence of frequency on radical generation was negligible, whereas its effect on emulsification was pronounced. Micrographs of the state of emulsification are shown in Fig. 5 [11]. Many spherical monomer droplets were seen at 28 kHz and many coagulated droplets at 45 kHz. The polymerization was thought to have been affected by these differences in the initial emulsion. Therefore, the frequency was changed with irradiation time in order to investigate the effects of emulsion stability on the polymerization. The process operating conditions are shown in Table 2, and characteristics of polymers obtained under these three sets of conditions are shown in Table 3.

Table 3
Characteristics of polymer (Part A)

No.	x (%)	Characteristics of polymer		
		M_w (g/mol)	M_n (g/mol)	M_w/M_n
1	4.5	2.12×10^6	9.35×10^5	2.36
2	0.0			
3	0.0			

Polymerization occurred under the first set of conditions, whereas no polymerization was observed under conditions labeled “2” and “3” in Table 2. It was therefore inferred that the formation of a stable emulsion in the initial stages was important for the polymerization.

Next, the effects of degradation in the second stage were investigated. Investigations on the polymerization under steady-state irradiation showed that polymer chain scission was more pronounced at $d = 10$ and 45 mm than at 20 mm. The position of the reactor was therefore changed with irradiation time. The process operating conditions are shown in Table 4, and characteristics of the polymers obtained under four sets of conditions are shown in Table 5.

The molecular weight under conditions “4” was larger than for conditions “7”. Thus, it was thought that molecular weight increased by attenuating the energy of polymer chain scission over the course of the polymerization. However, it was found that polymer yield was reduced under conditions “4”, because the yield was almost the same for conditions “4” and “6”. The

Table 2
Process operating conditions (Part A)

No.	Process operating conditions							
	First step				Second step			
	t (min)	f (kHz)	d (mm)	$d + h$ (mm)	t (min)	f (kHz)	d (mm)	$d + h$ (mm)
1	0–30	28	5	20	30–120	45	5	20
2	0–120	45	5	20	–	–	–	–
3	0–30	28	5	20	–	–	–	–

Table 4
Process operating conditions (Part B)

No.	Process operating conditions							
	First step				Second step			
	t (min)	f (kHz)	d (mm)	$d+h$ (mm)	t (min)	f (kHz)	d (mm)	$d+h$ (mm)
4	0–30	28	45	60	30–120	28	20	35
5	0–60	28	45	60	60–120	28	20	35
6	0–120	28	20	35	–	–	–	–
7	0–120	28	45	60	–	–	–	–

Table 5
Characteristics of polymer (Part B)

No.	x (%)	Characteristics of polymer		
		M_w (g/mol)	M_n (g/mol)	M_w/M_n
4	19.3	3.54×10^6	1.86×10^6	1.90
5	31.7	2.84×10^6	1.28×10^6	2.23
6	16.8	4.01×10^6	1.75×10^6	2.28
7	41.9	2.67×10^6	1.06×10^6	2.52

yield improved under conditions “5”, but the molecular weight was almost the same for conditions “5” and “7”.

Finally, the position of the reactor and the frequency were changed with irradiation time in order to investigate the possibility of improving the ultrasonic polymerization. Operating conditions for these processes are shown in Table 6, and characteristics of the polymers obtained under these two conditions are shown in Table 7.

Conditions “8” and “9” were the most efficient process operating conditions in this study for obtaining high molecular weight polymer.

3.3. Polymerization under variable indirect ultrasonic irradiation

The results described above indicated that the performance of ultrasonic polymerizations could be improved by changing irradiation conditions during different stages of the polymerization.

Table 7
Characteristics of polymer (Part C)

No.	x (%)	Characteristics of polymer		
		M_w (g/mol)	M_n (g/mol)	M_w/M_n
8	17.7	3.50×10^6	1.60×10^6	2.19
9	11.9	3.29×10^6	1.50×10^6	2.23

The effect of reactor’s position on OH radical generation was investigated using KI oxidation dosimetry. When a KI solution is irradiated with ultrasound, I^- ions are oxidized to I_2, which reacts with excess I^- in solution to form $I_3{}^-$ ions. The absorbance of I^- at 355 nm was measured using a UV–vis spectrometer. KI oxidation dosimetry indicated that the $I_3{}^-$ absorbance $d = 10$ and 45 mm was greater than at 20 mm. Therefore, because of the position of the reactor in the first stage, the ultrasound generated a high concentration of radicals, resulting in improved polymer yield. Next, because the reactor’s position in the second step led to reduced-chain scission by ultrasound irradiation, the resulting molecular weight was high. Thus the overall polymer yield could be improved and the molecular weight could be controlled by varying the irradiation time in the first step and the reactor’s position in the second step.

