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RATRP of MMA in AIBN/$FeCl_3$/PPh_3 initiation system under microwave irradiation

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Summary

Reverse atom transfer radical polymerization (RATRP) of methyl methacrylate (MMA) under microwave irradiation (MI), using azobisisobutyronitrile (AIBN) /$FeCl_3$/triphenylphosphine (PPh_3) as the initiating system, was successfully carried out in N, N-dimethylformamide (DMF) at 69°C. Plots of ln ($[M]_0/[M]$) vs. time and molecular weight evolution vs. conversion showed a linear dependence. A polymer for reaching 82% conversion, with molecular weight (M_n) 34,000 and polydispersity index (PDI) 1.37, was obtained under MI (90W) with the ratio of $[MMA]_0/[AIBN]_0/[FeCl_3]_0/[PPh_3]_0$ = 1600/2/4/8 in only 60 min; while 840 min was required under conventional heating (CH) process for reaching 82 % conversion (M_n = 48,000 and PDI = 1.31) at identical polymerization conditions, indicating a significant enhancement of the polymerization rates and apparent initiator efficiencies under MI.

Key words: reverse atom transfer radical polymerization (RATRP); microwave irradiation; methyl methacrylate; living polymerization; iron-catalyzed polymerization

Introduction

Recently, the transition-metal-catalyzed atom transfer radical polymerization (ATRP) of vinyl monomers has been introduced as a versatile chemistry enabling the synthesis of a wide range of tailor-made polymers with predetermined degrees of polymerization and narrow polydispersities [1- 4].

ATRP of MMA has been widely investigated using a large variety of transition metal compounds as catalyst: Cu(I) [5]; Ru(II) [1,6]; Ni(I) [7]; Rh(II) [8] systems. It has been reported that the PMMA with well-controlled molecular weights and narrow molecular weight distributions could be obtained with iron-based catalyst systems that is RX/$FeCl_2$/PPh_3 [9], RX/$FeBr_2$/dNbipy [4,4′-bis(5-nonyl)-2,2′-bipyridine] or $N(nBu)_3$ [10].

Though the above-mentioned direct ATRP method is an efficient way to maintain living/controlled radical polymerization of various vinyl monomers, this type of ATRP suffers two major drawbacks: firstly, the use of a halide species RX, which often is toxic or not easily handled or obtained; secondly, the oxidation of the catalyst by the oxygen included in air. To circumvent this problem, alternative/reverse ATRP was introduced [11-13] and a well-controlled polymerization was observed although often with low initiator

efficiencies. Teyssié [12] reported that the AIBN (azobisisobutyronitrile) /$FeCl_3$/PPh_3 (triphenylphosphine) system could be used for the synthesis of well-defined PMMA in bulk and solution polymerization of MMA, but a higher polymerization temperature (85°C) was used. If the polymerization was conducted at a lower temperature (i.e., below 70°C), some additional measures should be taken to keep a higher rate of polymerization.
Microwaves, as a peculiar source of energy, have been widely applied to enhance chemical reactions [14-15]. The reported results have shown that, in comparison with conventional heating (CH) process, polymerization under microwave irradiation (MI) has the advantages of higher reaction rates and greater polymer yields within a shorter period of time; therefore microwave irradiation may act as the additional measures mentioned above.
In this work, we introduced microwaves into RATRP system, and report the solution RATRP of methyl methacrylate (MMA) in N, N-dimethylformamide (DMF) under self-improved domestic microwave oven irradiation with an initiating system of AIBN/$FeCl_3$/PPh_3. With the help of dielectric heating and "no-thermal effect" [16,17] provided by MI, the reactivities of polymerization system may be raised, the polymerization rate was then promoted, which allows reaction to be conducted at a lower temperature.

