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Holographic polymer dispersed liquid crystal reflection gratings formed by visible light initiated thiol-ene photopolymerization

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Abstract

Visible laser light of wavelengths 442, 488 and 532 nm was used to write holographic reflection gratings with notches into the infra-red spectral region in polymer dispersed liquid crystals (H-PDLC). The gratings were formed by the spatially periodic phase separation of nematic liquid crystal during thiol-ene photopolymerization. An organic titanocene based complex, Rhodamine 6G (Rh6G) and Pyrromethene 597 (Pym) dyes in combination with benzoyl peroxide, were used as initiators. Using visible laser light and a single prism, electrically switchable reflection gratings with notches in the blue, green, yellow, red, and near infra-red (NIR) spectral regions were fabricated using angle tuning. The photophysics of the initiator dyes was studied by absorption and fluorescence spectroscopy. Morphology studies by TEM showed a periodic distribution of discrete nematic droplets of nearly spherical shape. The development of visible photoinitiator systems broadens the range of fabrication wavelengths of dynamic reflection filters using inexpensive visible lasers.

Keywords: Visible photoinitiator; Liquid crystals; Holography

1. Introduction

Recently, there has been much interest in holographic polymer-dispersed liquid crystals (H-PDLC) formed by non-homogeneous spatial illumination of monomer/LC mixtures [1–3]. Constructive interference of laser beams on a pre-polymer syrup containing multi-functional monomers, nematic LC, dye and a co-initiator results in the anisotropic distribution of polymer and LC-rich layers leading to a periodic refractive index modulation which can be electrically modulated. The resulting reflection gratings are electrically switchable and have high potential for devices in a variety of display and communication applications [4]. Typical H-PDLC gratings exhibit high switching fields (∼10 V/μm), high contrast ratios, good transmission in the on and off states and fast switching speeds on the order of a few hundred microseconds.

Highly crosslinked acrylate polymers have been previously employed as hosts for H-PDLCs [1–3]. Use of multifunctional acrylate monomers as hosts has some disadvantages including very early gelation and subsequent vitrification, low monomer conversion, and post-polymerization issues [5]. Dark polymerization leads to a blue shift of the notch owing to an increase of shrinkage [6]. Modeling studies of grating formation and the non-symmetrical shape of the reflection notches seem to indicate non-uniform shrinkage of the polymer host, which contributes to a chirping of the refractive index profile limiting the peak diffraction efficiency [7]. In addition, the use of additives including surfactants and chain extenders is typical to optimize performance [3].

Recently, we have shown that most of the problems associated with the use of acrylates as hosts for H-PDLC's can be overcome by thiol-ene chemisty [8]. Thiol-ene polymers are well known for their role in the preparation of UV curable coatings and adhesives [9]. Thiol-ene polymers are formed by the combination of step growth and free radical reactions between multifunctional aliphatic thiols and vinyl monomers containing 'ene' groups. Free radical producing photoinitiaton triggers the polymerization, which is followed by H-atom abstraction and step-chain growth. The thiol-ene reaction is

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based on a stoichiometric relation between the reacting components; either the thiol or ene must have a functionality >2 for polymer formation and cross-linking. The thiol-ene reaction mechanisms, polymerization kinetics and reactivities of different thiol systems have been reviewed by Jacobine and more recently by Hoyle [9,10].

Reflection gratings have been previously written using a single-beam prism-coupled holographic geometry and ultraviolet (UV) light from the 364 nm line of an argon-ion laser [8]. Unfortunately, using this chemistry limits the upper end of the wavelength of the reflection notch that can be written. Notch wavelengths above 800 nm are difficult to write due to the poor overlap of the beams induced by the severe angles needed to red-shift the periodicity. The use of visible light lasers (532–900 nm) as the writing source could extend the wavelength capability for the reflection notches from the red (600 nm) into the short wave infra-red (1–2 μm).

Most of the work on thiol-ene chemistry is based on UV initiated curing [9,10]. There are only a few reports on thiol-ene polymerization initiated by visible initiators [11,12]. In these cases, however, visible initiation was not observed with monochromatic wavelength irradiation. White light with filters was used for irradiation. Finding suitable dyes for visible laser initiation is indeed challenging since the highly reactive aliphatic thiols react with conventional dyes like xanthene-type systems in the dark. In the present work, we demonstrate the development of different visible initiators for writing H-PDLC reflection gratings with 442, 488, and 532 nm laser lines and a single prism technique. We have observed that the laser dyes Rhodamine 6G and Pyrromethene 597 function as photoinitiators for visible laser lines when combined with benzoyl peroxide. We have also used the commercially available Irgacure 784, a titanocene organo-metallic complex in combination with benzoyl peroxide as the initiator system. Reflection notches as far as 1.6 μm were written. We discuss the photophysics and photochemical processes enabling the initiation of thiol-ene polymerization.

