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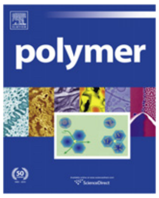

Photoinitiated dispersion polymerization using polyurethane based macrophotoinitiator as stabilizer and photoinitiator

Jianbo Tan [a,b], Bo Wu [a], Jianwen Yang [a,b], Yedan Zhu [a], Zhaohua Zeng [a,b,*]

[a] Key Laboratory for Polymeric Composite and Functional Materials of Ministry of Education, School of Chemistry and Chemical Engineering, Sun Yat-Sen University, Guangzhou 510275, China

[b] Key Laboratory of Designed Synthesis and Application of Polymer Material, School of Chemistry and Chemical Engineering, Sun Yat-Sen University, Guangzhou 510275, China

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ABSTRACT

Polyurethane based macrophotoinitiator (PU-PI) had been designed and synthesized, and applied to photoinitiated dispersion polymerization of methyl methacrylate as both photoinitiator and stabilizer, with ethanol/water mixture as reaction medium. Monomer conversion over 90% was achieved within 25 min of UV irradiation at room temperature, and monodisperse PMMA microspheres were obtained. The structure of the microspheres had been analyzed by XPS, showing that about 50% of surface of the microspheres were covered with the stabilizer. PU-PI effectively stabilized the polymeric particles in photoinitiated dispersion polymerization due to the unique stabilization process. The size and size distribution of the microspheres became insensitive to the reaction condition such as stabilizer/initiator concentration, initial monomer concentration and reaction medium. The size of the microspheres obtained changed in the range from 0.88 μm to 1.06 μm at different reaction condition, with polydispersity index as low as 1.011. The research may provide a quick and facile approach to prepare monodisperse microspheres with tailored functional surface.

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1. Introduction

Dispersion polymerization is one of the effective methods for preparing polymeric microspheres with narrow size distribution [1–4]. In dispersion polymerization, thermal initiated free radical polymerization is commonly adopted. Due to the long half-life of thermal initiator, reaction period up to 24 h is commonly needed to achieve high monomer conversion. Researchers have developed several ways to reduce the reaction period, such as introducing γ-ray [5,6] or UV irradiation [7,8] to initiate dispersion polymerization and the assistance of microwave in thermal initiated free radical polymerization [9].

Photoinitiated free radical polymerization is a very rapid procedure, in which photoinitiator decomposes and then produces free radicals very quickly under UV or visible light irradiation [10]. Temperature insensitivity is another advantage of photoinitiated polymerization in addition to the high reaction rate. The reaction can be carried out at room temperature or lower. This character is in favor of the "bottom-up" preparation procedures of polymeric microspheres containing thermally labile materials (e.g. some kinds of proteins and drugs). Short reaction time and low reaction temperature inhibit the degradation or inactivation of thermally labile materials. For this reason, photoinitiating technology has been introduced into the microsphere generating procedures, such as microemulsion polymerization [11], emulsion polymerization [12–17] and precipitation polymerization [18–20].

In comparison with photoinitiated emulsion polymerization and precipitation polymerization, the report of photoinitiated dispersion polymerization is scarce. In our past work, we had investigated photoinitiated dispersion polymerization of methyl methacrylate (MMA) using poly(N-vinylpyrrolidone) (PVP) as stabilizer [8]. It has been found that conversion up to 90% was achieved within 30 min of UV irradiation at room temperature, and microspheres around 1 μm with narrow size distribution were obtained. Further work revealed that stabilizers other than PVP, e.g. macromonomers and block copolymers, were not very effective for obtaining monodisperse microspheres in photoinitiated dispersion polymerization. The primary cause is the very high polymerization rate. Nucleation occurs so quickly that there is not enough time for the stabilizer to capture and stabilize the nuclei and growing particles effectively. Apparently, for the application and promotion of photoinitiated dispersion polymerization, it is necessary to develop stabilizers with satisfying effect.

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* Corresponding author at: Key Laboratory of Designed Synthesis and Application of Polymer Material, School of Chemistry and Chemical Engineering, Sun Yat-Sen University, Guangzhou 510275, China. Tel./fax: +86 20 84111138.
E-mail address: ceszzh@mail.sysu.edu.cn (Z. Zeng).

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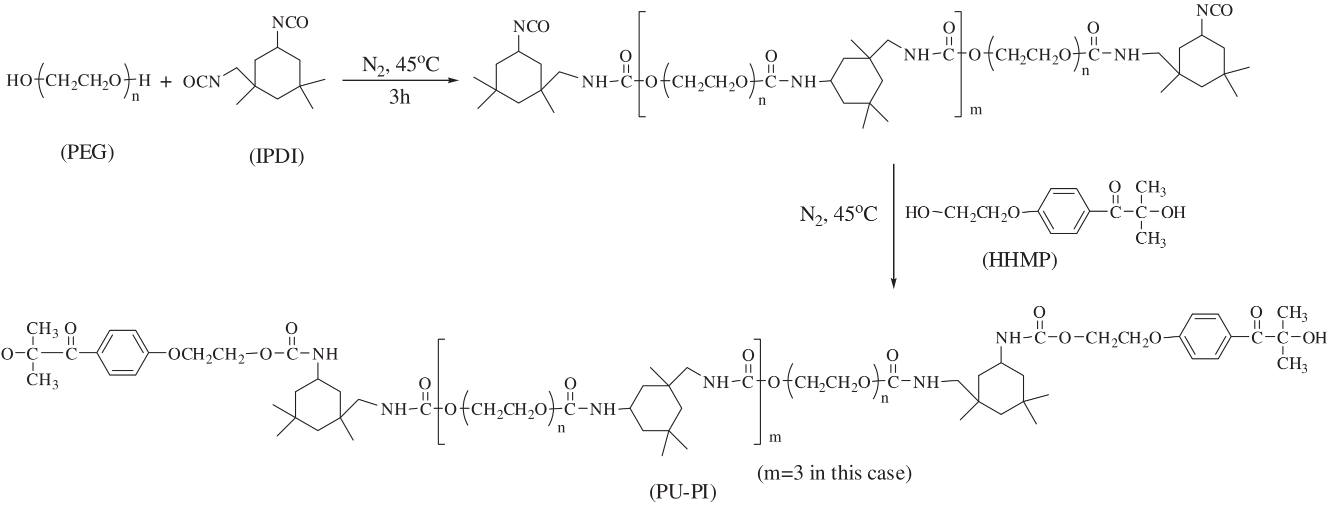