Experimental

Apparatus

The self-improved domestic microwave oven, M9D88 SANSUNG, was used. Microwave irradiation power is from 90W to 900W. The reactor is a two-neck bottle (500ml) with refluxing solvent used for controlling the reaction temperature. The dry sealed glass tube filled with reaction mixture was placed into the refluxing solvent to let polymerization take place.

Materials

Methyl methacrylate (MMA) (chemically pure; Shanghai Chemical Reagent Co., LtD.) was purified by extracting with 5% sodium hydroxide aqueous solution, followed by washing with deionized water and dried with sodium sulfate anhydrous overnight, and finally distillated *in vacuo*. Azobisisobutyronitrile (AIBN) (chemically pure; Shanghai Chemical Reagent Co., LtD.) was recrystallized with ethanol anhydrous. Triphenylphosphine (PPh_3) (chemically pure; Shanghai Chemical Reagent Co., LtD.) was recrystallized from ethanol to remove triphenylphosphine oxide. $FeCl_3.6H_2O$ and $FeCl_2.4H_2O$ (analytical reagent; Shanghai Chemical Reagent Co., LtD.), N, N-dimethylformamide (DMF) (analytical reagent; Shanghai No.1 Chemical Reagent Factory), tetrahydrofuran (THF) (analytical reagent; Shanghai Chemical Reagent Co., LtD.), hydrochloric acid (HCl) (analytical reagent; Jiangsu Jincheng Chemical Reagent Co., LtD.), and methanol (commercially available) were used as received.

General Procedures for the Solution RATRP of MMA in DMF

MI process: A dry glass tube was filled with $FeCl_3.6H_2O$, PPh_3, DMF, AIBN and MMA. Three freeze-pump-thaw cycles were performed, and the tube was sealed *in vacuo* and placed into the self-improved microwave oven with reflux of hexane (69°C). The polymerization was stopped at a desired time by the tube being cooled in ice water. Afterwards, the tube was opened, and contents were dissolved in THF and precipitated into a large amount of methanol/HCl (100/0.05 v/v). The dried product was then characterized gravimetrically.

CH process: The sealed tube *in vacuo* was placed in an oil bath held by a thermostat at the desired temperature (69°) for polymerization. The other procedures were identical to those used for MI.

Characterizations

Conversion of monomer was determined by gravimetry. Molecular weights and molecular weight distributions were measured using Waters 1515 gel permeation chromatography (GPC) instrument with THF as a mobile phase and with a column temperature of 30□. Polystyrene standards were used to calibrate the columns. ^{1}H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ with an Inova 400MHz spectrometer at ambient temperature.

Results and Discussion

Comparison of RATRP of MMA under MI and CH

Figure 1 shows kinetics of solution RATRP of MMA in DMF under MI (A) and CH (B) at different concentrations of initiator. The resulting slopes indicate the polymerizations proceeded with an approximately constant number of active species for the duration of the polymerization under both cases. As expected, increasing the values of n, namely

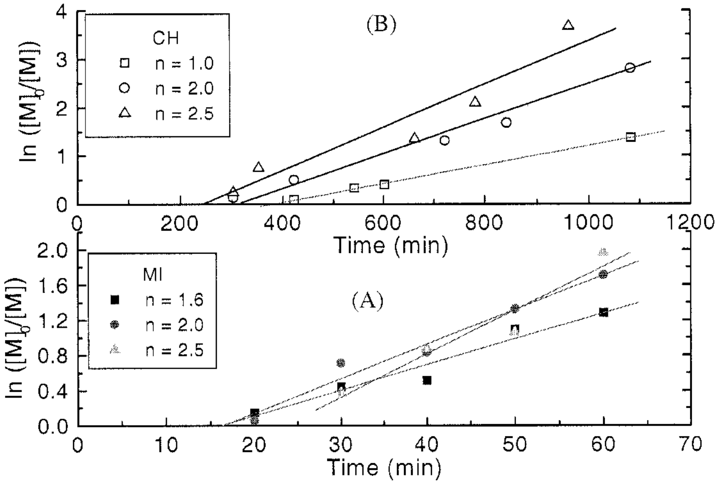

Figure 1. Kinetics of solution RATRP of MMA in DMF under MI (A) and CH (B) at different concentrations of initiator. Conditions: $[MMA]_0/[AIBN]_0/[FeCl_3]_0/[PPh_3]_0$ = 1600/n/4/8 (n = 1, 1.6, 2, 2.5); MMA/DMF = 10/1 (v/v); 69°; 90W(MI).