2. Experimental

Rhodamine 6G dye (Rh6G) and benzoyl peroxide (BzO_2) were obtained from Aldrich. Pyrrromethene 597 dye (PyM) was a gift from Prof. Paras Prasad, State University of New York at Buffalo. The titanocene complex bis(cyclopentadien-1-yl)-bis(2,6 difluro-3-(1H-pyrrol-1-yl)-phenyl)titanium, commercially known as Irgacure 784 was a gift from Ciba-Geigy. NOA65 containing a tristhiol and a tetraallylether ene is a product of Norland Optical Adhesives, Inc., and the nematic liquid crystal BL037 was obtained from EM Industries. The liquid crystal BLO37 is an eutectic mixture of cyano substituted biphenyls and terphenyls. It has a birefringence of 0.282 and a nematic to isotropic transition temperature of 109 °C. Both plain glass and ITO coated glass cells were used as substrates. The pre-polymer syrup containing 15 or 25 μm diameter glass spacers, 2 wt% Irgacure 784, 2.5% benzoyl peroxide and 24% BL037 was placed between two glass slides and attached to the prism with index matching liquid. In the case of the fluorescent dyes Rh6G and PyM, the dye concentration was of the order of 1×10^{-5} M and BzO_2 concentrations 1.5–2.0% by weight. The pre-polymer syrup also contained 5% *N*-vinyl pyrrolidinone (NVP) as a reactive diluent. NVP serves as a homogenizer for the pre-polymer syrup and is expected to react with the thiols and therefore form part of the thiol-ene polymer network. A single-beam prism-coupled holographic geometry was used for writing reflection gratings using He–Cd, Argon ion, and Verdi-diode lasers with output wavelengths of 442, 488, and 532 nm, respectively. Laser powers ranged from 10 to 3500 mW/cm^2, the exposure time was 45 s, and gratings with notches in the visible and NIR were written by changing the incident beam angle. Post-curing was achieved by exposing the grating in white light for an hour. Optical characterization of the gratings was done with an Ocean Optics spectrophotometer and a Cary UV–vis–IR spectrometer. For electrical switching, a square wave signal at 1 kHz operating from 0 to 200 V RMS was applied, and changes in DE were noted. Samples for microscopy were embedded in flat molds using epo-fix resin and cured overnight in a 60 °C oven. The blocks were trimmed and ultramicrotomed at room temperature using an RMC ultramicrotome. Sections of 50–60 nm thickness were cut with a 35° Diatome diamond knife, picked up onto 400 mesh grids and vapor stained with RuO_4. The sections were then imaged using bright field transmission electron microscopy (BFTEM) performed on a FEI CM200FEG TEM.

3. Results and discussion

Using a single prism geometry and an expanded laser beam simplifies writing of holographic gratings. This technique also minimizes the vibrational disturbances which affect the fringe stability and consequently the overlap of two beams. However, for writing longer wavelength reflection notches, steeper incident angles of the beam are involved which reduce the efficiency of the overlap as shown in Fig. 1. Although,

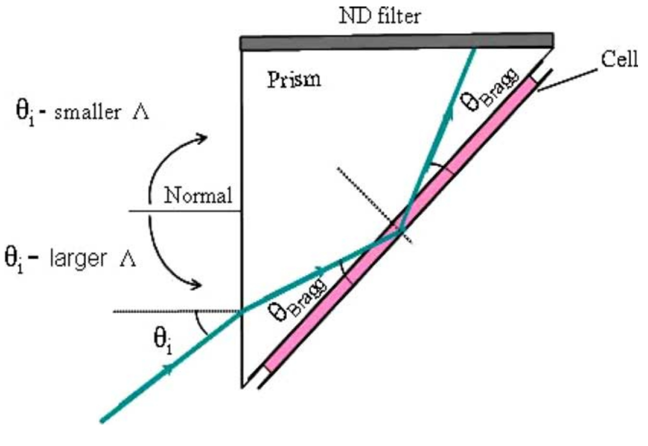


Fig. 1. Visible laser light writing geometry, showing the single beam incident on the prism attached to the cell.

theoretically, there is no limit of the wavelength of the notch that can be written by this technique [13], experimentally, there are difficulties due to the steep angles. The accessible notch wavelengths depend on the size and the refractive index of the prism and also the thickness of the cell. Using Snell's law and Bragg's relation [13], a relation to estimate the wavelength of reflection notches can be obtained. To avoid multiple reflections inside the prism assembly, the reflected beam must exit the opposite prism window and for standard prism materials this condition is satisfied for incident angles less than 50°. Pushing the writing wavelength to 532 nm enables, in theory, notch wavelengths out to approximately 2100 nm, almost double what can be obtained using a UV writing laser. In practice, the longest wavelength achievable using a 364 nm writing line is approximately 900 nm.

We have chosen the initiators so that the absorption spectrum covers the region from 400 to 550 nm and thus are suitable for He–Cd (442 nm), argon ion (476, 488, 514 nm) and Verdi (532 nm) laser lines. As an example, Fig. 2 shows reflection notches written with the 532 nm laser line using the Rh6G and BzO_2 initiator system. The high end of the notch wavelengths accessible (~1600 nm) are considerably higher than those obtained with UV writing. Thiol-ene polymerization undergoes a free radical step-growth mechanism as shown in Scheme 1. The presence of oxygen does not affect the polymerization significantly. For these thiol-ene systems where the thiol functionality is 4 and the ene functionality is 3, the gel point does not occur until conversions exceed 41% [13]. The late gelation facilitates almost 100% final conversion of double bonds, and because most of the double bonds are consumed while the precursors are in the liquid state, the adverse consequences of shrinkage are not manifested in the films. The notches are well characterized by a good baseline, symmetrical shapes and the notch width depends on the film thickness. The DE decreases as expected as the writing angle and the notch wavelength is increased. The bleaching of the dyes was very efficient. The performance of the three initiators in this context is discussed separately.

3.1. Irgacure 784 initiator

The commercial thiol-ene monomer NOA65 contains a few percent benzophenone as a UV initiator. Benzophenone, however, does not absorb the laser visible wavelengths used in this work. We also found that the absorption maximum and shape of all three visible initiators employed here, Irgacure 784, Rh6G and PyM597, were unaltered by the addition of NOA65. This indicates that there is no interference in the photochemistry due to the benzophenone. By combining Irgacure 784 with BzO_2, reflection gratings in all colors with DE's in the range of 65–75% were formed with a variety of visible writing lines as shown in Fig. 3. In the absence of BzO_2, very low DE's were observed (<3%). Because, Irgacure 784 has an absorption peak near 440 nm (close to He–Cd laser line) but little absorption at 532 nm as shown in Fig. 4, a high concentration of 3% (by weight) is needed to get high DE's for 532 nm writing. Notches with wavelengths as far as 1500 nm were written. The gratings were electrically switchable with switching fields of 12 V/μm (Fig. 5) and similar in behaviour to those of UV laser line written gratings. The gratings were stable and no aging