Thus, introducing dynamic changes in the process operating method (changing irradiation conditions over the course of the polymerization) was a useful method for intensifying an emulsion polymerization process. In the future, the effects of irradiation conditions (frequency and reactor’s position) on emulsification and degradation will be investigated in detail, with a focus on developing an efficient process for producing high molecular weight polymer.

4. Conclusions

The polymer yield and molecular weight in a polymerization carried out under indirect ultrasonic irradiation were influenced by frequency and reactor’s position. The ultrasonic irradiation process was divided into three stages, and the effects of the ultrasonic energy on the reaction changed over the course of the polymerization. Polymer yield was improved by changing frequency and reactor’s position with irradiation time in two stages, with the formation of a stable emulsion in the first stage. The con-

Table 6
Process operating conditions (Part C)

No.	Process operating conditions							
	First step				Second step			
	t (min)	f (kHz)	d (mm)	$d+h$ (mm)	t (min)	f (kHz)	d (mm)	$d+h$ (mm)
8	0–30	28	10	25	30–60	45	20	35
9	0–30	28	45	60	30–60	45	20	35

trol of molecular weight was achieved by changing the reactor's position with irradiation in two stages, maintaining low chain scission energy in the second stage. The dynamic process operating method (changing irradiation conditions over the course of the polymerization) was an efficient means of intensifying the emulsion polymerization process.

Acknowledgements

This research was supported in part by a Grant-in-Aid for Scientific Research (No. 17206079) from the Ministry of Education, Culture, Sports, Science and Technology, Japan and also in part by a 21st Century COE program "Creation of Molecular Diversity and Development of Functionalities".

References

[1] A.I. Stankiewicz, J.A. Moulijn, Process intensification: transforming chemical engineering, Chem. Eng. Prog. 96 (2000) 22–34.
[2] C. Tsouris, J.V. Porcelli, Process intensification—has its time finally come? Chem. Eng. Prog. 99 (2000) 50–55.
[3] K.V.K. Boodhoo, R.J. Jachuck, Process intensification: spinning disk reactor for styrene polymerization, Appl. Thermal Eng. 20 (2000) 1127–1146.
[4] G.J. Price, Recent developments in sonochemical polymerisation, Ultrason. Sonochem. 10 (2003) 277–283.
[5] S.V. Ley, C.M.R. Low, Ultrasound in Synthesis, Springer-Verlag, Berlin, 1989.
[6] S. Biggs, F. Grieser, Preparation of polystyrene latex with ultrasonic initiation, Macromolecules 28 (1995) 4877–4882.
[7] S.K. Ooi, S. Biggs, Ultrasonic initiation of polystyrene latex synthesis, Ultrason. Sonochem. 7 (2000) 125–133.
[8] S.R. Soudagar, S.D. Samant, Semiquantitative characterization of ultrasonic cleaner using a novel piezoelectric pressure intensity measurement probe, Ultrason. Sonochem. 2 (1995) S49–S53.
[9] S. Koda, T. Kimura, T. Kondo, H. Mitome, A standard method to calibrate sonochemical efficiency of an individual reaction system, Ultrason. Sonochem. 10 (2003) 149–156.
[10] D. Kobayashi, H. Matsumoto, C. Kuroda, Indirect ultrasonic irradiation in polymerization of styrene, in: Proceedings of the 7th World Congress of Chemical Engineering, vol. C9-006, 2005, pp. 1–10.
[11] D. Kobayashi, H. Matsumoto, C. Kuroda, Emulsion Polymerization of Styrene under Indirect Ultrasonic irradiation, vol. 332, Kagaku Kogaku Ronbunshu, Japanese, 2006, pp. 88–92.
[12] G.J. Price, Ultrasonically enhanced polymer synthesis, Ultrason. Sonochem. 3 (1996) S229–S238.
[13] Y. Liao, Q. Wang, H. Xia, X. Xu, S.M. Baxter, R.V. Slone, S. Wu, G. Swift, D.G. Westmoreland, Ultrasonically initiated emulsion polymerization of methyl methacrylate, J. Polym. Sci. Part A 39 (2001) 3356–3364.