

Unexpected Visible-Light-Induced Free Radical Photopolymerization at Low Light Intensity and High Viscosity Using a Titanocene Photoinitiator

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ABSTRACT: Most visible-light photoinitiators are based on electron transfer processes and are comprised of two or more components. These initiators can lose effectiveness in viscous systems because the underlying reactions are diffusion controlled. In this contribution, the visible-light photoinitiator bis(cyclopentadienyl) bis[2,6-difluoro-3-(1-pyrryl)phenyl]titanium is characterized for polymerization of viscous systems and low light intensities. This compound absorbs visible light at wavelengths up to 550 nm, and does not rely on diffusion-controlled electron transfer reactions because it undergoes unimolecular decomposition. In contrast to trends observed for other photoinitiators, the effectiveness of the compound is found to increase markedly with the addition of protonic acids and with increasing system viscosity. For a given concentration of initiator and acid, a remarkably low optimal light intensity for effective polymerization is observed. The origins of these surprising results are discussed in terms of the mechanism of decomposition of the photoinitiator. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

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INTRODUCTION

Photopolymerizations have become the state-of-the-art for rapid room-temperature cure of coatings, adhesives, and printed images.^{1,2} In a typical photopolymerization, a small amount of a light-activated initiator is dissolved in a monomer. When this system is exposed to light with the right wavelength, the monomer is converted to polymer within seconds to minutes. Photopolymerizations are highly desired because the use of light affords great temporal and spatial control over the polymerization as light can be directed to a location of interest and shuttered at will. Photopolymerizations also offer environmental advantages such as low energy requirements, high polymerization rates, and solvent-free compositions which alleviates the need to remove solvent in a subsequent step. Because of these characteristics, photopolymerizations are attractive for new applications in medical devices including coatings for artificial implants and structural elements in bone and tissue restoration.^{3–5} Free radical photoinitiators have traditionally been based on the benzoyl chromophore, which absorbs light in the ultraviolet (UV) region of the spectrum. Some common classes

of these photoinitiators include benzoin ethers, dialkoxyacetophenones, hydroxy alkyl ketones, benzoyl oxime esters, amino ketones, and morpholino ketones. When illuminated with UV light, these unimolecular photoinitiators produce active centers efficiently by the well-known α -cleavage process. However, UV light is undesirable for many applications. For instance, in biological and medical applications, visible light is preferable due to the damaging effects of UV radiation. In addition, to photopolymerize adhesives through a polyimide film (e.g., Kapton, Toray), visible light whose wavelength is higher than 500 nm is required because this film absorbs light at wavelengths below 500 nm. Furthermore, visible-light-initiated cure is attractive because of the ready availability of inexpensive, reliable, mercury-free light sources such as light-emitting diodes (LEDs).

A major challenge in this field is that although UV photoinitiators are unimolecular and their initiation is unaffected by viscosity of the monomer, visible-light-induced photopolymerizations require multicomponent photoinitiator systems. Visible-light initiators are generally based on electron-transfer processes due to the relatively low energy of a visible photon.^{6–20} Because

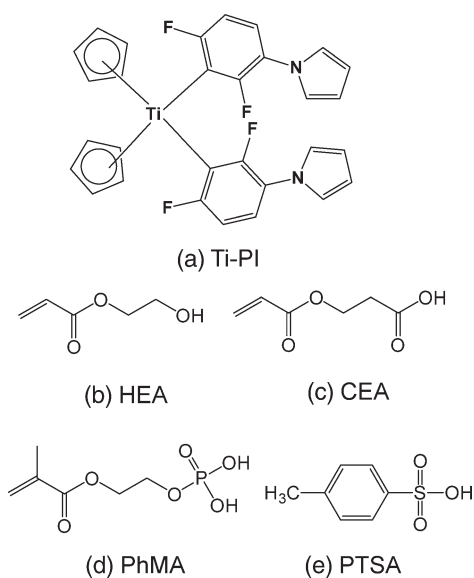


Figure 1. Chemical structures of the reaction components: (a) bis(cyclopentadienyl) bis[2,6-difluoro-3-(1-pyrryl)phenyl]titanium (Ti-PI), (b) HEA, (c) CEA, (d) PhMA, and (e) PTSA.

visible-light electron-transfer photoinitiator systems generally require two or more components, they rely on bimolecular collisions during an excited state lifetime to facilitate the electron transfer process. Although common unimolecular UV photoinitiators are relatively insensitive to viscosity, the bimolecular electron transfer reactions in the multicomponent systems tend to be diffusion-controlled and are highly influenced by the viscosity of the solvent.^{21,22} Hence, it can be difficult to achieve a complete cure in viscous formulations that contain oligomers for enhancement of mechanical properties.

