A Water-Soluble Supramolecular-Structured Photoinitiator between Methylated β-Cyclodextrin and 2,2-Dimethoxy-2-phenylacetophenone

Yuanlong Wang, Xuesong Jiang, Jie Yin

Research Institute of Polymer Materials, School of Chemistry and Chemical Technology, State Key Laboratory for Composite Materials, Shanghai Jiao Tong University, Shanghai 200240, People's Republic of China

ABSTRACT: A water-soluble supramolecular-structured photoinitiator (SSPI) was synthesized by supramolecular self-assembling between methylated β-cyclodextrin (MβCD) and hydrophobic 2,2-dimethoxy-2-phenylacetophenone (DMPA). The structure of SSPI was characterized by X-ray diffraction, FTIR, ^{1}H NMR, UV–vis, and fluorescence spectra. The results indicated that MβCD and DMPA had formed 1 : 1 inclusion complex in methanol solution. The binding constant (K) for the complex was $7.51 \times 10^2 M^{-1}$. SSPI could be dissolved in water easily and its water-solubility was 15.3 g/ 100 mL. SSPI was the more efficient photoinitiator than DMPA for the photopolymerization of acrylamide (AM) in homogeneous aqueous system. The conversion for photopolymerization of trimethylolpropane triacrylate system initiated by SSPI was similar to that initiated by DMPA. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 105: 3817–3823, 2007

Key words: cyclodextrin; 2,2-dimethoxy-2-phenylacetophenone; supramolecular-structured; photoinitiator; photopolymerization; water-soluble

INTRODUCTION

Ultraviolet–visible photopolymerization science and technology have assumed an increasing relevance in many applications, ranging from the production of paper, board, and coating to photoresist.[1–3] In conventional ultraviolet–visible photopolymerization systems, reactive diluents are used to reduce the viscosity of the resin. Because of environmental and legislation constrains, efforts have been made in the last 20 years to develop water as a diluent to replace conventional diluents.[4,5] Water has lots of advantages such as low cost, availability, nontoxicity, and nonflammability. Among photopolymerization system, the photoinitiators are very important components. Great attention has been paid to synthesize new water-soluble photoinitiators in recent years.[6–10] It was well known that the water solubility of oil-soluble photoinitiators could be increased through two methods: firstly, introduction of hydrophilic groups, such as ethoxyethers, to photoinitiator molecules; secondly, attachment of ionic groups, such as quaternary ammonium salts, carboxylic acids, or sulphonic acid, to photoinitiator molecules.[6,11,12] Ritter et al. have reported that hydrophobic monomers became water-soluble owing to the self-assembly between monomer and cyclodextrin (CD).[13–15] The method of self-assembly to getting water-soluble photoinitiator from common photoinitiator is very rapid and effective.

CDs are cyclic oligosaccharides formed by six, seven, or eight units of α-D-(+)-glucopyranose and are called α-, β- or γ-CD, respectively. They possess the ability to encapsulate a wide variety of organic and inorganic compounds into their hydrophobic cavity to form supramolecules.[16–18] This property has been used in industry to increase bioavailability, to mask unpleasant taste, and to increase the solubility of drugs in aqueous solution.[19–23] The structure of β-CD is the most rigid among CDs because of the hydrogen bonds formed between the —CH$_2$OH groups and the —CH$_3$OH groups of the neighboring glucopyranose units. So β-CD shows a low solubility in water. But, methylated β-cyclodextrin (MβCD) as one of β-CD derivative shows higher solubility than β-CD in water.

Benzoin ethers are important commercial radical-type photoinitiators.[24] These compounds undergo α-cleavage to generate benzoyl and substituted benzyl radicals upon irradiation.[25] But most of benzoin ethers are hydrophobic, such as benzoin isobutyl ether, benzoin butyl ether, and 2,2-dimethoxy-2-phenylacetophenone (DMPA). This solubility problem limits their applications as UV-radiation curing materials in homogenous aqueous system.

Recently, Wu et al. reported a water-soluble complex of the MβCD and DMPA and gave a preliminarily result about the mechanism of acrylamide (AM) polymerization.[9] Our research is to develop water-soluble benzoin ethers through self-assembled between MβCD and DMPA to form supramolecular-structured photoinitiator (SSPI). We characterized and confirmed the supramolecular-structure of SSPI further by X-ray diffraction, FTIR, ^{1}H NMR, UV–vis, and fluorescence spectra. We also studied water-solubility of SSPI. Two kinds of commercial monomers, AM and trimethylolpropane triacrylate (TMPTA), were chosen to evaluate the properties of SSPI. Kinetics for photopolymerization of TMPTA initiated by SSPI were also studied through photo-DSC.