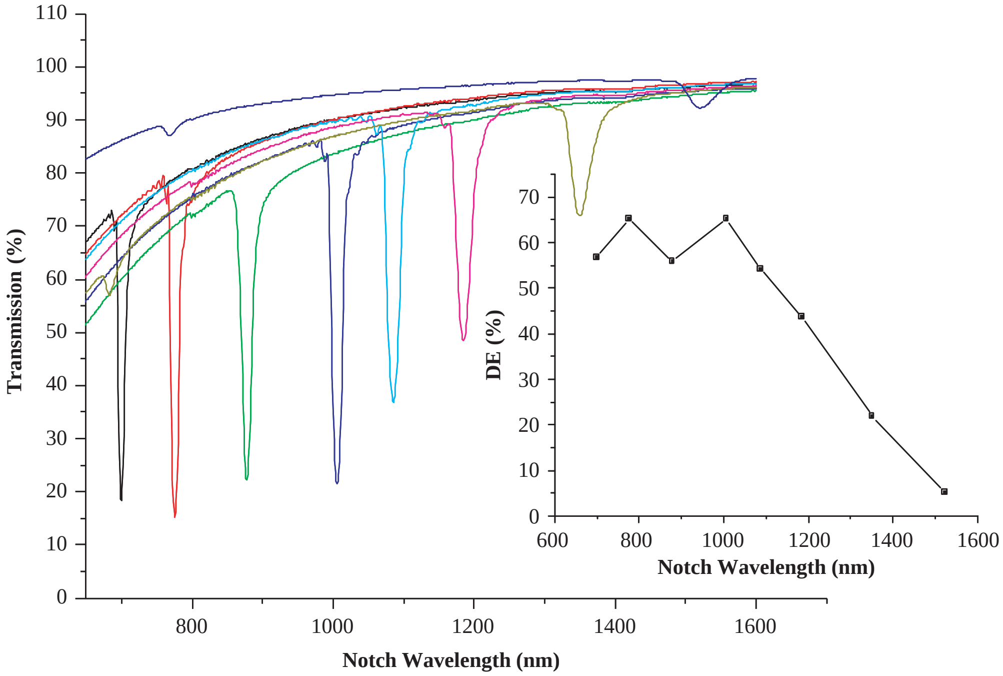
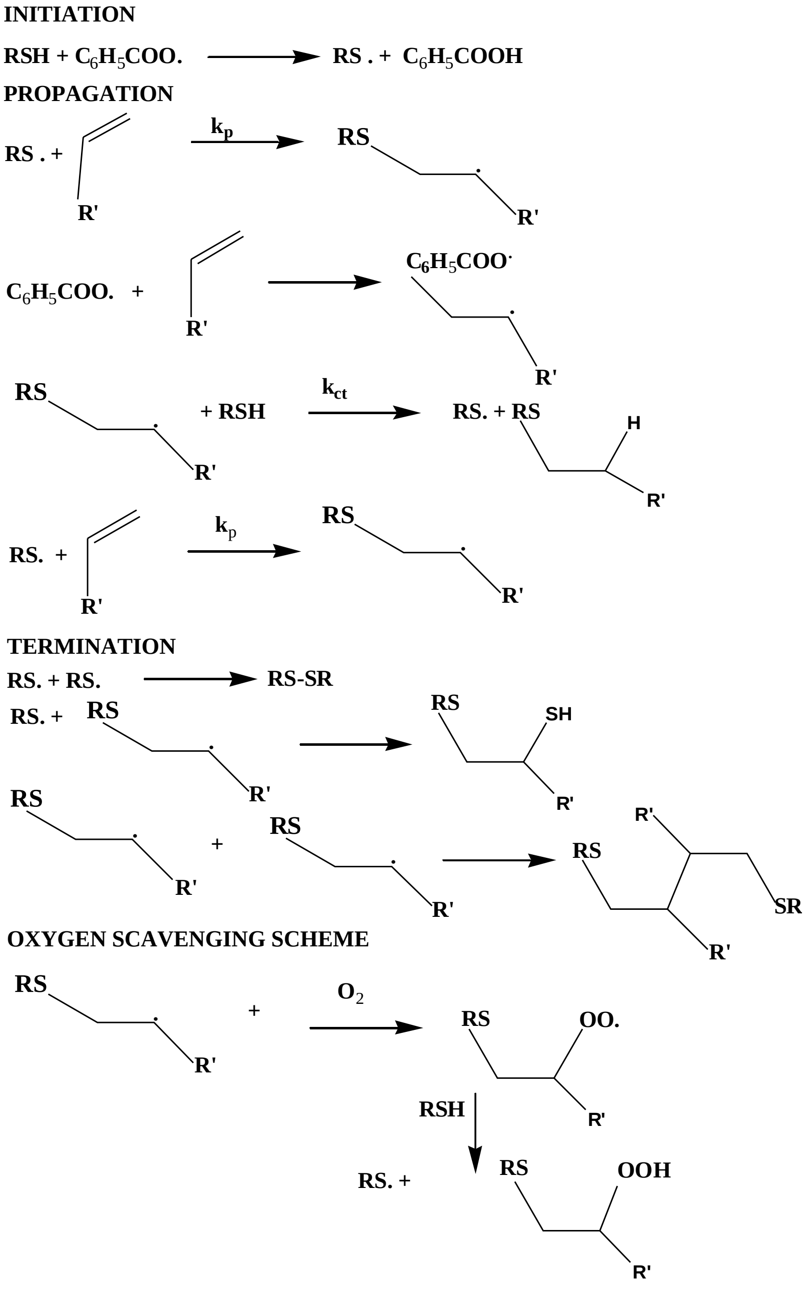


Fig. 2. Near infra-red reflection notches written with 532 nm laser line using the Rhodamine 6G and benzoyl peroxide system. Inset: diffraction efficiency of these notches as a function of the notch wavelength.