Scheme 1. Preparation route of PU-PI.

In this paper, a polyurethane based macrophotoinitiator has been designed and synthesized, and applied to photoinitiated dispersion polymerization as both photoinitiator and stabilizer. Monodisperse microspheres have been successfully obtained with monomer conversion over 90% within 25 min of UV irradiation.

2. Experimental

2.1. Materials

Methyl methacrylate (MMA, Tianjing Kermel Chemical Reagents Development Centre) was purified by distilling under reduced pressure and stored in a refrigerator prior to use. Polyethylene glycol (PEG) with number-average molecular weight 600 g/mol was supplied by Shantou Long Hua Company. 2-Hydroxy-4′-hydroxy-ethoxy-2-methylpropiophenone (HHMP or Irgacure 2959, Ciba Company) and Isophorone diisocyanate (IPDI, Shanghai YuTian Company) were used without further purification. All other chemicals used were analytical grade and used without further purification.

2.2. Synthesis procedure of macrophotoinitiator

The polyurethane based macrophotoinitiator, named PU-PI, was synthesized by a two-step reaction procedure. Scheme 1 illustrates the synthetic route for PU-PI. IPDI (11 g) was charged in the three-neck flask and bubbled N_2 for 30 min. Then the mixture of PEG 600 (20 g) and 2-butanone (proper amount) was dropped slowly into the flask. The temperature was raised to 45 °C and the reaction mixture refluxed for 3 h. Then HHMP (4.29 g) 2-butanone solution was dropped slowly into the flask and refluxed for another 3 h. Finally 2-butanone was removed by rotary evaporation. The product obtained was stored in the refrigerator and avoided light irradiation. The chemical structure of the synthesized PU-PI was confirmed by ^{1}H NMR (Fig. 1).

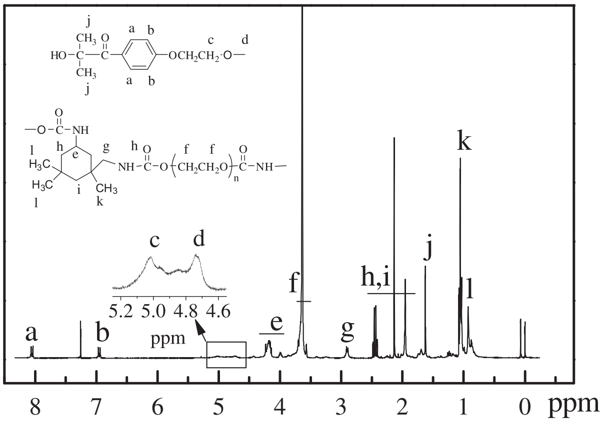


Fig. 1. ^{1}H NMR spectrum of PU-PI.

2.3. Photoinitiated dispersion polymerization

The apparatus for photoinitiated dispersion polymerization is shown in Fig. 2. In a typical experiment procedure, MMA (10 wt.% relative to the system) and PU-PI (15 wt.% relative to MMA) were dissolved in the reaction medium (ethanol/water mixture with 40wt% ethanol). The reaction mixture obtained was introduced into the glass pipe and then gently purged with nitrogen for 15 min in order to remove oxygen prior to irradiation. Then the glass pipe was sealed and immerged into water bath to maintain the temperature at 30 °C. A 400-W high-pressure mercury lamp was employed to irradiate the mixture from the top of reaction cell. UV intensity was measured by a UV-radiometer (type UV-A, from Photoelectric Instrument Factory, Beijing Normal University) which is sensitive in the wavelength range of 320–400 nm. Typical light intensity used in the experiment was 1.0 mW cm^{-1}. The reaction period was proceeded for 1 h. The product was precipitated by centrifugation and rinsed with methanol and centrifuged repeatedly to remove residual PU-PI, dried in a vacuum oven for 24 h to gain fine powder, then weighed for calculating the reaction conversion.

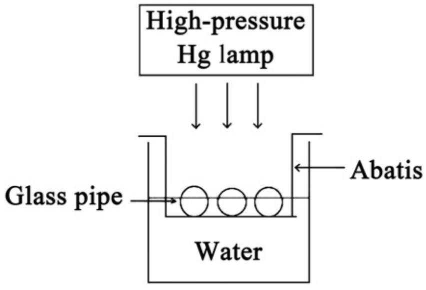


Fig. 2. Apparatus for photoinitiated dispersion polymerization.

