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RESEARCH ARTICLE

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Controlled/living photopolymerization of methyl methacrylate in miniemulsion mediated by HTEMPO

Abstract Controlled/living photopolymerization of methyl methacrylate (MMA) in miniemulsion mediated by 4-hydroxy-2,2,6,6-tetramethyl-piperidinyloxy (HTEMPO) was carried out at ambient temperatures. MMA miniemulsion was prepared by using an anionic surfactant with cetylalcohol as a co-stabilizer. The photopolymerization led to stable lattices and they were obtained with no coagulation during synthesis and no destabilization over time. It was found that the obtained MMA homopolymers exhibited relatively narrow molecular weight distribution ($PDI = 1.27 - 1.36$) which was characterized by GPC. The plots of number-average molecular weight in (M_n) *vs.* conversion and $\ln([M_0]/[M])$ *vs.* time both were linear indicating that the reaction was a controlled/living free radical polymerization.

Keywords methyl methacrylate (MMA), controlled/living photopolymerization, miniemulsion, 4-hydroxy-2,2,6,6- tetramethyl-piperidinyloxy (HTEMPO)

1 Introduction

The primary mechanism of nitroxide-mediated living free radical polymerization is to control the bimolecular termination reaction of growing polymer chain radicals by forming dynamic reversible equilibrium between nitroxide radicals and growing polymer chain radicals. Prodpran [1,2], MacLeod [3] and their coworkers had been able to successfully apply 2,2,6,6-tetramethyl-1-piperdinyloxy (TEMPO) as a stable radical in a living free radical miniemulsion polymerization of styrene (St). Nitroxide-mediated living free radical polymerization (NMP) technique in miniemulsion polymerization has rapidly developed both in studies and in industry. Pan et al. [4] used TEMPO-terminated oligomers of polystyrene as a macroinitiator to initiate the miniemulsion polymerization of styrene at 125°C and found that the molecular weight distribution of the PS products was not narrow. Cunningham [5] compared miniemulsion polymerization of styrene in TEMPO/benzoyl peroxide (BPO), TEMPO/potassium persulfate (KPS), 4-hydroxy-2,2,6,6-tetramethyl-piperidinyloxy (HTEMPO)/BPO and HTEMPO/KPS four different systems. They also studied the influence of the rate-accelerating additive camphorsulfonic acid (CSA) in heterogeneous styrene miniemulsion polymerizations with TEMPO/BPO and HTEMPO/BPO systems, respectively [6]. Enright [7] first used a continuous tubular reactor apparatus and studied styrene miniemulsion polymerizations at 135°C using oligomers of polystyrene as a cosurfactant. The results indicated obvious living characteristics of polymerization and the polydispersity index (PDI) of the product was less than 1.4. Zetterlund [8] investigated miniemulsion co-polymerization of styrene and divinylbenzene (DVB) in the presence of a polystyrene-TEMPO macroinitiator at 125°C. Farcet [9] had reported free-radical polymerization of *n*-butyl acrylate (*n*-BA) in the miniemulsions with the use of the acyclic SG1 nitroxide [*N*-*tert*-butyl-*N*-(1-diethylphosphono-2,2-dimethyl-propyl) nitroxide] as a mediator. At 112°C and 125°C, the molecular weight of poly(*n*-butyl acrylate) (PBA) linearly increased with the monomer conversion increasing and PDI was as low as 1.2. Controlled free-radical homopolymerization of *n*-BA and its copolymerization with styrene had also been reported in the miniemulsion, using SG1 as a mediator. The well-defined PBA homopolymers and poly(*n*-butyl acrylate-*co*-styrene) gradient copolymers had been successfully synthesized and their PDI could reach 1.23 [10].

Controlled/living radical polymerization in the miniemulsion could proceed at higher temperatures (> 120°C) in the presence of stable nitroxide radicals such as TEMPO derivatives and SG1, and the research focused on styrene

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monomers. Photopolymerization has many advantages such as proceeding at lower temperatures (ambient temperature), reducing the reaction time, equipment simplification and ease of operation. We had successfully carried out a controlled/living photopolymerization of 4-methacryloyloxy-1,2,2,6,6-pentamethyl-piperidine (MP MP), and synthesized the MPMP homopolymers which exhibited a narrow molecular weight distribution (PDI = 1.06 − 1.39) [11]. We also studied the controlled/living photopolymerization of MMA [12] and *n*-butyl methacrylate (*n*-BMA) [13] mediated by HTMPO. The literatures about inverse emulsion heterogeneous polymerization systems had been widely reported [14], but literatures about miniemulsion systems were reported less, in comparison.

