

Preparation and characterization of an amphiphilic macrophotoinitiator based on 2-hydroxyl-2-methyl-1-phenylpropanone

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ABSTRACT: On the basis of 2-hydroxyl-2-methyl-1-phenylpropanone (HMPP) and poly(ethylene glycol) (PEG), we prepared amphiphilic macrophotoinitiators (HMPP-PEG-HMPP) by first reacting HMPP with isophorone diisocyanate and subsequently reacting it with PEGs with different chain lengths. Fourier transform infrared spectroscopy, high-performance liquid chromatography, and ¹H-NMR were used to confirm the structure of the amphiphilic macrophotoinitiators. Ultraviolet (UV) absorption spectra showed that the amphiphilic macrophotoinitiators had maximum absorption wavelengths that were similar to those of the low-molecular-weight photoinitiator HMPP. The photolysis rate of the amphiphilic macrophotoinitiators was slightly lower than that of HMPP, but the migration rate of the amphiphilic macrophotoinitiators from a UV-cured matrix was much lower compared to that of HMPP. Because of their amphiphilic nature, these macrophotoinitiators may play roles as both photoinitiators and emulsifiers, and they have been applied to the solution polymerization of water-soluble monomer acrylamide in water and the emulsion polymerization of methyl methacrylate. © 2016 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 43910.

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INTRODUCTION

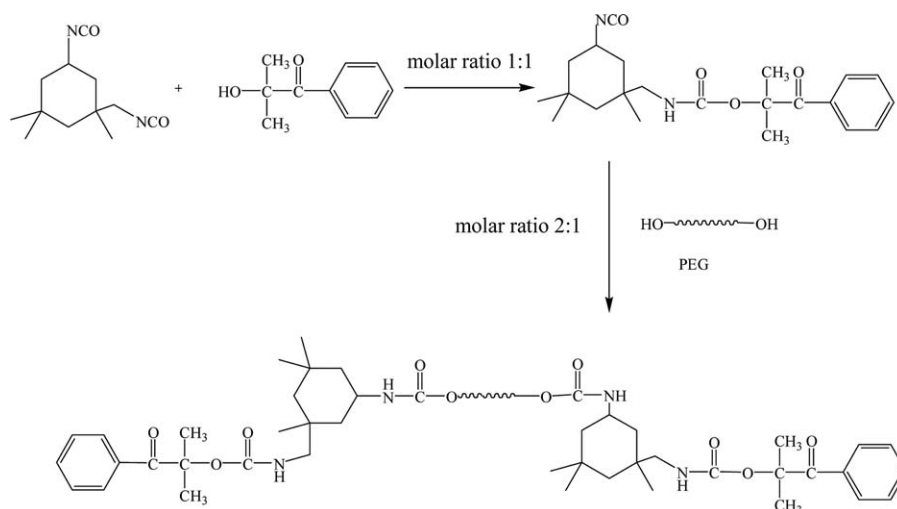
Ultraviolet (UV) curing technology, which is based on a photoinitiator generating radicals under UV radiation to initiate the curing process of oligomers, prepolymers, and various crosslinkers, has found a wide range of industrial applications; these include applications in coatings, adhesives, photoresists, printing inks, encapsulation of electronic components, and the manufacturing of printed circuits.^{1–3} As an indispensable component of UV curing systems, macrophotoinitiators have obtained much attention recently because they have several advantages over photoinitiators with low molecular weights; these advantages include a low odor, low migration, low toxicity, and good compatibility with the matrix.^{4–6} With the increasing awareness of environmental protection, much effort has been paid to the minimization or elimination of the use of toxic substances such as organic solvents and reagents. At the same time, great efforts have been focused on waterborne curing systems because of their prominent superiority in environmental protection.^{7–9} Naturally, waterborne macrophotoinitiators have become a subject of great interest to many scientists.

There are, at least, three methodologies that bring oil-soluble photoinitiators into water. One is the introduction of hydrophilic

groups or oligomers onto an oil-soluble photoinitiator.^{10–17} The second method is the formation of supermolecules of an oil-soluble photoinitiator with β -cyclodextrin.^{18–24} The third approach is the copolymerization of water-soluble monomers, such as acrylamide (Am), with an oil-soluble photoinitiator.^{9,25–29}

2-Hydroxyl-2-methyl-1-phenylpropanone (HMPP) has been widely used in UV curing systems as a low-cost and efficient type I photoinitiator. A series of hyperbranched HMPP-based macrophotoinitiators were synthesized through the reactive hydroxyl group of HMPP.^{30,31} In addition, an HMPP-based macrophotoinitiator with a higher water solubility was also obtained by a supermolecular approach with HMPP and methylated β -cyclodextrin.¹⁹