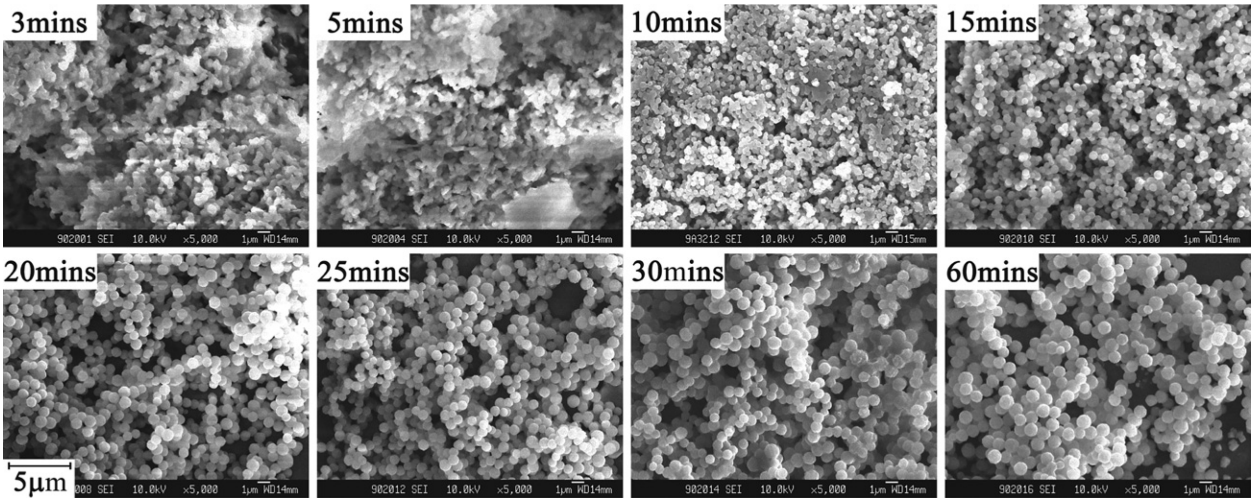


Fig. 3. SEM images of PMMA microspheres obtained by photoinitiated dispersion polymerization of MMA with different UV irradiation time (marked in the images).

2.4. Characterization

Morphology analysis was carried out on a JSM-6330F Field Emission Scanning Electron Microscope(FMSEM) at 10 kV. Samples were gold-coated after dispersed in water and dropped onto glass slides.

All the clear microspheres for each sample in FESEM images, 300–400 counts in most cases, were measured in software named Image-Pro Plus 6.0 (Media Cybernetics, Inc., USA), and the number-average diameter (D_n), weight-average diameter (D_w), and polydispersity index (PDI) were calculated as follows:

$$D_n = \sum_{i=1}^{n} n_i D_i / n \tag{1}$$

$$D_w = \left(\sum_{i=1}^{n} D_i^4\right) \Big/ \left(\sum_{i=1}^{n} D_i^3\right) \tag{2}$$

$$PDI = D_w / D_n \tag{3}$$

The particle distribution is considered to be monodisperse when the polydispersity index is between 1.0 and 1.1 [20,21].

X-ray photoelectron spectroscopy (XPS) analysis was performed on a Thermo Electron Corporation Escalab 250 spectrometer. A Al K Alpha X-ray source was used. The determination was operated at 20 eV pass energy.

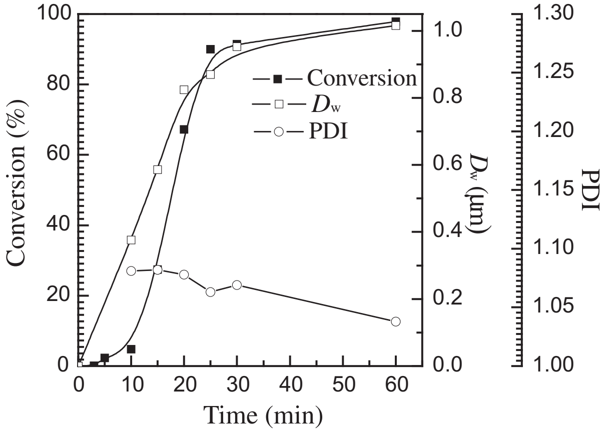


Fig. 4. Plots of MMA conversion, weight-average diameter (D_w) and PDI versus irradiation time for PMMA microspheres obtained from photoinitiated dispersion polymerization of MMA with typical condition described in Experimental section.

The molecular weight and polydispersity were determined by Waters 1515 GPC instrument with tetrahydrofuran as the mobile phase. The flow rate of tetrahydrofuran was 1.0 mL/min. Narrow distribution linear polystyrenes were used as the standard to calibrate the apparatus, the molecular weight of the samples were measured using universal calibration.

^{1}H NMR spectra were taken on Varian Unity Inova 500 spectrometers.