EXPERIMENTAL

Materials

2,2-Dimethoxy-2-phenylacetophenone (DMPA) was obtained from Shanghai Jiahe Chemical Co. and recrystallized in 50% isopropyl alcohol aqueous solution. MβCD was purchased from Shandong Xinda Fine Chemical Co. and used without further purification. TMPTA (Nantong Litian Chemical Company) were used as received. AM and methanol (Shanghai Solvent Co.) were purified under standard methods. The water was distilled and deionized.

Measurements

Powder X-ray diffraction patterns for all samples were obtained using X-ray diffractometer (a Rigaku III Dmax 2500) under the following conditions: target Cu; filter Ni; using a Ni filtered Cu-kα radiation as source. Powder samples were mounted on a sample holder and scanned with a step size of $2\theta = 0.01°$ between $2\theta = 5°$ and $50°$.

^{1}H NMR spectra were recorded on a Mercury Plus 400 MHz spectrometer with D_2O as the solvent. FTIR spectra were measured with a Perkin–Elmer Paragon 1000 spectrometer. The samples were prepared as cast films on KBr discs or as KBr pellets.

UV–vis spectra were recorded in methanol solution by a Perkin–Elmer Lambda 20 UV–vis spectrophotometer. The molar extinction coefficient values ε are expressed as $1 \text{ mol}^{-1} \text{ cm}^{-1}$ L.

Fluorescence spectra were recorded in methanol solution by a Perkin–Elmer LS50B luminescence spectrophotometer. The fluorescence spectra of DMPA and SSPI were obtained by exciting at the isosbestic point with emission maximum at 270 nm.

Molecular weight measurement for polyacrylamide was performed with gel permeation chromatography on a Perkin–Elmer Series 200 apparatus on the basis of linear polyglycol standards using water as the eluent.

Preparation of SSPI

MβCD (0.1 mol) was dissolved in 10 mL of methanol and 0.1 mol of DMPA was added. The mixture was sonicated for 20 min, followed by standing overnight at room temperature. DMPA and MβCD were all dissolved in methanol at first. The solution was transparent and then gradually turned turbid. The precipitate was filtered and washed with methanol several times to remove those nonincluded materials. The solid SSPI was dried under vacuum.

UV: $\lambda_{max} = 252$ nm, log ε $(\text{mol}^{-1} \text{ cm}^{-1} \text{ L}) = 4.017$. ^{1}H NMR ($D_2O$, 400 MHz): δ = 8.04–8.02 (2H, aromatic), 7.48–7.44 (3H, aromatic), 7.38–7.34 (3H, aromatic), 7.26–7.22 (2H, aromatic), 5.055–4.885 (7H, —CH=), 3.72–3.67 (21H, —CH=), 3.60–3.41 (28H, —CH—), 3.23–3.12 (12H, —CH=). FTIR (KBr): 3400 (O—H), 2844 (H3C—O), 1644 (C=O), 1500–450 cm^{-1} (glucopyranose ring).

Photopolymerization of AM in water

The equimolar of uncomplexed photoinitiator $(2.5 \times 10^{-2} \text{ mol/L})$ DMPA or SSPI $(2.5 \times 10^{-2} \text{ mol/L})$ was added to an aqueous solution of AM (20 wt %). Photopolymerization was carried out at 25°C in thermostated water bath. The light source was a high-pressure Hg lamp, set at a distance of 40 cm from the sample. The intensity of light was about 0.5 mW/cm^2 and the maximum absorption wavelength was about 365 nm. Photopolymerization was stopped after 60 min. The produced polymer was precipitated with methanol, filtered, and dried *in vacuo* and analyzed.

Photocalorimetry (photo-DSC)

The photopolymerization kinetics was carried out by DSC 6200 (Seiko Instrument) photo-DSC with incident light of 365 nm. The experimental setup was described in prior publication.[26–28] The sample contained photoinitiator ([PI] =0.08M) and TMPTA. Approximately 1.2 mg sample was placed in the aluminum DSC pans. By integrating the area under the exothermic peak, the conversion of the vinyl groups (C) or the extent of reaction could be determined according to:

$$C = \Delta H_t / \Delta H_0^{\text{theor}} \tag{1}$$

where ΔH_t is the reaction heat evolved at time t, and $\Delta H_0^{\text{theor}}$ is the theoretical heat for complete conversion. For an acrylic double bond, $\Delta H_0^{\text{theor}} = 86$ kJ/mol.[29] The rate of polymerization (R_p) is directly related to the heat flow (dH/dt) by the following equation:

$$R_p = dc/dt = (dH/dt)/\Delta H_0^{\text{theor}} \tag{2}$$
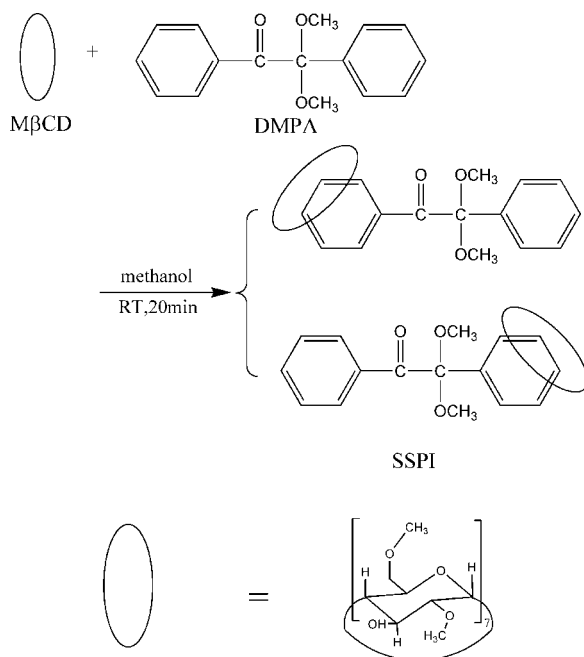
Scheme 1 Synthesis of SSPI by self-assembly.

RESULTS AND DISCUSSION

Synthesis and characterization of SSPI

SSPI was synthesized by reacting MβCD with DMPA, as shown in Scheme 1. DMPA and MβCD were all dissolved in methanol. The solution was transparent and then gradually turned turbid. The appearance of precipitate is considered the formation of SSPI between MβCD and DMPA, which is characterized by XRD, IR, ^{1}H NMR, UV–vis, and fluorescence.[30,31]

Powder XRD is used to measure the crystallinity of SSPI.[32] Figure 1 represented the powder X-ray diffraction patterns of pure MβCD and DMPA, their physical mixture, and SSPI. The diffraction pattern of SSPI was very different from that of the physical mixture. Jiao et al. and Braga et al. reported the formation of a diffuse diffraction pattern, appearance of new peaks, and disappearance of characteristic peaks of the guest as evidence for formation of inclusion complex with CDs.[33,34]

Figure 2 is the IR spectra of MβCD, DMPA, and SSPI. The spectrum of SSPI had typical bands of MβCD, indicating no chemical modification of the CD host. However, the band at about 1689 cm^{-1}, which corresponds to the carbonyl vibrations of DMPA, shifted to 1644 cm^{-1} in SSPI. This phenomenon is probably because of the formation of hydrogen bonds.[18] It is thought that hydrogen bonds can be formed between the hydroxyl groups of MβCDs as well as between the hydroxyl groups of MβCDs and the carbonyl groups of DMPAs. Furthermore, the band at about 2828 cm^{-1}, related to the methyl
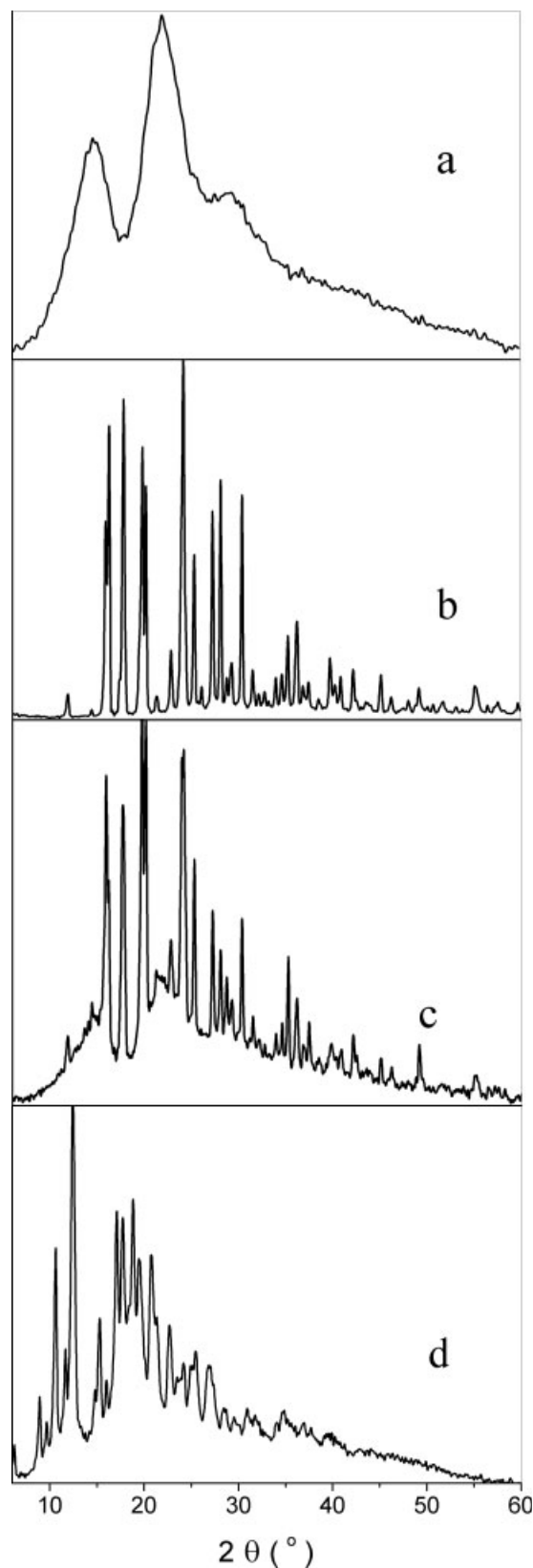