In this study, we obtained HMPP-based macrophotoinitiators easily by first reacting HMPP with isophorone diisocyanate (IPDI) and subsequently reacting it with poly(ethylene glycol)s (PEGs) with different chain lengths (see Scheme 1). The structural characterization and reactivity determination of these macrophotoinitiators in an aqueous solution polymerization of the water-soluble monomer Am were then carried out. Because of the hydrophilicity of PEG, the HMPP-based macrophotoinitiators had amphiphilic properties. In other words, they were not only



Scheme 1. Synthesis of HMPP-PEG-HMPP.

macrophotoinitiators but could also act as macromolecular surfactants. Therefore, these macrophotoinitiators could also be applied to the UV-initiated emulsion polymerization of methyl methacrylate (MMA), and their role as a surfactant was tested as well.

EXPERIMENTAL

Materials

IPDI, Am, and PEG with different molecular weights were purchased from Sinopharm Chemical Reagent Co., Ltd. The catalyst dibutyltin dilaurate was purchased from Aladdin Reagent Co. (Shanghai, China). Trimethyl propane triacrylate (TMPTA) was obtained from Shin-Nakamura Chemical Co., Ltd. HMPP (Ciba) was used as received. MMA was obtained from Tianjing Kermel Chemical Reagents Development Center. All other reagents were used without any further purification.

Synthesis and Purification of HMPP-PEG-HMPP

A series of amphiphilic macrophotoinitiators were synthesized according to Scheme 1. IPDI (0.02 mol), the catalyst dibutyltin dilaurate (0.04 g), and ethyl acetate (12.24 g) were first added to a 100-mL, three-necked flask equipped with a reflux condenser, nitrogen inlet, and magnetic stirrer. HMPP (0.02 mol) was then added dropwise to the previous mixture at 65 °C under a nitrogen atmosphere. An amount of 0.01 mol of PEG was added finally after the mixture was stirred for 3.5 h. A Fourier trans-

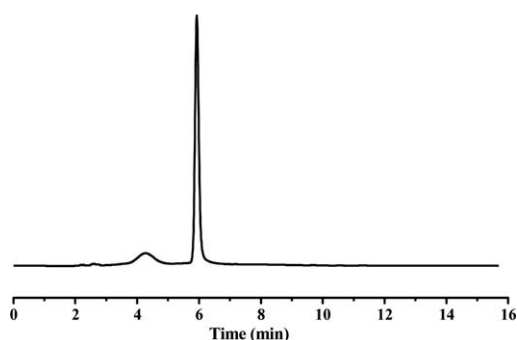


Figure 1. HPLC results for HMPP-PEG4k-HMPP.

form infrared (FTIR) spectrometer was used to monitor the whole process of the reaction. When the isocyanate band around 2256 cm^{-1} disappeared, the mixture was cooled down to room temperature. The solvent ethyl acetate was removed by rotational evaporation. The crude products were purified by precipitation in an excess amount of ether and dried in a high vacuum at room temperature. The final products were protected from light irradiation.

Instrumentation

FTIR spectra were obtained on Nicolet 6700 instrument (Nicolet Instrument, Thermo Co.) at a resolution of 4 cm^{-1} at room temperature. $^1\text{H-NMR}$ spectra were recorded with a 400-MHz Inova NMR spectrometer with CDCl_3 as a solvent and tetramethylsilane as an internal standard. The UV absorption spectra were recorded on a Hitachi U-3900/3900H UV-visible spectrophotometer with ethanol as a reference. A cell path length of 0.5 cm was used. The UV radiation intensity was detected with a UV radiometer (Photoelectrical Instrument Factory, Beijing Normal University, Beijing, China). High-performance liquid chromatography (HPLC) chromatograms were recorded on an

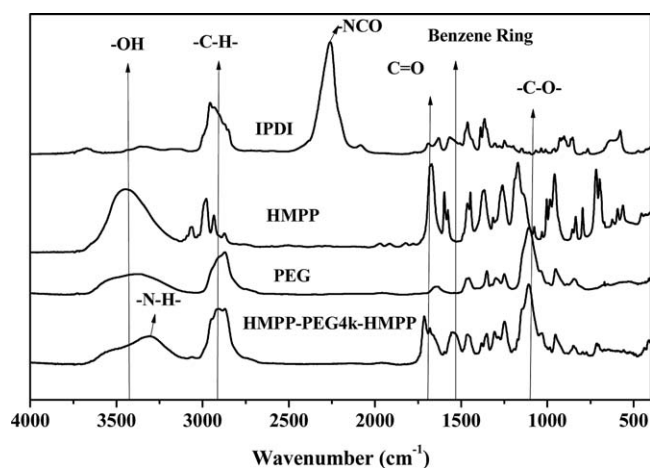


Figure 2. FTIR spectra of the raw materials and the product HMPP-PEG4k-HMPP.