increasing the concentrations of initiator (AIBN), increases the apparent rate constant of polymerization, k_p^{app}, as determined from the kinetic slopes, indicating the increase of the rate of polymerization. From Figure 1, an induction period of polymerization at low temperature (69°C) can also be observed under both processes and becomes shorter under CH with increasing of the concentrations of initiator. The induction period can be attributed to the establishment of dynamic equilibrium between active species and dormant species before ATRP may proceed or the consumption of residual oxygen and some impurities [18]. Shorter induction periods (about 16~22min) under MI, as compared with those (about 250~350 min) under CH indicate the significant enhancement of initiating rate of AIBN under MI.

According to the kinetic slopes, all k_p^{app} values can be calculated as listed in Table 1. At identical polymerization conditions, k_p^{app} under MI is $65.3\times10^{-5}s^{-1}$ for n = 2 and $82.7\times10^{-5}s^{-1}$ for n = 2.5, respectively; while under CH, it is $5.47\times10^{-5}s^{-1}$ and $6.93\times10^{-5}s^{-1}$, respectively. The former is 11.9 times higher than the latter for both n = 2 and 2.5, indicating that a great enhancement of polymerization rate under MI. In addition, as compared with that the k_p^{app} ($2.57\times10^{-5}s^{-1}$) of RATRP of MMA in DMF (50%, v/v) reported by Yan [19] using AIBN/$FeCl_3$/isophthalic acid as initiating system ($[MMA]_0/[AIBN]_0/[FeCl_3]_0/[\text{isophthalic acid}]_0$ = 500/1/2/4), and that the k_p^{app} ($\sim8\times10^{-5}s^{-1}$) of RATRP of MMA in solution (~36%, v/v) estimated from the results reported by Teyssié [12] using AIBN/$FeCl_3$/PPh_3 as initiating system ($[MMA]_0/[AIBN]_0/[FeCl_3]_0/[PPh_3]_0$ = 2460/1/4/12), though their polymerization temperatures were higher (110°C for Yan and 85°C for Teyssié, but only 69°C in our work), the k_p^{app} values were largely smaller than those under MI in this work. Therefore, the polymerization temperature of RATRP of MMA can significantly be lowered under MI. It can be believed that, under MI, the molecules in reaction system would rotate and

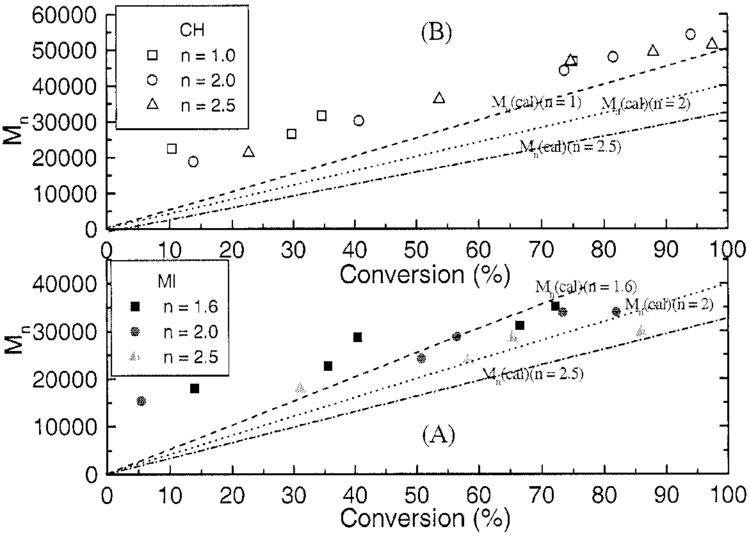

Figure 2. Dependence of molecular weight, M_n, on monomer conversion in DMF under MI (A) and H (B) at different concentrations of initiator. Conditions were identical to Figure 1.

