Preparation of a Novel Infrared Photoinitiator and Kinetic Monitoring of Photopolymerization by Real Time FT-IR Spectroscopy

Bin LI,[†] Shihai ZHANG, Liming TANG, and Qixiang ZHOU

*Department of Chemical Engineering, Materials Research Center,
Tsinghua University, Beijing 100084, People's Republic of China*

(Received October 10, 2000; Accepted December 25, 2000)

ABSTRACT: In this paper, a novel cationic cyanine dye-borate complex, 1,3,3,1',3',3'-hexamethyl-11-chloro-10,12-propylenetricarbocyanine triphenylbutylborate was prepared and used as the photoinitiator in infrared laser-induced photopolymerization of acrylates. It had a maximum electron absorption at 786 nm, which matched well with the output wavelength of the adopted infrared laser diode, with a maximum molar extinction coefficient of $1.4 \times 10^5 \text{ L mol}^{-1} \text{ cm}^{-1}$ in chloroform solution. Under the irradiation of infrared laser the polymeric samples based on phthalicdiglycol diacrylate (PDDA), binder, photoinitiator and solvent polymerized and the polymerizing process was monitored through Real Time FT-IR spectroscopy (RTFT-IR). The double bond conversion was determined from the reduction of the absorption of acrylate monomer at 1635 cm^{-1} and 1620 cm^{-1} ($\text{CH}_2=\text{CH}$ stretching) in FT-IR spectra during laser irradiation. As the concentration of photoinitiator rose, the polymerization rate (R_p) increased rapidly but then decreased when the concentration reached a critical value. R_p and the ultimate double bond conversion of sample increased when the infrared laser power was enhanced, whereas they fell greatly as the thickness of the polymeric sample layer increased.

KEY WORDS Infrared Laser / Photoinitiator / Phthalicdiglycol Diacrylate / Real Time / FT-IR /

It is well known that photopolymerization has many distinct virtues such as rapid reaction rate, low energy or space requirements for processing and little pollution to the environment.¹ In the past decades study on photopolymerization induced by UV irradiation was well developed and traditional UV light sources were widely used for various industrial applications, *e.g.*, photosensitive polymer materials including photoresists, photocurable varnishes, fast-drying inks, photocurable adhesives and information-recording media. But for the use of imaging such as in offset process, there must be a stage where multiple pieces of paper become film or negative pages when using traditional UV source. On the other hand, such a cost- and time-consuming process can be avoided by the use of laser sources. An image from the computer can be directly written on the pre-sensitized plates by the scanning of laser beam (such a technology was called "Direct-To-Plate" or "Computer-To-Plate" (CTP) in industry).^{2–6} So savings in costs and improvements in efficiency can be brought through CTP. Infrared laser diode is small, compact and easy to operate, so it's a suitable laser source to be used in this technology. But the most superiority of it lies in its cheap price. As soon as the commodity of infrared laser diode became available, it was regarded highly competitive to be utilized for achieving CTP.

However, there were few photoinitiators matching well with the wavelength of infrared light, which strongly impeded the development of infrared laser-induced polymerization. In the past years there were a few investigations on the synthesis of infrared photoinitiators but they were all reported in patents.^{7–12} There are no commercial infrared photoinitiators available at present.

The kinetics study of photopolymerization has been the main subject of researches on photopolymerization all the while. Many traditional discrete methods such as IR spectroscopy¹³ and FT-IR photoacoustic spectroscopy¹⁴ or continuous measuring like in methods based on dilatometry,¹⁵ differential photocalorimetry¹⁶ and laser interferometry¹⁷ have been developed. However, these methods can only monitor the photopolymerization in large time scale, that is, the one that proceeds slowly. As for photopolymerization induced by laser with high energy density, since the reaction takes place so rapidly that it can be finished within a fraction of second, the methods above become unsuitable. In the past years there were a few novel analytical methods favorable for ultra-fast photopolymerizations appeared, including Real Time FT-IR spectroscopy (RTFT-IR),^{18–23} Real Time Fluorescence Probe methodology (RTFP)²⁴ and Real Time Attenuated Total Reflectance FT-IR spectroscopy (RTATR).²⁵ These new methods ended the study of fast photopolymerization fresh sight. Among them RTFT-IR provided us a convenient way to monitor the residual double bonds in the polymerizing system directly and so it was employed in many studies.