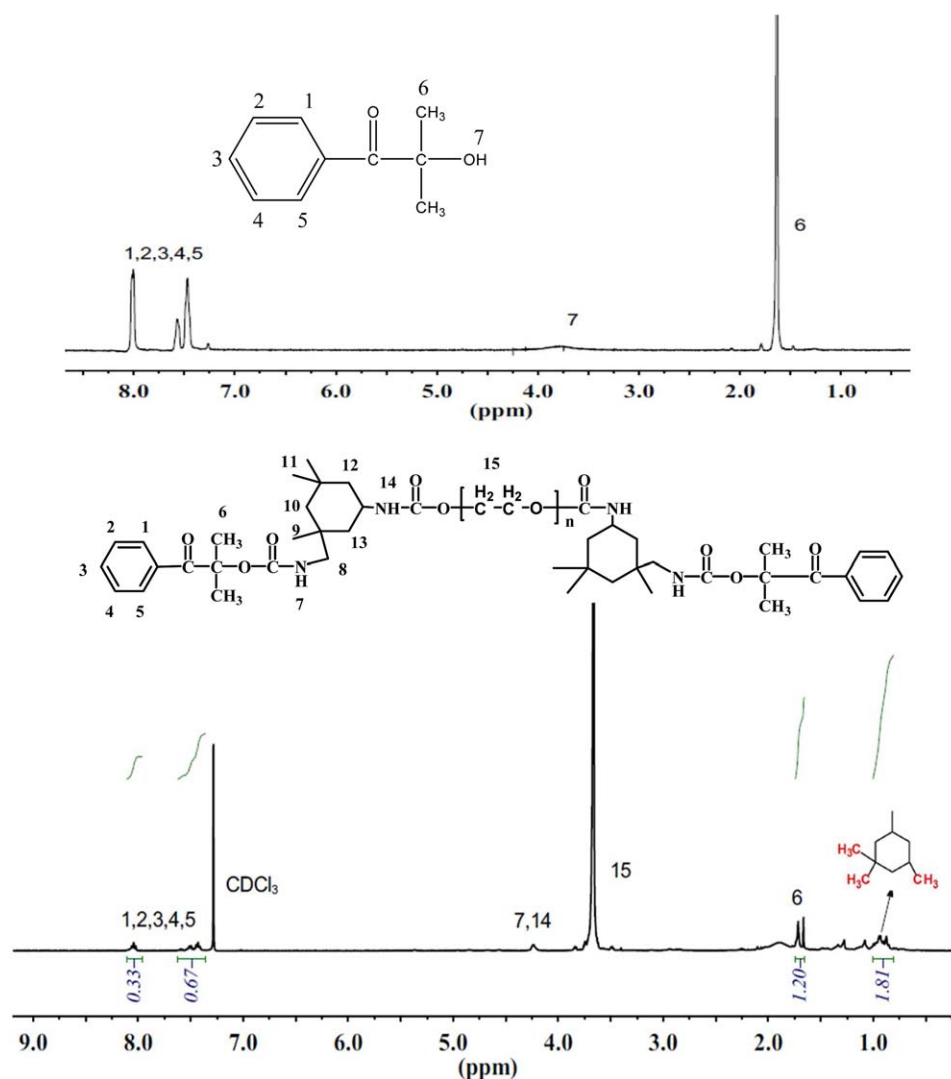


Figure 3. ^1H NMR spectra of HMPP and HMPP-PEG4k-HMPP. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Agilent 1260 with a mixture of acetonitrile and H_2O (acetonitrile/ H_2O = 50:50) as the eluent at a flow rate of 1.0 mL/min. Scanning electron microscopy (SEM) photographs were obtained with a Hitachi scanning electron microscope.

Photopolymerization of Am

Photopolymerizations of Am were carried out in aqueous solution. Bottles with Am solutions containing a given amount of amphiphilic macrophotoinitiators were irradiated with a 350-W,

high-pressure Hg lamp. At the end of a given time, the polymer obtained was transferred into a large amount of methanol, filtered, and dried in a high vacuum to a constant weight. Conversions were determined gravimetrically.

