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# Articles

## Photopolymerizations of Thiol−Ene Polymers without Photoinitiators

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ABSTRACT: A thiol monomer is shown to copolymerize with vinyl ether, allyl, acrylate, methacrylate, and vinylbenzene monomers. These thiol−ene polymerizations are photoinitiated without the use of photoinitiator molecules. It is seen that the polymerization proceeds more readily when initiatorless samples are irradiated with light centered around 254 nm as compared to 365 nm light. To demonstrate resistance to oxygen inhibition, thin polymer films of 3−15 $\mu$m are polymerized while exposed to ambient air. Without photoinitiator molecules present, light is attenuated only by the monomer and polymer. This feature leads to greater penetration of ultraviolet light and allows for the polymerization of extremely thick polymers. Thick cures of up to 25 in. are obtained using a thiol−vinyl ether system.

### Introduction

The field of photopolymerizations has been one of the most rapidly growing industries in recent years, with the majority of the growth involving polymerization of acrylic systems. Photopolymerizations of acrylic monomers have the advantages of solventless processing, energy efficiency, and spatial and temporal control of the polymerization. As such, these materials have found widespread use as coatings, imaging materials, photoresists, and polymeric materials for many other applications.

The traditional disadvantages of acrylic photopolymerizations involve oxygen inhibition and the use of photoinitiator molecules. Thiol−ene photopolymerizations represent a unique class of polymerizations that are not significantly inhibited by oxygen[1,2] and are polymerizable without the use of additional photoinitiator molecules.[3]

Thiol−ene photopolymerizations are step-growth radical polymerizations involving a reaction between multifunctional thiol and ene (vinyl) monomers. The reaction proceeds via propagation of a thiyl radical through a vinyl functional group. This reaction is followed by chain transfer of the radical to a thiol functional group, regenerating a thiyl radical, which then restarts the process. This successive propagation/chain transfer mechanism is the basis for step-growth thiol−ene polymerizations.[2,4,5] Previous work on these systems has shown that real-time FTIR successfully monitors the conversion of both the thiol and ene functional groups independently.[3] Monitoring consumption of both functional groups is a valuable tool for determining conversion in polymerizing systems in which significant homopolymerization of the ene monomer occurs.

Acrylate, methacrylate, and vinylbenzene monomers all homopolymerize via a radical chain growth mechanism. The kinetics and polymer properties of these systems have been extensively explored.[6,7] The copolymerization of these systems with thiol monomers adds chain transfer as a significant influence in the polymerization mechanism. The addition of thiol monomer affects polymer properties, molecular weight evolution, and the rate of reaction. The incorporation of small amounts of thiol monomers into acrylic photopolymerizations yields polymers with similar properties to those of bulk acrylic polymerizations[3] while reducing the effects of oxygen inhibition and eliminating the need for a photoinitiator. Moreover, the properties of thiol−ene and thiol−acrylate systems are tailorable for a wide range of mechanical properties by using different monomer chemistry and functionality or varying stoichiometric ratios of thiol and acrylate functional groups.

Photopolymerizations traditionally require the use of a photoinitiator molecule, which upon absorption of ultraviolet or visible light leads to the generation of radical centers. The use of photoinitiators results in several disadvantages for photopolymerizations. Photoinitiators generally degrade during long-term exposure to sunlight, producing a yellowing effect in polymer clear coats. This degradation makes photoinitiated systems undesirable for outdoor applications. Another disadvantage is that curing depths in photopolymerizations are limited by the attenuation of ultraviolet or visible light by the photoinitiator. Photoinitiator molecules can also be toxic and expensive.

Photoinitiation in thiol−ene systems is also achieved through the generation of radical centers. Benzophenone and its derivatives have been the most thoroughly explored photoinitiators for thiol−ene systems.[5] Cleavage-type photoinitiators or maleimides will also readily

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initiate the polymerization.[3,8,9] However, a photoinitiator molecule is not required for initiation of a photopolymerization when thiol monomers are present in radically polymerizable vinyl systems. Photopolymerization without the use of photoinitiator molecules leads to unique polymer properties. Polymers without photoinitiators do not exhibit degradation/yellowing that generally results from the initiator molecules, and therefore, the polymer ages much more slowly during long-term exposure to sunlight. Achievable polymerization depths are increased because light is attenuated only by absorbance of the monomer and polymer rather than the photoinitiator molecules.

