

Synthesis and Evaluation of 4-Benzophenone Methoxyl Methacrylate As a Polymerizable Photoinitiator

By Guangyu HOU,¹ Suqing SHI,² Shiji LIU,¹ and Jun NIE^{1,*}

Synthesized 4-benzophenone methoxyl methacrylate (BMM) was used as a polymerizable photoinitiator in combination with 2-(*N,N*-dimethylamino) ethylmethacrylate (DMEM) to initiate the UV photopolymerization of the mixture of 70 wt % 2,2-bis[4-(2-hydroxy-3-methacryloxypropoxy)phenyl]-propane (Bis-GMA) and 30 wt % triethylene glycol dimethylacrylate (TEGDMA). Real time infrared spectroscopy (RTIR) was used to monitor the extent of polymerization and dynamic mechanical analyzer (DMA) was used to measure the mechanical properties of the cured samples. Water sorption and solubility of cured samples were tested according to ISO4049's standards. The obtained results indicated that increasing the concentration of DMEM or BMM led to the increase of double bond conversion and the rate of polymerization. Comparing with the non-polymerizable photoinitiating system in the same curing condition, benzophenone(BP)/ethyl 4-dimethylamino-benzoate (EDMAB), BMM/DMEM showed the slightly higher initiating reactivity. The glass transition temperature (T_g), storage modulus, water sorption and solubility of the cured samples initiated by BMM/DMEM were slightly lower than that of samples initiated by BP/EDMAB.

KEY WORDS: Polymerizable Photoinitiator / FT-IR / Kinetics / Photopolymerization /

The technology of photoinduced polymerizations is widely used in several industrial fields. Important advantages offered by this technology such as high curing speed, reduced release of volatiles compounds because of no solvents, low cost of equipment, good mechanical properties, inertness to solvents and resistance to abrasion of the obtained polymer could be achieved through a high degree of cross-linking reaction.¹⁻⁶

The photoinitiator system is a key component in the formulation, which is capable of absorbing the incident UV and/or visible radiation wavelengths to produce reactive species, then convert the monomer or prepolymer system into a linear or highly crosslinked network.^{3,4} In recent years, the studies were focused on the development of polymeric and polymerizable photoinitiators with reactive functionalities, which could led to higher activity or greater curing speed coupled with lower migration rates and/or water solubility.⁷⁻⁹

The free radical photopolymerizations are usually performed in presence of photoinitiators of "cleavage" type (type I) or hydrogen abstraction type (type II).^{3,4,10} The latter was generally used in dental restorative, contact lens, food-packaging materials, and so on. Benzophenone derivatives as one of the most commonly used photoinitiator could initiate the polymerization of vinyl monomers with an amine as a coinitiator to speed up the reaction.^{11,12} However, the free radical generated by the benzophenone moiety and synergistic amine may actually cause some problems for biomedical or food packaging materials. Some evidence of carcinogenic activity of benzophenone was found by feeding a groups of 50 males and 50 females F344 rats and B6C3 mice with diets containing 0, 312, 625 and 1520 ppm benzophenone for 105

weeks.¹³ Thus, if both the photoinitiator and the synergist could be incorporated into a polymer, the biocompatibility of the polymer would be greatly improved.^{9,14-17}

In this study, the mixture of benzophenone-containing methacrylate and a polymerizable amine is expected to have more biocompatibility because it should be incorporated into the final polymer.^{14,15} Real time infrared spectroscopy (RTIR) was used to monitor the extent of polymerization, and dynamic mechanical analyzer (DMA) was used to measure the glass transition temperature (T_g) and modulus of the resin system. Water sorption and solubility were measured according to ISO 4049's standards.

MATERIALS AND METHODS

Materials

2,2-Bis[4-(2-hydroxy-3-methacryloxyprop-1-oxo) phenyl]-propane (Bis-GMA, Sartomer), triethylene glycol dimethacrylate (TEGDMA, Sartomer), 2-(*N,N*-diamino)ethyl methacrylate (DMEM, AcrOs Organics), benzophenone (BP, AcrOs Organics), and ethyl 4-(dimethylamino)benzoate (EDMAB, Aldrich) were used as received. Other chemicals were analytical reagent and used without further purification. Chemical structures of monomers and photoinitiator system were shown in Figure 1.

Methods

NMR. ¹H NMR spectra were recorded on a Bruker AV600 unity spectrometer operated at 600 MHz, with CDCl₃ as solvent.