Migration of the Macrophotoinitiators

To determine the migration extent of macrophotoinitiators in the cured matrix, TMPTA was polymerized under UV radiation with the previously obtained macrophotoinitiators and then

Table I. Cloud Points, HLB Values, and Turbidity of the Macrophotoinitiators

	Macrophotoinitiator				
	PEG1k	PEG2k	PEG4k	PEG6k	OP-10
Cloud point ($^{\circ}\text{C}$)	58.32	65.44	75.40	78.51	65.51
HLB ^a	11.29	14.43	16.67	17.72	13.50
HLB ^b	8.35	11.63	14.16	15.24	11.54
Turbidity (g/mL)	0.1963×10^{-3}	3.631×10^{-3}	6.918×10^{-3}	15.14×10^{-3}	2.470×10^{-3}

^a Calculated with the Griffin method.

^b Obtained with the water number method.

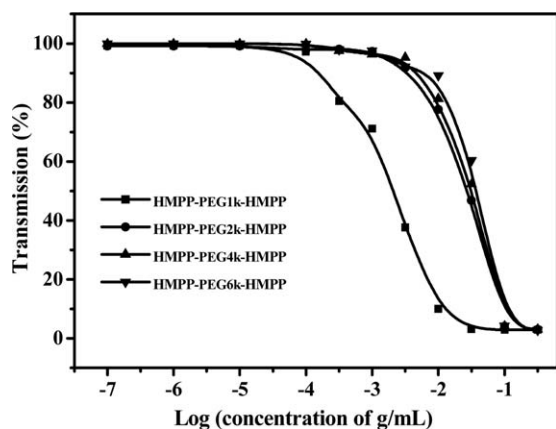


Figure 4. UV transmission of macrophotoinitiators with different PEG chain lengths.

immersed into ethanol. The ethanol solution was sampled at certain sampling intervals, and its UV absorption spectrum was measured. The extracted amount of the macrophotoinitiator from the cured TMPTA matrix (c) was calculated according to eq. 1:

$$A = \epsilon cL \quad (1)$$

where A is the absorption of the ethanol solution of the macrophotoinitiator; ϵ is the molar extinction coefficient of the macrophotoinitiator, which can be determined on the basis of the UV spectra of the macrophotoinitiator's solutions with known concentrations; and L is the cell path length (0.5 cm).

RESULTS AND DISCUSSION

Purification and Characterization of the Amphiphilic Macrophotoinitiators

The synthetic route of the HMPP-based amphiphilic macrophotoinitiators is shown in Scheme 1. Figure 1 shows the HPLC results of the amphiphilic macrophotoinitiator HMPP-PEG4k-HMPP as an example after purification. A single intensive peak appeared at an elution time of about 6 min (the small peak around 4.5 min corresponded to the elution time of the solvent); this indicated that the product had a relatively high purity.

Figure 2 shows the IR spectra of the raw materials and the product HMPP-PEG4k-HMPP. Comparing the IR spectrum of

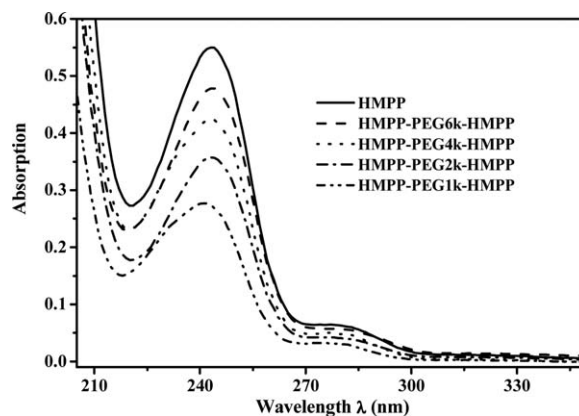


Figure 5. UV spectra of HMPP and HMPP-PEG-HMPP with different PEG chain lengths (concentration of HMPP in ethanol = 5.0×10^{-5} mol/L).

HMPP-PEG4k-HMPP with the raw materials, one can see that the final product HMPP-PEG4k-HMPP was obtained; this could be confirmed by the appearance of the —N—H— , C=O , benzene ring, and —C—O— bands and the disappearance of the —NCO and —OH bands.