Scheme 1. Mechanism of thiol-ene polymerization.

effects or changes were noticed in DE, the notch wavelength, or the switching field voltage for up to three months. By angle tuning the prism, reflection notches in the near IR were easily written. Using the 532 nm laser line, the initiator efficiency dropped considerably and much higher powers were needed to write gratings. This may be understood in terms of the very low absorption at 532 nm (Fig. 4). The mechanism of thiol-ene polymerization initiated by benzoyl oxy radical is shown in Scheme 1.

The mechanism of initiation of photopolymerization by Irgacure 784 (I784) is illustrated in Scheme 2. No luminescence was observed for I784, which is not surprising since very few organometallic complexes exhibit fluorescence or phosphorescence. We propose that complexation of BzO_2 with the excited Ti-complex (II) occurs through the keto group followed by decomposition of the complex to give benzoyl oxy radicals (VII) capable of free radical initiation and also hydrogen abstraction from the thiol bond. In the polymerization of acrylates by titanocenes, a similar complexation of the keto group of the acrylates was proposed [14]. It has been concluded from previous studies that the allyl pyrrolidino radical (IV) acts as a radical scavenger and not as an initiating species [14]. The flash photolysis studies support the formation of the dimer from (IV) [14]. We attempted different peroxides and found that BzO_2 gave the best results.

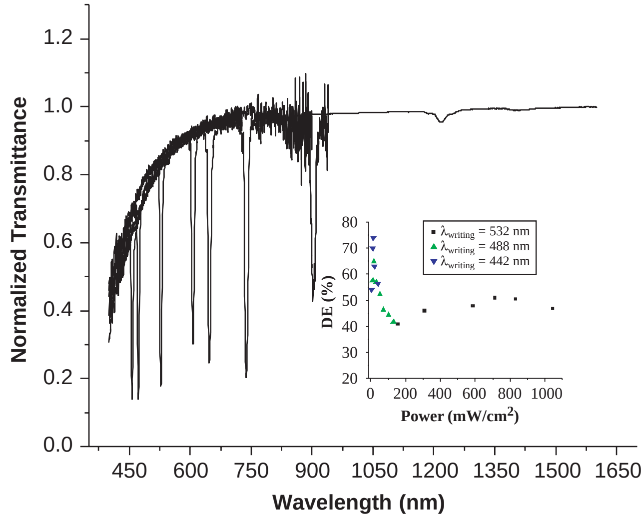


Fig. 3. Reflection notches written with the Irgacure 784 and benzoyl peroxide system. Inset: comparison of diffraction efficiencies of a 750 notch written with different laser wavelengths (442, 488, 532 nm).

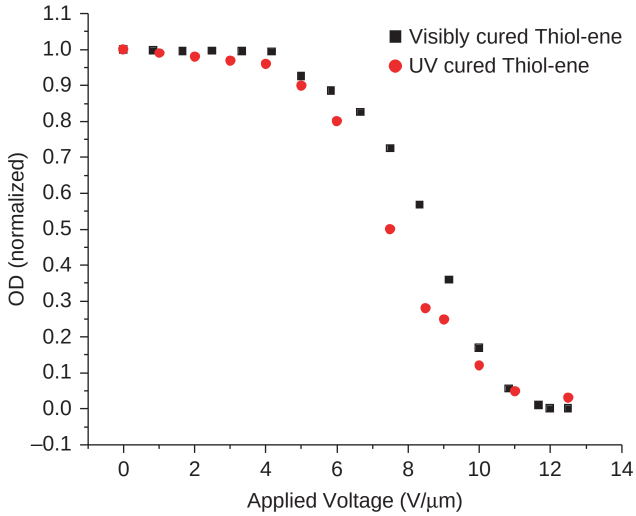


Fig. 5. Electrical switching of UV and visibly written thiol-ene reflection notch of 705 nm.

It should be noted that the mechanism proposed (Scheme 2) shows that each titanocene molecule yields four initiating radicals and thus an enormous concentration of free radicals can be produced in a short time. It is likely that high monomer conversion and thus gelation are reached much faster in the case of He–Cd writing where a main absorption peak of Irgacure 784 is close to the 442 nm wavelength of the laser. It is interesting to note that using much lower powers (<10 mW/cm^2) of the He–Cd compared to UV writing yields notches with higher DE.

3.2. Rhodamine 6G initiator

We have demonstrated in Fig. 2 that the well known laser dye Rhodamine 6G (Rh6G) in combination with BzO_2 is an efficient initiator of thiol-ene photopolymerization as notches out to 1500 nm were demonstrated. Rh6G shows an absorption maximum around 530 nm in most well-known solvents and is thus suited for 532 nm laser radiation. An increase of absorption was noticed when BzO_2 in the concentration range 1×10^{-5}–1×10^{-3} M was added in *N*-vinyl pyrrolidinone as a solvent as shown in Fig. 6. Since, BzO_2 has no absorption beyond 280 nm, this is indicative of a ground state association or complex formation between Rh6G and BzO_2. However, no significant red shift characteristic of a charge transfer complex was evident. A similar observation was made in the photopolymerization of methyl methacrylate using the Rh6G and BzO_2 combination [15]. Fluorescence studies conducted by us support the ground state association between Rh6G and BzO_2. The emission intensity increases for the BzO_2 addition in the concentration range 1×10^{-5}–1×10^{-3} M. It is possible that the increase of fluorescence may be due to the excited complex or a fluorescent exciplex formed from Rh6G and BzO2 or even the combination of both. Fluorescence lifetime studies which are beyond the scope of the present investigation may lead to more insight for the mechanism. Based on these observations, we propose a mechanism for initiation involving ground state complexation between the Rh6G and BzO_2. The excitation of the complex at 532 nm results in an excited state complex which may then decay to the singet excited state of Rh6G. Electron transfer to the BzO_2 takes place in the singlet excited state followed by cleavage of BzO_2 to give a benzoyl-oxy radical capable of initiating the polymerization as shown in Scheme 3.