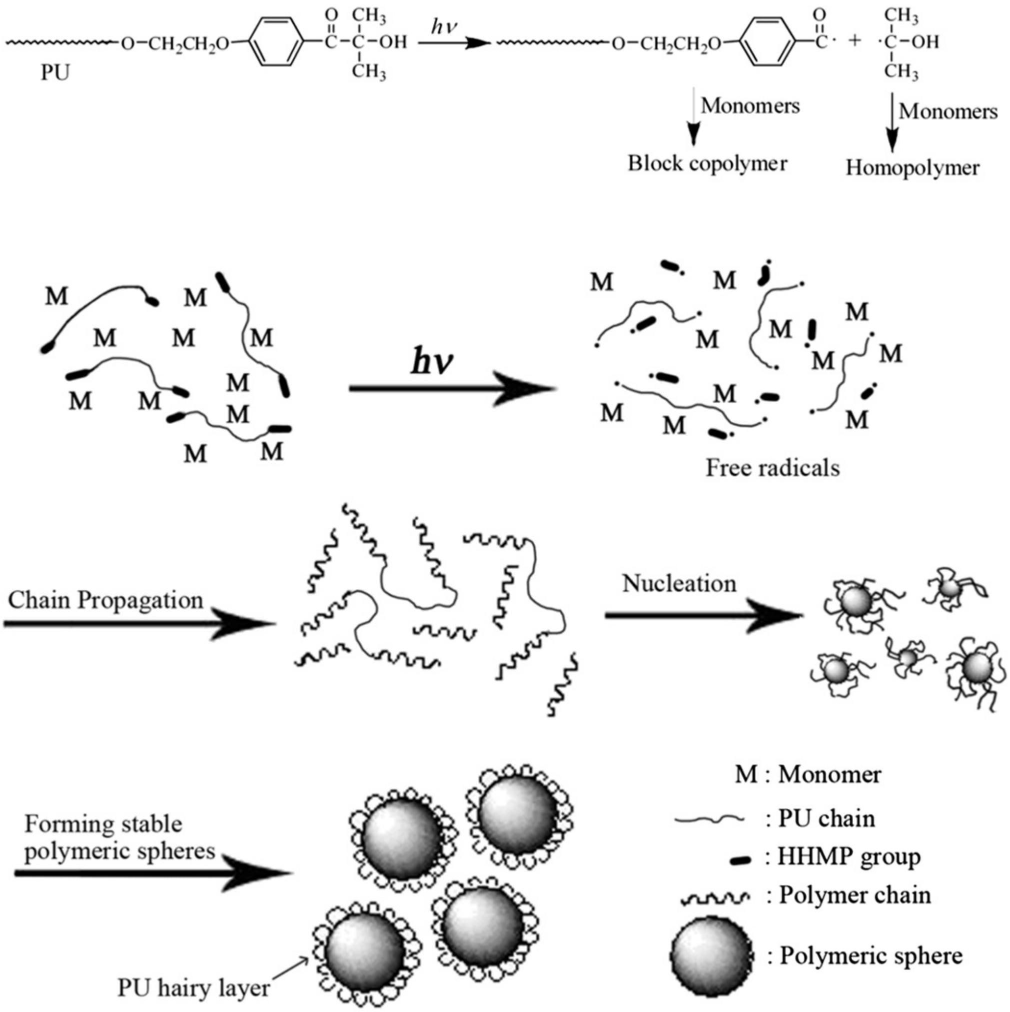
3. Result and discussion

Photoinitiated dispersion polymerization of MMA was carried out in a mixture of ethanol and water as the dispersion medium. The photoinitiator-capped polyurethane (PU-PI) was used as both stabilizer and photoinitiator. The reaction mixture was clear at the beginning and became opalescent after about 3 min of UV irradiation, and turned into a white, stable dispersion as the reaction proceeded.

Fig. 3 presents the morphology of the products at different reaction time. It shows that only irregular particles were generated at the early stage (3 min and 5 min), which may be the nucleation stage. As the time increased, uniform microspheres were obtained. Fig. 4 shows that the monomer conversion increases quickly after UV irradiation, and reaches to 90.0% at 25 min and 97.9% at 60 min. The microsphere diameter (D_w) increases synchronically and reaches to 1.02 μm at 60 min, with PDI of 1.038. The results indicate that the photoinitiated dispersion polymerization stabilized with PU-PI is similar to that stabilized with PVP [8] on reaction rate and the characters of the final microspheres. While the nucleation stage of these two systems is quite different. For PVP stabilized system [8], the clear solution became opalescent after only 20 s of UV irradiation, but it spent about 3 min for PU-PI stabilized system. Considering that photoinitiators used in these two systems have the same photoinitiating unit and thus possess similar photoinitiating activity, the delay of opalescence for PU-PI stabilized system may be correlated to the nucleation mechanism of PU-PI stabilized system.

3.1. Mechanism

PU-PI is composed of a water/ethanol affinitive polyurethane chain and two photoinitiating end groups.Under UV irradiation, the



Scheme 2. Mechanism of the formation of microspheres.

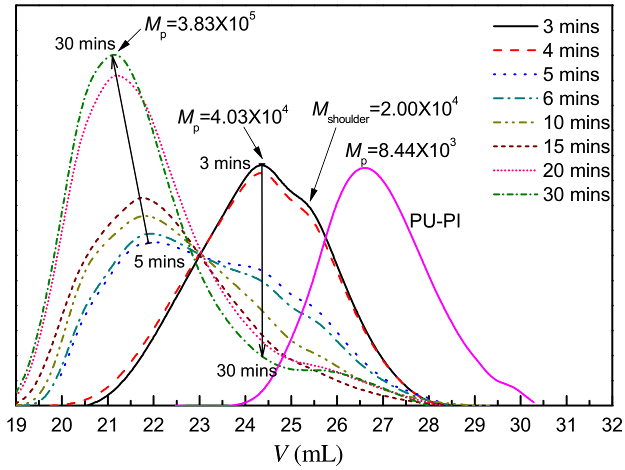


Fig. 5. GPC results of the microspheres obtained by photoinitiated dispersion polymerization of MMA with different UV irradiation time (marked in the images).