The successful synthesis of the product HMPP-PEG4k-HMPP was further verified by the $^1\text{H-NMR}$ spectra of HMPP-PEG4k-HMPP and HMPP, as shown in Figure 3. The peak shifts at 7.45–8.12 and 1.60–1.70 ppm were attributed to the hydrogen atoms of the phenyl ring and —CH_3 in HMPP, respectively. The peak shifts at 0.82–1.0, 3.70, and 4.24 ppm were assigned to —CH_3 in IPDI, $\text{—CH}_2\text{—}$ in PEG, and —N—H— in the product HMPP-PEG-HMPP, respectively. In addition, the ratio of the peak area at 7.45–8.12 ppm to that at 0.82–1.0 ppm was also consistent with the theoretical value shown in Scheme 1.

Because of the amphiphilic nature of these macrophotoinitiators, they exhibited typical properties, such as the cloud point, hydrophilic-lipophilic balance (HLB) value, and turbidity (Table I and Figure 4), of a surfactant.

As shown in Table I, the cloud point and HLB value of these macrophotoinitiators increased with increasing PEG molecular weight, and correspondingly, the turbidity of these macrophotoinitiators decreased. This was apparently the result of the increasing hydrophilicity of the macrophotoinitiators with increasing PEG molecular weight. We also noticed that the

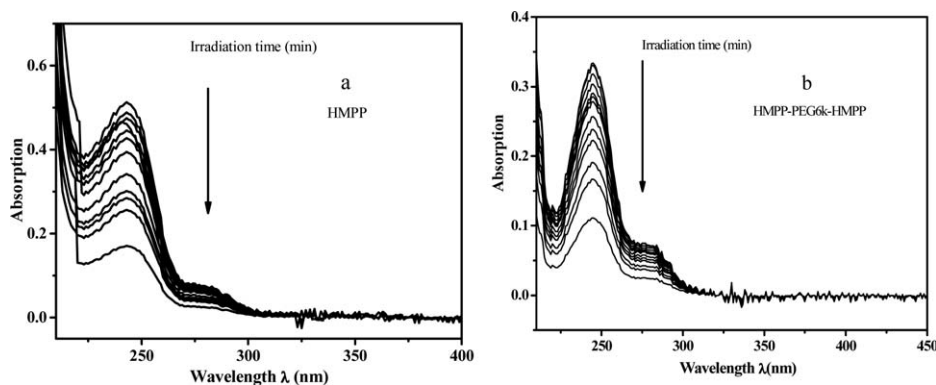


Figure 6. Photolysis of (a) HMPP and (b) HMPP-PEG6k-HMPP.

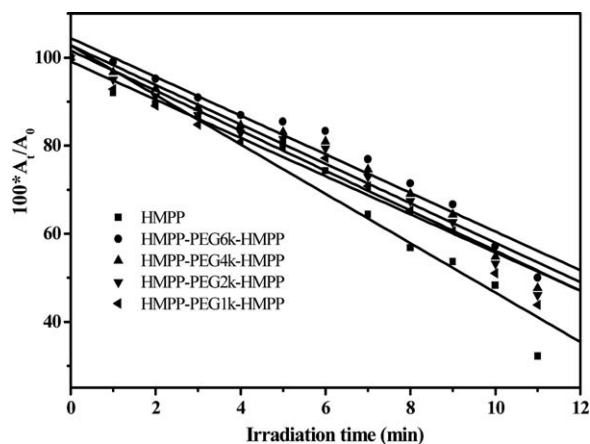


Figure 7. Decay rate of HMPP and HMPP-PEG-HMPP with different PEG chain lengths.

cloud point, HLB value, and turbidity of the macrophotoinitiator HMPP-PEG2k-HMPP was very close to that of the common surfactant OP-10.

UV Absorption Spectra and Photolysis

As found previously, the combination of PEG and HMPP made the final HMPP-PEG-HMPP products typical surfactants and macrophotoinitiators. Naturally, it was important to know whether there was any effect of the PEG chain on the photoinitiation properties of HMPP, that is, whether there was any difference between HMPP and HMPP-PEG-HMPP. The UV absorption spectra of HMPP and HMPP-PEG-HMPP with different PEG chain lengths in ethanol are shown in Figure 5. Compared with that of HMPP, the maximum absorption wavelength of HMPP-PEG-HMPP with different PEG chain lengths showed no change; this suggested that the PEG chain had no effect on the UV absorption wavelength of HMPP.

The UV photolysis of HMPP and HMPP-PEG-HMPP with different PEG chain lengths was also performed in ethanol with a high-pressure Hg lamp. The UV spectra were detected at different irradiation times (only the photolyses of HMPP and HMPP-PEG6k-HMPP are shown in Figure 6). The decay rate (Figure 7) was determined according to eq. 2¹⁷:

$$\text{Decay rate} = 100 \times A_t / A_0 \quad (2)$$

where A_0 is the initial absorption of the initiator solution and A_t is the absorption of the initiator solution at irradiation time t .