Figure 1 X-ray powder patterns of (a) MβCD, (b) DMPA, (c) physical mixtures, and (d) SSPI.
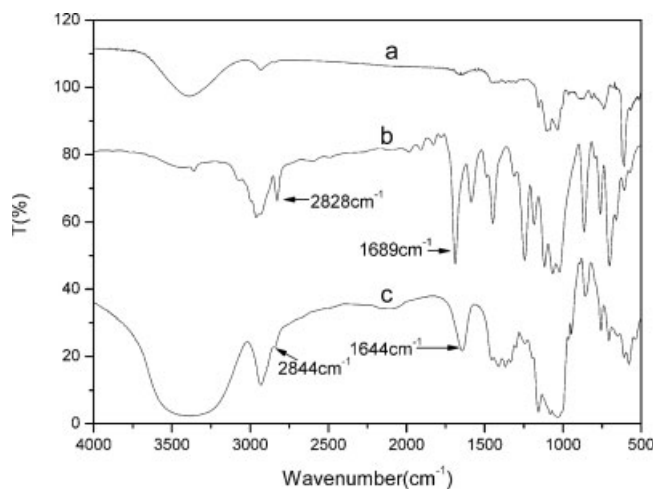
Figure 2 The FTIR spectra of (a) MβCD, (b) DMPA, and (c) SSPI.

vibrations of DMPA, shifted to a higher frequency by ~16 cm^{-1} (from 2828 to 2844 cm^{-1}). These can also be considered as proofs for the formation of SSPI, which are in agreement with the result of the XRD spectra. Meanwhile, carbonyl and methyl in DMPA were both affected by the presence of MβCD. These phenomena might indicate that one of the two DMPA benzene rings was included into MβCD cavity.

The ^{1}H NMR spectroscopy of SSPI and MβCD in D$_2$O indicated the presence of the hydrophobic photoinitiator (Fig. 3). Figure 3(1a) showed proton shifts of SSPI. Figure 3(2a) showed proton shifts of MβCD. The typical shifts of MβCD protons in SSPI, which may be because of the effect of DMPA, indicate that supramolecular-structured is formed between MβCD and DMPA.[13] Moreover, the integral ratio illustrates that the radio of MβCD and DMPA is 1 : 1.
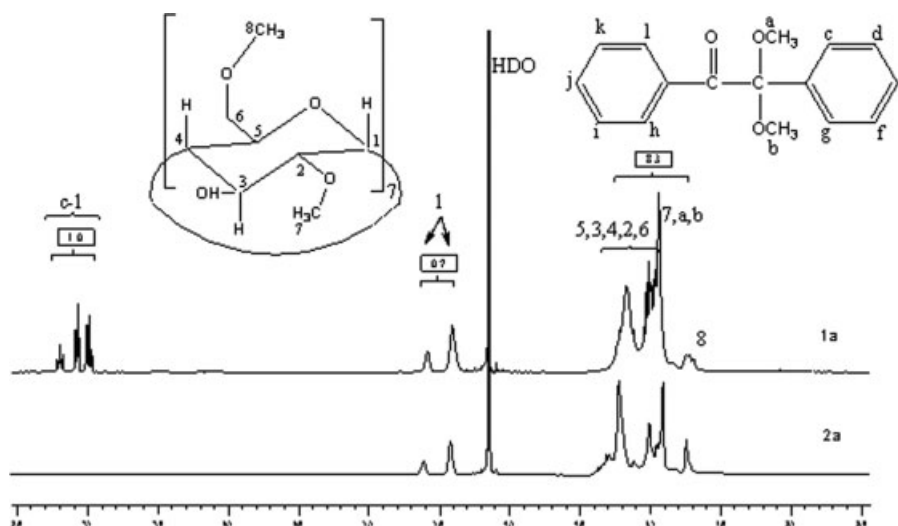
Figure 4 was the UV–vis absorption spectra of DMPA and SSPI in methanol. SSPI exhibited the usual characteristic absorption of DMPA and had the similar maximum UV–vis absorption at 252 nm. This showed that the structure of SSPI did not influence the UV–vis absorption of DMPA.