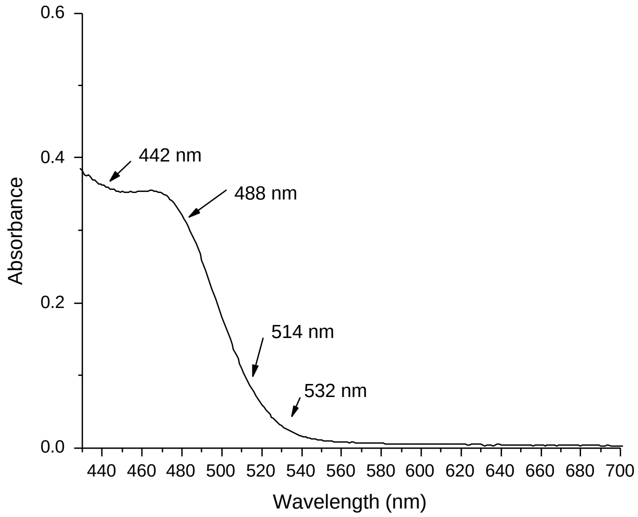
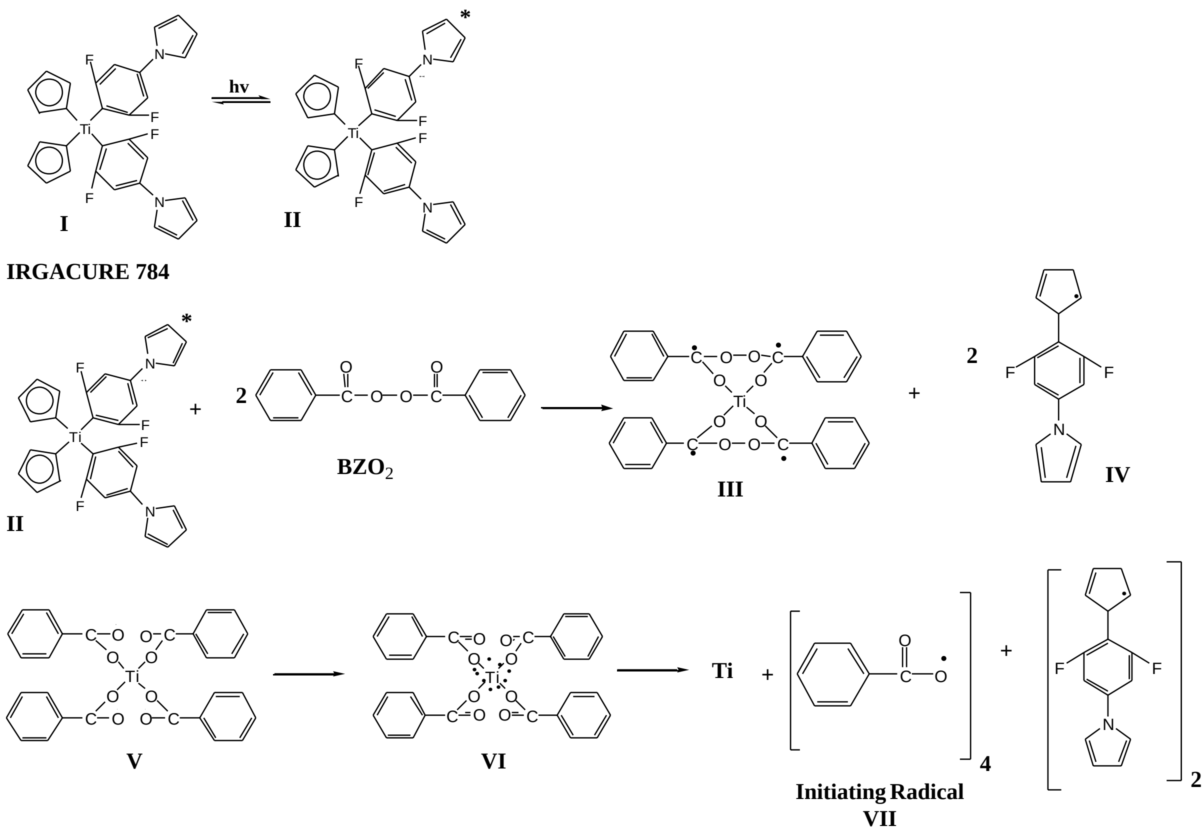


Fig. 4. Absorption spectrum of Irgacure 784 in *N*-vinyl pyrrolidinone. The laser wavelengths are shown in the absorption spectrum.

Rh6G with BzO_2 is efficient for writing near IR notches from 700 to 1400 nm as shown in Fig. 2. High power densities (above 250 mW/cm^2) of 532 nm laser light are needed to obtain DE's higher than 50%. The optimum concentration of BzO_2 was found to be 1.5 wt%. The writing power was varied from 100 mW to 3500 mW/cm^2



Scheme 2. Mechanism for the formation of initiating radicals.

and DE values began to level off for powers around 1500 mW/cm^2.

3.3. Pyrromethene initiator

Pyrromethene dyes were synthesized 20 years ago and are known for their high quantum yields for fluorescence and stability towards bleaching and therefore are used as laser dyes [16]. We employed Pyrromethene 597 (PyM), where 597 refers to its lasing wavelength, as an initiator for the 532 nm laser line. BzO_2 was used in combination as a coinitiator. The photophysics in terms of fluorescence quenching by BzO_2 was different from that of Rh6G. There is no evidence of ground state association for BzO_2 concentrations below 0.15 M as no change in the absorption or the maximum wavelength of absorption was noticed as indicated in Fig. 7. Dynamic quenching of fluorescence is observed at low concentrations evidenced by the Stern–Volmer relation as shown in Fig. 8. At higher concentrations (>0.2 M), static quenching is indicated by an increase in the slope. The fluorescence quenching of PyM can be explained on the basis of a photoinduced electron transfer from the singlet excited dye to BzO_2 ground state. The prepolymer syrup used for writing gratings contained ~ 0.06 M BzO_2. Under the experimental concentration range of BzO_2 employed, we propose that electron transfer occurs from the singlet excited state of PyM to BzO_2, followed by bond breaking that leads to the production of a benzoyl-oxy radical [16] as shown in Scheme 4.