Ganster et al.²³ reported a visible-light photoinitiator, diacyldialkylgermanium compounds, which may be used, for example, in dental materials. These germanium compounds are highly efficient, cleavable photoinitiators for visible-light curing, and show an excellent bleaching behavior. However, these compounds absorb wavelengths less than 470 nm. Therefore, another photoinitiator which can be activated by higher than 500-nm light to polymerize the adhesive described above is still desired.

In this article, we report the successful polymerizations of viscous acrylates at low intensities of visible light using a unimolecular titanocene compound. The photoinitiator is bis(cyclopentadienyl) bis[2,6-difluoro-3-(1-pyrryl)phenyl]titanium [henceforth referred to as Ti-PI, Figure 1(a)]. This initiator is a commercially available organometallic complex which absorbs light at wavelengths up to 550 nm and is known to produce radicals when exposed to visible light.^{24–32} Although the mechanism of decomposition of Ti-PI to yield radicals is not well understood, it is known that it decomposes by a unimolecular pathway and that the resulting polymerization rate is enhanced by the presence of acid.^{29,33–36} In this contribution, we demonstrate that Ti-PI can rapidly polymerize monomers to high conversion with surprisingly low levels of visible light in the presence of acids. In this article, we report a result that has not been seen by others: at relatively low light intensities, the rate of

polymerization with Ti-PI increases as the intensity of light is increased; but for light intensities higher than an optimum value, the rate actually decreases as the intensity of light is further increased. The optimal intensity of light to quickly reach a high conversion was remarkably low for Ti-PI in the polymerization of acrylates (~ 8 mW/cm²). This result was unexpected, and a detailed mechanism to explain it was explored.

In prior work by others,^{29,33} it was shown that the presence of acids affect the polymerizations of acrylates using Ti-PI, but only the physical properties (i.e., gelation) of the resulting material were studied rather than the rate of polymerization or conversion. In this contribution, we have provided a more detailed investigation of the effect of a variety of acids on the rate and final conversion of the polymerization. Finally, we have demonstrated that Ti-PI is effective in viscous medium where other visible-light photoinitiators fail.

EXPERIMENTAL

Materials

The monomer 2-hydroxyethyl acrylate (HEA) [Figure 1(b)] (Sigma-Aldrich, St Louis, MO) was used as the base monomer in these experiments. A viscous urethane acrylate oligomer (CN9002, Sartomer, Exton, PA) was mixed with HEA to prepare viscous reactive formulations. Ti-PI (commercial name Irgacure 784) was supplied by BASF (Ludwigshafen, Germany). Additives used in this study including 2-carboxyethyl acrylate (CEA) [Figure 1(c)], phosphoric acid 2-hydroxyethyl methacrylate ester (PhMA) [Figure 1(d)], *p*-toluenesulfonic acid (PTSA) [Figure 1(e)], and triethylamine (TEA) were purchased from Sigma-Aldrich. CEA and PhMA are polymerizable protonic acids. Eosin Y spirit soluble (EYss), *N*-methyldiethanolamine (MDEA), and diphenyl iodonium chloride (DPI), supplied by Sigma-Aldrich, were used to form a visible-light-induced multicomponent photoinitiator system.¹⁵

Methods

The photopolymerization rate was characterized using real-time Fourier transform infrared spectroscopy (RT-FTIR) at room temperature with a modified Bruker 88 FTIR spectrometer designed to accommodate a horizontal sample.³⁷ The RT-FTIR used a 520-nm LED lamp (UHP-MIC-LED-520, Prizmatix, Modiin Ilite, Israel) or 150-W xenon lamp (MAX-150, Asahi Spectra, Tokyo, Japan) equipped with a 520-nm bandpass filter to illuminate the samples. The light spectrum of the lamp was measured using an Ocean Optics (Dunedin, FL) USB 4000 fiber optic spectrometer. The samples were prepared by placing a droplet of the monomer mixture between two rectangular IR grade sodium chloride salt crystals, with 15 μ m Teflon beads placed between the salt plates to serve as spacers. The infrared absorption spectra during photopolymerization were collected *in situ* at 1.1-s intervals with four signal averaged scans for each spectrum. The carbon-carbon double bond infrared absorbance peak at 812 cm⁻¹, associated with an out-of-plane vibration, was monitored during the reaction to determine the acrylate conversion. The conversion was calculated using the ratio of current peak height to peak height before polymerization. Because the reactive monomer or oligomer samples are confined between salt plates, they are initially saturated with dissolved