Complex binding constant of SSPI

Figure 5 was the emission spectra of DMPA (1 × 10^{-5}M) in methanol solutions of MβCD. The emission was red shifted with enhancement in fluorescence intensity on increasing the MβCD concentration. It is easy to note that the increase in fluorescence intensity of DMPA with the increase in the MβCD concentration is because of the incorporation of DMPA into the nonpolar cavity.

The complex binding constant (K) for SSPI of DMPA and MβCD was analyzed by the Benesi–Hildebrand plot[35] as given in the following form:

$$F^0/(F - F^0) = 1/([M\beta CD]KA) + 1/A \qquad (3)$$

where K is the complex binding constant, F^0 is the initial fluorescence intensity of free DMPA, F is the maximum value reached by the fluorescence intensity of SSPI, and A is a constant.

Figure 6 showed the plot of $F^0/(F - F^0)$ versus $1/[M\beta CD]$. The linearity of the plot reflects the formation of a 1 : 1 complex between DMPA and MβCD. From the slope and intercept of the curve it is possible to calculate the complex binding constant (K) of 7.51 × 10^{2}M^{-1}.

Water-solubility of SSPI

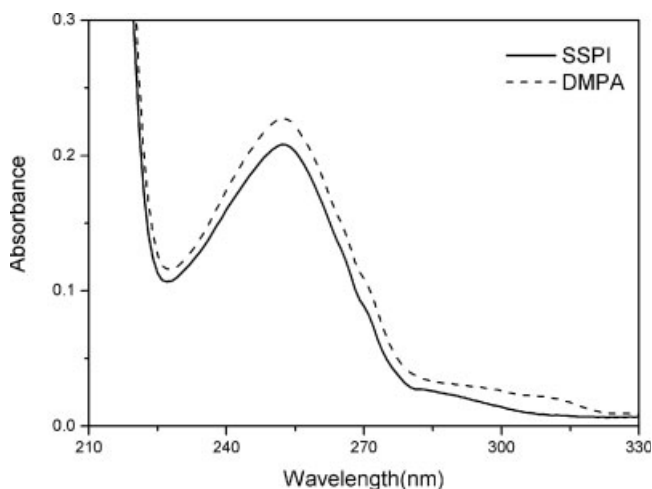As showed in Figure 7, UV–vis absorption was used to study the water-solubility of SSPI. With increasing

Figure 3 400 MHZ ^{1}H NMR spectra of SSPI (1a) and MβCD (2a) in D$_2$O.

Figure 4 UV–vis absorption spectra of DMPA and SSPI in methanol solution ([DMPA] = $2 \times 10^{-5}M$; [SSPI] = $2 \times 10^{-5}M$).

Figure 6 Double reciprocal curve of 1 : 1 inclusion complex of DMPA with MβCD.

the concentration of DMPA in water, the mixture became more and more turbid. But with increasing the concentration of SSPI in water, the solution was still clear. A dramatic decrease in transmission with increase in the concentration of DMPA in water was regarded as a consequence of scattering of light. Water solubility of SSPI was 15.3 g/100 mL

Photopolymerization of AM and TMPTA systems

The photopolymerization of AM in aqueous medium can be realized using SSPI as photoinitiator. Table I showed the results for the photopolymerization of AM initiated by SSPI and DMPA.

The photopolymerization initiated by SSPI ended up with higher yields than the photopolymerization
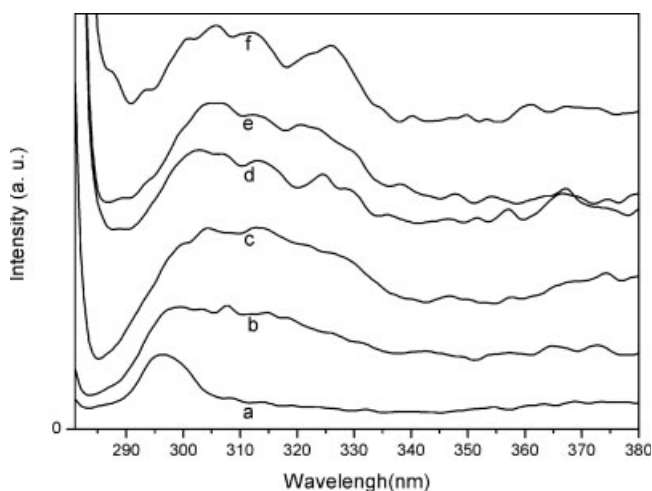
initiated by DMPA. This is probably because SSPI had better water-solubility than DMPA. However, the volume of radicals yielded from SSPI was higher than the volume of radicals yielded from DMPA, which might lead to the higher dispersity of polymer.