Using 532 nm radiation, the efficiencies of the three initiators were compared by writing the same wavelength notch at 705 nm shown in Fig. 9. The absorption of the prepolymer syrup at 532 nm for all three initiators were kept approximately equal. At power densities >500 mW/cm^2, Rh6G gives higher DEs than either the Irgacure 784 or PyM initiators. The sharp drop in DE for PyM with writing power

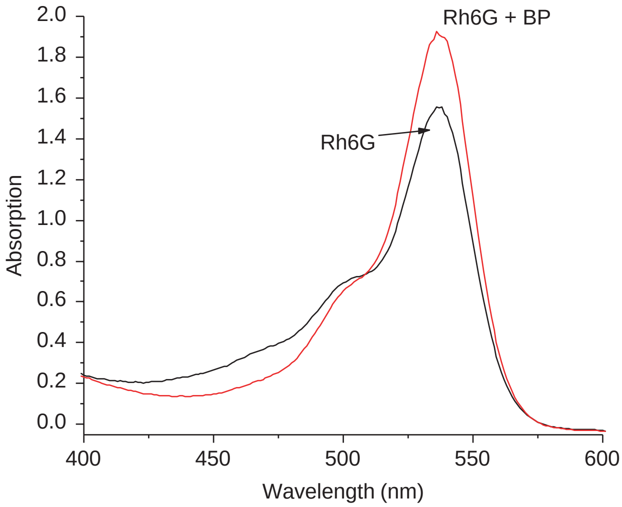
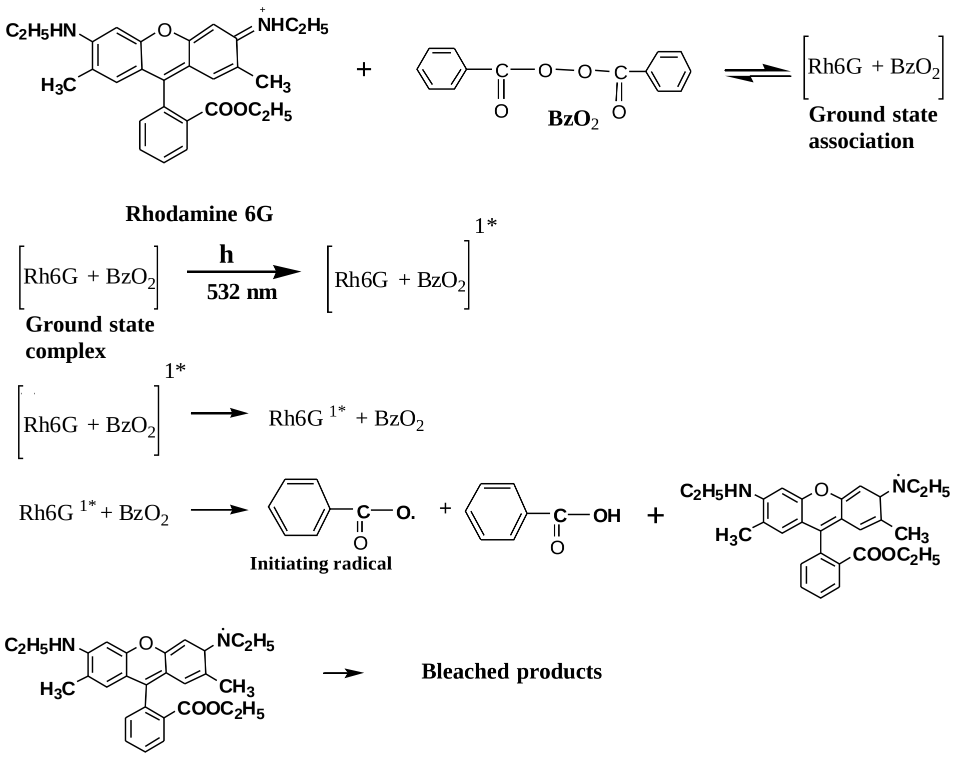


Fig. 6. Absorption spectrum of Rhodamine 6G in *N*-vinyl pyrrolidinone with and without benzoyl peroxide.



Scheme 3. Mechanism of initiation by Rhodamine 6G.

is not easily understood. Faster gelation in thiol-ene polymers can lead to poorer phase separation and a lowering of the final index modulation. In general, laser dye initiator systems require higher powers for 532 nm than the UV-initiated systems.

The decrease of DE with increase of notch wavelength (see inset in Fig. 2) may be due to various reasons. The overlap of the beams is less efficient for the steep angles required for writing in a single-prism geometry. Also, to compensate for the increase of the grating spacing, the thickness of the films must be increased to increase the number of layers. Finally, the birefringence of the LC decreases at longer wavelengths due to the dispersion of the refractive index.

The interior morphology of the reflection gratings was probed in detail with transmission electron microscopy, both bright field transmission (BFTEM) and scanning transmission electron microscopy (STEM) were used for the study. Fig. 10 shows phase separated spherical shaped

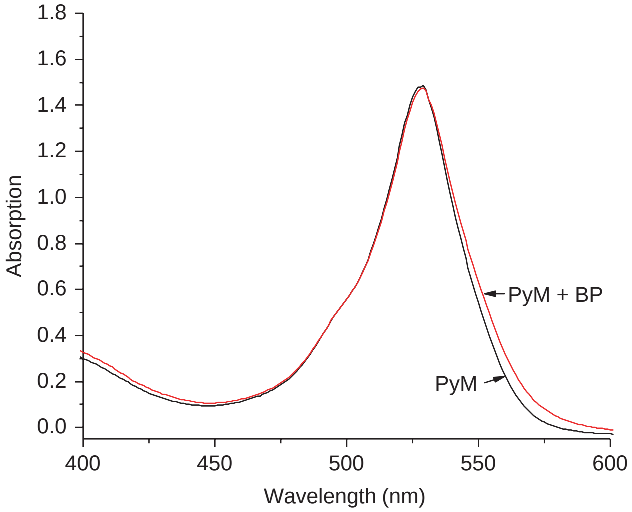


Fig. 7. Absorption spectrum of Pyrromethene 597 in *N*-vinyl pyrrolidinone with and without benzoyl peroxide.