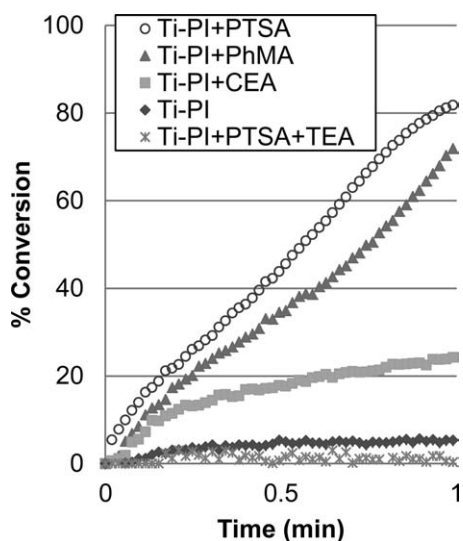


Figure 2. HEA photopolymerization conversion profiles in the presence of various additives: 1.0 wt % (0.053M) PTSA (○); 1.5 wt % (0.067M) PhMA (▲); 1.5 wt % (0.105M) CEA (■); no additives (◆); 1.0 wt % (0.053M) PTSA plus 1.0 wt % (0.100M) TEA (*). All samples contain 2.6 wt % (0.050M) Ti-PI. Light intensity: 2 mW/cm².

oxygen, but the oxygen is consumed by free radicals and is not replenished from the atmosphere.

RESULTS AND DISCUSSION

Effect of a Protonic Acid on the Photopolymerization Rate Using Ti-PI as a Visible-Light Initiator

Figure 2 shows the conversion profiles, as monitored by RT-FTIR spectroscopy, for HEA polymerizations photoinitiated using Ti-PI (2.6 wt %; 0.050M) and mixtures of Ti-PI with four different protonic acid additives. The figure contains plots of the experimentally observed conversions as a function of time for neat HEA monomer, and the monomer systems containing the protonic acids. For these experiments, the xenon lamp with the 520-nm bandpass filter was used as the light source and the light intensity was 2 mW/cm².

Figure 2 clearly shows that the polymerization rate and conversions of monomer were strongly affected by the presence of acid. The photoinitiator system containing Ti-PI without any protonic acid (the curve labeled with solid diamonds) does not undergo appreciable polymerization. In contrast, the systems with acids present have significantly enhanced polymerization rates and ultimate conversions of monomer. Both values follow the trend: Ti-PI+CEA < Ti-PI+PhMA < Ti-PI+PTSA that correlate with the pKa of a carboxylic acid (approximate pKa of 4.0), phosphoric ester (pKa of phosphoric acid is 2.1), and PTSA (pKa of -2.8). This figure further illustrates that if a base (TEA) is added to the Ti-PI+PTSA system to quench the acid, the photopolymerization rate and ultimate conversion drop significantly and the conversion profile becomes similar to that of a photoinitiator system containing only Ti-PI. Therefore, it can be concluded that the presence of the protonic acid in the Ti-PI photoinitiator system is critical to achieve high overall photopolymerization and the enhancement in polymerization depends

Table I. Ultimate Conversions of Photopolymerization Profiles in Figure 2 after 6 min of illumination

	Ultimate conversion (%)
Ti-PI	8.2
Ti-PI+CEA	70.4
Ti-PI+PhMA	99.6
Ti-PI+PTSA	96.7
Ti-PI+PTSA+TEA	3.0

on the acidity of the protonic acid additive. It is important to note that this enhancement of photopolymerization by the addition of the acid is not observed in other photoinitiating systems including 1-hydroxy-cyclohexyl-phenyl-ketone, which is a common free-radical unimolecular photoinitiator. This enhancement is unique to Ti-PI.

Table I summarizes the ultimate conversions of the systems illustrated in Figure 2. The ultimate conversion is defined as the maximum or plateau conversion after 6 min of illumination. Importantly, the systems containing PTSA or PhMA reached ultimate conversions in excess of 95% which is highly desired for many applications of photopolymerizations.

The stability of solutions of HEA and Ti-PI with either PhMA or PTSA were investigated to learn if these solutions were stable in the absence of light. When the solution containing PTSA was allowed to sit for 1 day in the dark and then exposed to light, the photopolymerization reached low monomer conversions. In contrast, the solution with PhMA showed a high photopolymerization reactivity and a long shelf life after a month of storage in the dark. Therefore, the protonic acid PhMA was used for the remainder of the work reported in this article.