The decay rates of HMPP-PEG-HMPP with different PEG chain lengths were almost identical but were slightly lower than

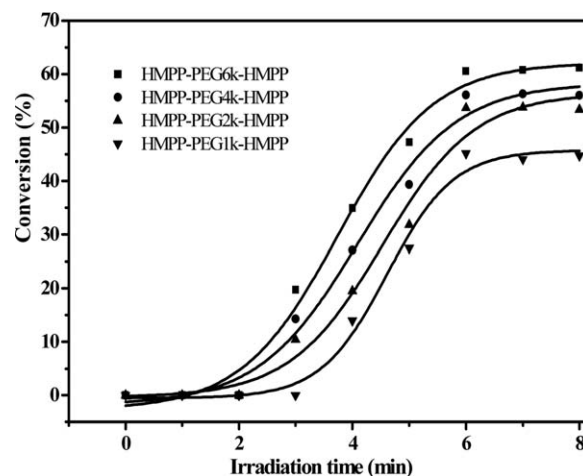


Figure 8. Photopolymerization of Am with HMPP-PEG-HMPP macrophotoinitiators (UV intensity = 8.5 mW/cm²; macrophotoinitiator concentration = 2.5×10^{-5} mol/L in terms of the HMPP moieties; [Am] = 1.0 mol/L).

that of HMPP; this suggested that the PEG chain length had a minor effect on the UV photolysis of HMPP.

Migration of the Macrophotoinitiator

The results shown in Table II are the amounts of HMPP and HMPP-PEG-HMPP that could be extracted by ethanol within 1–7 days. This value could be taken as the maximum amount of photoinitiator that could migrate to the surface of the matrix. Apparently, the amphiphilic macrophotoinitiators had a much lower migration ratio than HMPP. Meanwhile, the migration ratio of HMPP-PEG-HMPP decreased when the molecular weight of PEG increased. These results were attributed to the lower mobility and higher entanglement of PEG chains with a higher molecular weight.

Photopolymerization

To test the efficiency of these amphiphilic macrophotoinitiators in waterborne systems, the photopolymerization of a water-soluble monomer Am was first used as an example. Figure 8 shows the conversion–time curves for the photopolymerization of Am initiated by HMPP-PEG-HMPP with different PEG chain lengths. Both the polymerization rate and the final conversion of Am increased with changing molecular weight of PEG from 1000 to 6000; this indicated that HMPP-PEG6k-HMPP had the highest initiation efficiency. This was counterintuitive because amphiphilic macrophotoinitiators with higher PEG molecular weights will give rise to lower concentrations of HMPP for a certain molar concentration of the macrophotoinitiator. In other words, HMPP-PEG6k-HMPP was expected to have the lowest initiation efficiency among these amphiphilic

Table II. Migration Ratios of HMPP and HMPP-PEG-HMPP with Different PEG Chain Lengths within 1–7 Days

	1 day	2 days	3 days	4 days	5 days	6 days	7 days
HMPP (%)	5.54	6.35	7.34	8.15	9.62	11.10	12.50
HMPP-PEG1k-HMPP (%)	3.36	4.47	5.48	6.85	7.28	7.41	7.52
HMPP-PEG2k-HMPP (%)	2.84	3.67	4.16	5.16	6.12	6.71	6.84
HMPP-PEG4k-HMPP (%)	2.04	2.95	3.23	4.32	5.34	5.90	6.03
HMPP-PEG6k-HMPP (%)	1.94	2.14	2.83	3.56	4.05	4.22	4.31

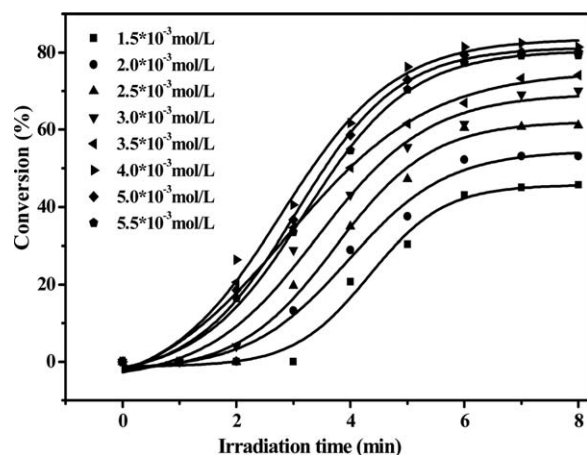


Figure 9. Photopolymerization of Am with concentrations of HMPP-PEG6k-HMPP ranging from 1.5×10^{-5} to 5.5×10^{-5} mol/L (UV intensity = 8.5 mW/cm^2 ; [Am] = 1.0 mol/L).