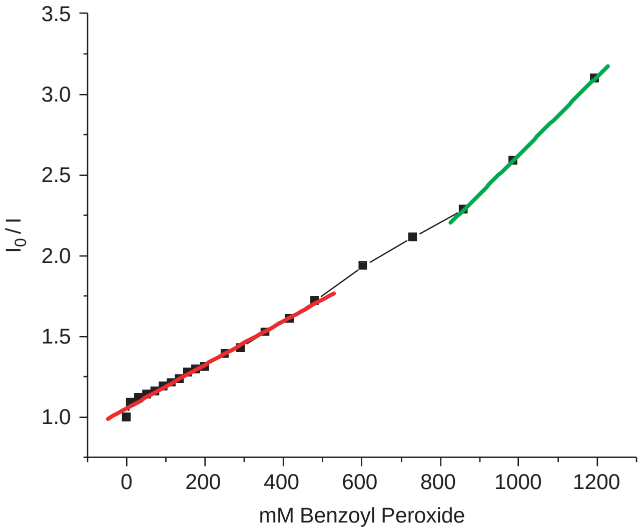
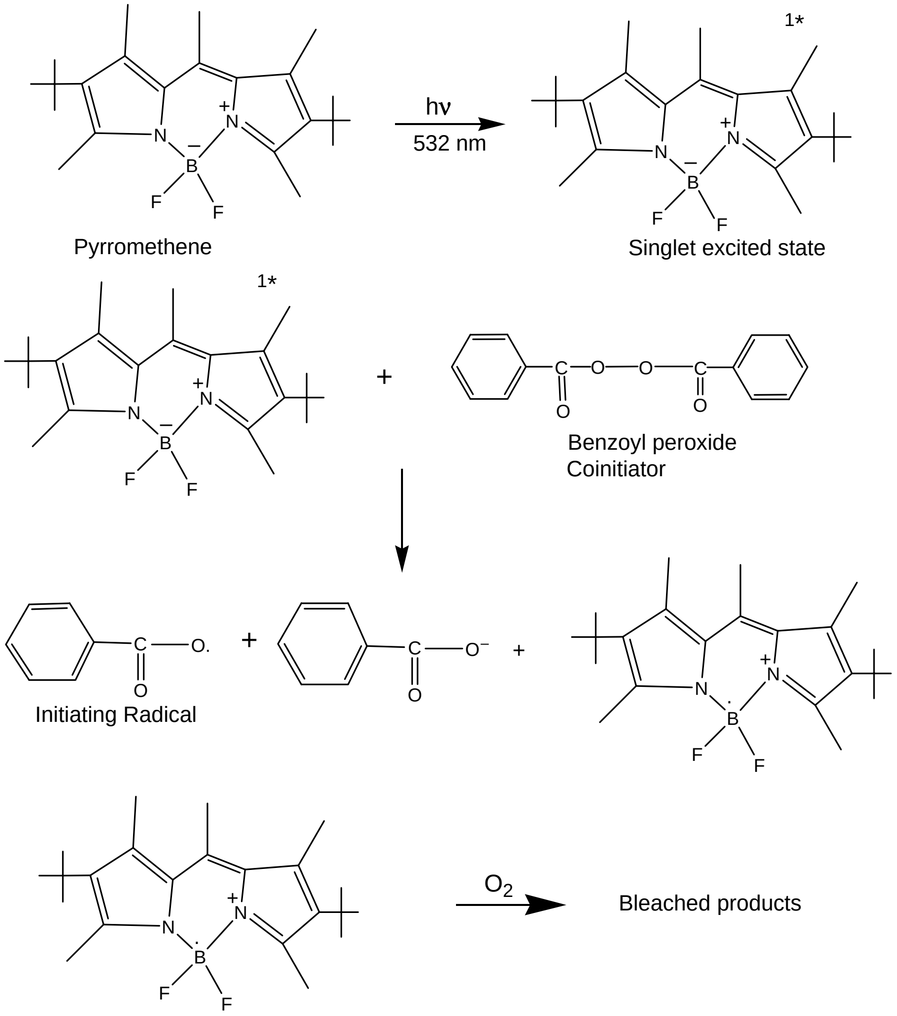


Fig. 8. Stern–Volmer plot of fluorescence quenching of Pyrromethene by benzoyl peroxide in *N*-vinyl pyrrolidinone.



Scheme 4. Mechanism of initiation by Pyrromethene 597.

discrete nematic droplets periodically dispersed in the polymer. The droplets are similar in shape and the interface between the droplets and polymer was very smooth. Thiol-ene polymerization involves a free radical step-growth mechanism in which the monomer is converted to oligomers early in the reaction. As the number of oligomers increases above a critical concentration, phase separation of an oligomer- rich liquid from an LC-rich liquid occurs. Because both phases are liquid and the viscosity is low, the discontinuous phase typically is spherical in shape as a result of surface tension effects. Fig. 10 gives morphology of three gratings with notch wavelengths 750, 1033, and 1327 nm with grating spacings 244, 336 and 432 nm respectively. Good agreement was observed between the spacing obtained optically and from the micrograph. The average droplet sizes were 140, 160, and 190 nm for the three notches. Though, the grating spacing increased 77% from 750 to 1327 nm notch, only a small increase in the droplet size was seen. This decrease in droplet density with spacing leads to lower index modulation, consistent with the drop in DE from 75 to 23% for these three systems.

