Free Radical Polymerization of Butyl Acrylate in Monodispersed Droplets: Comparison Between Two Heating Strategies

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ABSTRACT: Monodispersed droplets could be easily generated in coaxial microdevice, and a reaction based upon these discrete droplets is an attractive approach thanks to isolated reaction units, efficient mixing, and precise residence time control. In this work, free radical polymerization of butyl acrylate was conducted in monodispersed droplets of several hundred microns. Two different heating methodologies, microwave heating and conventional heating with oil bath were adopted to initiate polymerization, respectively. The polymerization under conventional heating could be regarded as an isothermal process, while the polymerization under microwave heating gradually underwent a temperature increase. So the poly (butyl acrylate) obtained by microwave heating has larger average molecular weight and higher polydispersity index. Meanwhile, the conversion of butyl acrylate was significantly improved by microwave heating compared with conventional heating, even though the reaction temperature under microwave heating might be lower than the temperature of the oil bath. This remarkable enhancement was a direct proof of the nonthermal effect of the microwave field for free radical polymerization. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

INTRODUCTION

Droplet-based technology has for decades been a powerful tool to perform reactions and make analysis for chemists and biologists.[1,2] But only with the advent of microfluidics technologies in more recent years, reaction in droplets have regained its vitality and obtained broad investigation.[3–5] In microfluidics devices, versatile methods for preparation of droplets could be realized through the use of T-junctions,[6–9] flow focusing geometries,[10,11] and coaxial microdevices.[12,13] Different from droplet generation in conventional bulk reactors where turbulence dominates the flow state, formation of droplets in microfluidic devices is controlled by combined action between surface tension and sheath force.[14,15] This new generation mechanism endows microfluidics systems to conveniently, efficiently and controllably generate droplets that are highly uniform in size and chemical composition. In addition, the discrete droplets flow with the continuous phase is very effective to eliminate the residence time distribution. So monodispersed droplets generated by microfluidics technologies could provide a promising platform for chemical or biological processes investigation and development. In literatures, applications of microfluidics-based monodispersed droplets have been successfully attempted for the synthesis of organic molecules,[16,17] nanoparticles preparation,[18,19] protein crystallization,[20,21] as well as data acquisition in chemical kinetics.[22,23]

In polymer industry, free radical polymerization is the most widely used commercial process to produce polymers with high molecular weight, which can be applied to almost all vinyl monomers under mild reaction conditions over a wide temperature range.[24] However, free radical polymerization also bears conspicuous drawback of poor control on process and product in conventional macroscale reactors due to large amount heat released, severe variation in viscosity and diffusion controlled termination mechanism.[25,26] Heating is commonly used for initiating the free radical polymerization. For conventional heating method, polymerization temperature having critical influence on the molecular weight of product should be higher than the thermal decomposition temperature of initiator. The thermal decomposition of initiator being usually slower than the chain propagation may lead to nonuniform chain propagation with polymerization proceeding. As an alternative heating method, microwave heating has been widely used in many technical applications in chemical and related industries, in particular like

Additional Supporting Information may be found in the online version of this article.

food-processing,[27,28] drying,[29] and organic synthesis.[30–32] Different from conventional heating that transports heat from high-temperature place to low-temperature place through conduction-convection mechanism, microwave transforms electromagnetic energy into thermal energy through the internal friction between polar molecules undergoing perpetual reorientation cycles with high frequency. So, microwave heating has several advantages over conventional heating such as instantaneous and rapid bulk heating, noncontact heating, selective heating and energy saving. Because of these advantages, microwave-assisted chemical reactions have been intensively investigated for the purpose of reducing processing time, saving energy consumption and improve selectivity. Moreover, some reactions that cannot be realized through conventional heating were reported to be successfully performed under microwave radiation.[33] Specific to its application in polymer synthesis, microwave-assisted polymerization has been found exhibiting spectacular improvements like decreasing polymerization time,[34,35] providing structural control[36,37] and prompt polymerization successfully without inert gas protection.[38]