When photoinitiators are not utilized, the mechanism by which initiation occurs has not been clearly identified. A charge-transfer complex between the thiol and ene functional groups has been shown to be responsible for dark initiation of the reaction[10−13] whereas thiols have been reported to cleave into thiyl and hydrogen radicals upon irradiation by 254 nm light.[14,15] Disulfide impurities and other products may also play a role in initiation as they also cleave into thiyl radicals upon absorption of UV light or reaction with hydrogen and thiyl radicals.[16] Thiyl and hydrogen radicals generated by cleavage of thiols or disulfides should readily initiate a polymerization. However, these previous investigations do not address or attempt to explore the possible photoinitiation of a thiol−ene polymerization via these mechanisms. It is likely that initiation is achieved from thiol monomer decay into thiyl and hydrogen radicals upon absorption of ultraviolet light. An interaction between the thiol and ene functional groups, such as a charge-transfer complex,[2,11,12] may also facilitate photoinitiation.

When oxygen is present during thiol−ene polymerizations, the reaction proceeds more slowly than under a nitrogen blanket but is not significantly inhibited.[17] Oxygen is incorporated into the polymerization by reacting with a carbon radical to form a peroxy radical. The peroxy radical is much less reactive than the carbon radical and serves to quench the reaction for acrylic polymerizations. Thin films of acrylic polymers are thus impractical to achieve without an inerting blanket. However, in a thiol−ene polymerization, the peroxy radical abstracts a hydrogen from a thiol monomer, regenerating a thiyl radical in a manner that does not dramatically inhibit the rate of the polymerization.[1,2]

This work describes the photopolymerization of thiol monomers with a wide variety of vinyl monomers. Thiol monomers are polymerized with allyl, vinyl ether, vinylbenzene, acrylate, and methacrylate systems. To demonstrate the unique properties afforded by these systems, the photopolymerizations are carried out in the absence of photoinitiators and in the presence of oxygen, demonstrating advantages relative to the common drawbacks associated with radical photopolymerizations.

## Experimental Section

The monomers pentaerythritol tetrakis(3-mercaptopropionate) (thiol), triallyl triazine trione (allyl), and divinylbenzene were purchased from Aldrich (Milwaukee, WI). Divinylbenzene was further purified with a 10 wt % aqueous sodium hydroxide solution and then washed with distilled water to remove the excess sodium hydroxide. Triethylene glycol divinyl ether (vinyl ether) was donated by ISP Technologies Inc. (Wayne, NJ). Hexanediol diacrylate (HDDA) and hexanediol dimethacrylate (HDDMA) were donated by UCB Chemicals (Smyrna, GA). The photoinitiator, 2,2-dimethoxy-2-phenylacetophenone (DMPA), was purchased from Ciba-Geigy (Hawthorne, NY). All monomers (except divinylbenzene) and the photoinitiator, DMPA, were used as received.

FTIR studies were conducted using a Nicolet 750 Magna FTIR spectrometer with a KBr beam splitter and an MCT/A detector. Series scans were recorded, taking spectra at the rate of approximately 2.5 scans/s. The FTIR sample chamber was continuously purged with dry air. Samples were irradiated until the reaction was completed, as indicated by the functional group absorption spectra no longer decreasing. Thiol conversion was monitored using the S−H absorption peak at 2570 $cm^{-1}$. Allyl and methacrylate conversions were monitored using the carbon−carbon double bond absorption peak at 1636 $cm^{-1}$. The vinyl ether functionality has absorption peaks at 1619 and 1636 $cm^{-1}$, and the acrylate functionality has absorption peaks at 1636 and 1640 $cm^{-1}$. Conversions were calculated using the ratio of peak areas to the peak area prior to polymerization. Analyses and apparatus for FTIR experiments are previously described in greater detail.[18,19] All reactions were performed at ambient temperature.

Monomer samples without initiator were placed between NaCl crystals in a horizontal transmission apparatus.[18] Polymerizations were initiated via an EFOS Novacure light source (EXFO, Mississauga, Ontario) with a 320−500 nm filter. Irradiation intensities were measured with a Cole-Parmer Instruments Co. series 9811 radiometer.