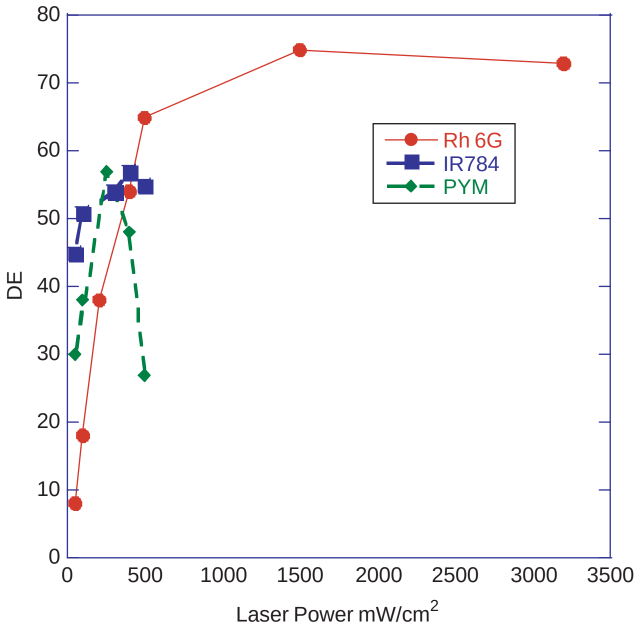


Fig. 9. Comparison of the performance of three photoinitiators at the writing laser wavelength 532 nm. The reflection notch was at 705 nm.

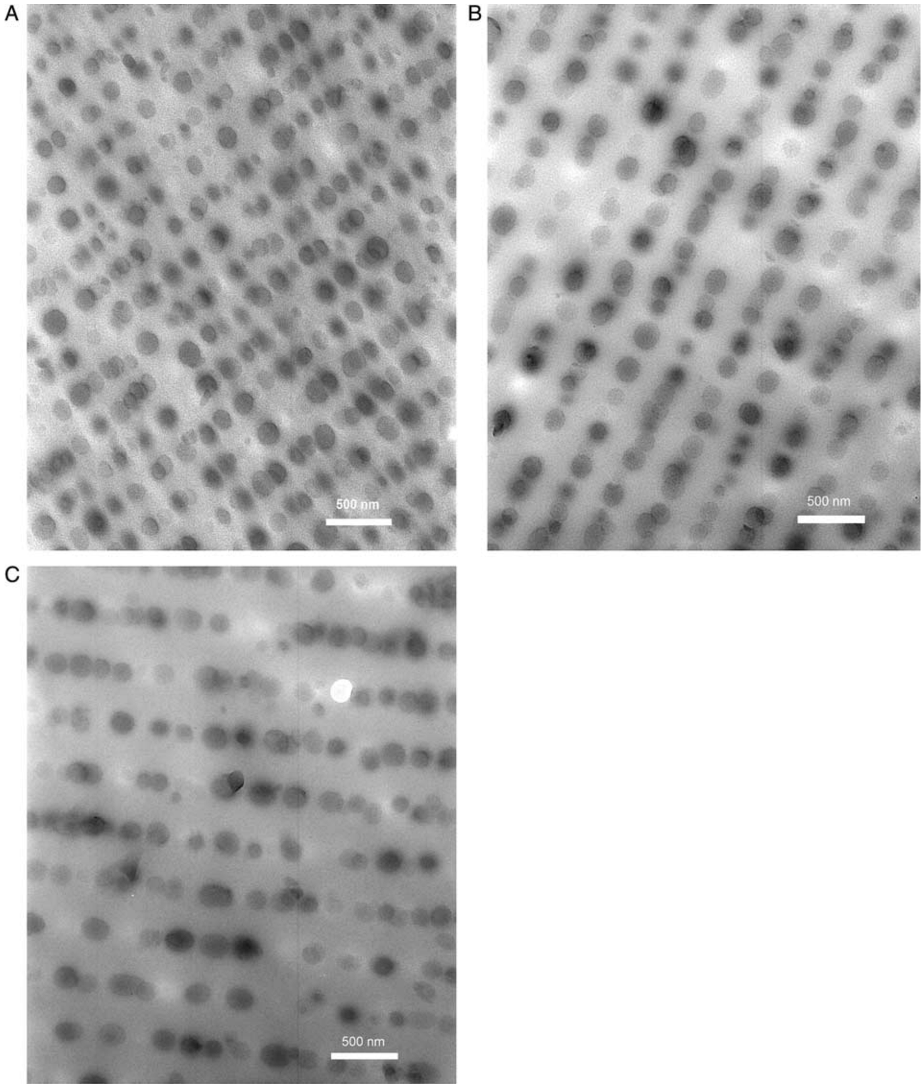


Fig. 10. Bright-field transmission electron micrographs of near IR reflection gratings. (A) Reflection notch at 750 nm. (B) Notch at 1033 nm. (C) Notch at 1327 nm. Scale bar 500 nm.

4. Conclusion

We have demonstrated the capability of three visible initiator systems for thiol-ene photopolymerization using laser wavelengths between 442 and 532 nm. The commercially available titanocene complex is efficient for laser light wavelengths <500 nm. In addition, the well known laser dyes Rhodamine 6G and Pyrromethene 597 are suitable for 532 nm laser, and in combination with benzoyl peroxide, exhibit chemical reactivity through a singlet excited state. Efficient bleaching of the dyes was observed. Benzoyl oxy radicals produced are very efficient as they abstract hydrogen from thiols and also can add on to the olefinic bond. By employing a single-beam prism-coupled holographic geometry with visible lasers, reflection gratings in the near-IR with high diffraction efficiencies were written. Interesting differences in the photophysics and in the production of the initiating species were observed for the three initiators. Rh6G showed better performance than the other two initiators for 532 nm laser writing. Given the low cost and easy availability of CW lasers, development of initiators for CW visible wavelength lasers for practical applications is important. Work is now underway to develop photoinitiators for 633 and 647 nm lasers.

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