The reasons for outstanding enhancements observed in microwave-assisted reaction have been intensively investigated in recent years.[39–41] Generally, two groups of theories, so called "thermal effect" and "nonthermal effect" (also called "specific microwave effect") respectively, are used to explain the acceleration of reaction rate under microwave radiation. The first group considers that the microwave radiation does not change the kinetics and mechanism of the reactions, and the reduction of the reaction time is due to a sudden and uncontrollable temperature rise of the reaction medium under microwave radiation.[42–44] Otherwise, proponents of nonthermal effect suggest that rate increase for microwave assisted reactions could not be adequately explained by temperature. They propose that microwave has direct interaction with reaction medium, including reactant or product molecules, and eventually changes the kinetic or thermodynamic parameters of the reaction. Based on the Arrhenius reaction rate equation, some researchers speculated that microwave field can lead to an increase in molecular vibration and hence in the Arrhenius preexponential factor A.[41,45] Meanwhile, a decrease in the activate free energy promoted by microwave irradiation was also suggested.[46–48] However, a major difficulty in temperature measurement of the reaction medium under microwave radiation hinders to clearly reveal the existence of nonthermal effect.[49] For one thing, experiments in most published works were conducted in bulk vessels. Under microwave radiation, it is hardly possible to maintain uniform temperature profile in the vessels as microwave decays within the reaction medium exponentially. For another, most of temperature sensors used in microwave reactor including shielded thermocouple, IR-sensor and fiber optics cannot detect the temperature distribution within the reaction medium. The magnetic resonance imaging (MRI) adopted to map temperature in three dimensions is not possible to use directly inside the metallic microwave cavity.[50,51] Because of these limitations, temperature measurement in microwave reactor through current approaches could not accurately represent the actual temperature within the reaction medium, and those experimental data obtained under these conditions were not sufficient to understand the reaction performance in details.

Combination of microwave heating and microfluidic system has created considerable interest in recent years. It enables continuous flow processing and addresses problems in microwave-assisted synthesis stemmed from limited penetration depth of microwave irradiation into absorbing materials. Several publications describing this combined technology have shown significant improvements including reaction rate acceleration and catalytic activity increasing.[52,53] In further, the excellent controlling on temperature and residence time of monodispersed microdroplets generated by microfluidics devices may provide in-depth insight into the characteristics of microwave heating.

To our knowledge, microwave-induced miniemulsion polymerization performed in droplets has already been reported,[54] but these droplets therein had distributed size and residence time due to the generation mechanism of mechanic stirring. In this work, we prepared highly uniform flowing butyl acrylate (BA) droplets of several hundred microns as ideal polymerization units with precise temperature and residence time control, and presented free radical polymerization of BA initiated by conventional heating and microwave heating, respectively. Based on the easy-to-reach local temperature within the droplets, the effect of microwave on the free radical polymerization was investigated and discussed by comparing the properties of the products like molecular weight and molecular weight distribution.

EXPERIMENTAL SETUP AND PROCEDURES

Materials

Butyl acrylate (BA), 2,2-azobis(isobutylronitrile)(AIBN), sodium dodecyl sulfate (SDS), polyvinyl alcohol (PVA), sodium hydrate (NaOH), and sodium sulfate (Na_2SO_4) were of analytical grade. BA and AIBN were obtained from Sinopharm Chemical Reagent (Beijing, China) and TongGuang Fine Chemicals Company (Beijing, China), respectively. Other chemicals were all from Beijing Chemical Works (China). To remove inhibitor, BA was washed with 1 M NaOH three times, washed with water three times, and dried with Na_2SO_4. Before use, BA monomer and water were stripped with N_2 to remove dissolved O_2 for at least 1 h. Other materials were used as obtained commercially.