oscillate at a high speed, then become polarized and even deformed; this might enhance the reactivities of reaction system, further increase the rate constant of propagation, resulting in the acceleration of the polymerization process.

Table 1. Comparison of k_p^{app} for the solution RATRP of MMA at different concentrations of initiator

n	k_p^{app} (MI) (s^{-1})	k_p^{app} (CH) (s^{-1})	k_p^{app}(PMI)/ k_p^{app}(CH)
1	---	3.25×10^{-5}	---
1.6	48.6×10^{-5}	---	---
2	65.3×10^{-5}	5.47×10^{-5}	11.9
2.5	82.7×10^{-5}	6.93×10^{-5}	11.9

Conditions were identical to Figure 1.

Figure 2 shows the dependence of molecular weights on monomer conversion in DMF under MI (A) and CH (B) at different concentrations of initiator. For all concentrations of initiator, M_ns, determined by GPC against linear polystyrene standards, increase linearly with conversion. Under CH, M_ns are higher than those expected M_n(cal)s (M_n(cal) = $[MMA]_0/(2[AIBN]_0)\times MW(MMA)\times$Conversion), indicating a low apparent initiator efficiency [f; f = M_n(cal)/M_n(GPC)] in those conditions, and f increases with conversion. At the same time, it can also be observed from Figure 2 (B) that f decreases with increasing of concentrations of initiator. Under MI, however, high f (close to 1) can be obtained at higher conversions [Figure 2 (A)]. The low f could be due to the slower decomposition of AIBN at a lower temperature [20] (69□ in this work). However, under MI, the rate of decomposition of AIBN should increase due to the "no-thermal effect" of MI, leading to the increase of f. In addition, all the plots do not go through the origin (Figure 2), which is similar to the results of Teyssié [12]. This is probably due to the slow initiation of AIBN.

Figure 3 shows the dependence of molecular weight distributions on monomer conversion

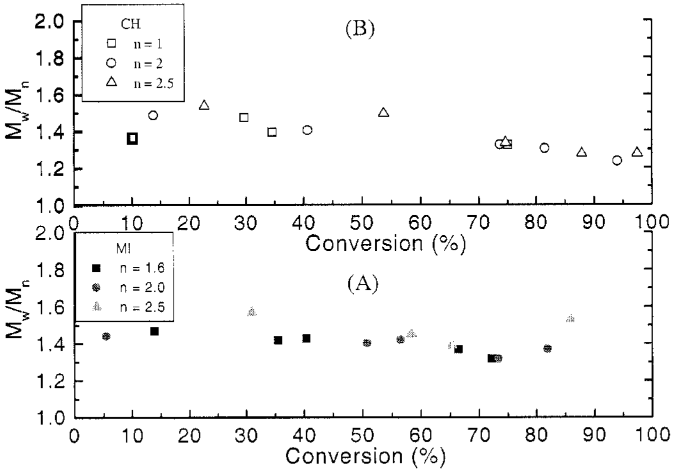

Figure 3. Dependence of molecular weight distributions on monomer conversion in DMF under MI (A) and CH (B) at different concentrations of initiator. Conditions were identical to Figure 1.

in DMF under MI (A) and CH (B) at different concentrations of initiator. PDIs at both cases are narrow, M_w/M_n□1.5 and almost decrease with conversion, indicating a good control over the polymerization of MMA under this initiating system of AIBN/$FeCl_3$/PPh_3, especially under MI.