In this article, we prepared a kind of cationic cyanine dye-borate complex (CBC), 1,3,3,1',3',3'-hexamethyl-11-chloro-10,12-propylenetricarbocyanine triphenylbutylborate, which was employed as the photoinitiator for the infrared laser-induced polymerization of phthalic diglycol diacrylate (PDDA). The influence of polymerization parameters including concentration of photoinitiator, laser energy and thickness of the sample layer on the kinetics of photopolymerization of PDDA was studied through RTFT-IR.

[†]To whom correspondence should be addressed.

Figure 1. Chemical formula of the photoinitiator and monomer.

EXPERIMENTAL

Materials

Triphenylborane was purchased from Aldrich Chem. Co. and used as received. Phthalic diglycol diacrylate (PDDA) (Figure 1) was a largess from Dongfang Chemical Engineering Factory, Beijing. It was used without removing of the stabilizers because it seemed that this procedure resulted in little instability in the polymerizing system. The copolymer of acrylic acid (AA), methyl methacrylate (MMA), styrene (St) and butyl acrylate (BA) (AA/MMA/St/BA = 20/45/10/25 (wt ratio)) was used as the binder in the polymerizing system in order to improve the adhesion of polymeric sample to the substrate. All the other compounds were of analytically pure grade and were used without further purification.

Synthesis of the Photoinitiator

Cationic Cyanine Dye. The cationic cyanine dye 1,3,3,1',3',3'-hexamethyl-11-chloro-10,12-propylenetricarbocyanine iodide was prepared according to the procedure reported in ref 26. Mp 258–259°C. Anal. Calcd. for $C_{32}H_{36}N_2ClI$: C, 62.90; H, 5.90; N, 4.59. Found: C, 62.68; H, 6.00; N, 4.55. IR (KBr): 1610, 1550, 1510, 1450, 1390, 770 cm^{-1} . 1H NMR (DMSO): 1.55–2.00 (s, 12H), 2.58–3.00 (m, 6H), 3.20–3.80 (s, 6H), 6.16–6.55 (m, 4H), 7.13–8.48 (m, 8H). The maximum absorption wavelength, λ_{max} , for the dye in methanol is 774 nm with a maximum molar extinction coefficient, ϵ_{max} , of $2.7 \times 10^5 L mol^{-1} cm^{-1}$.

Tetramethylammonium *n*-Butyltriphenylborate. The triphenylborane was dissolved in 100 mL dry benzene (1 M) under nitrogen atmosphere. The flask was placed in a cool water bath and *n*-BuLi (1.1 equiv of theoretical) was added *via* syringe while stirring strongly. A white precipitate soon formed after addition was started. Stirring was continued for about 45–60 min. The mixture was diluted with 50 mL hexane and filtered, then washed with hexane. This resultant lithium *n*-butyltriphenylborate salt was slightly air-unstable. The white powder was dissolved in about 200 mL deionized water and the aqueous solution of tetramethylammonium chloride (1.2 equiv of theoretical in 200 mL) was added into it with vigorous stirring. A thick white precipitate immediately formed. This aqueous mixture was stirred for 30 min at room temperature and then filtered. The collected white solid was washed with deionized water and dried it to get the product. Mp 248–250°C. Anal. Calcd. for $C_{26}H_{36}NB$: C, 83.87; H, 9.68; N, 3.76.

Found: C, 83.58; H, 9.43; N, 3.87.

Cationic Cyanine Dye-Borate Complex (Photoinitiator). A very fine suspension of the tetramethylammonium *n*-butyltriphenylborate ($0.1 g mL^{-1}$) in methanol was made under vigorous stirring. The flask was protected from light by wrapping it with aluminum foil. The temperature of the reacting system was kept at around 50°C by using a water bath. Then 1 equiv of the above cationic cyanine dye was added into the flask while stirring. After stirring for 30 min the mixture was cooled to room temperature, then diluted with 10 volumes of ice water. The resultant solid was filtered and washed with deionized water until the washing was colorless. The solid was suction-filtered to dryness and the so-obtained photoinitiator compound was completely dried at room temperature in a vacuum drying oven to get an olive powder product. Mp 140°C, Decomposing temperature 178°C. Anal. Calcd. For $C_{54}H_{60}N_2ClB$: C, 82.81; H, 7.67; N, 3.58. Found: C, 81.99; H, 7.68; N, 3.22.