The effect of different concentrations of PhMA on the rates of polymerization and conversions of monomer was investigated

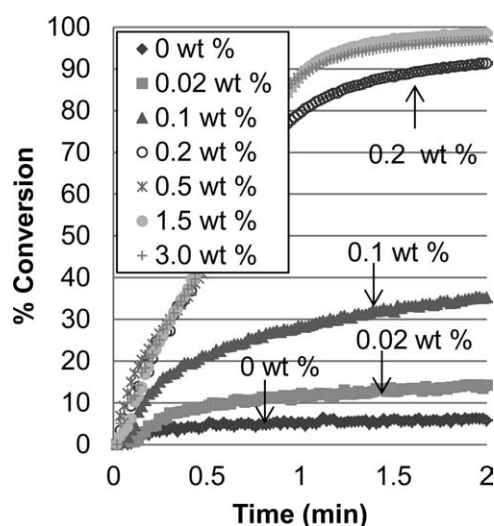


Figure 3. HEA photopolymerization conversion profiles for eight different concentrations of the protonic acid PhMA. All samples contain 2.6 wt % (0.050M) Ti-PI. Light intensity: 2 mW/cm².

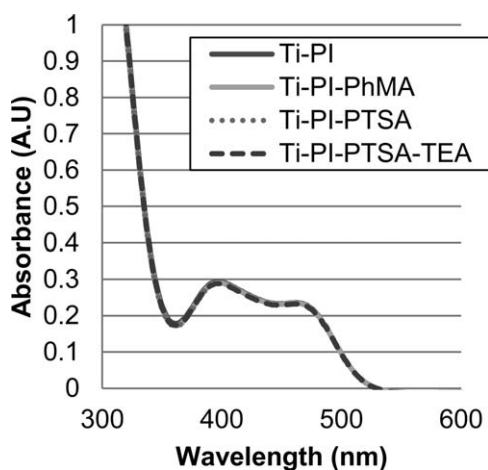


Figure 4. Absorbance spectra with and without the acid additives in ethyl acetate. For all samples, Ti-PI = 0.01 wt %, PhMA = 0.006 wt %, PTSA = 0.005 wt %, and TEA = 0.01 wt %.

to determine the optimal concentration of PhMA. Figure 3 contains profiles of the photopolymerization conversion as a function of time for HEA compositions containing 2.6 wt % (0.050M) Ti-PI and various concentrations of PhMA ranging from 0 to 3.0 wt % (0–0.133M). The rate of polymerization and conversion of monomer increase when the concentration of PhMA increases from 0 to 0.5 wt % but above a value of 0.5 wt %, the rate and conversions are unchanged.

The enhancement in polymerization rate and conversion of monomer when an acid was added to a solution of monomer with Ti-PI was studied for other acrylate monomers including 1,6-hexandiol acrylate. The same enhancements were observed for this monomer. In contrast, for polymerizations of nonacrylate monomers, the effect of a protonic acid on photopolymerization was negligible. For example, for styrene photopolymerizations initiated using Ti-PI, the addition of acid had no effect on the resulting conversion profiles.

Origin of the Effect of Acid on the Polymerization Rate

It was hypothesized that the rate of polymerization was increased when an acid was added to a solution of Ti-PI because the acid increased the absorption of Ti-PI. This hypothesis was investigated by collecting the UV-Vis absorbance spectrum of the Ti-PI photoinitiator as shown in Figure 4. The figure illustrates that the presence of the three different protonic acid additives had no measurable effect on the observed Ti-PI absorbance spectra. Therefore, the enhancement in the photopolymerization rate shown in Figure 2 did not result from enhanced absorbance of the incident light.

The effect of the protonic acid on the effectiveness of Ti-PI likely arises from a change in the photolysis products resulting from the presence of an acid. It is well known that the identity of the chemical substituents on the aromatic ligands of a titanocene complex can have a marked effect of the photolysis products. For example, several investigators^{24,26–28} have characterized the difference in photolysis products between diphenyltitanocene and perfluorodiphenyltitanocene (Figure 5). This comparison is interesting because the two titanocene complexes differ

only in the substituents on the aromatic ligands, with the replacement of the hydrogen of the diphenyltitanocene with electronegative fluorine to yield perfluorodiphenyltitanocene. Previous work by others showed that the primary radicals (yields higher than 93%)^{24,27} generated from photodecomposition of perfluorodiphenyltitanocene (Structure 4) were titanium diradicals containing both a cyclopentadienyl group and a perfluorophenyl group (Structure 5), and pentafluorophenylcyclopentenyl (Structure 6) which was not a radical. In contrast, the primary radicals (yields of higher than 80%)^{24,27} generated from photodecomposition of diphenyltitanocene (Structure 1) were phenyl radical (Structure 2) and titanium monoradical (Structure 3). Roloff²⁴ and collaborators²⁶ reported that the titanium diradical (Structure 5) is the most effective initiating radical of the photolysis products shown in Figure 5, and this hypothesis is consistent with the observation that the perfluorodiphenyltitanocene is a more effective photoinitiator than diphenyltitanocene. As shown in Figure 3, protonic acid concentrations higher than 0.2 wt % appear to favor the production of the titanium diradical, which produce propagating active centers on reaction with the acrylate monomers to form a ketene acetal type diradical capable of initiating polymerization.^{26,27}