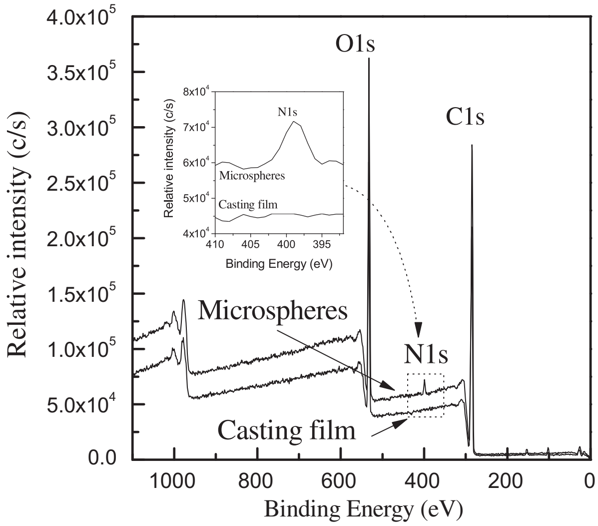


Fig. 6. XPS survey spectra of PMMA microspheres and the casting film. The microspheres were prepared according to the Experimental description.

Table 1
PU-PI content on the surface of PMMA microspheres and casting film.

Sample	PU-PI content[a]		
	$C_{(N)}$	$C_{(\gamma,\ \alpha)}$	$C_{(\gamma,\ \beta)}$
Original microspheres	47.0%	49.3%	52.1%
Casting film	–	4.7%	5.0%

[a] $C_{(N)}$ is calculated from the nitrogen concentration, $C_{(\gamma,\ \alpha)}$ from the relative content of oxygen γ and α, $C_{(\gamma,\ \beta)}$ from the relative content of oxygen γ and β (Fig. 7).

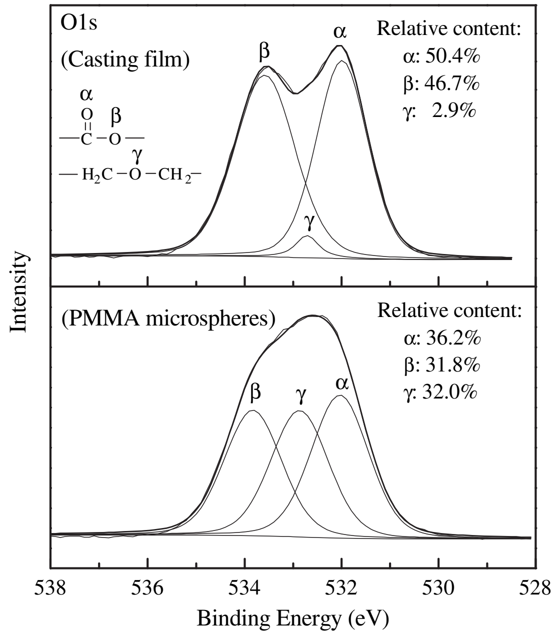


Fig. 7. XPS (O 1s) spectra of PMMA microspheres and the casting film. The microspheres were prepared according to Experimental section. The relative content of different type of oxygen calculated from the peak area is marked in the figure.

photoinitiating end group decomposes and two free radicals are formed (Scheme 2). One radical stays at the end of PU chain and another gets into the dispersion medium as a small fragment, both of which can initiate free radical polymerization of vinyl monomers, forming block copolymer and homopolymer (PMMA). The free radicals on the propagating chains of block copolymer can transfer to monomers, generating new homopolymer chains. Nucleation occurs as the homopolymer chains propagate to the critical chain length, following with the formation of polymeric microspheres, just like a normal dispersion polymerization.

The block copolymers formed in situ act as stabilizer in this process. PMMA homopolymer chain and MMA block of the copolymer generated from the same photoinitiating group will be very close with each other. As a result, the homopolymer chains congregate with stabilizer before forming nuclei, and thus the reaction mixture keeps clear for longer time at starting stage, even though the polymer chains propagate to the critical chain length. It also ensures that the nuclei and growing particles are stabilized effectively with stabilizer.

Fig. 5 presents the GPC results of PU-PI and the PMMA microspheres obtained at different UV irradiation time. The GPC curve for the microspheres formed after 3 min irradiation shows a peak and a shoulder. The corresponding molecular weights of the peak and the shoulder are 4.03×10^4 and 2.00×10^4 $g \cdot mol^{-1}$ respectively, both higher than the peak molecular weight (M_p) of PU-PI. Thus we can deduce that the microspheres are composed of two kinds of polymers, one is the block copolymer derived from PU-PI, and another is the homopolymer (PMMA). As the irradiation time increases to 5 min, the peak weakens and becomes a shoulder, and a new peak at high molecular weight appears. This new peak rises and the shoulder weakens with increasing irradiation time. The change trend of molecular weight with increasing irradiation time may be attributed to the difference in polymerization surrounding at different stage. At early stage (irradiation less than 5 min), the polymer chains are primary produced in the solution.This is the nucleation stage. Due to the lower monomer concentration and the effect of chain transfer to solvent, the molecular weight of the polymers formed in this stage is lower. As the nuclei form and propagate, the monomers are attracted to the microspheres. These monomers polymerize in or around the microspheres, and the molecular weight of the polymer chains formed in this condition is relative high due to the higher monomer concentration and less effect of chain transfer to solvent. As the irradiation time extends, more and more monomers polymerize in this manner, and polymer chains with high molecular weight become the dominant products at the later stage.