Sample Preparation and Photopolymerization Conditions

To prepare the sample for photopolymerization the photoinitiator, PDDA monomer and binder were first dissolved in butanone. For all of the samples in this article the concentration of PDDA and binder was set constant with monomer *vs.* binder being 1:1 (wt/wt). The concentration of PDDA was $0.7 mol L^{-1}$. The mixture was purged with nitrogen for 15 min while stirring to exclude the oxygen. A drop of the mixture was applied as a uniform layer on a NaCl crystal tablet. The thickness of the layer was controlled by one or more frames made by aluminum foil, which was 20 μm of thickness. The samples were covered with another NaCl tablet and sealed the sides around the two tablets with inert silicone grease in order to prevent the diffusion of atmospheric oxygen into the polymeric layer.

The FT-IR spectra were obtained with a NICOLET 560 FT-IR spectrometer at a resolution of $8 cm^{-1}$. The *in situ* spectra were taken every 10 s with a scan speed of 1 $s scan^{-1}$. The sample for photopolymerization was fixed in the FT-IR sample chamber to ensure the analyzing area not changed during the experimental procedure. The infrared laser source was an infrared laser diode purchased from Institute of Semiconductors, Chinese Academy of Sciences, which had output wavelength at 796 nm. The infrared laser beam was imported to the chamber through an optical fiber. The output laser beam was adjusted to suitable size in favor of the choice of analyzing area during FT-IR measurement. Energy output of the laser beam at the exporting port was determined with LPE-1 energometer (Institute of Physics, Chinese Academy of Sciences). The sample polymerized under the irradiation of laser beam in the FT-IR sample chamber with its IR spectra being measured instantaneously. In this way RTFT-IR was realized. Figure 2 schematically describes the experimental setup in order to expose the sample to the infrared laser beam, which induces the photopolymerization, and the analytical IR beam, which monitors the drop of the absorbance of the reactive group, at the same time.

The absorbance of acrylate monomer at the double-peak of $1635 cm^{-1}$ and $1620 cm^{-1}$ ($CH_2 = CH$

Figure 2. Schematic experimental setup for photopolymerization kinetics study by RTFT-IR spectroscopy.

stretching) was used for calculating the conversion of double bond during photopolymerization. The conversion of acrylic double bond (γ) was determined from the change of the absorbance before and after infrared laser irradiation according to

$$\gamma = (A_0 - A_1)/A_0 \times 100\% \quad (1)$$

where A_0 and A_1 were the absorbance at 1635 cm^{-1} and 1620 cm^{-1} before and after infrared laser irradiation, respectively.

The rate of polymerization (R_p) was obtained from the slope (γ/t) of the linear part of the time-conversion curve below a 10% of conversion according to eq 2,

$$R_p = [M](\Delta\gamma/\Delta t) \quad (2)$$

where $[M]$ is the molar concentration of PDDA monomer before laser irradiation. Units: R_p , $\text{mol L}^{-1} \text{ s}^{-1}$; $[M]$, mol L^{-1} ; t , s.

Electron Spinning Resonance (ESR)

ESR was performed in Bruker ER 200 D-SRC spectrometer with 2-Methyl-2-Nitroso-Propane (MNP) as a radical capturing agent. CBC and MNP were dissolved

in toluene to form a saturated solution. The solution was purged with nitrogen for 10 min to get rid off the oxygen, then it was irradiated under the infrared laser for 5 min at a laser power density of 7.0 mW cm^{-2} . ESR spectrum was collected from this irradiated solution with central magnetic field intensity of 347 mT and scanning range of 4 mT at room temperature.