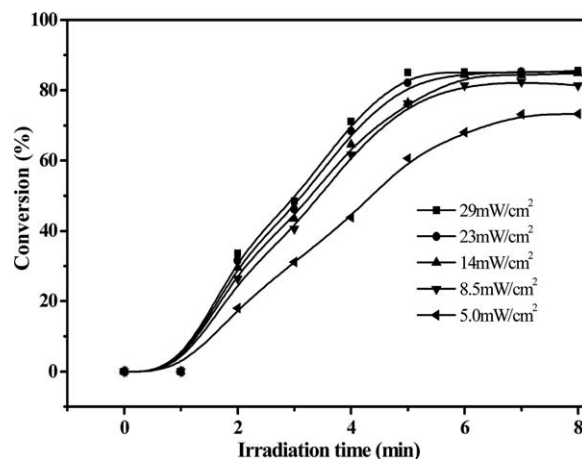


Figure 10. Effect of the UV intensity on the polymerization of Am ([HMPP-PEG6k-HMPP] = 4.0×10^{-3} mol/L; [Am] = 1.0 mol/L).

macrophotoinitiators. There were at least two reasons for such abnormal behavior. One was that longer PEG chain led to higher solubility in these amphiphilic macrophotoinitiators in water; this facilitated their initiation on a water-soluble monomer such as Am. The other reason was that an amphiphilic macrophotoinitiator with a higher PEG molecular weight pro-

duced an aqueous solution with a higher viscosity, and this gave rise to a stronger gel effect.

The effects of the macrophotoinitiator concentration and UV intensity on the polymerization of Am are shown in Figures 9 and 10, respectively. Obviously, they followed the regular rule of free-radical polymerization.