Droplet Generation in Microreactor

Microdroplets were prepared by homemade coaxial capillary microreactor. Figure 1 shows the scheme of the coaxial capillary microreactor. A quartz capillary was inserted as the main channel for introducing continuous phase and providing reaction space, while another thinner quartz capillary was coaxially inserted inside the outer capillary as the dispersed phase flow channel. The outer and inner diameter of the main channel was 0.70 and 0.53 mm, respectively; and, the outer and inner diameter of the inserted channel was 0.29 and 0.19 mm, respectively. Two gastight syringe needles were inserted from each side of the PMMA substrate as continuous phase inlets. The fabrication method of the device can be found in elsewhere.[55]

BA monomer with certain ratio of AIBN (0.8%, mole ratio based on monomer) was used as the dispersed phase. Water containing surfactants and stabilizer (SDS, 0.5 wt %; PVA, 0.5 wt %; Na_2SO_4, 0.3 wt %) was used as the continuous phase.
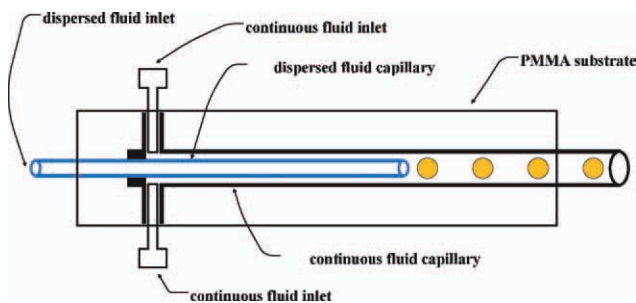
Figure 1. Scheme of coaxial capillary microreactor. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

All the operational conditions in this work allowed that experiments carried out in the uniform droplet flow regime, as shown in Figure 2.

Polymerization Using Different Heating Strategies
Figure 3 shows the sketch map of the experimental procedures for polymerization. The BA monomer solution was first dispersed into uniform droplets by the sheath focusing of water phase flow from the two side channels. After the droplet flow was generated in the coaxial microdevice, one of two heating tools—oil bath and microwave reactor—was used to provide initiation condition for butyl acrylate polymerization in subsequent quartz capillary tube. The residence time was determined by the ratio of capillary tube length in the oil bath or microwave reactor and the total flowrate of two phases. After the polymerization was processed for a certain reaction time, the flow passed through a cold water bath to stop polymerization. The product collected at the end of the capillary was washed and dried under vacuum to remove monomer and water. Because of uniform droplet size, fast heat transfer and stable flow pattern, polymerization conducted in these ideal nanoliter reactors can exhibit high reproducibility.[56] This polymerization set-up therefore can be stably operated regardless of the heating method, enabling reliable comparison between experimental results obtained under both heating strategies.

Description of Microwave Reactor and Temperature Evaluation Procedure
In this work, a multimode microwave reactor (XO-50A, Nanjing SINOTECH, China) was used, which has the following specifications: cavity volume, 23.18 dm^3; dimensions, 28 cm × 36 cm × 23 cm ($W \times L \times H$); microwave frequency, 2450 MHz; output power, 0–800 W, adjustable. As the electromagnetic field in the multimode microwave reactor distributes nonuniformly, a supported stand made by polytetrafluoroethylene (PTFE, Teflon)

was used to ensure that the quartz capillary tube stayed in the same place of the cavity throughout all the experiments.

We used a Pt-100 thermocouple with an accuracy of ±0.01°C to measure the temperature of continuous water phase flowing out of the microwave cavity. A calibration procedure conducted in oil bath (see Supporting Information) was adopted to compensate the heat loss between temperature measuring point and the outlet of the microwave cavity and determine the temperature of the latter. Because the temperature of continuous phase increases along the capillary in general, the temperature at the outlet of microwave cavity is approximately the upper value within the whole capillary tube.

Analysis
GPC analysis was carried out on Waters-515 gel permeation chromatograph equipped with an RI detector. The molecular weight (M_n) and the polydispersity index (PDI, referred as M_w/M_n) of synthesized polymers were determined at 40°C in THF using polystyrene standard samples for calibration.

The conversion was measured by gravimetrical method. The weight of monomer was calculated according to operating duration and the set flowrate of the monomer pump. The weight of final polymer product was obtained by collecting the final polymer product within the same time duration and weighing. Before weighing, the product was washed and dried under vacuum to remove monomer and water. The conversion for each experimental run was characterized in triplicate.