Based on studies of the controlled/living photopolymerization of acrylate monomers, in this article we expand the research on acrylate monomers to the miniemulsion system. The result indicated that the MMA miniemulsion system was very stable through all polymerization processes and the average molecular weight (M_n) *vs.* conversion and ln([M_0]/[M]) *vs.* time relationships both exhibited linear kinetic characteristics. The obtained MMA homopolymers had low PDI (PDI = 1.27 − 1.36) and could be effectively controlled through the whole reaction process indicating that the reaction was a controlled/living free radical polymerization.

2 Experimental

2.1 Materials

Methyl methacrylate (MMA, China Medicine Shanghai Chemical Reagent Corporation) was purified before use by alkali cleaning, drying and decompression distillation. 4-hydroxy-2,2,6,6-tetramethyl-piperidinyloxy (HTEMPO, Wenzhou plastic additives factory, 99.3% purity) was used as received. 1-Hydroxy cyclohexyl phenyl ketone (Irgacure184, Ciba) was used as received. Sodium dodecyl sulfate (SDS, Tianjin Baishi Chemical Co., Ltd) was used after recrystallization. Cetyl alcohol (CA, Tianjin Yongda Reagent Development Center) was used as received. Sodium hydrogen carbonate ($NaHCO_3$, Guangdong Guanghua Chemical Factory Co., Ltd) was used as received.

2.2 Analyses

The following instruments were used: As3120 serial ultrasonic bench top cleaner (frequency output 40 kHz, Power 120 W, Tianjin Automatic Science Instrument Co., Ltd, China), BGH-250 330W UV light source (Mejior Precision Inc., Japan), UV-A radiometer with sensitive wavelength range 320−400 nm (Photoelectric Instrument Factory of Beijing Normal University, China), JEOL JSM-6360LA SEM. The molecular weight and PDI of samples were measured by Waters-515 Gel Permeation Chromatography (GPC, USA). Toluene was used as the eluent at a flow rate of 1.0 mL/min and the operational temperature was 35°C with polystyrene as standard ($M_n = 28{,}000$).

2.3 Procedure

SDS (1.215 g) and CA (2.655 g) were dissolved in distilled water (100 mL) by stirring at 55°C for 30 min in a 250 mL conical flask. The mixture solution was cooled to room temperature and then ultrasonically dispersed for 5 min to break the gel phase. MMA (30 mL) was slowly added into the above mixture to make them mix fully under high-speed stirring at 1000 r/min before the pH value of the formed system was adjusted to weak alkalinity using $NaHCO_3$ solution. Then the emulsion underwent ultrasonic emulsification for 20 min to get stable miniemulsion.

The stable miniemulsion which was prepared according to the predefined formula was charged in a brown bottle. We weighted out the total mass of the bottle and the miniemulsion and then added gauging initiator Irgacure184 and HTEMPO as the nitroxide stable free radical agent. The above mixture solution was treated by ultrasonication for 10 min. Afterward, deoxygenation was performed with nitrogen for 30 mi before withdrawing a quantitative sample by microliter syringe. The sample was then put into a home-made quartz tube having an inner diameter of 40 mm and its nozzle was encased with two layers of biaxial oriented polypropylene (BOPP) films. The schematic diagram of apparatus is plotted in Fig. 1.

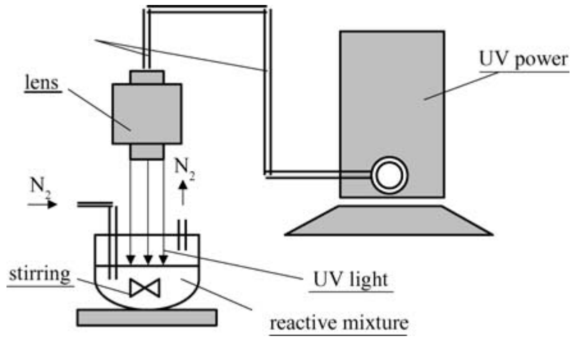


Fig. 1 Schematic diagram of the apparatus for the photopolymerization of MMA in miniemulsion

The light source was warmed-up for 20 min and the light intensity was put on static stall (using 365 nm light intensity for detection). The quantitative sample was irradiated under N_2 cyclation through the whole reaction at room temperature. The UV light was turned off once the engaging irradiation time was reached, and the sample was promptly put into a refrigerator for termination of the reaction. Then the monomer conversion ratio was determined by the weighting method after dulcification, washing, depositing and vacuum drying.

