Copolymeric Photoinitiators Containing In-Chain Thioxanthone and Coinitiator Amine for Photopolymerization

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ABSTRACT: Two kinds of copolymeric macromolecular photoinitiator, PTXPM and PTXPC, were prepared by introducing methylacryloyl or cinnamoyl groups to the side chain of PTXP. The photopolymerizations of poly(propylene glycol)diacrylate (PPGDA) and trimethylolpropane triacrylate (TMPTA), using PTXPM and PTXPC as photoinitiators, were studied by photo-DSC. PTXPM and PTXPC have UV–vis spectra similar to that of PTXP with blue-shift absorption maxima. The photopolymerization behavior of TMPTA, initiated by three photoinitiators, appears similar to that of PPGDA. Compared with PTXP and PTXPC, PTXPM gives higher polymerization rate and final conversion, in photopolymerization of PPGDA and TMPTA, which shows that the introduction of methyl acrylate to the PTXP chain has a greater effect on photopolymerization of PPGDA and TMPTA than that of cinnamoyl acrylate. The polymerization rate and final conversion, for photopolymerization of PPDGA initiated by PTXP, can be more effectively increased by the introduction of methyl acrylate group to the PTXP chain, than are those for TMPTA. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 94: 2395–2400, 2004

Key words: polymeric photoinitiator; thioxanthone; photopolymerization; initiators; chain

INTRODUCTION

Photopolymerization science and technology have assumed in recent years an increasing relevance in many applications, such as curing of coatings on various materials, adhesives, printing inks, and photoresists.[1–3] This technology is based on the use of photoinitiator systems absorbing light radiation of appropriate wavelength and producing primary radical species that are able to initiate polymerization. The performance of the photoinitiation system is related to high absorptivity, high efficiency in terms of both quantum yield for radical formation and high reactivity toward the monomer, low odor and toxicity, and good storage stability. A possible way to achieve most of the above-mentioned requirements is to develop polymeric photoinitiators[4–12] that contain pendant or in-chain chromophores. There are usually two types of free-radical photoinitiators: photofragmentation (Type I photoinitiators) and hydrogen-abstracting chromophores (Type II photoinitiators). Among them, thioxanthone is one of the most widely used bimolecular photoinitiators in vinyl polymerization and its photoinitiation activity can be promoted by the presence of tertiary amine.[13–20] The incorporation of both thioxanthone and coinitiator amine into the same polymer chain has obvious advantages such as intramolecular reactions responsible for the formation of more reactive species and protecting the active species by a polymer chain, attributed to the polymer effect.[5]

The other important research field in photopolymerization is the polymerization of multifunctional monomers, which determines the structure and physical properties of final polymer networks. This has been the subject of many investigations[21–27] that have shown that the photopolymerization of multifunctional monomers can exhibit unique reaction behavior including unequal functional group reactivity and autoacceleration induced by diffusion-controlled propagation and termination.

In our previous work, we synthesized a polymeric photoinitiator (PTXP) containing in-chain thioxanthone and coinitiator amine by step-growth polymerization.[20] In this context, we continued to modify this photoinitiator through the introduction of methylacryloyl and cinnamoyl groups to the side chain of PTXP to synthesize copolymeric photoinitiator and then studied the photopolymerization, of poly(propylene glycol)diacrylate (PPGDA) and trimethylolpropane triacrylate (TMPTA) using them as photoinitiators, by photo-DSC.

EXPERIMENTAL

Materials

The polymeric photoinitiator (PTXP, $M_n = 8.6 \times 10^3$) was synthesized in our laboratory according to a previous publication.[20] Methacryloyl chloride and cinnamoyl chloride were obtained from Acros Organics (Morris Plains, NJ), PPGDA was from Aldrich (Milwaukee, WI), and TMPTA was from Nantong Litian Chemical Co. (China). Other chemicals were of analytical grade except as noted.