RESULTS AND DISCUSSIONS
Thermal Condition of Polymerization Process
In this work, the average droplet size generated in the capillary of I.D. 530 μm was about 360 μm, and the distance between droplets was larger than 2200 μm. Under conventional heating in a thermostat bath, a CFD simulation in our previous work has proved that in such cases the temperature of reaction system reaches100°C (oil bath temperature) within 1 s and the highest temperature during the polymerization is 101°C, indicating that the polymerization under conventional heating almost undergoes an isothermal process.[56] On the contrary, the microwave can heat the medium consistently, so the temperature of medium under microwave heating increases with the radiation time increasing until vaporization. Compared with water, butyl acrylate droplet has higher boiling point and rather weaker thermal effect than water under microwave radiation (the relative permittivity of water at 293 K is 80.1, and butyl acrylate about 5.3). It is easier for the continuous phase to vaporize in experiments. As the vaporization will destroy the stable
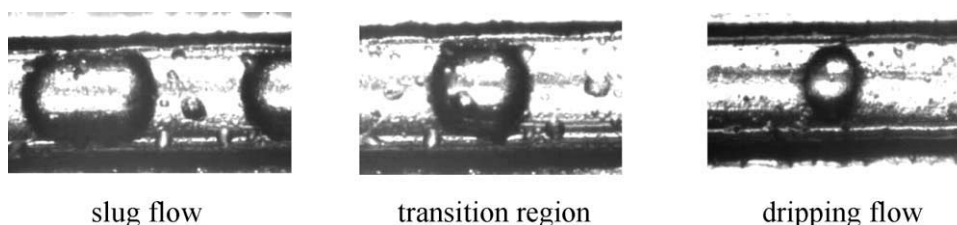
Figure 2. Different flow patterns in capillary tube.
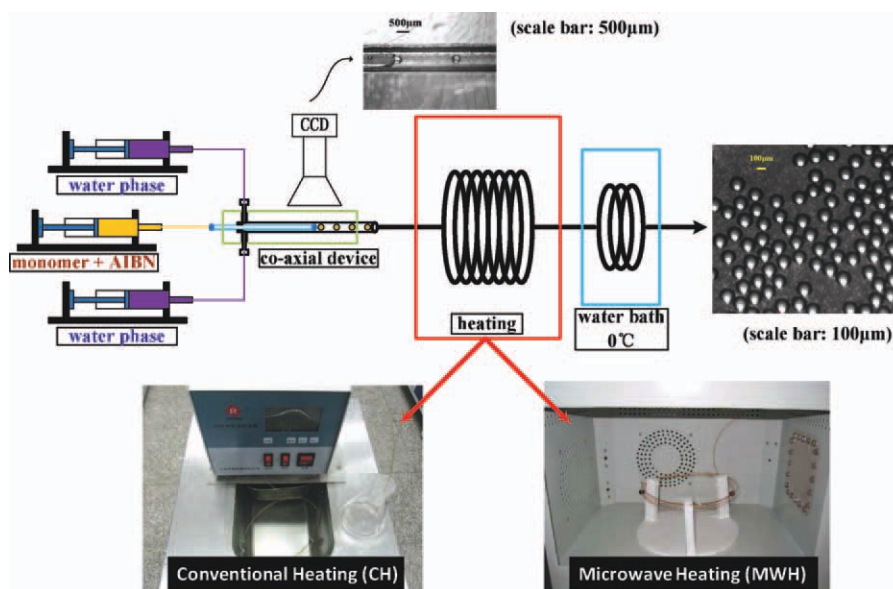
Figure 3. Outline of experimental procedure for polymerization under conventional heating (CH) and microwave heating (MWH). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

droplet flow, the microwave power has to be controlled at a low level to avoid vaporization within microwave reactor. Thus, for a continuous process operated in microwave cavity, the polymerization undergoes a nonisothermal process that the temperature of reaction system increases gradually from the inlet to the outlet, always below the vaporization temperature. However, the temperature within BA droplet was nearly uniform and identical with that of the continuous phase surrounded. Table I shows the experimental conditions and results under microwave heating. The increasing of microwave power can increase the outlet temperature. The increasing of reaction time has the same effect.
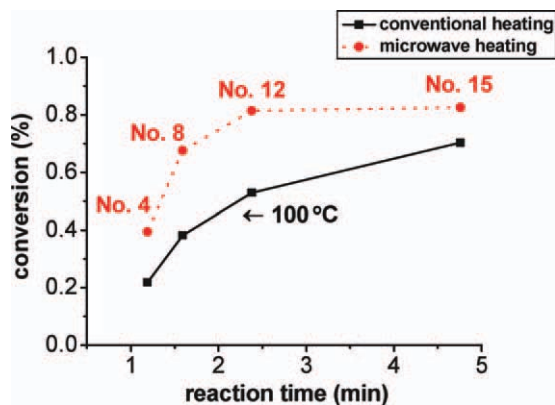
Conversion