3 Results and discussion

3.1 Particle morphology and size distribution

Figure 2 gives the SEM micrographs of miniemulsion MMA particles before polymerization (Fig. 2(A)) and latex particles after photopolymerization of MMA (Fig. 2(B)). The results indicated that the diameters of the both particles were 70−150 nm and their size distribution had no obvious difference. The monomer diffusion in water phase was no longer the prerequisite of polymerization because the reaction within the monomer droplets was predominant through the whole miniemulsion polymerization process. In the stable miniemulsion polymerization, the latex particle size and number were mainly determined by the size and number of droplets before polymerization which was kept basically constant during polymerization [15].

3.2 Influence of photoinitiator content on polymerization

Figure 3 shows the influence of the photoinitiator content on the monomer conversion plots under the condition of $n(\text{HTEMPO})/n(\text{Irgacure184}) = 1.1$. It could be seen that the plots of monomer conversion had obvious differences with the changing of photoinitiator content. At the photoinitiator weight percentage of 2.0%, the conversion increased quickly during the early stage of polymerization. But at the late stage, the equilibrium between HTEMPO and propagating chains led to a slow increase in monomer conversion (Eq. (1)).

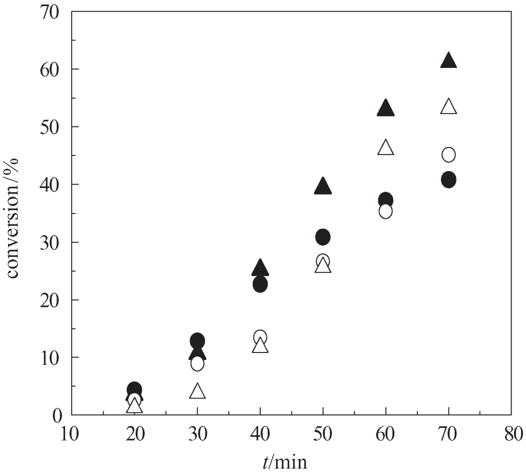
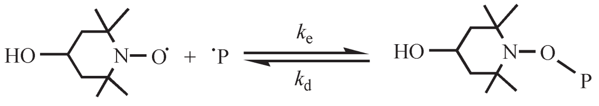


Fig. 3 Influence of photoinitiator content on monomer conversion
w (Irgacure184): • 2.0% ▲ 2.5% ○ 3.0% △ 3.5%



(1)

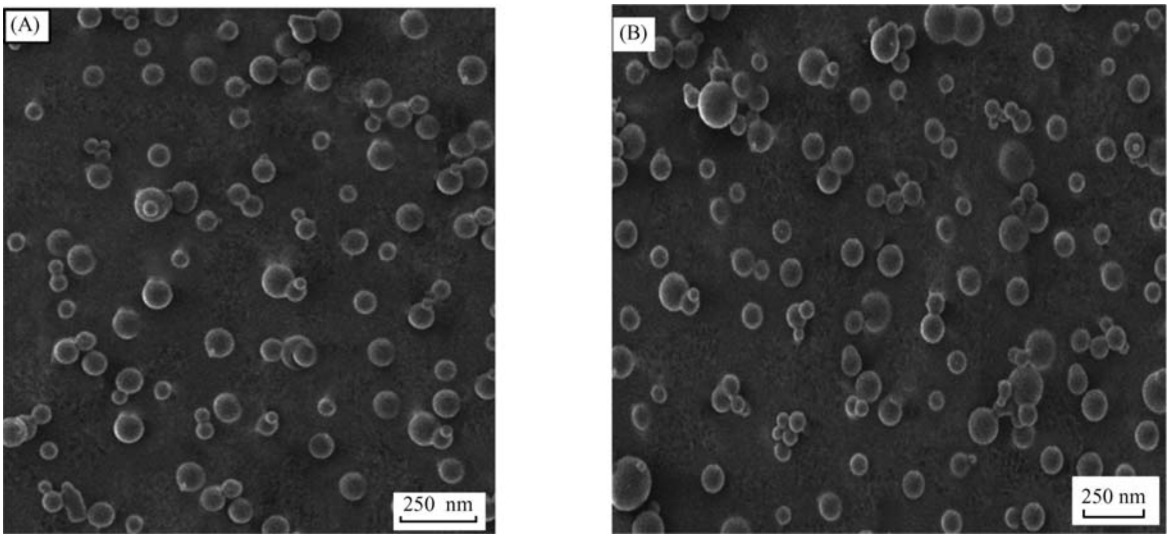


Fig. 2 SEM images of MMA particles (A) and latex particles after the photopolymerization of MMA for 70 min (B) in miniemulsion irradiation time: 70 min, monomer conversion ratio: 58.76%