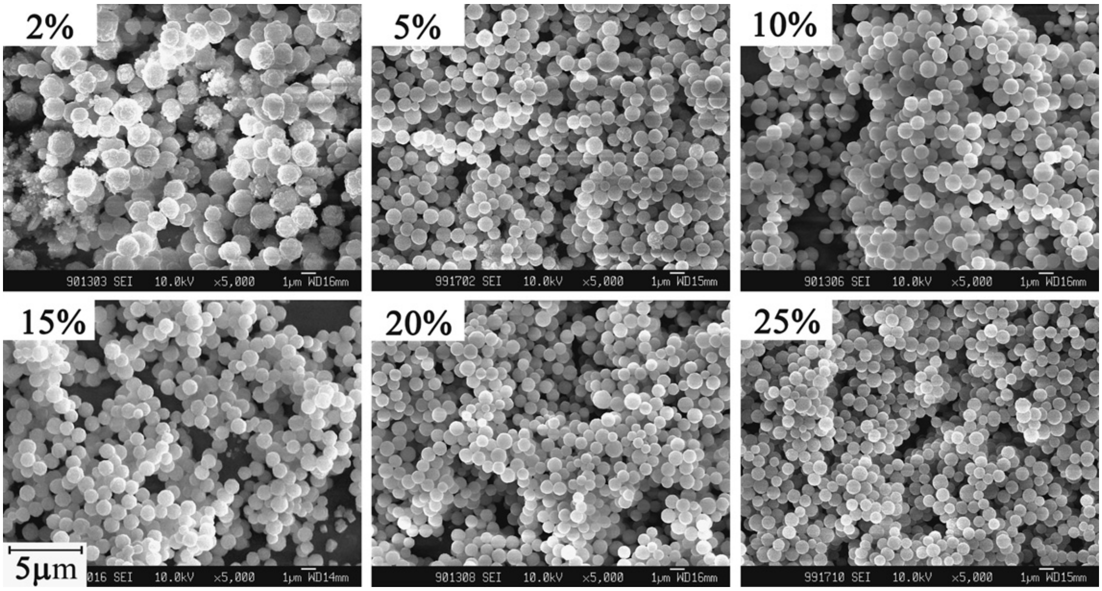


Fig. 8. SEM images of PMMA microspheres obtained by photoinitiated dispersion polymerization of MMA with different stabilizer concentration (wt%, marked in the images).

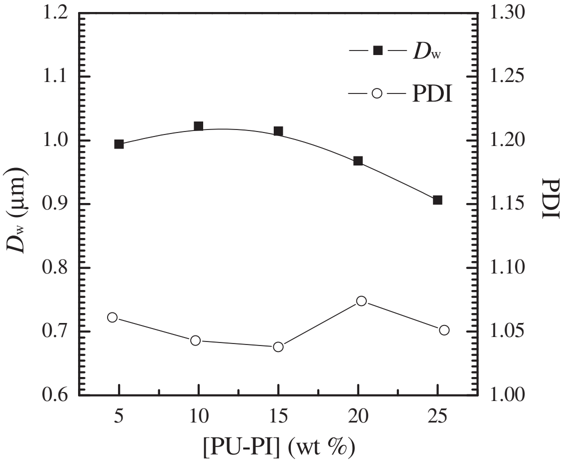


Fig. 9. Weight-average diameter and PDI versus PU-PI concentration for PMMA microspheres obtained from photoinitiated dispersion polymerization of MMA with typical condition described in Experimental section.

3.2. *Structure of the microspheres*

The composition of the surface of PMMA microspheres was analyzed by X-ray photoelectron spectroscope (XPS). For comparison, another sample (casting film) was prepared by dissolving the microspheres to chloroform to form a homogeneous solution and then casting from the solution to form a dry film. XPS analysis of this film sample can be used to estimate the average composition of the whole microsphere, including the inside and the surface. By comparing the XPS spectra of these two samples, we can obtain the structure information of the microspheres.

XPS wide survey spectra of the original microspheres and the casting film are shown in Fig. 6. Strong carbon peaks (C 1s, around 285eV) and oxygen peaks (O 1s, around 532eV) are found in both spectra of the two samples. A weak nitrogen peak (N 1s, 399.6eV) exists in the spectrum of the microspheres. The nitrogen concentration based on the peak areas is 1.66%, corresponding to 47.0% of PU-PI (Table 1). No nitrogen peak is found in the spectrum of the casting film.

Fig. 7 shows the XPS (O 1s) spectra of PMMA microspheres and the casting film. The three peaks are attributed to three type of oxygen (tagged as α, β and γ in Fig. 7). The relative content of different type of oxygen calculated from the peak area is marked in the figure. Because the ether units only exist in PU-PI, the content of PU-PI on the surface of the samples can be calculated by comparing the relative content of ether oxygen (γ) with other type of oxygen (α or β in ester unit). The results are listed in Table 1. PU-PI content on the surface of the microspheres is around 50%, close to the value based on nitrogen signal. PU-PI content on the surface of the casting film is around 5%. Considering the very likely surface richening effect, this result may not accurately represent the average composition of the microspheres. For this reason, we have also tested ^{1}H NMR spectrum of the solution of microspheres in $CDCl_3$, by which PU-PI content is calculated. The result is 5.7%, close to XPS result of the casting film. It is obvious that PU-PI is basically on the surface of the microspheres, as it is expected. The results also reveal that about 50% of surface of the microspheres is covered with PU-PI. This value is greatly higher than that in PVP stabilized system in which only about 13% of surface of the microspheres were covered with PVP when the same amount of stabilizer (15% relative to monomer) was used [8].