Under a certain microwave power, increasing radiation time can lead to higher conversion of BA (for example, comparing conversion of BA between No. 1, No. 5, No. 10, and No. 15 in Table I). Meantime, evaluated outlet temperature shared the same trend that it also increased with radiation time. For the same radiation time, the conversion of BA depended on the microwave power. The increasing of output microwave power that certainly leads to higher water temperature results in higher conversion of BA as well. Obviously, increasing the temperature of continuous phase contributed to faster conversion of

Table I. Experimental Results for Polymerization Under Microwave Heating (MWH)

No.	Radiation time (s)	MW power (W)	Conversion of BA (%)	M_n	PDI	Evaluated outlet temperature[a] (°C)
1	1.19	130	0	NA[b]	NA	66.9
2		150	1.51	NA	NA	75.5
3		170	13.5	338067	2.69	86.4
4		190	39.43	219231	2.72	89.3
5	1.59	130	2.22	NA	NA	68.2
6		150	11.96	242931	2.89	81.8
7		170	54.94	234899	3.34	89.1
8		190	67.53	219535	3.07	91.3
9	2.38	110	3.65	NA	NA	58.7
10		130	11.96	268988	2.96	72.4
11		150	77.58	245933	3.53	89.7
12		170	81.4	227068	3.31	94.5
13	4.76	90	10.07	230883	3.44	87.9
14		110	18.46	218343	3.63	92.7
15		130	82.53	206440	3.31	94.6

[a]The procedure for temperature evaluation was described in Description of Microwave Reactor and Temperature Evaluation Procedure section., [b]NA means not analyzed.
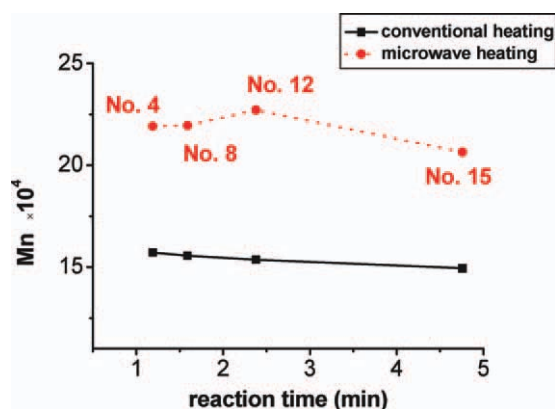
Figure 4. Comparison of conversion of BA between conventional heating (CH) and microwave heating (MWH). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

monomer to polymer. However, it is not enough to conclude that temperature rise is the sole reason, since a nonthermal effect of microwave radiation might be exist and improve BA conversion as well.

For a certain radiation time, an upper limit of microwave power was detected through CCD camera according to the stability of flow pattern. Correspondingly, the highest conversion of BA was determined for the each radiation time (like No. 4, No. 8, No. 12, and No. 15).

Whether the polymerization rate of microwave-assisted polymerization compared with conventionally heated polymerization was improved is the first thing the researchers concern. In Figure 4, conversion data obtained under upper limit microwave power for each radiation time were compared with those obtained in 100°C oil bath environment. As seen, conversion of BA was significantly improved under microwave radiation.

This result really deserves attention. It is worthy to point out that even under microwave radiation of upper limit power the outlet temperature of continuous phase was under 100°C, meaning that the average temperature of water that encompasses the BA droplet was far lower than 100°C. Because the

water temperature under conventional heating was kept constant at 100°C, the enhancement of BA polymerization seems unexplainable under microwave radiation if microwave heating has only thermal effect. Actually, the significant improvements were not only specific to conditions under upper limit microwave power. Conversion for experiments of No. 3, No 7, and No. 11 in Table I were also higher than their counterpart experiments in 100°C oil bath. These phenomena are thought to be solid evidences for the nonthermal effect of microwave in free radial polymerization.