At the late stage of polymerization the photoinitiator content gradually decreased with the reaction consumption, but the HTEMPO concentration was relatively high which resulted in a positive trend for the processing of the above equilibrium reaction and depression of the chain growth. So the increasing trend of conversion slowed down. In the system with higher initiator concentration (3.5%), a relatively rapid increase of the conversion was observed at the middle and late stages of the reaction. The result was that the number of reactive radicals was relatively higher than that of residual nitroxides. At the photoinitiator weight percentage of 2.5%, the plot of conversion versus time kept a good linearity under higher conversions. The result indicated that chain termination was effectively controlled in the reaction system. So, the proper photoinitiator concentration of 2.5% was used in this work.

Influence of different photoinitiator content on monomer conversion at the early stage of polymerization is shown in Fig. 4. With the photoinitiator content increasing, the induction period was also, accordingly, prolonged. The reason for the abnormal phenomenon was that the nitroxide concentration increased with the increasing photoinitiator content. Once the photoinitiator was irradiated by UV light, the primary radicals would be capped by HTEMPO (Eq. (2)).

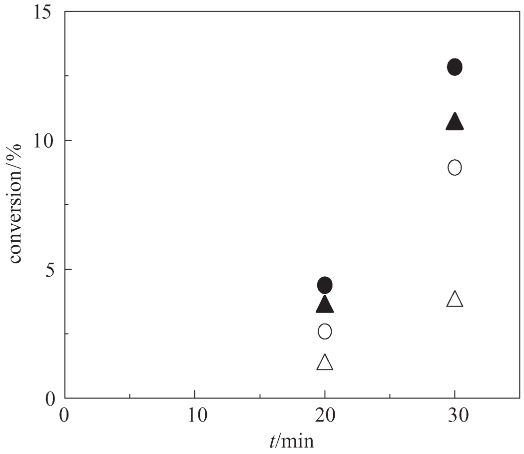


Fig. 4 Influence of photoinitiator content on monomer conversion at the early stage of polymerization
w (Irgacure184): • 2.0% ▲ 2.5% ○ 3.0% △ 3.5%

$$T^{\bullet} + R^{\bullet} \underset{K_{\cdot c}}{\overset{K_c}{\rightleftharpoons}} X \qquad (2)$$

where R· was the initiator primary free radical, T·was HTEMPO, X was the dormant species which was the primary free radical capped by HTEMPO.

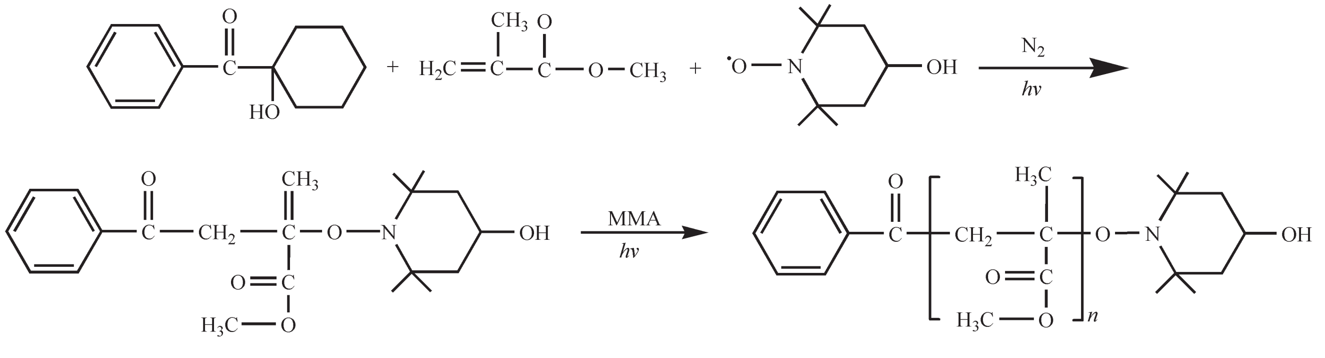
The time of HTEMPO releasing from X was much longer than the time of monomer polymerization. So, the induction period was also accordingly prolonged with the increase of the initiator content. In this research the mechanism of MMA photopolymerization in the miniemulsion is shown in Scheme 1 [16,17].

3.3 Influence of the ratios of HTEMPO/photoinitiator

At the same initiator content, we investigated the influence of different *n*(HTEMPO)/*n*(Irgacure184) ratios (1.0−1.3) on MMA monomer conversion. The results are shown in Fig. 5. It could be found that the polymerization induction period was prolonged and the monomer conversion decreased with the HTEMPO consumption increasing. However, the control effect could be strengthened.