UV−vis spectra of the thiol were taken on a Hewlett-Packard 8452A diode array spectrophotometer. Scans were taken with the thiol monomer dissolved in tetrahydrofuran (THF) at a concentration of 0.005 mol/L in a 1 cm path length quartz cuvette.

Thin cures were exposed to ambient air by spreading the monomer sample on a NaCl crystal with a 6 $\mu$m wire-wound wet film applicator rod (Paul N. Gardner Co., Inc., Pompano Beach, FL). Samples were polymerized with an EFOS Acticure (EXFO, Mississauga, Ontario) at 14 $mW/cm^2$ with a 365 nm filter. After polymerization, polymer films were measured with a micrometer and found to vary from 3 to 15 $\mu$m.

Thick cures were performed in rectangular glass test tubes that were 2.5 × 6 mm wide by 305 mm deep irradiated from the top using an EFOS Acticure with a 365 nm filter and a light intensity of 1.8 $W/cm^2$. The light intensity was measured by an EFOS UV/vis R5000 250−600 nm radiometer (EXFO, Mississauga, Ontario). Conversions were calculated with FTIR using near-IR spectroscopy.[18] A near-IR spectrum (5000−7000 $cm^{-1}$) was collected (KBr beam splitter and DTGS detector) and conversion of the vinyl groups determined from the area of the =C−H peak at approximately 6190 $cm^{-1}$.

Differential scanning calorimetry (DSC) experiments were carried out in a Perkin-Elmer DSC 7 (Norwalk, CT). Approximately 4 mg of monomer was placed into aluminum pans (TA Instruments, New Castle, DE) and placed inside the DSC chamber. Samples were held at 25 °C and purged continuously with 20 sccm nitrogen throughout the polymerization and for 10 min prior to polymerization. The 365 nm light was generated using an EFOS Novacure with a 365 nm filter. The 254 nm light was generated using a Mineralight Short Wave UV 254 nm, UVG-54 light source (UVP, Upland, CA). Light intensity was experimentally verified with the DSC by monitoring the amount of heat absorbed by carbon disks (Perkin-Elmer, Norwalk, CT) placed in the sample holder.

## Results and Discussion

Two common thiol−ene systems, thiol−vinyl ether and thiol−allyl, were polymerized without photoinitiators. Conversion vs time results for stoichiometric mixtures of these monomers are shown in Figure 1. Irradiated at 15 $mW/cm^2$, the thiol−vinyl ether reaction is complete in less than 300 s while the thiol−allyl system reaches full conversion in approximately 500−800 s. These systems are traditional thiol−ene systems in that the ene does not readily homopolymerize via a

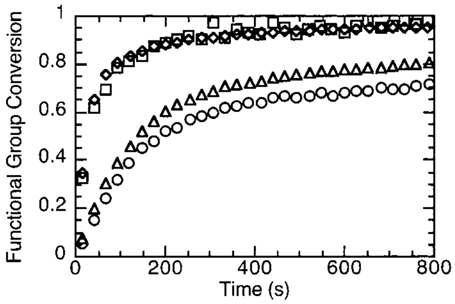


**Figure 1.** Conversion of 1:1 stoichiometric mixtures of thiol−vinyl ether (thiol [□], vinyl ether [◇]) and thiol−allyl (thiol [○], allyl [△]) with no added photoinitiator. Samples irradiated at 15 mW/cm$^2$.