Molecular Weight and Molecular Weight Distribution

Comparison of molecular weight of obtained PBA corresponding to Figure 4 between conventional heating and microwave heating was shown in Figure 5. As seen, the molecular weight of PBA under microwave radiation was in general higher than that of PBA produced in oil bath. As reported, molecular weight of polymer has key relationship with polymerization temperature for free radial polymerization. At other conditions like concentrations of monomer and initiator kept the same, higher molecular weight means lower polymerization temperature. So, through comparison in Figure 5, it is inferred that the polymerization of BA droplets under microwave heating carries out in a lower temperature than that under conventional heating. This result in return is another evidence to support the existence of nonthermal microwave effect, as it demonstrates that the actual polymerization temperature of BA droplet in microwave heating was indeed lower than the polymerization temperature under conventional heating.

Comparison of polydispersity indices (PDI) of obtained PBA between conventional heating and microwave heating was also made. As seen in Figure 6, the PDIs in microwave heating condition were much higher than those in conventional heating condition. The reason for this difference is obvious. As discussed above, conventionally heated polymerization is an isothermal process, whereas microwave-assisted polymerization is a nonisothermal process. In our previous work,[56] it was demonstrated that heat transfer within the droplets had the key influence on the molecular weight distribution of the final poly
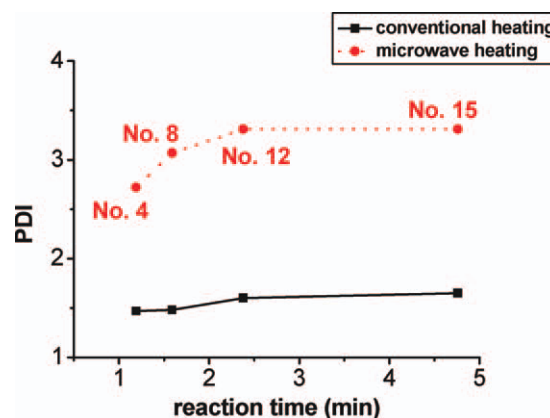

Figure 5. Comparison of molecular weight of obtained PBA between conventional heating (CH) and microwave heating (MWH). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 6. Comparison of PDI of obtained PBA between conventional heating (CH) and microwave heating (MWH). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

(butyl acrylate), and more uniform temperature distribution within the droplets could bring narrower molecular weight distribution and hence smaller value of PDI. Considering the whole polymerization process under microwave radiation, the temperature of BA droplet varies along the capillary. As a consequence, wider profile of temperature generates broader the molecular weight distribution.

The Initiator Decomposition

Through above comparisons, it is still not easy to elucidate the reason why the rate for microwave-assisted polymerization of butyl acrylate was enhanced. In literatures, effect of microwave radiation on kinetics of radical initiator like potassium persulfate has been reported, and the result showed that decomposition rate of initiator was increased under microwave radiation.[57,58] So, in this work, to further investigate this phenomenon, decomposition kinetics of AIBN in droplet flow under two different heating strategies was studied as well. According to earlier publications,[59] the decomposition kinetics of AIBN was independent from the choice of solvent. So in the experiments, butyl acrylate was replaced by toluene as the inner phase to eliminate the effect of polymerization reaction. Besides, with regard to dielectric property, toluene is of the same level as butyl acrylate, which ensures that no conspicuous microwave thermal effect of toluene could influence the decomposition of AIBN. All other operational conditions like flow rates, microwave output power and initial AIBN concentration etc. were kept the same as polymerization experiments. The concentration of AIBN in toluene was analyzed by optical method, which was already described in detail elsewhere.[59]

Figure 7 shows the result for decomposition of AIBN under different heating methods. For one thing, as seen, both of decomposition rates obtained in our experiments were faster than decomposition rate in reported reference, which is possible due to that in our experiments, AIBN in toluene droplets were encircled by water as the continuous phase and AIBN has slight solubility in water. For another, and also the key point, decomposition rate of AIBN under microwave radiation was faster than that in oil bath heating. Because of the difficulty in conducting isothermal experiments in microwave heating environment, comprehensive kinetic investigation of AIBN decomposition is still a tough task and beyond the scope of this work. Although in what a way that microwave influences the decomposition of AIBN is still unclear, one possible reason the authors inferred to be responsible to this enhancement is that under high-frequency electromagnetic oscillation the diffusion of chemical species in AIBN decomposition reaction was increased and hence accelerate the overall decomposition rate.