¹Key Lab. of Beijing City on Preparation and Processing of Novel Polymer Materials, College of Material Science and Engineering, Beijing University of Chemical Technology, Beijing, 100029, P. R. China

²Department of Chemistry, Northwest University, Xi'an, 710069, P. R. China

*To whom correspondence should be addressed (Tel: +86-10-64421310, Fax: +86-01064421310, E-mail: niejun@mail.buct.edu.cn).

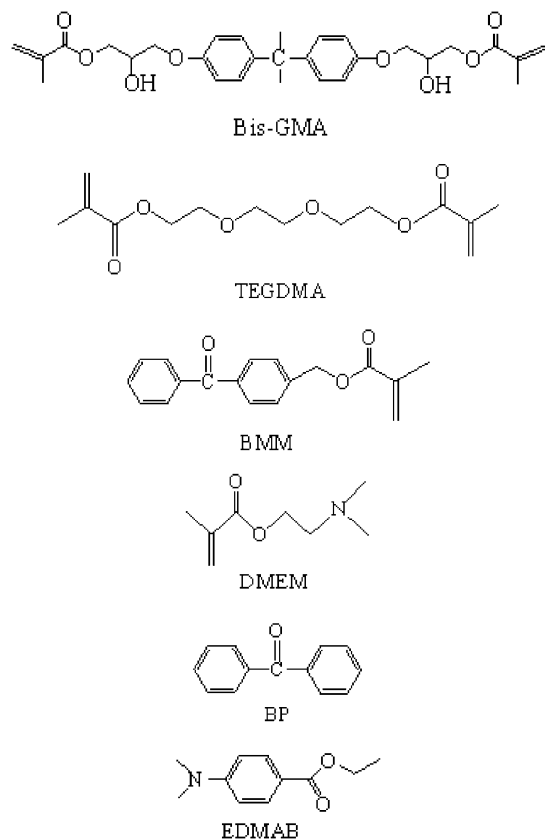


Figure 1. Chemical structure of monomers and photoinitiator system.

FT-IR. The mixture of monomer and photoinitiator was placed in a mold made from glass slides and spacers with 8 ± 0.5 mm in diameter and 1.2 ± 0.1 mm in thickness. The samples were irradiated by UV spot light source (EFOS Lite, with 320–390 nm filter and 5 mm crystal optical fiber, Canada) at room temperature with various light intensities (UV Light Radiometer, Beijing Normal University, China). FT-IR (Nicolet 5700, Thermo Electron, USA) was used to monitor absorbance change of =C-H peak area from 6107 to 6227 cm^{-1} in the near IR range which was correlated to the extent of polymerization. For each sample, the series FT-IR runs were repeated three times.

DMA. A dynamic mechanical analyzer (DMA) (Rheometric, USA) was used to measure the mechanical properties. The samples were photocured at room temperature with a UV light source (EFOS Lite, 320–390 nm filter, light intensity = 20 mW/cm^2) for 15 min in a mold made from glass slides and spacers. The polymerized samples were put at room temperature for 5 d after curing to ensure that postpolymerization process was complete. The samples used for DMA were thin rectangular films of 1.2 mm thickness and dimensions of 7 mm \times 35 mm. Dynamic mechanical analysis was performed over a temperature range from -50 to 200 $^{\circ}\text{C}$ with a ramping rate of 5 $^{\circ}\text{C}$ per minute using extension mode. The loss and storage modulus and the loss tangent ($\tan \delta$, ratio of loss to storage modulus) were recorded as a function of temperature,

and the glass transition temperature (T_g) was taken to be the maximum of the loss tangent versus temperature curve.

Water Sorption and Solubility. Water sorption and solubility were measured according to ISO 4049's standards. The specimens, 15 ± 1 mm in diameter and 1.2 ± 0.1 mm in thickness, were stored in a desiccator that contained anhydrous calcium chloride. The samples were maintained at 37 ± 1 $^{\circ}\text{C}$ for 24 h. The temperature was then decreased to 23 $^{\circ}\text{C}$ for 1 h and the samples were subsequently weighed to an accuracy of ± 0.2 mg. This process was repeated until a constant mass m_1 was obtained. The specimens were then immersed in water and maintained at 37 $^{\circ}\text{C}$ for 7 d. After this time, the samples were taken out, washed with water, blotted to remove surface water, waved in air for 15 s, and weighed 1 min after removal from water. This measurement was recorded as m_2 . Following this weighing, the specimens were replaced into the desiccator, and the cycle described previously was repeated until a final constant mass was obtained (m_3). For each polymer system, the value taken was the average of five specimens. The specimen volumes (V) were also measured. To calculate the water sorption (W_{sp}) and solubility (W_{sl}), the following equations were used:

$$W_{\text{sp}} = (m_2 - m_3)/V \quad (1)$$

$$W_{\text{sl}} = (m_1 - m_3)/V \quad (2)$$

All samples were cured with a UV light source (EFOS Lite, 320–390 nm, light intensity = 20 mW/cm^2) for 10 minutes before measurement.