The literature studies on diphenyltitanocene and perfluorodiphenyltitanocene suggest that the addition of a protonic acid increases the effectiveness of Ti-PI is by shifting the distribution of photolysis products. In the absence of added acid, the unprotonated Ti-PI is likely to have a photolysis product distribution resembling that of diphenyltitanocene [Figure 6(a)]. In this state, the pyrrole groups of the 2,6-difluoro-3(1H-pyrrol-1-yl)phenyl side chains are electron donating and the molecule most closely resembles diphenyltitanocene. In the presence of acid, the nitrogen in the pyrrole functional group can be reversibly protonated which will make the pyrrole ring strongly electron withdrawing which will make the pyrrole ring strongly electron withdrawing [Figure 6(b)]. When the protonated Ti-PI was illuminated with light, the photolysis product distribution was similar to that of perfluorodiphenyltitanocene (with five electron-withdrawing fluorines). Thus, in the presence of acid, Ti-PI would favor generation of highly active titanium diradicals.

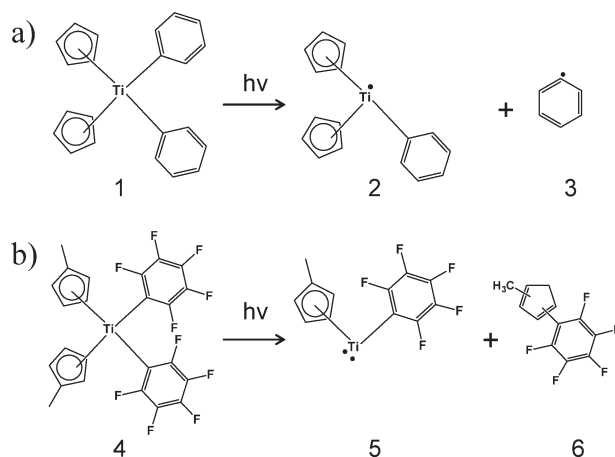


Figure 5. The products of the light-activated decomposition of (a) diphenyltitanocene differ from those of (b) perfluorodiphenyltitanocene.

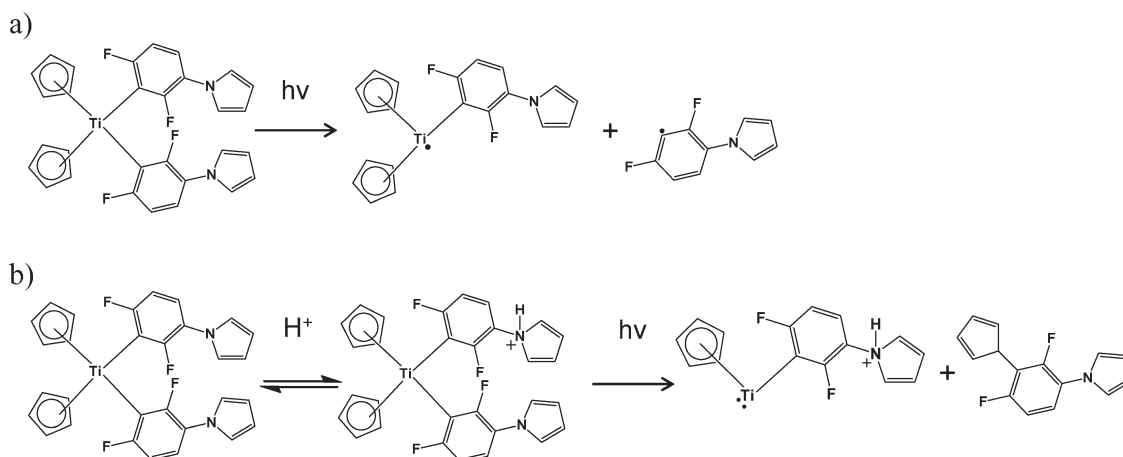


Figure 6. (a) When Ti-PI is not protonated by external acid, the degradation products resemble those from diphenyltitanocene. (b) In the presence of an acid to protonate the nitrogen on Ti-PI, the degradation products change and resemble those of perfluorodiphenyltitanocene.