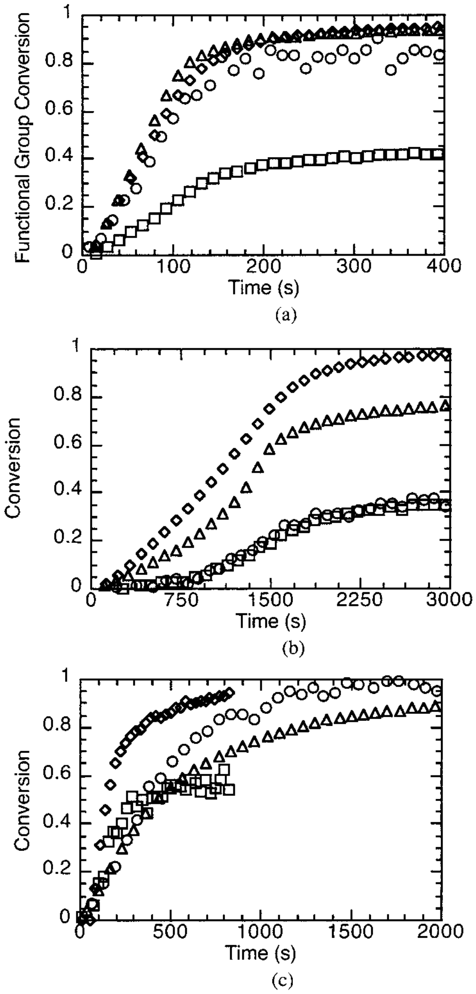


**Figure 2.** Conversion of thiol−HDDA, thiol−HDDMA, and thiol−vinylbenzene systems with no added photoinitiator: (a) 1:1 stoichiometric mixture of thiol (□), and acrylate (◇) functional groups and 1:4 stoichiometric mixture of thiol (○) and acrylate (△) functional groups; (b) 1:1 stoichiometric mixture of thiol (□) and methacrylate (◇) functional groups and 1:4 stoichiometric mixture of thiol (○) and methacrylate (△) functional groups; (c) 1:1 stoichiometric mixture of thiol (□) and vinylbenzene (◇) functional groups and 3:7 stoichiometric mixture of thiol (○) and vinylbenzene (△) functional groups. Samples irradiated at 15 mW/cm$^2$.

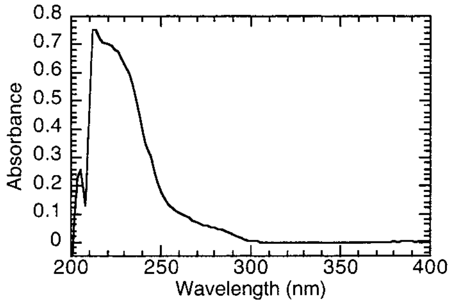


**Figure 3.** UV−vis spectra for the absorbance of the thiol monomer in THF at 0.005 mol/L.

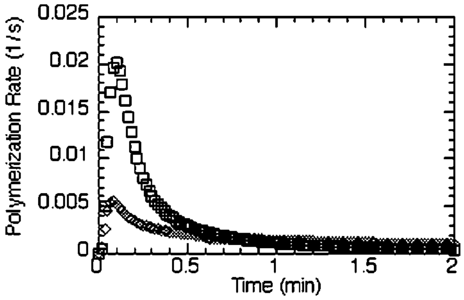
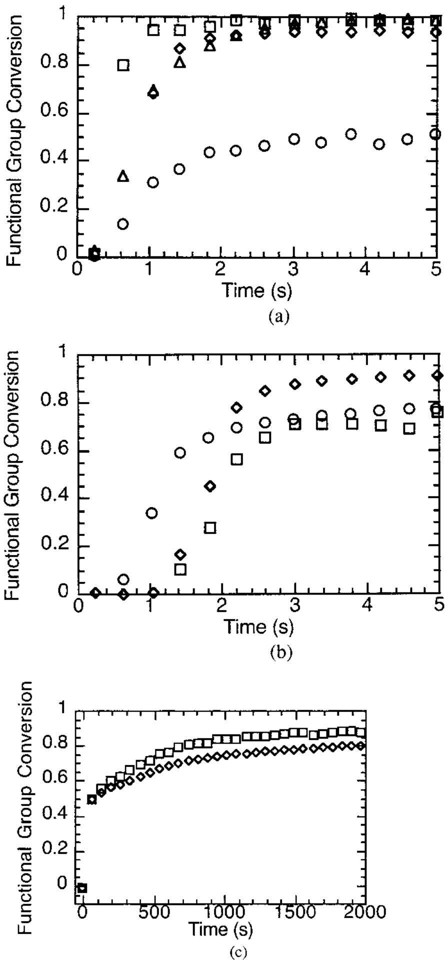


**Figure 4.** Polymerization rate for tetrathiol and divinyl ether with no initiator polymerized with 254 nm light at 0.8 mW/cm$^2$ (□) and 365 nm light at 80 mW/cm$^2$ (◇).

radical mechanism, and thus, step-growth is the dominant polymerization mechanism. The step-growth mechanism is clearly evidenced in the thiol−vinyl ether polymerization where the thiol and vinyl ether functional groups are equally consumed. In the thiol−allyl polymerization, the allyl monomer undergoes some homopolymerization as evidenced by 80% final conversion of allyl functional groups compared with 72% for the thiol functional groups.