With *n*(HTEMPO)/*n*(Irgacure184) = 1:1, initiator content = 2.5%, light intensity = 3.5 mW/cm^2, the plot of monomer conversion *vs.* polymerization time was linear for photopolymerization of MMA in the miniemulsion. Under high conversions the kinetic plot also kept the first stage linearly increasing trend (Fig. 6) which was one of the kinetic characteristics of living polymerization. The GPC results of the products are shown in Fig. 7 and Fig. 8.

Form Fig. 7, we could find that M_n linearly increased with the increasing monomer conversion and the



Scheme 1 Main reaction course for MMA photopolymerization in the miniemulsion

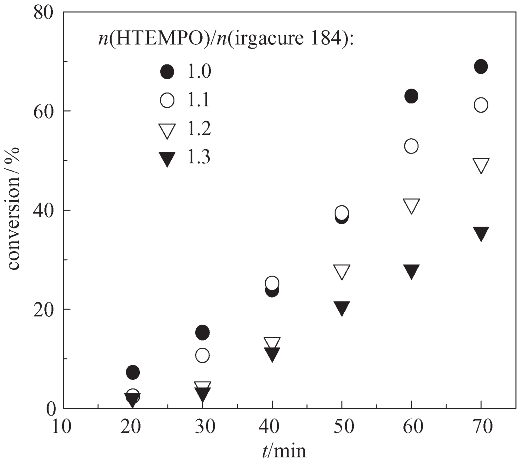


Fig. 5 Influence of the molar ratio of HTEMPO/initiator on conversion for photopolymerization of MMA in the miniemulsion

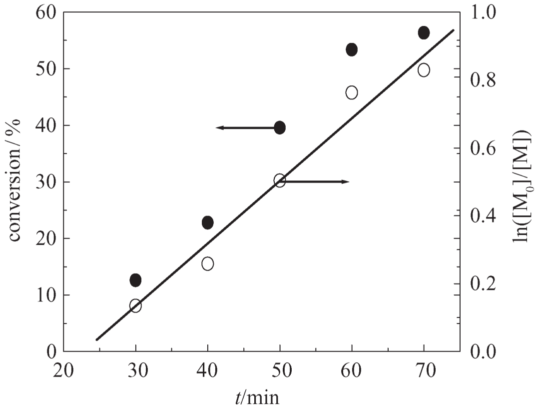


Fig. 6 ln([M$_0$]/[M]) *vs.* time plots for photopolymerization of MMA in the miniemulsion

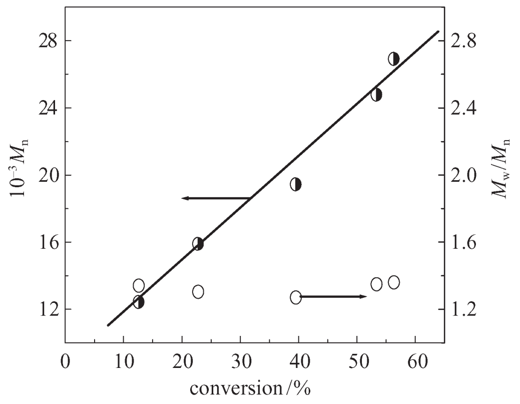


Fig. 7 GPC data of the MMA homopolymers prepared by photopolymerization

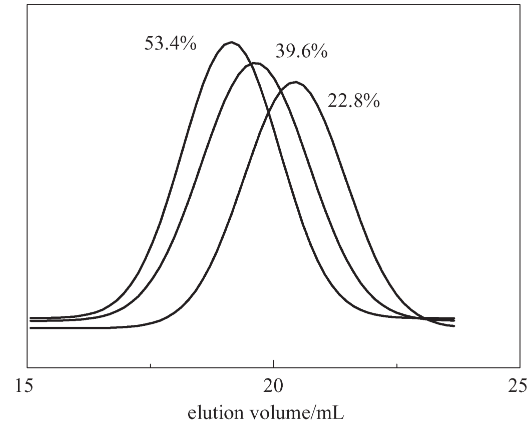


Fig. 8 GPC data of the MMA homopolymers with different conversion

molecular weight distribution (PDI < 1.36) was narrow during the whole polymerization process. The lowest value of PDI was 1.27. As shown in Fig. 8. The plots of molecular weight distribution were basically identical for samples at different monomer conversion. The PDI value always kept in a range from 1.27 to 1.36 which indicated that TEMPO had obvious kinetic control on the photopolymerization of MMA at ambient temperature.

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