Effect of Light Intensity and Photoinitiator Concentration on the Photopolymerization Rate and Conversion of Monomer

A series of experiments were performed to investigate the effect of light intensity on the observed photopolymerization rate and ultimate conversion. Figure 7 contains RT-FTIR conversion profiles as a function of time in HEA monomer for a photoinitiator system composed of 2.6 wt % (0.050M) Ti-PI and 1.5 wt % (0.067M) PhMA when irradiated by 520-nm light of different light intensities. The data in Figure 7 illustrate a surprising trend. The lowest polymerization rate is observed for the highest light intensities investigated, and there is a light intensity threshold above which higher light intensities result in poor polymerization. Specifically, if the light intensity is higher than

30 mW/cm², the photopolymerization rates are relatively low, and the observed ultimate conversions are less than 30% (see Table II). In contrast, for light intensities below 18 mW/cm², a high ultimate conversion of >99% is observed, and the photopolymerization rate is relatively high. The data in Figure 7 illustrate that the maximum photopolymerization rate was observed for a light intensity of 8 mW/cm², and the rate is lower for light intensities above or below this value.

The low polymerization rate and ultimate conversion for light intensities above 18 mW/cm² is surprising, and the reason for this effect is not obvious. One possible explanation is that the rapid photodegradation of the Ti-PI leads a lower concentration of propagating radicals due to an increase in the rate of radical-radical combination reactions. At the relatively high light intensities, radical combination reactions could dominate thereby preventing effective polymerization. At low light intensities, the rate of formation of radicals from Ti-PI is reduced, thereby leading to lower radical concentrations, and a reduction in the rate of the radical combination reactions. Therefore, the concentration of propagating radicals may actually increase with decreasing light intensity due to a shift in the probability of propagation relative to radical combination before propagation can occur. The optimal polymerization rate at a low terminate

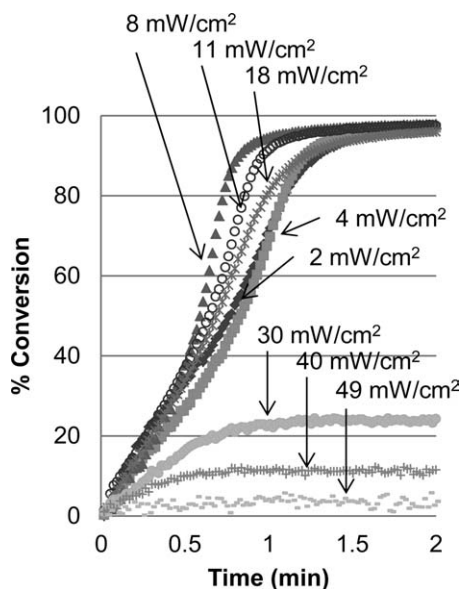


Figure 7. HEA photopolymerization conversion profiles for seven different light intensities: 2 mW/cm² (◆), 4 mW/cm² (■), 8 mW/cm² (▲), 11 mW/cm² (○), 18 mW/cm² (*), 30 mW/cm² (●), 40 mW/cm² (+), and 49 mW/cm² (—). For all systems, Ti-PI = 2.6 wt % (0.050M), PhMA = 1.5 wt % (0.067M).

Table II. Ultimate Conversions of Photopolymerization Profiles in Figure 7

Light Intensity (mW/cm ²)	Ultimate conversion (%)
2 mW/cm ²	99.2
4 mW/cm ²	99.2
8 mW/cm ²	99.1
11 mW/cm ²	99.0
18 mW/cm ²	97.9
30 mW/cm ²	23.9
40 mW/cm ²	12.5
49 mW/cm ²	5.3

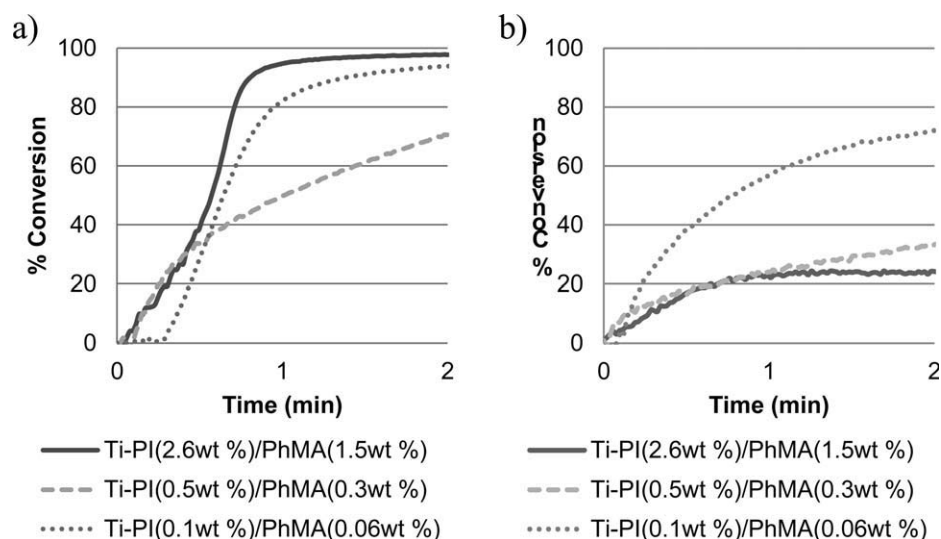


Figure 8. HEA photopolymerization conversion profiles for three different Ti-PI/PhMA concentrations and two different light intensities: (a) 8 mW/cm² and (b) 30 mW/cm².