The thiol monomer was also polymerized with HDDA, HDDMA, and vinylbenzene. Each of these systems was polymerized using a 1:1 stoichiometric ratio of thiol and acrylate, methacrylate, or vinylbenzene functional groups. In all cases, this lead to incomplete conversion of the thiol monomer as the vinyl functional groups were consumed via homopolymerization as well as by propagation/chain transfer with thiol. This result has been observed previously in thiol−acrylate[3] and thiol−methacrylate[20] systems with photoinitiators. In the case of the thiol−acrylate, thiol−methacrylate, and thiol−vinylbenzene polymerizations, there are two competing mechanisms. They are chain growth homopolymerization of the vinylic monomers and chain transfer/propagation between the thiol and vinyl monomers. Homopolymerization of the vinyl group leads to incomplete conversion of the thiol functional groups when initially 1:1 stoichiometric mixtures of functional groups are polymerized. A 1:4 stoichiometric mixture of thiol to acrylate functional groups leads to roughly equivalent conversion of both functional groups, indicating that they are being consumed at equal rates during the polymerization. In thiol−methacrylate polymerizations, there are still significant quantities of unconsumed thiol functional groups with a 1:4 ratio of thiol to methacrylate functional groups. Smaller functional group ratios of 1:5 and 1:8 also yielded incomplete consumption of thiol functional groups. Lesser ratios should yield equivalent consumption; however, the rates of polymerization became extremely slow. In the thiol−vinylbenzene system, a 3:7 stoichiometric mixture yields roughly equivalent functional group conversions.

In Figures 1 and 2, photoinitiation for all of the thiol−ene systems is achieved via irradiation with light centered around 365 nm. However, as seen in Figure 3, thiols absorb light much more readily at lower wave-



(a)

(b)

(c)

**Figure 5.** Conversion of thiol–vinyl ether and thiol–HDDA systems with 1 wt % DMPA. (a) Films of 1:1 stoichiometric mixture of thiol (□) and vinyl ether (◇) and 1:1 stoichiometric mixture of thiol (○) and acrylate (△) are spread on NaCl crystals with a 6 $\mu$m roller and polymerized under ambient conditions. (b) Films of 1:4 stoichiometric mixture of thiol (□) and acrylate (◇) and bulk HDDA (○) are sandwiched between NaCl crystals such that they are not exposed to ambient air during polymerization. (c) Films of 1:4 stoichiometric mixture of thiol (□) and acrylate (◇) are spread on NaCl crystals with a 6 $\mu$m roller and polymerized under ambient conditions. Samples are irradiated at 14 mW/cm$^2$.

lengths. Because of differences in absorption of UV light, the polymerization rate in thiol–ene systems is highly dependent on the wavelength of the irradiating light. At lower wavelengths, light is absorbed more readily, leading to a greater radical generation rate. Figure 4 illustrates polymerizations with the irradiating light centered at 365 nm vs 254 nm. The intensity of 365 nm light is a full order of magnitude greater than the 254 nm light, yet the maximum rate of polymerization is one-quarter at 365 nm of the maximum rate when 254 nm light is utilized.

Thiol–ene reactions are not significantly inhibited by oxygen, and thus extremely thin polymer films are achievable even when exposed to ambient oxygen. We have illustrated this effect by spreading thin films of monomers onto NaCl windows. Using 1 wt % DMPA as an initiator, the thiol–vinyl ether system reached full conversion in less than 2 s when irradiated at 14 mW/cm$^2$ (Figure 5a). This polymerization occurred faster than bulk HDDA that was not exposed to ambient oxygen (Figure 5b). The 1:1 thiol–acrylate system also proceeded nearly uninhibited in the presence of oxygen (Figure 5a), reaching full conversion in less than 3 s. When a 1:4 mixture of thiol–acrylate functional groups is used, the polymerization exhibits significant oxygen inhibition, requiring approximately 15 min for full conversion (Figure 5c). However, the polymerization is not completely quenched, as is the case when bulk HDDA is exposed to ambient oxygen under identical conditions to those in Figure 5.