Synthesis of BMM. BMM was synthesized by the following procedure (Figure 2). A mixture of 0.0691 mol (14.61 g) of 4-(hydroxymethyl)benzophenone (HBP), 0.076 mol (7.86 g) of triethylamine and 150 mL of toluene was added into a three-necked flask, equipped with stirrer, thermometer, dropping funnel. Under ice-water bath cooling (0 – 5 $^{\circ}\text{C}$), 0.076 mol (7.96 g) of methacryloyl chloride dissolved in 10 mL of toluene was added during 4 h. Then, the mixture was allowed to stand overnight. The precipitate was filtered off. The organic phase was washed with 100 mL of 1 mol/L HCl, 100 mL of 1 mol/L NaHCO_3 , and 150 mL of water for three times. The organic phase was dried overnight with Na_2SO_4 . Subsequently, the organic phase was evaporated under vacuum to remove the solvent. The slight yellow crude product was purified by column chromatography (silica gel 200–300 mesh) using ethyl acetate/hexane 2/1 (wt/wt) as elution to give the colorless liquid product. The yield was 4.53 g (56%). The final product was identified with FT-IR and ^1H NMR.

FT-IR 2957, 2928 cm^{-1} (CH), 1720 cm^{-1} (C=O), 1637 cm^{-1} (C=C), 816 cm^{-1} (=C-H). ^1H -NMR (CDCl_3 , δ) 1.99 (-CH₃, 3H), 5.28 (-CH₂-OC(=O), 2H), 5.63, 6.20 (=CH₂, 2H), 7.26–7.82 (-benzene, 9H).

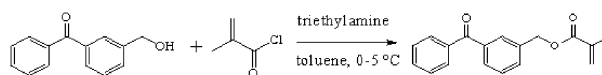


Figure 2. Synthesis process of BMM.

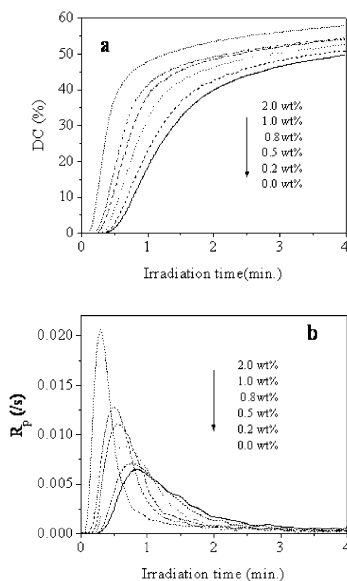


Figure 3. Effect of [DMEM] on DC and R_p of Bis-GMA/TEGDMA (70/30 wt %), [BMM] = 1.0 wt %, $I = 20 \text{ mW/cm}^2$.

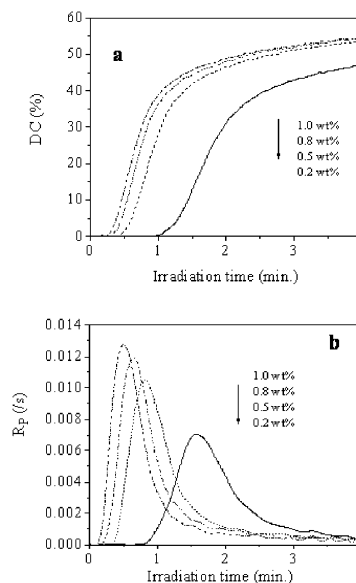


Figure 4. Effect of [BMM] on DC and R_p of Bis-GMA/TEGDMA (70/30 wt %), [DMEM] = 1.0 wt %, $I = 20 \text{ mW/cm}^2$.

RESULTS AND DISCUSSION

Photopolymerization Kinetics

The real-time IR (RTIR) technology has been widely used to measure the double bond conversion of (meth)acrylate monomers under irradiation.^{18,19} The decrease of the =C-H near IR absorption peak area from 6107 to 6227 cm^{-1} accurately reflects the extent of polymerization. The rate of polymerization (R_p) could be calculated by the time derivative of the double bond conversion (DC).