rate was found at ~ 8 mW/cm². It should be noted that the surprising effect of increasing light intensity on the ultimate conversion was also observed for photopolymerizations initiated using other light sources including a xenon lamp which emits a broad wavelength spectrum.

The general trends of an enhancement in photopolymerization with the addition of the acid and the decrease in ultimate conversion with an increase in light intensity were observed in other (meth)acrylates including 1,6-hexandiol acrylate, 2-hydroxyethyl methacrylate, and a HEA/urethane acrylate mixture. In addition, reports in the literature³⁸ have illustrated that photopolymerization profiles of 1,6-hexandiol acrylate initiated using 2,2-dimethoxy-2-phenylacetophenone were not affected by addition of a strong acid. Therefore, the phenomena shown in Table II and Figure 7 are not limited to any particular acrylic monomer but are instead associated with the Ti-PI photoinitiator.

A series of experiments were completed to investigate the effect of the photoinitiator concentration on the observed polymerization rate and ultimate conversion. These studies were completed using PhMA as the protonic acid, and the molar ratio of the PhMA to Ti-PI was maintained at a value of 1.4–1. Figure 8 contains profiles for the conversion as a function of time for three different photoinitiator concentrations (0.1, 0.5, and 2.6 wt % Ti-PI) and two different light intensities (8 and 30 mW/cm²). The data in the figure illustrate that, for both light intensities, the observed profiles for conversion versus time depend strongly on the photoinitiator concentration; however, the nature of the dependence is very different at the low light intensity than at the high light intensity. Specifically, Figure 8(a) illustrates that at the low light intensity of 8 mW/cm² the most rapid photopolymerization is observed for the highest photoinitiator concentration (2.6 wt % Ti-PI, solid line in the figure), and a significant inhibition period (due to oxygen) is observed for the lowest photoinitiator concentration (0.1 wt %, dotted line in the figure). The intermediate photoinitiator concentra-

tion (0.5 wt %, dashed line) shows no appreciable inhibition period, but a relatively sluggish polymerization. All three photoinitiator concentrations resulted in the same ultimate limiting conversion of over 91% after 6 min illumination.

Figure 8(b) illustrates that a very different trend is observed for the higher light intensity of 30 mW/cm². Here, the lowest Ti-PI concentration (0.1 wt %, dotted line) shows a small inhibition period followed by a relatively high polymerization rate, and the two higher photoinitiator concentrations lead to ineffective polymerization. The ultimate limiting conversions after 6 min illumination for the samples containing 0.1, 0.5, and 2.6 wt % Ti-PI were 24, 49, and 79%, respectively.

The trends described in the previous paragraphs are consistent with the postulate that the photolysis of Ti-PI leads to the production of high concentration of radical species that leads to fast termination reactions at high light intensities. Therefore, the highest polymerization rates and highest ultimate limiting conversions are observed for the combination of low light intensity and relatively high initiator concentration. At higher light intensities, lower photoinitiator concentrations are required to achieve appreciable polymerization.

Comparison of Ti-PI to a Three-Component Visible-Light Photoinitiator System

A series of experiments were conducted to compare the performance of the Ti-PI photoinitiator to a three-component visible-light photoinitiator. Multicomponent photoinitiator systems are commonly used for visible-light-induced photopolymerization. The energy of a visible photon is generally lower than the bond dissociation energy of most organic molecules, therefore visible-light-induced photoinitiator systems are primarily two-component photoinitiator systems in which the active centers are produced via an electron transfer followed by a proton transfer from the electron donor (typically an amine) to the excited light-absorbing component. The polymerization rate is further enhanced by the addition of a third component such as