Synthesis of copolymeric photoinitiator modified by methacryloyl chloride (PTXPM)

Methacryloyl chloride (2.0 g, 0.019 mol) in N,N-dimethyl formamide (DMF, 10 mL) was added dropwise to a solution of PTXP (1.0 g) and triethylamine (1.9 g, 0.019 mol) in DMF (30 mL) which was then cooled to 0°C, for 30 min. The resulting mixture was stirred at room temperature for 24 h under a nitrogen atmosphere. The solution was poured into 10-fold diluted aqueous solution of NaOH and filtered to give the product, which was dried *in vacuo* to obtain PTXPM.
^{1}H-NMR (DMSO-d_6, 400 MHz): δ = 8.24–7.08 (6H, aromatic), 5.99–5.95 (3.24H, CH$_2$=C), 4.37–4.22 (6H, –OCH$_2$, —OCH), 2.48–2.41 (12H, –NCH$_2$), 1.83 (4.9H, CH$_3$). FTIR (KBr): 3401 (O—H), 2923, 2813 (C—H), 1716 ($_R\!\!\overset{O}{\underset{|}{C}}\!\!_O$) 1628 cm^{-1} ($_{Ar}\!\!\overset{O}{\underset{|}{C}}\!\!_{Ar}$) T_g (DSC in N$_2$, 20°C/min): 53.1°C.

Synthesis of copolymeric photoinitiator modified by cinnamoyl chloride (PTXPC)

Cinnamoyl chloride (3.1 g, 0.019 mol) in N,N-dimethyl formamide (DMF, 10 mL) was added dropwise to a solution of PTXP (1.0 g) and triethylamine (1.9 g, 0.019 mol) in DMF (30 mL), which was then cooled to 0°C, for 30 min. The resulting mixture was stirred at room temperature for 24 h under a nitrogen atmosphere. The solution was poured into 10-fold diluted aqueous solution of NaOH and filtered to give the product, which was dried *in vacuo* to obtain PTXPC.
^{1}H-NMR (DMSO-d_6, 400 MHz): δ = 8.24–7.11 (15H, aromatic and CH=CH), 6.65–6.69 (0.82H, CH=CH), 4.27–4.01 (6H, –OCH$_2$, —OCH), 2.48–2.41 (12H, –NCH$_2$), FTIR (KBr): 3401 (O—H), 2923, 2813 (C—H), 1691($_{Ar}\!\!\overset{O}{\underset{|}{C}}\!\!_O$) 1628 cm^{-1} ($_{Ar}\!\!\overset{O}{\underset{|}{C}}\!\!_{Ar}$) T_g (DSC in N$_2$, 20°C/min): 39.6°C.

Measurements

^{1}H-NMR spectra were recorded on a Mercury Plus 400 Hz spectrometer (Varian Associates, Palo Alto, CA) with DMSO-d_6 as solvent.

FTIR spectra were recorded on a Perkin–Elmer Paragon1000 FTIR spectrometer (Perkin Elmer Cetus Instruments, Norwalk, CT). The samples were prepared as KBr discs.

Differential scanning calorimetric (DSC) analysis was conducted on a Pyris 1 DSC (Perkin Elmer Cetus Instruments).

UV–vis spectra were recorded in ethanol solution by a Perkin–Elmer Lambda 20 UV–vis spectrophotometer.

Photocalorimetry

The photopolymerization of PPGDA and TMPTA was carried out by a DSC 6200 (Seiko Instruments Inc., Torrance, CA) photo-DSC with an incident light of 365 nm. A sample mixture (~ 2 mg) was placed in aluminum DSC pans. The whole process was conducted according to procedures reported in the literature.[19]

Heat flow versus time (DSC thermogram) curves were recorded in an isothermal mode under a nitrogen flow of 50 mL/min. The reaction heat, liberated in the polymerization, was directly proportional to the number of vinyl groups reacted in the system. 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.[28] The rate of polymerization (R_p) is directly related to the heat flow (dH/dt) by the following equation:
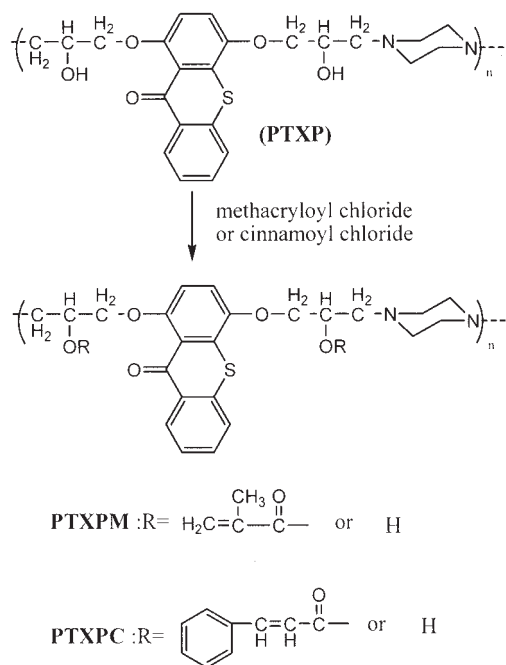
$$R_p = dC/dt = (dH/dt)/\Delta H_0^{\text{theor}} \tag{2}$$