In this study, a Bis-GMA/TEGDMA (70/30 wt %) was photopolymerized as resin mixture with various BMM/DMEM photoinitiator system. Figure 3 was the kinetics of Bis-GMA/TEGDMA at constant [BMM] (1.0 wt %) and different [DMEM] (0, 0.2, 0.5, 0.8, 1.0 and 2.0 wt %). Increasing the concentration of DMEM ([DMEM]) led to the increase of both DC and the rate of polymerization. When the [DMEM] was increased from 0 to 2.0 wt %, the final double conversion for 4 min exposure increased from 46% to 58% and the rate of polymerization increased as well. This was because higher co-initiator concentration yielded more radicals, thus led to the higher polymerization rate and DC. On the other hand, this might be due to the free volume effect, which was caused by the volume shrinkage.²⁰ The volume shrinkage occurred at very fast rate of polymerization and resulted in an increase of free-volume formation which increased the mobility of the residual double-bond and led to a higher double bond conversion. The induction period was shortened with the increase of [DMEM] at the same time, because photopolymerization carried out in the presence of air, the initiating radicals were scavenged by oxygen molecules dissolved in the formulation. When the oxygen was consumed, the monomer molecules become capable of successfully reacting with the initiator radicals,

thus initiating polymerization. Increase [DMEM] could produce large amounts of free radicals rapidly to overcome oxygen inhibition.

The kinetics of Bis-GMA/TEGDMA at the same [DMEM] concentration (1.0 wt %) and different [BMM] (0.2, 0.5, 0.8, and 1.0 wt %) were shown in Figure 4. When the concentration of BMM was increased from 0.2 wt % to 0.5 wt %, the final double conversion for 4 min exposure increased from about 45% to 55%, and the rate of polymerization was greatly increased from 0.007 s^{-1} to 0.011 s^{-1} . The induction period was greatly shortened as well. However, continuing increasing [BMM] only caused the slight increase of final double bond conversion and the rate of polymerization. This was because at the higher initiator concentration the initiating efficiency of the initiator system was greatly affected by the light screening of the initiator itself and its photolysis products.

Figure 5 showed the kinetics of Bis-GMA/TEGDMA initiated by 0.5 wt % BMM and 1.0 wt % DMEM] with different UV light intensity. It was observed that increasing the UV light intensity increased both the double bond conversion and the rate of polymerization. When the UV light intensity was increased from 5 to 40 mW/cm^2 , the final double conversion for 4 min exposure increased from 20% to 58% and the maximum rate of polymerization increased from 0.002 s^{-1} to 0.011 s^{-1} . This was because the higher light intensity could yield more radicals which led to the increase in polymerization rate and final double bond conversion. At the same time, the more radicals yielded by the increase of light intensity could overcome oxygen inhibition more efficiently, resulting in the shortening of the induction period.

Figure 6 was the comparison of kinetics of Bis-GMA/TEGDMA (70/30 wt %) initiated by BMM/DMEM (0.5/1.0 wt %) and BP/EDMAB (0.5/1.0 wt %). It was observed that BMM/DMEM and BP/EDMAB could reach the same DC

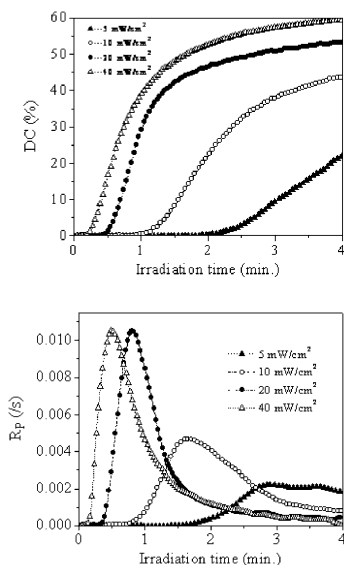


Figure 5. The effect of light intensity on the kinetics of Bis-GMA/TEGDMA (70/30 wt %) [BMM] = 0.5 wt %, [DMEM] = 1.0 wt %.