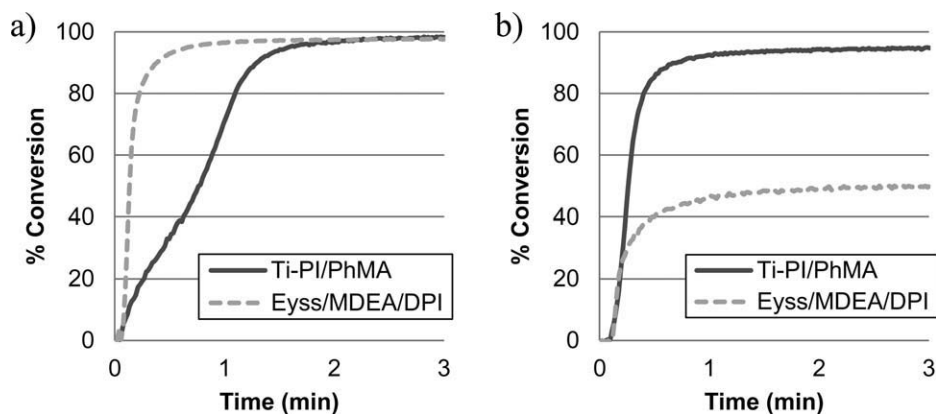


Figure 9. Photopolymerization conversion profiles for Ti-PI/PhMA photoinitiator system (Ti-PI = 2.6 wt %, PhMA = 1.5 wt %) and EYss/MDEA/DPI photoinitiator system (EYss = 0.074 wt %, MDEA = 3.77 wt %, DPI = 0.072 wt %) for two different monomer systems: (a) neat HEA monomer, (b) high viscosity urethane acrylate/HEA mixture (urethane acrylate = 70 wt %, HEA = 30 wt %). Light intensity: 2 mW/cm².

DPI into the two-component photoinitiator systems, as described by a number of investigators.^{12–20}

The polymerization observed for the Ti-PI/PhMA photoinitiator system is compared to that observed for the EYss/MDEA/DPI three-component photoinitiator system for monomer mixtures of two different viscosities (Figure 9). Figure 9(a) corresponds to photopolymerization of the neat HEA monomer which exhibits a relatively low viscosity of 0.005 Pas (measure with a Brookfield digital viscometer). In this case, both photoinitiators resulted in a high ultimate limiting conversion of 98%; however, the three-component initiator system reached this limiting conversion more rapidly. Figure 9(b) corresponds to a high viscosity mixture of the HEA monomer with a urethane acrylate oligomer (30 wt % HEA, 70 wt % oligomer) which exhibits a viscosity of 3.5 Pas. For this high viscosity system, the Ti-PI/PhMA photoinitiator is more effective, and leads to an ultimate limiting conversion of more than 95%, while the three-component photoinitiator EYss/MDEA/DPI leads to a final conversion of only ~50%. The sensitivity of multicomponent photoinitiator systems to the monomer viscosity is well known and arises from the fact that the electron transfer process that leads to the production of active centers is diffusion controlled and becomes less efficient as the viscosity is increased. For the EYss/MDEA/DPI, photoinitiator system requires diffusion-controlled bimolecular encounters to occur between the excited EYss and MDEA or DPI during the lifetime of the EYss excited state.¹⁵ The probability of this encounter decreases as the viscosity is increased. In contrast, the photolysis reaction of Ti-PI is unimolecular, and will be relatively insensitive to the system viscosity. In fact, comparison of the solid line in Figure 9(a) to the solid line in Figure 9(b) reveals that the TI-PI photoinitiator is more effective at the higher viscosity, perhaps due to a decrease in the fraction of active centers which participate in radical combination reactions on photolysis.

CONCLUSIONS

This contribution has provided a characterization of the photopolymerization effectiveness of the visible-light photoinitiator Ti-PI for a variety of reaction compositions and conditions. The

experimental results demonstrate that a carefully selected combination of a protonic acid additive and light intensity is important to achieve effective photopolymerization using the Ti-PI photoinitiator system. As the acidity of the additive increases, the overall photopolymerization achieved by the Ti-PI-containing photoinitiator system increased accordingly, and the protonic acid PhMA provided an excellent combination of reactivity and shelf life. For a given concentration of the initiator and the acid, a relatively low optimal light intensity for effective polymerization was observed, and light intensities above a threshold yield no effective polymerization at all. This implies that, although careful light intensity control is required to reach a high conversion, this photoinitiator system has great potential to realize safe and low energy photopolymerization using visible-light sources including visible LEDs. Furthermore, with careful selection of the light intensity gradient within the sample, some interesting cure scenarios could be created. For example, in thick systems such as adhesives and sealants, the deep regions (where the intensity is lower), might undergo more rapid polymerization than the shallow regions. As a result, low shrinkage stress of the thick system may be achieved. Finally, this initiator is very promising for visible-light-induced polymerizations of viscous systems. Most visible-light photoinitiators are based on electron transfer processes and are comprised of two or more components. These initiators can lose effectiveness in viscous systems because the underlying reactions are diffusion controlled. In contrast, the Ti-PI containing photoinitiator systems achieved high conversion in viscous oligomer-containing compositions, and the polymerization effectiveness actually increased with increasing viscosity.

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