The high stabilizer covering can be attributed to the unique stabilizing mechanism of PU-PI as described above. This character can provide a facile approach to prepare microspheres with tailored functional surface.

3.3. *Effect of PU-PI concentration*

Fig. 8 shows the SEM images of PMMA microspheres with different concentration of PU-PI. The size and size distribution of the microspheres as the function of PU-PI concentration are shown in Fig. 9.

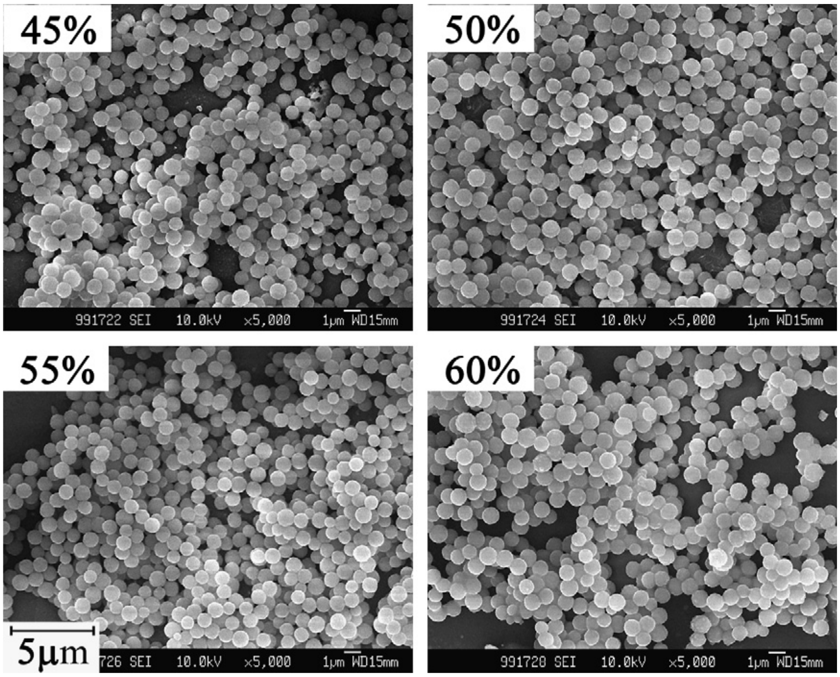


Fig. 10. SEM images of PMMA microspheres obtained by photoinitiated dispersion polymerization of MMA with different ethanol content (marked in the images). For the image of 40% ethanol, refer Fig. 7 (15% stabilizer).

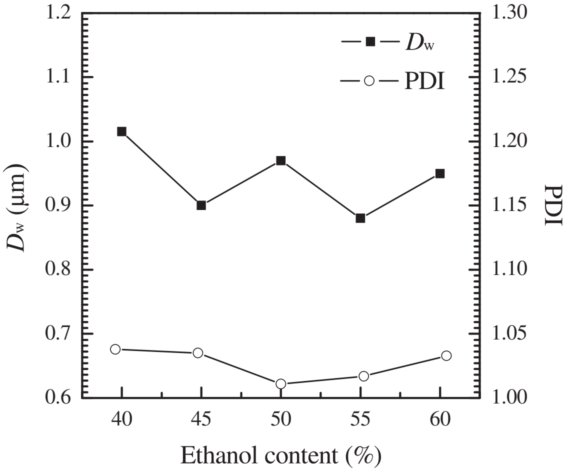


Fig. 11. Weight-average diameter and PDI versus ethanol content for PMMA microspheres obtained from photoinitiated dispersion polymerization of MMA with typical condition described in Experimental section.

For a normal dispersion polymerization system, both stabilizer concentration and initiator concentration affect the size of microspheres generated. Higher stabilizer concentration induces faster adsorption of stabilizer, which reduces the aggregation of the nuclei and thus smaller microspheres are obtained [22]. And higher initiator concentration generates large amount of oligomeric species with low molecular weight which are inclined to stay in the medium and hard to be absorbed by stabilizer, resulting in the reduced number of primary particles during the nucleation stage and hence larger particle size [23].

For PU-PI stabilized system, PU-PI acts as both stabilizer and photoinitiator in dispersion polymerization. Increasing PU-PI concentration leads to synchronous increase in stabilizer concentration and photoinitiator concentration. The former reduces the particle size while the latter increases it. The competition of these two reverse factors results in a maximum of particle size, as shown in Fig. 9. At lower PU-PI concentration, the effect of photoinitiator is dominant, the particle size increases with increasing PU-PI concentration. At higher PU-PI concentration, stabilizer effect becomes dominant and the particle size decreases.

Although the tendency of particle size with changing PU-PI concentration can be explained by the competition of the two reverse factors, it should not be ignored that both two factors are correlated with the adsorption of stabilizer. For PU-PI stabilized system, the propagating chains are easy to be absorbed by the block copolymer chains due to the unique stabilizing process of PU-PI as described above. This may induce less sensitivity of particle size to the change of PU-PI concentration. As shown in Fig. 9, D_w changes in the range of 0.91–1.02 μm as PU-PI concentration increases from 5% to 25%. The size distribution keeps very narrow (PDI 1.038–1.074) due to the sufficient stabilization. Insufficient stabilization occurs only at very low PU-PI concentration (2%), leading to large particles with irregular shape and unclean surface (Fig. 8).