RESULTS AND DISCUSSION

Synthesis of PTXPM and PTXPC

Copolymeric photoinitiators PTXPM and PTXPC were synthesized by reacting the hydroxyl group of PTXP with methacryloyl or cinnamoyl chloride, as shown in Scheme 1.

The structures of PTXPM and PTXPC were confirmed with ^{1}H-NMR and FT-IR. The appearance of the signal related to CH=CH in ^{1}H-NMR was considered as evidence of success of the acidulation reaction, and the composition of the two copolymeric polymeric photoinitiators was determined by ^{1}H-NMR spectra through the ratio of peak area of CH$_3$ or aromatic with –NCH$_2$ signal. From the ^{1}H-NMR spectra of PTXPM and PTXPC, about 80% of hydroxyl groups were acidulated by acyl chloride. Figure 1 shows the FTIR spectra of PTXP, PTXPM, and PTXPC. Compared with the spectrum of PTXP, the signal of other carbonyl groups at 1716 cm^{-1}, in the spectrum of PTXPM, and 1691
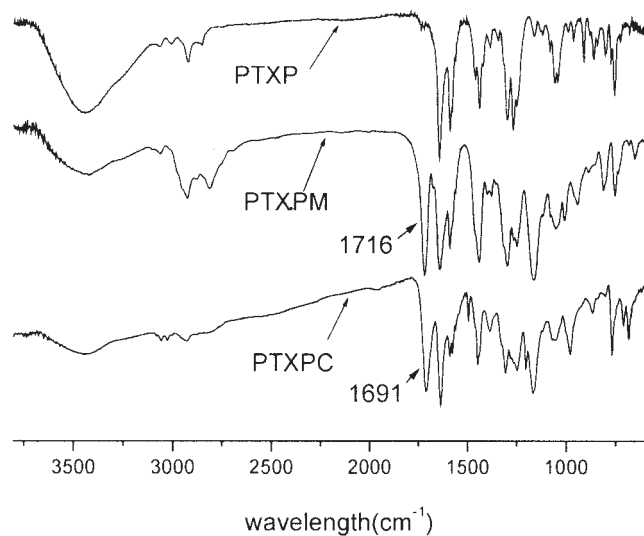
Scheme 1

Figure 2 UV–vis absorption spectra of PTXP, PTXPM, and PTXPC in ethanol solution (the concentration is 5×10^{-5} M with reference to thioxanthone moieties).
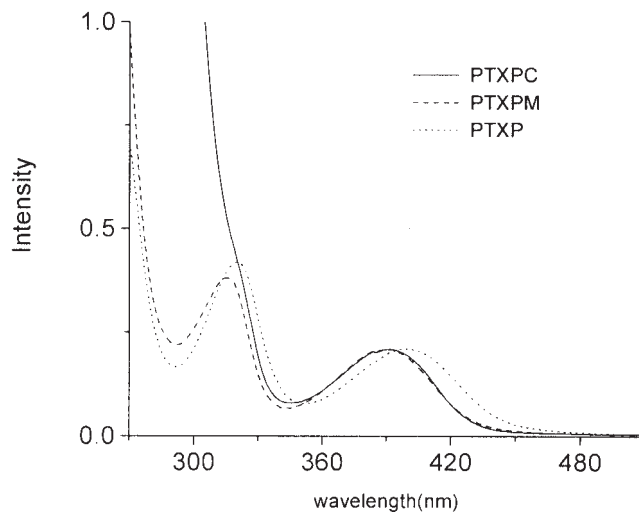
cm^{-1}, in the spectrum of PTXPC, showed that the methylacryloyl and cinnamoyl groups were successfully introduced into PTXP. Furthermore, the smaller hydroxyl signal (3400 cm^{-1}), in the spectra of PTXPM and PTXPC, also showed this result.