The photo-DSC method is widely used in studying the photopolymerization of multifunctional monomers.[36] Figure 8(a) showed the photo-DSC exotherms for the photopolymerization of the UV-curable TMPTA systems using different photoinitiator systems cured at 25°C by UV light with an intensity of 50 mW/cm². Figure 8(b) displayed plots of the conversion versus irradiation time. Figure 8(c) showed plots of the polymerization rate versus conversion of TMPTA for DMPA and SSPI. Photo-DSC results of TMPTA initiated by these photoinitiators

Figure 5 Fluorescence spectra of $1 \times 10^{-5}M$ DMPA at different MβCD concentrations: (a) [MβCD] = $0M$, (b) $0.002M$, (c) $0.004M$, (d) $0.005M$, (e) $0.006M$, and (f) $0.008M$.
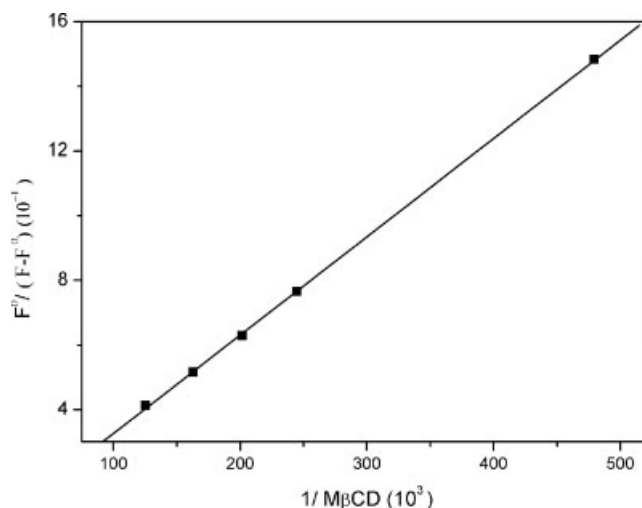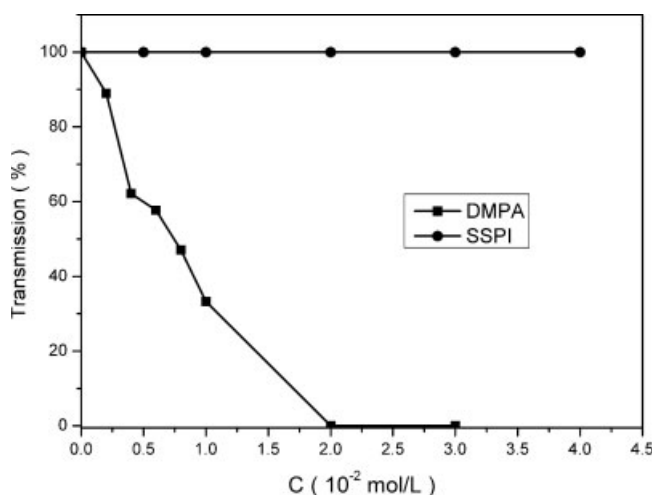

Figure 7 Transmission at 700 nm of the aqueous dispersions of DMPA and the solution of SSPI at different photoinitiator concentrations.

TABLE I
**Results of the Photopolymerization of
AM Aqueous Solution**

Initiator	Yield (%)	$\overline{M}_w$ (g/mol)	$\overline{M}_n$ (g/mol)	$\overline{M}_w/\overline{M}_n$
SSPI	72	9.89×10^6	2.53×10^6	3.90
DMPA	41	1.34×10^7	5.67×10^6	2.36

TABLE II
**Photopolymerization of TMPTA Initiated by SSPI
and DMPA and Cured at 25°C by UV Light with
an Intensity of 50 mW/cm²**

Photoinitiator	$R_{p,\max}$ (s⁻¹)	Final conversion (%)	$H_{\max}$ (mW/mg)	$T_{\max}$ (s)
SSPI	0.036	32.23	36.82	7.0
DMPA	0.041	37.53	48.10	6.4

The photoinitiator concentration is 0.08M.

were shown Table II. It was observed that SSPI could photoinitiate the polymerization of TMPTA quite efficiently. Meanwhile, it was also obvious that the systems with DMPA exhibited a slightly higher exotherm and ultimate percentage conversion as well as faster reaction rate than the systems of SSPI. These results maybe caused by the larger molecular size and the slower diffusion of SSPI because of the high viscosity of TMPTA polymerization system. The photo-DSC profiles had very similar shape, which indicated that these two photoinitiators might have the same decomposition mechanism (Scheme 2). DMPA decomposed into benzoyl and substituted benzyl radicals under UV-irradiation. Benzoyl radicals almost exclusively contributed to the initiation process. Substituted benzyl radicals would further recombine into noninitiating compounds.[37] So the photopolymerization of SSPI initiated system was mainly attributed to the supramolecular-structured benzoyl radical (R_1) and benzoyl radical (R_3).