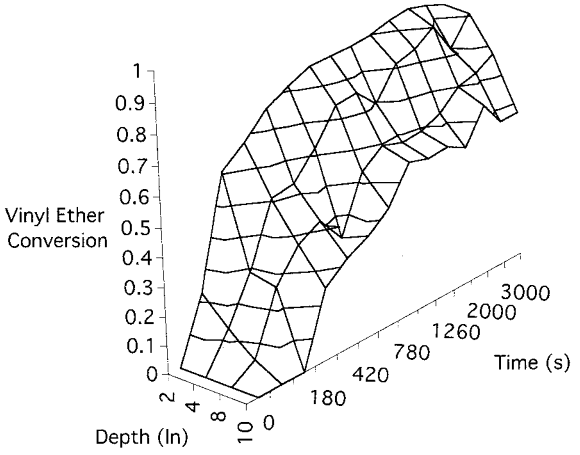


**Figure 6.** Vinyl ether conversion vs depth and time for a thiol–vinyl ether polymerization. Samples are irradiated from the top with 365 nm light at 1.8 W/cm$^2$.

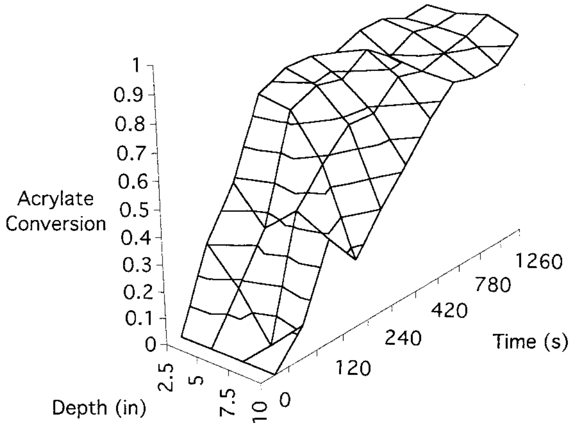


**Figure 7.** Acrylate conversion vs depth and time for a 1:5 stoichiometric mixture of thiol and acrylate functional groups in a thiol–acrylate polymerization. Samples are irradiated from the top with 365 nm light at 1.8 W/cm$^2$.

Extremely thick cures are also achievable in certain thiol–ene systems due to light not being attenuated by the photoinitiator molecules. The thiol–vinyl ether system has shown the greatest affinity for achieving thick cures. We have polymerized a thiol–vinyl ether system of 25 in. in depth. Conversion vs time and depth for a similar system 12 in. in depth is shown in Figure 6. Conversion vs time and depth is also profiled for the thiol–acrylate system in Figure 7. In the thiol–acrylate polymerization, the exothermic heat released by the polymerization produces a thermal front. Temperatures in the sample reach 160 °C, causing a thermally initiated polymerization that was responsible for the majority of the polymerization. In contrast, there is very little increase in temperature in the thiol–vinyl ether system during the polymerization. Curing temperatures did not increase more than 10 °C above ambient temperature, indicating that the polymerization was primarily photoinitiated.

## Conclusions

Thiol monomers are photopolymerizable with a wide variety of vinyl monomers. In this work we have highlighted the polymerization of a thiol monomer with vinyl ether, allyl, acrylate, methacrylate, and vinylbenzene monomers. Photoinitiator molecules were not required to initiate the photopolymerization in any of these systems. The thiol−vinyl ether and thiol−allyl polymerizations were shown to be true stoichiometric step-growth reactions, while the thiol−acrylate, methacrylate, and vinylbenzene polymerizations proceed via a combination of step-growth and vinyl homopolymerization reactions. Although the polymerizations proceed with irradiated light centered around 365 nm, the reaction was significantly faster when 254 nm light was utilized. Thin films of 3−15 $\mu$m were polymerized in the presence of ambient oxygen, demonstrating resistance to oxygen inhibition. In the presence of ambient oxygen, thiol−vinyl ether and thiol−acrylate systems with an initially stoichiometric ratio of functional groups had greater polymerization rates than inerted bulk HDDA. Thick cures of up to 25 in. are obtained for the thiol−vinyl ether system. These experiments demonstrate a wide variety of achievable polymers without the common disadvantages imparted by oxygen inhibition and photoinitiator molecules.

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