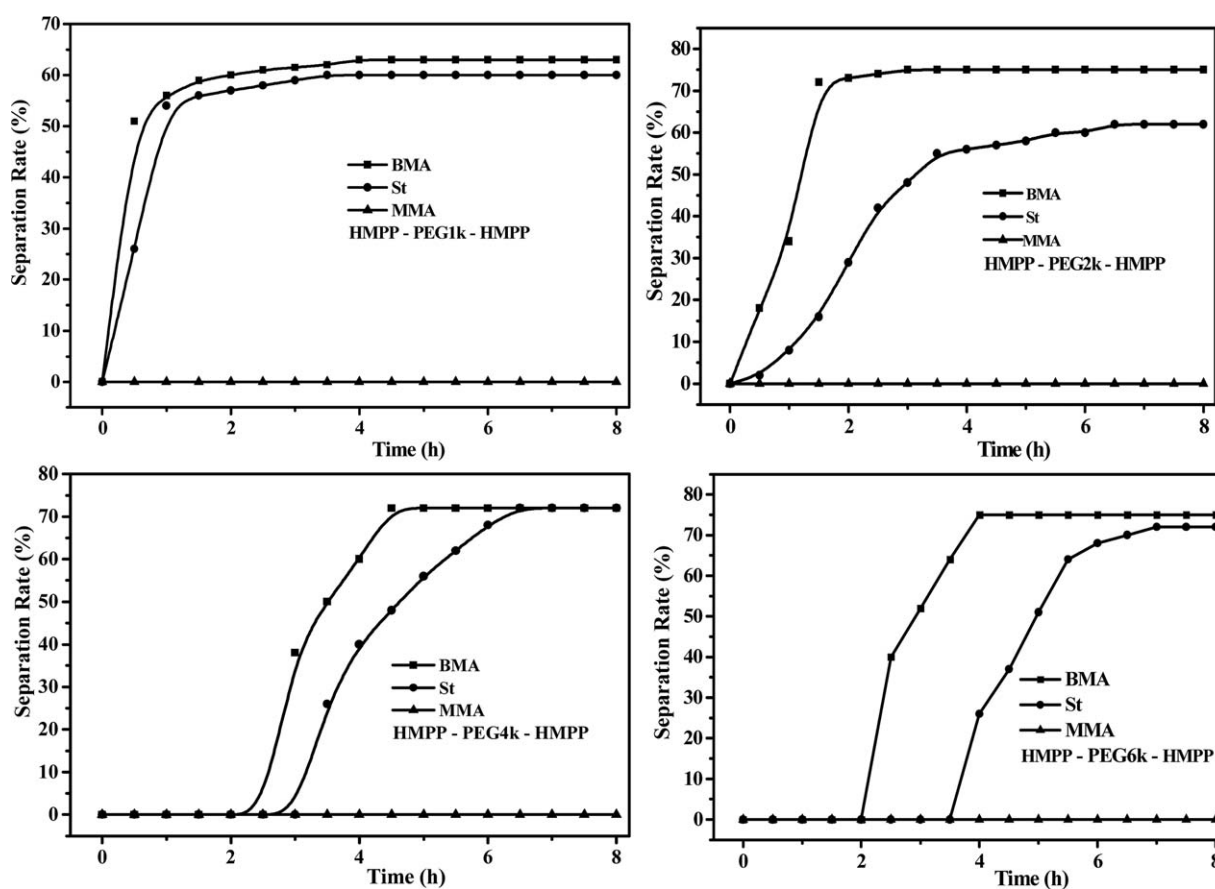


Figure 11. Emulsifying properties of the macrophotoinitiators with different PEG chain lengths. St = styrene.

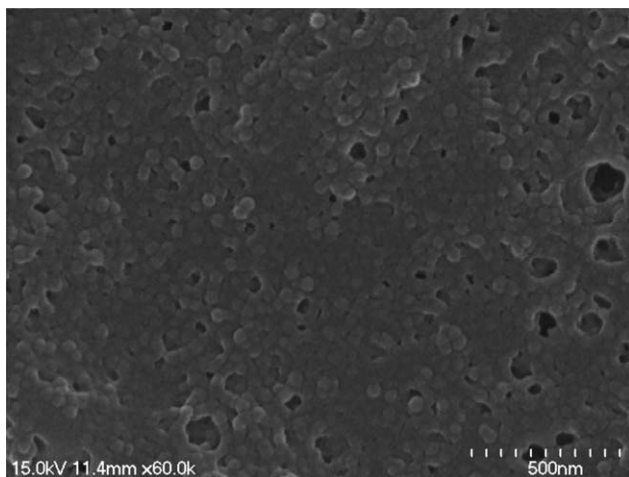


Figure 12. SEM image of a PMMA microsphere obtained by the UV-initiated emulsion polymerization of MMA under low-intensity magnetic stirring.

UV-Initiated Emulsion Polymerization

Before the emulsion polymerization, the stabilization of the macrophotoinitiators on three monomer emulsions were carried out, and the results are shown in Figure 11.

No measureable phase separation of the monomer emulsions was found within 2 h when the macrophotoinitiators HMPP-PEG4k-HMPP and HMPP-PEG6k-HMPP were used; this indicated that these two macrophotoinitiators had the high potential to stabilize the emulsion polymerization of these monomers. HMPP-PEG4k-HMPP was then used to carry out the emulsion polymerization of MMA as an example under UV radiation. An amount of 0.1 g of MMA was added to 4 mL of a 2.5×10^{-5} mol/L HMPP-PEG4k-HMPP aqueous solution. This mixture was pre-emulsified for 30 min and then irradiated with a 350-W high pressure mercury lamp under magnetic stirring. Figure 12 shows an SEM image of the poly(methyl methacrylate) (PMMA) microspheres obtained. It was clear that the PMMA microspheres had a size of about 50 nm, but serious agglomeration was observed. Obviously, in the previous UV-initiated emulsion polymerization of MMA, the amphiphilic macrophotoinitiator HMPP-PEG4k-HMPP acted as both a photoinitiator and an emulsifier because of its amphiphilic structure, although the stability of the latex was not good enough under such low-intensity magnetic stirring. This result inspired us to make polymeric particles by dispersion polymerization with these amphiphilic macrophotoinitiators, and this is under investigation.

CONCLUSIONS

Amphiphilic macrophotoinitiators were prepared through the introduction of the PEG chains with different molecular weights into HMPP. The UV absorption spectrum and photolysis of the amphiphilic macrophotoinitiators were similar to that of HMPP, but the migration rate from the cured matrix was lower compared to that of HMPP. These amphiphilic macrophotoinitiators were successfully used in the polymerization of Am in its aqueous solution, and we found that both the polymerization

rate and the final conversion increased with increasing molecular weight of PEG in macrophotoinitiators. The macrophotoinitiator HMPP-PEG4k-HMPP was also used to carry out the emulsion polymerization of MMA as an example under UV radiation and microspheres with a size of about 50 nm were obtained; this demonstrated that the macrophotoinitiator HMPP-PEG4k-HMPP acted as both a photoinitiator and an emulsifier because of its amphiphilic structure.

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