UV–vis absorption of PTXP, PTXPM, and PTXPC

UV–vis absorption spectra of three kinds of photoinitiator are shown in Figure 2. They exhibit the usual characteristic absorption of thioxanthone. PTXPM and PTXPC possess absorption similar to that of PTXP, which shows that the introduction of methylacryloyl and cinnamoyl groups has no significant influence on UV–vis absorption of thioxanthone moieties of PTXP. The absorption peak, at about 300 nm in the absorption spectrum of PTXPC, is different from the absorption spectra of PTXP and PTXPM, which can be ascribed to absorption by the styryl group of cinnamoyl in PTXPC, and also shows the success of the introduction of cinnamoyl group to PTXP.

Compared with the maximum of absorption (λ_{max} = 399 nm) in the UV–vis absorption spectrum of PTXP, λ_{max} of PTXPM and PTXPC is 395 nm. This

Figure 1 FTIR spectra of PTXP, PTXPM, and PTXPC. Samples were prepared as KBr discs.
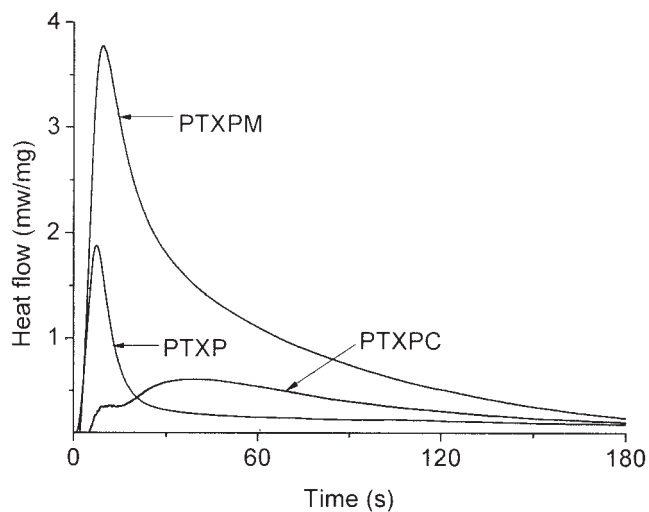
Figure 3 Photo-DSC profiles for PTXP, PTXPM, and PTXPC in PPGDA, cured at 25°C by UV light with an intensity of 50 mW/cm^2 (the photoinitiator concentration is 2 mM with reference to thioxanthone moieties).

TABLE I
Photopolymerization of PPGDA Initiated by PTXP, PTXPM, and PTXPC, Cured at 25°C by UV Light with an Intensity of 50 mW/cm² [a]

Photoinitiator	$R_{p\max} \times 10^3$ (s^{-1})	Final conversion (%)
PTXP	5.4	9.9
PTXPM	11.4	51.7
PTXPC	1.5	16.9

[a] The photoinitiator concentration was 2 mM with reference to thioxanthone moieties.

result may be attributable to the introduction of methylacryloyl and cinnamoyl groups into the PTXP chain. The methylacryloyl and cinnamoyl groups, connected to side chains of PTXPM and PTXPC, can cause microenvironment TX moieties to be less polar, resulting in a blue-shift of the maximum absorption.
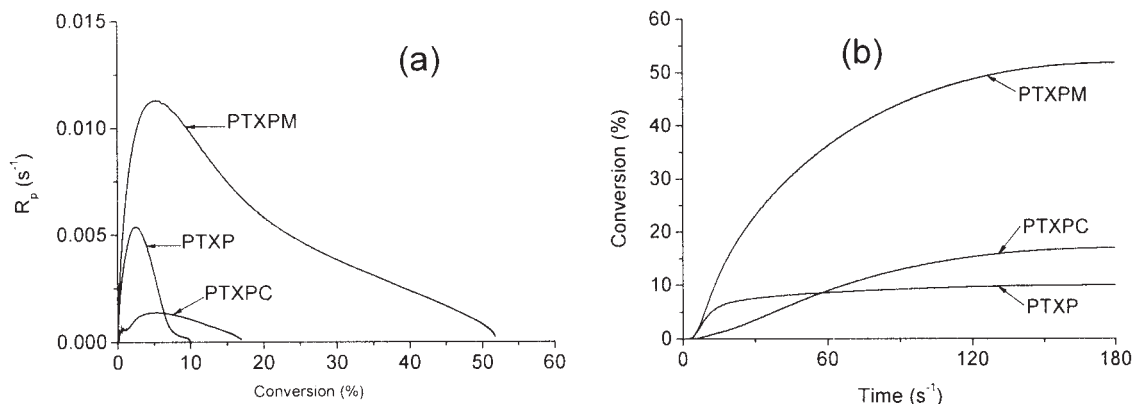
Photopolymerization of PPGDA