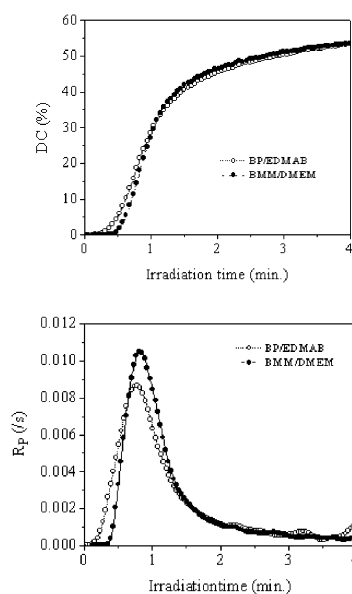


Figure 6. Comparison of BMM/DMEM (0.5/1.0 wt %) with BP/EDMAB (0.5/1.0 wt %) for the Bis-GMA/TEGDMA (70/30 wt %), $I = 20 \text{ mW/cm}^2$.

(55%). But the former led to slightly higher maximum R_p , which meant that the reactivity of BMM/DMEM was relatively higher than that of BP/EDMAB in the same curing condition.

DMA Characteristics

The DMA results for two different resin mixtures were shown in Figure 7. The storage modulus of Bis-GMA/TEGDMA/BMM/DMEM sample was slightly lower than that of Bis-GMA/TEGDMA/BP/EDMAB sample. The glass transition temperatures (T_g) of the Bis-GMA/TEGDMA/BMM/DMEM was 75°C , also lower than that of Bis-GMA/TEGDMA/BP/EDMAB (86°C). This might relate to the

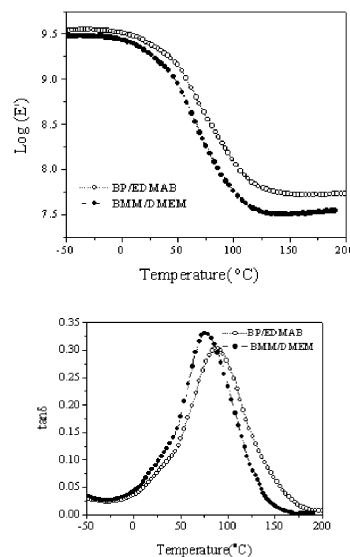


Figure 7. Storage modulus and glass transition temperature of Bis-GMA/TEGDMA/BMM(0.5 wt %)/DMEM(1.0 wt %) and Bis-GMA/TEGDMA/BP(0.5 wt %)/EDMAB(1.0 wt %).

Table I. Water sorption and solubility of Bis-GMA/TEGDMA/BMM(0.5 wt %)/DMEM(1.0 wt %) and Bis-GMA/TEGDMA/BP(0.5 wt %)/EDMAB(1.0 wt %), average of five samples \pm Standard Deviation ($\mu\text{g/mm}^3$)

	Water sorption	Solubility
Bis-GMA/TEGDMA/BMM(0.5 wt %)/DMEM(1.0 wt %)	27.33 ± 0.48	2.55 ± 0.07
Bis-GMA/TEGDMA/BP(0.5 wt %)/EDMAB(1.0 wt %)	28.85 ± 0.56	2.86 ± 0.06

network formation. For Bis-GMA/TEGDMA/BMM/DMEM, copolymerization of BMM and dimethacrylate monomer system led to relatively lower mobility of the free radical reactive species. It might cause the relatively looser network and lead to the lower T_g .

Water Sorption and Solubility

Table I gave the results of water sorption and solubility of Bis-GMA/TEGDMA/BMM(0.5 wt %)/DMEM(1.0 wt %) and Bis-GMA/TEGDMA/BP (0.5 wt %)/EDMAB(1.0 wt %). The results indicated that the water sorption and solubility of BMM system was slightly lower than BP system. It might be due to the incorporation of BMM and/or DMEM moiety into the polymer chain. The incorporation of the predominant part of a benzophenone-based photoinitiator and tertiary amine coinitiator into the polymer chain reduced the possibility of their diffusion from the resin into water or other surrounding solution. Thus, a considerably lower toxicity of the resulting resins than that of resins cured with nonpolymerizable low molecular weight initiator system could be expected.

CONCLUSIONS

BMM could be synthesized by common method as a polymerizable photoinitiator. Increasing the concentration of BMM or DMEM could lead to the increase of double bond

conversion and rate of polymerization. Compared with the nonpolymerizable initiator system (BP/EDMAB), BMM/DMEM reached the same final double bond conversion (55%) for 4 min exposure but relatively higher rate of polymerization. Although the glass transition temperature and the storage modulus of BMM/DMEM system were slightly lower than that of BP/EDMAB system, the lower water sorption and solubility for BMM/DMEM system make it more biocompatibility and more promising in the application such as biomaterials and food package.

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