3.4. Effect of dispersion medium

Fig. 10 shows the SEM images of PMMA microspheres with different ethanol content (percentage in ethanol/water mixture). The size and size distribution of the microspheres as the function of ethanol content are shown in Fig. 11.

In dispersion polymerization, reaction medium is the poor solvent for the polymer chains and solvent for stabilizer, and its effect on the size of resulted particles is attributed to its solvency toward polymer chains [24] or stabilizer [25,26]. For photoinitiated dispersion polymerization of MMA stabilized by PVP, rising ethanol content and hence increasing the solvency of the medium toward PVP decreased the chance of nuclei to absorb PVP from the medium, leading to a less number of primary stabilized particles and hence a larger ultimate particle size [8]. Thus, rising ethanol content from 35% to 50% caused the increase of D_w from 0.81 μm to 1.84 μm. In the case of PU-PI stabilized system, the adsorption of stabilizer becomes very easy due to the unique stabilizing process

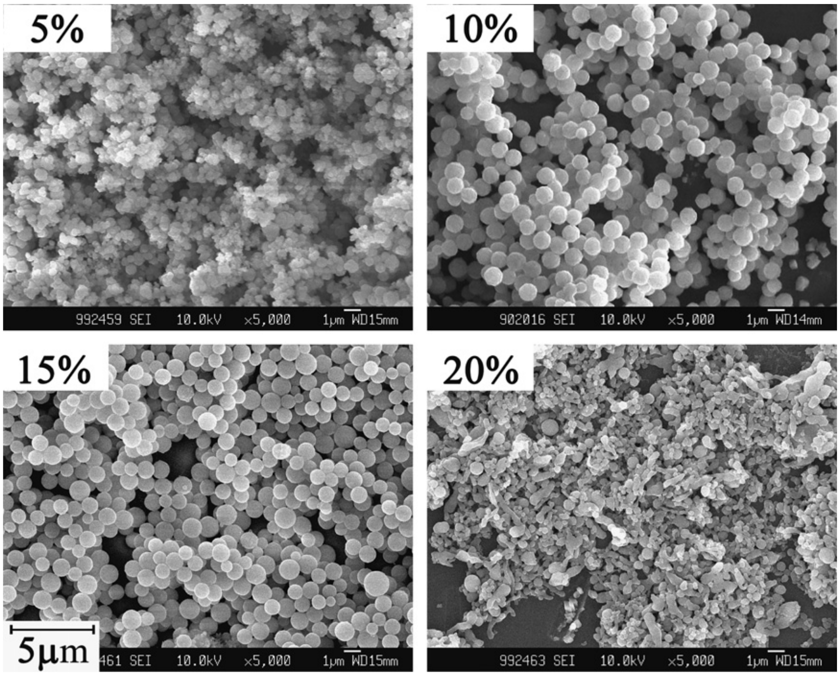


Fig. 12. SEM images of PMMA microspheres obtained by photoinitiated dispersion polymerization of MMA with different initial monomer concentration (wt%, marked in the images).

of PU-PI as described above. This may induce less sensitivity of particle size to the change of ethanol content. As shown in Fig. 11, D_W changes irregularly in a narrow range (0.88 μm–1.02 μm) as ethanol content increases from 40% to 60%. The sufficient stabilization gives very narrow size distribution (PDI 1.011–1.038).

3.5. *Effect of initial monomer concentration*

Fig. 12 shows the SEM images of PMMA microspheres with different initial monomer concentration. Microspheres were obtained at 10% and 15% initial MMA concentration, with D_W value of 1.02 μm and 1.06 μm, and PDI value of 1.038 and 1.070, respectively. At low initial MMA concentration (5%), only irregular particles were obtained because of the insufficient growth of particles, which is analogous to the case we have observed at early stage of the reaction with typical condition (images of 3 min and 5 min in Fig. 3). At high monomer concentration (20%), nucleation becomes difficult due to the higher solubility of PMMA chains in the medium, for MMA is a good solvent of PMMA. The forming polymer chains congregated around the block copolymer at early stage. With the consumption of monomers, the congregated polymer chains precipitated from the medium, giving irregular polymer lumps, as shown in Fig. 12.

4. Conclusions

Photoinitiated dispersion polymerization of methyl methacrylate has been carried out in ethanol/water mixture, using polyurethane based macrophotoinitiator (PU-PI) as both photoinitiator and stabilizer. Monodisperse PMMA microspheres were obtained in 25 min with monomer conversion over 90%. PU-PI stabilized the polymeric particles with good effect in photoinitiated dispersion polymerization due to the unique stabilization process. The size and size distribution of the microspheres became insensitive to the reaction condition such as stabilizer/initiator concentration, initial monomer concentration and reaction medium. Polydispersity index of 1.011 was achieved, which is the lowest PDI value we have found for photoinitiated dispersion polymerization. This type of photoinitiating stabilizer suits for any kind of photopolymerizable monomers, and can be used in different type of dispersion media by tuning the solvent affinity of the stabilizer backbone. XPS results reveal that about 50% of surface of the microspheres were covered with PU-PI. This character can provide a facile approach to prepare microspheres with tailored functional surface.

Acknowledgements

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