The photo-DSC profiles, of the polymerization of PPGDA for three kinds of photoinitiator systems, are shown in Figure 3. This polymerization behavior appears similar to that of other multifunctional monomers.[22,29–32] In the photopolymerization of multifunctional monomers, gelation often occurs at an early stage of the reaction. The formation of a three-dimensional gel structure restricts the diffusion and mobility of both macroradicals and pendant double bonds, slowing down the radical termination rate. This results in a buildup of radical species, promoting the rate of polymerization, leading to autoacceleration. However, when the reaction continues, the increased crosslinking level eventually limits the monomer mobility. The propagation reaction then also becomes diffusion controlled along with radical termination and, thus, the overall polymerization rate begins to
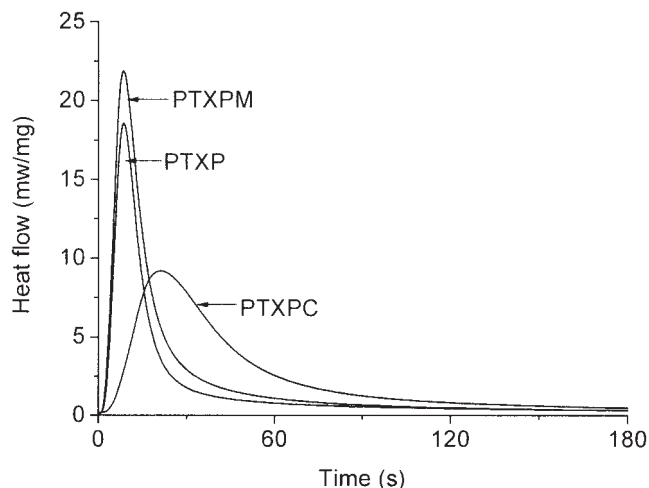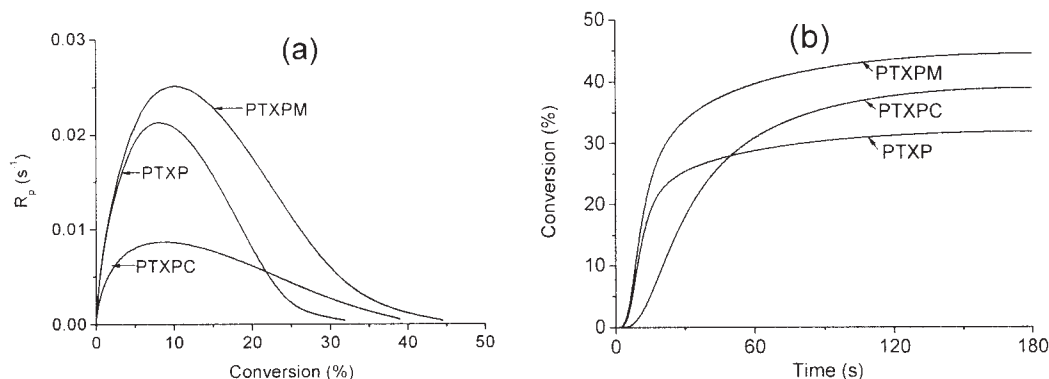
Figure 5 Photo-DSC profiles for PTXP, PTXPM, and PTXPC in TMPTA, cured at 25°C by UV light with an intensity of 50 mW/cm² (the photoinitiator concentration is 2 mM with reference to thioxanthone moieties).

decrease. As the mobility of the reaction system is further reduced, the reactive species become trapped, and the reaction eventually stops.