Figure 4 shows plot of ln (k_p^{app}) vs. ln $[AIBN]_0$ in solution RATRP of MMA in DMF under MI (A) and CH (B). From Figure 4, it can be observed that, for this system, the slopes of lines indicated the polymerization rate showed an apparent 0.88 and 1.18 order with respect to concentration of initiator under CH and MI, respectively. This may be due to the low initiator efficiency discussed above in this system. However, under MI, the order from 0.88 increasing to 1.18 can be attributed to the fact that the increase of f due to the contribution of MI.

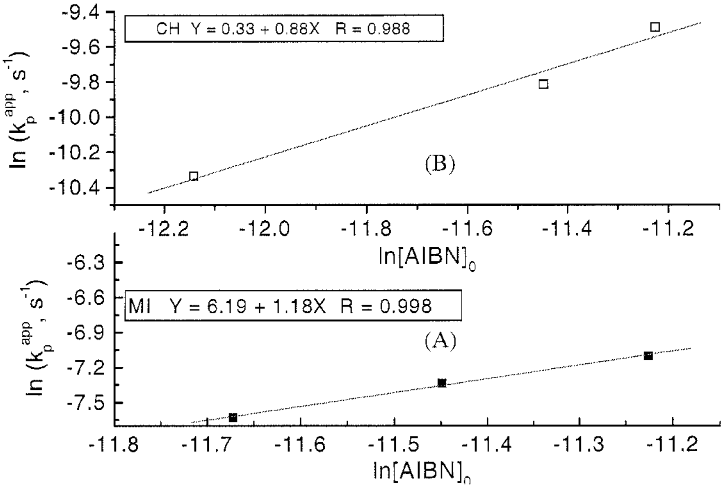

Figure 4. Plot of ln (k_p^{app}) vs. ln $[AIBN]_0$ in solution RATRP of MMA in DMF under MI (A) and CH (B). Conditions were identical to Figure 1.

End Group Characterizations

An additional method toward verifying the functionality of a polymer prepared by ATRP is its use as a macroinitiator for the same or other monomers. A chain extension of MMA with PMMA ($M_{n(GPC)}$ =22,000, M_w/M_n =1.35), prepared with initiation system of AIBN/$FeCl_3$/PPh_3 under MI, as the macroinitiator was performed ($[MMA]_0/[macroinitiator]_0/[FeCl_2]_0/[PPh_3]_0$ = 400/1/1/2; MMA/Toluene = 2/1 (v/v); T = 85°C; t = 5.7h.). The polymerization was conducted in toluene using $FeCl_2(PPh_3)_2$ as the catalyst. The M_n for 73 % conversion of the chain-extended PMMA increased to 47,000 and the polydispersity index decreased to 1.27. Furthermore, the ^1H NMR spectrum shows a signal at 3.76ppm corresponding to the methyl ester group at the chain end as mentioned by Sawamoto [9], which deviating the chemical shift (3.60ppm) of other methyl ester group in PMMA due to the electron-attracting function of ω-Cl. These thus demonstrate the quantitative presence of a Cl atom at ω of the chain. A signal at 125.84ppm was detected in ^{13}C NMR, proving the presence of the CN group of the AIBN moiety in the α of the chain.

Conclusion

Applying MI to the solution RATRP of MMA in DMF with initiating system of AIBN/FeCl$_3$/PPh$_3$ could significantly increase the rate of polymerization and initiator efficiency, which allows the polymerization to proceed under a lower temperature (i.e., 69□) but very fast polymerization rates (k_p^{app} more than $10^{-4}s^{-1}$) can be obtained. Plots of ln ($[M]_0/[M]$) vs. time and molecular weight evolution vs. conversion showed a linear dependence. Well-controlled polymerization with narrow polydispersities (1.3~1.5) and high initiator efficiency (close to 1) have been achieved under MI and the polymers obtained are α-functionlized by a nitrile group and ω-functionalized by a halide atom.

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