Nevertheless, results of AIBN decomposition experiments in Figure 7 could successfully interpret the significant enhancement of microwave-assisted polymerization of butyl acrylate in Figure 5. For free radical polymerization, chain initiation is the rate-determining step; while chain propagation and chain termination are both fast chemical processes. The chain initiation rate lies on initiator decomposition rate. So, significant improvement of BA conversion under microwave radiation could be ascribed to the fact that the decomposition rate of initiator was acceler-
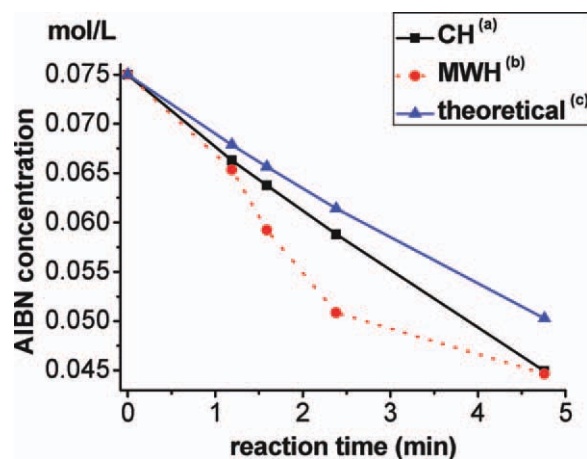
Figure 7. Results for decomposition of AIBN under different heating strategies. (a) conventional heating (CH) under constant temperature of 100°C; (b) microwave heating, reaction conditions for the four points in this figure corresponds to the points in Figure 5; (c) residual concentration of AIBN under 100°C calculated theoretically; the kinetics data for AIBN decomposition were from Ref. 59. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

ated through microwave heating method. Anyway, as discussed above, purely thermal effect of microwave radiation is not satisfied to interpret our experimental result. Through simply designed experiments in droplet, our result could provide creditable evidence in demonstration the existence of nonthermal microwave effect on free radical polymerization.

CONCLUSION

A coaxial capillary microreactor was used to prepare monodispersed droplets of several hundred microns in diameter. Advantages of experiments implemented in microfluidics-based droplets like remarkable heat transfer efficiency and precise residence time control enable them to be ideal polymerization units. Free radical polymerization of butyl acrylate was conducted in these droplets with two heating strategies—conventional heating and microwave heating to initiate polymerization, respectively. Characteristics of both heating strategies on free radical polymerization and their difference were reliably revealed.

Conventionally heated polymerization of butyl acrylate in monodispersed microdroplets undergoes an approximate an isothermal process due to good heat transfer performance and thermostat surrounding environment. Poly (butyl acrylate) with narrow molecular weight distribution can be obtained by this process. On the contrary, microwave-radiated polymerization in droplet flow was a nonisothermal process that temperature within the droplet varied consistently. For a certain radiation time, the microwave power has an upper limit, exceeding which the continuous phase water can vaporize and destroy stable flow pattern. Also due to the nonisothermal characteristics, the obtained polymer had broader the molecular weight distribution (the polydispersity indices are generally above 3).

Under the same polymerization time microwave assisted polymerization of butyl acrylate could reach higher conversion level

than can conventionally heated polymerization, though the temperature of polymerization system under microwave radiation was lower than that in 100°C oil bath. It reveals the existence of microwave nonthermal effect solidly. The promotion of microwave radiation on the decomposition rate of AIBN is verified by experiments to be responsible to the conspicuous enhancement in microwave-assisted polymerization of butyl acrylate somehow. The comprehensive kinetics of AIBN decomposition under microwave radiation and the mechanism of the nonthermal effect are still unclear and need further investigation.

ACKNOWLEDGMENTS

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