From Figure 3 and Table I, PTXPM is the most efficient photoinitiator for the photopolymerization of PPGDA. The higher photopolymerization rate of the PPGDA/PTXPM system may be attributable to good compatibility of PTXPM with PPGDA. Compared with PTXP and PTXPC, introduction of the methylacryloyl group into the PTXP chain enhances the compatibility of PTXPM to PPGDA, resulting in high mobility of macroradical chains in the PPGDA matrix. The major differences between PTXP and PTXPC photoinitators were that the polymerization rate of PTXP was higher than that of PTXPC at an early stage, but slower at a later stage. This is clear in Figure 4(a), which shows the relationship between the polymer-

Figure 4 (a) Rate versus conversion; (b) conversion versus time for polymerization of PPGDA for PTXP, PTXPM, and PTXPC systems, cured at 25°C by UV light with an intensity of 50 mW/cm² (the photoinitiator concentration is 2 mM with reference to thioxanthone moieties).

Figure 6 (a) Rate versus conversion; (b) conversion versus time for polymerization of TMPTA for PTXP, PTXPM, and PTXPC systems, cured at 25°C by UV light with an intensity of 50 mW/cm^2 (the photoinitiator concentration is 2 mM with reference to thioxanthone moieties).

ization rate and the conversion. This result may be attributed to the special structures of PTXP and PTXPC. Compared with PTXPC, the compatibility of PTXP to PPGDA is poor. At an early polymerization stage, the macroradicals of PTXPC can be trapped by styryl groups in PTXPC to produce unreactive styryl radicals, so the polymerization rate is slow and it takes a long period of time to form the gel structure that produces a maximum in the polymerization rate. On the other hand, gelation occurs at an earlier stage in the microenvironment of PTXP radicals because of their very poor compatibility with PPGDA, which results in the polymerization rate and conversion reaching maximum values in a very short time. This can also be seen in Figure 4(b), which shows the relationship between the conversion and time for the three photoinitiator systems. Polymerization for the PTXP photoinitiator system almost stops at the later stage. The final conversion for PTXP and PTXPC systems is much lower than that for the PTXPM system, which also shows that the introduction of methylacryloyl groups into the PTXP chain has a greater effect than the introduction of cinnamoyl groups.

Photopolymerization of TMPTA

The photopolymerization behavior of TMPTA, initiated by the three types of photoinitiator (Figs. 5 and 6),

appears similar to that of PPGDA. PTXPM can facilitate the photopolymerization of TMPTA most effectively because of its excellent compatibility with TMPTA, which is also seen in Table II. Compared with PPGDA, however, TMPTA can be photoinitiated efficiently by PTXP and PTXPC, which may be explained by the better compatibility of PTXP and PTXPC with TMPTA than with PPGDA. The introduction of methylacryloyl and cinnamoyl groups can enhance the compatibility of PTXP with TMPTA and leads to more efficient photopolymerization of TMPTA, but did not have a very obvious effect with respect to the photopolymerization of PPGDA. This may be attributed to the substantial compatibility between TMPTA and PTXP.

CONCLUSIONS

Two kinds of copolymeric photoinitiators, PTXPM and PTXPC, prepared by the introduction of methylacryloyl and cinnamoyl groups to the side chain of PTXP, have UV–vis spectra similar to that of PTXP with blue-shift absorption maxima. The photopolymerization behavior of TMPTA, initiated by three kinds of photoinitiator, appears similar to that of PPGDA. Compared with PTXP and PTXPC, PTXPM can facilitate the photopolymerization of PPGDA and TMPTA with higher polymerization rate and final conversion, which shows that the introduction of methylacryloyl group to the PTXP chain has a greater effect on the photopolymerization of PPGDA and TMPTA than that of the cinnamoyl group. The polymerization rate and final conversion, for the photopolymerization of PPDGA initiated by PTXP, can be more effectively increased by the introduction of methylacryloyl group to the PTXP chain than that of TMPTA. The introduction of ester groups of different chain lengths to PTXP is presently under investigation.

TABLE II
Photopolymerization of TMPTA Initiated by PTXP, PTXPM, and PTXPC, Cured at 25°C by UV Light with an Intensity of 50 mW/cm^2 [a]

Photoinitiator	$R_{p\max} \times 10^3$ (s^{-1})	Final conversion (%)
PTXP	21.5	31.8
PTXPM	25.3	44.5
PTXPC	8.9	38.9

[a] (The photoinitiator concentration was 2 mM with reference to thioxanthone moieties).

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