CONCLUSION

SSPI between DMPA and MβCD had been successfully prepared, which has high water-solubility. The supramolecular-structure of SSPI was characterized and confirmed and K is $7.51 \times 10^2 M^{-1}$. The radio of
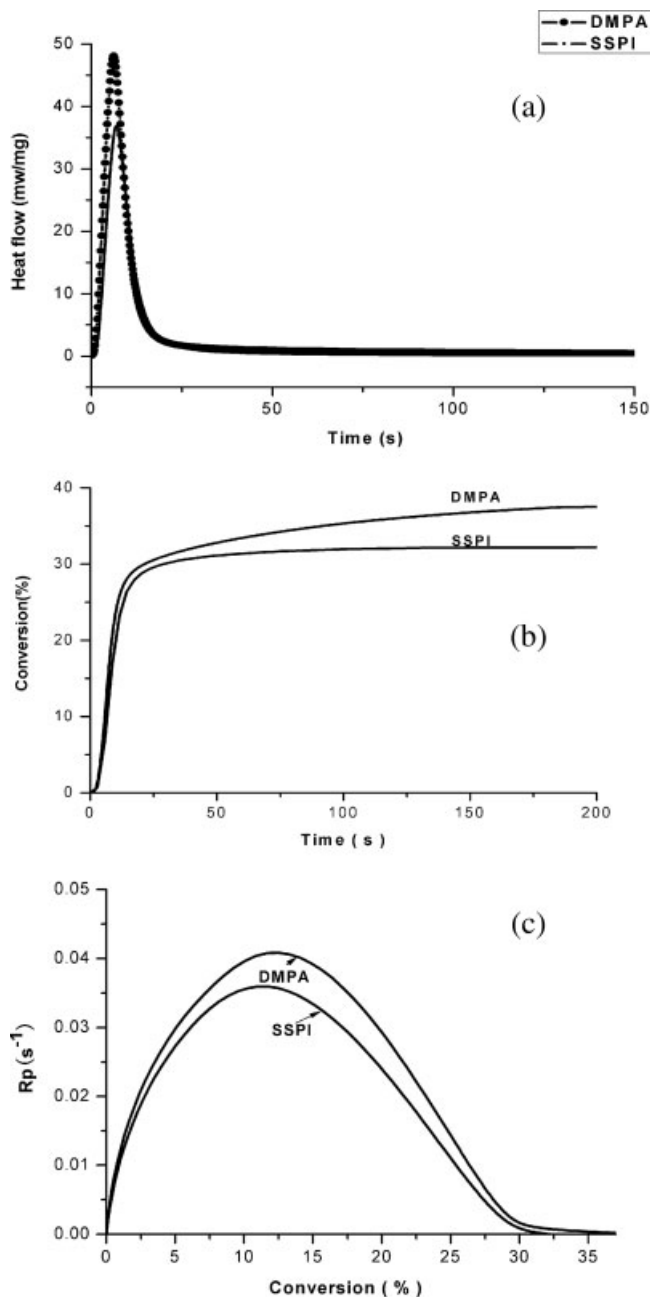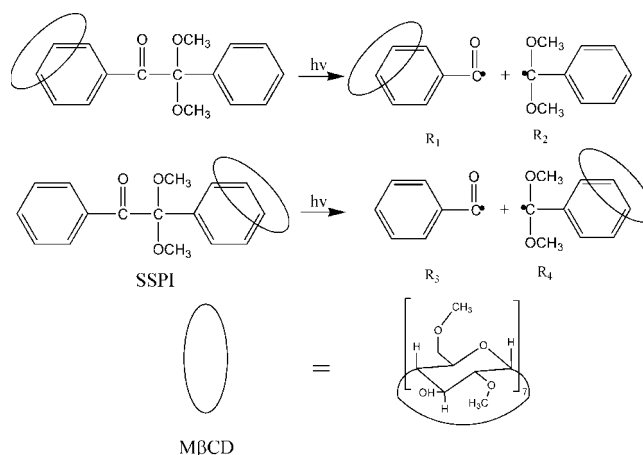

Figure 8 (a) Photo-DSC profiles for DMPA and SSPI in TMPTA, (b) conversion versus time, and (c) rate versus conversion for photopolymeizition of TMPTA for DMPA and the supramolecular-structured PI cured at 25°C by UV light with an intensity of 50 mW/cm² (DMPA = 0.08M; SSPI = 0.08M).

Scheme 2 Photoinitiation mechanism of SSPI.

DMPA to MβCD is about 1 : 1. One of the two DMPA benzene rings could be included into MβCD cavity. The photopolymerization of AM aqueous system with SSPI achieved higher conversion than the system with DMPA. SSPI can also photoinitiate the polymerization of TMPTA, but not as efficient as DMPA. The supramolecular-structured benzoyl radical (R_1) and benzoyl radical (R_3) played an important role in photopolymerization initiated by SSPI.

References

1. Moszner, N.; Salz, U. Prog Polym Sci 2001, 26, 535.
2. Nguyen, K. T.; West, J. L. Biomaterials 2002, 23, 4307.
3. Aydin, M.; Arsu, N.; Yagci, Y. Macromol Rapid Commun 2003, 24, 718.
4. Liska, R. J Polym Sci Part A: Polym Chem 2002, 40, 1504.
5. Corrales, T.; Catalina, F.; Peinado, C.; Allen, N. S. J Photochem Photobiol A: Chem 2003, 159, 103.
6. Kojima, K.; Ito, M.; Morishita, H.; Hayashi, N. Chem Mater 1998, 10, 3429.
7. Lougnot, D. J.; Turck, C.; Fouassier, J. P. Macromolecules 1989, 22, 108.
8. Alupei, I. C.; Alupei, V.; Ritter, H. Macromol Rapid Commun 2002, 23, 55.
9. Li, S. J.; Wu, F. P.; Li, M. Z.; Wang, E. J. Polymer 2005, 46, 11934.
10. Yang, J.; Zeng, Z.; Chen, Y. J Polym Sci Part A: Polym Chem 1998, 36, 2563.
11. Visconti, M.; Cattance, M. Prog Org Coat 2000, 40, 243.
12. Liska, R.; Knauo, S.; Gruber, H.; Wendrinsky, J. Surf Coat Int 2000, 6, 297.
13. Storsberg, J.; Ritter, H. Macromol Rapid Commun 2000, 21, 236.
14. Choi, S. W.; Ritter, H. Macromol Rapid Commun 2004, 25, 716.
15. Ritter, H.; Schwarz-Barac, S.; Stein, P. Macromolecules 2003, 36, 318.
16. Szejtli, J. Chem Rev 1998, 98, 1743.
17. Bernhardt, S.; Glöckner, P.; Theis, A.; Ritter, H. Macromolecules 2001, 34, 1647.
18. Indirapriyadharshini, V. K.; Karunanithi, P.; Ramamurthy, P. Langmuir 2001, 17, 4056.
19. Fischer, M.; Ritter, H. Macromol Rapid Commun 2000, 21, 142.
20. Uekama, K.; Hirayama, F.; Irie, T. Chem Rev 1998, 98, 2045.
21. Goyenechea, N.; Sánchez, M.; Vélaz, I.; Martin, C.; Martinez-Ohárriz, M. C.; González-Gaitano, G. Luminescence 2001, 16, 117.
22. Li, J. J.; Guo, Y. S.; Zografi, G. J Pharm Sci 2002, 91, 229.
23. Lima, S.; Goodfellow, B. J.; Teixeira-Dias, J. J. C. J Phys Chem A Polym Chem 2004, 108, 10044.
24. Kizilcan, N. J Appl Polym Sci 1999, 72, 927.
25. Fouassier, J. P. Photoinitiation, Photopolymerization and Photocuring Fundametals and Application; Hanser: New York, 1995.
26. Jiang, X. S.; Xu, H. J.; Yin, J. Polymer 2005, 46, 11079.
27. Cho, J. D.; Hong, J. W. J Appl Polym Sci 2004, 93, 1473.
28. Padon, K. S.; Scranton, A. B. J Polym Sci Part A: Polym Chem 2001, 39, 715.
29. Andrejewska, E.; Andrzejewski, M. J Polym Sci Part A: Polym Chem 1998, 36, 665.
30. Harada, A.; Li, J.; Kamachi, M. Macromolecules 1993, 26, 5698.
31. Li, J. Y.; Yan, D. Y. Macromolecules 2001, 34, 1542.
32. Veiga, M. D.; Diaz, P. J.; Ahsan, F. J Pharm Sci 1998, 87, 891.
33. Jiao, H.; Goh, S. H.; Valiyaveettll, S. Macromolecules 2001, 34, 8138.
34. Braga, S. S.; Ferreira, R. A. S.; Goncalves, I. S.; Pillinger, M.; Rocha, J.; Teixeira-Dias, J. J. C.; Carlos, L. D. J Phys Chem B Polym Phys 2002, 106, 11430.
35. Cho, D. W.; Kim, Y. H.; Kang, S. G.; Yoon, M.; Kim, D. J Phys Chem 1994, 98, 558.
36. Cho, J. D.; Ju, H.T.; Hong, J. W. J Polym Sci Part A: Polym Chem 2005, 43, 658.
37. Witte, R. P.; Black, A. J.; Palmer, C.; Kao, W. J. J Biomed Mater Res A 2004, 71, 508.