RESULTS AND DISCUSSION

Synthesis of the Photoinitiator

Synthesis of the photoinitiator is described in Scheme 1. The lithium salt of *n*-butyltriphenylborate was first prepared from triphenylborane and *n*-butyllithium. Since this lithium salt is a little unstable in air atmosphere, it further reacted with tetramethylammonium chloride to get a borate salt of tetramethylammonium, which was very stable and could be stored for more than one year. Then this borate salt was treated with the cationic cyanine dye through a kind of ion-exchange reaction, and eventually the cationic cyanine dye-borate complex (photoinitiator) was obtained.

The maximum absorption wavelength for the photoinitiator in chloroform is 786 nm with a maximum molar extinction coefficient of $1.4 \times 10^5 \text{ L mol}^{-1} \text{ cm}^{-1}$. Since the output wavelength of the infrared laser employed is 796 nm, the absorbance of the photoinitiator matches it well.

There have been many studies on the photophysics of reactions of carbocyanine alkyltriphenylborate salts up to present.^{27–29} They have shown that under the irradiation there is an intramolecular electron transfer from borate, the anionic part, to the triplet state of the cyanine, the cationic part of the salt. This process leads to the formation of alkyl radicals, which are responsible for the initiation of photopolymerization. The major difference between CBC in this paper and those absorbed in the visible region and used by S. Chatterjee *et al.*^{27,29} is that the former has more conjugated double bond number, so is sensitive to light with longer wavelength. It is reasonable to assume the CBC would also undertake the same intra-ion-pair electron transfer process (Scheme 2) under the irradiation of infrared laser beam because of the

Scheme 1. Synthesis of the photoinitiator.

Scheme 2. Schematic illustration of photolysis and photoinitiation of the photoinitiator.

similarity in their chemical structures. The resonance peaks shown in the ESR spectrum of CBC after irradiation of infrared laser (Figure 3) indicated that *n*-butyl radicals had been formed.

Photopolymerization of PDDA

Under infrared laser irradiation the photoinitiator in the polymeric sample absorbed photons and began to photolyze. Then the so-formed *n*-butyl radicals initiated

Figure 3. ESR spectrum of CBC after irradiation of infrared laser (Laser power density: 7.0 mW cm^{-2} , laser irradiation duration: 300 s).

the polymerization of PDDA monomer. Since the FT-IR spectra of the sample were obtained at the same time when the photopolymerization was proceeding, the drop of absorbance at the double-peak of 1635 cm^{-1} and 1620 cm^{-1} ($\text{CH}_2=\text{CH}$ stretching) or the single-peak at 810 cm^{-1} ($\text{CH}_2=\text{CH}$ twisting) exactly monitored the decrease of double bonds in the sample. The absorbance of photoinitiator at 793 cm^{-1} was also seen clearly reducing during irradiation of laser. Generally the change of absorbance at 1635 cm^{-1} and 1620 cm^{-1} or at 810 cm^{-1} could be used for calculating the percentage conversion of double bond. But since absorbance peak of the monomer at 810 cm^{-1} overlapped partially with that of the photoinitiator at 793 cm^{-1} , the absorbance at 1635 cm^{-1} and 1620 cm^{-1} was employed for determining the double bond conversion.

Figure 4 shows the spectra for a sample with photoinitiator concentration of 2.5% and irradiated under a laser energy density of 17.0 mW cm^{-2} for different time. It is clearly that the double bond decreased rapidly with the laser irradiation, then the polymerization rate slowed to reach a plateau. The double bond conversion reached around 65% after irradiated for 10 min. The exposed area changed to a fine film and could not be dissolved in solvents any more. This means that the sample polymerized and cured effectively as a result of infrared laser irradiation.

Figure 4. FT-IR spectra for the photopolymerization sample at different time (Concentration of PDDA: 0.7 mol L^{-1} , laser power density: 17.0 mW cm^{-2} , CBC content: 2.5 wt%, sample thickness: $20 \mu\text{m}$).

Figure 5. Double bond conversion of samples with different concentration of photoinitiator (Concentration of PDDA: 0.7 mol L^{-1} , laser power density: 17.0 mW cm^{-2} , sample thickness: $20 \mu\text{m}$).

Figure 6. Influence of CBC content on the double bond conversion of PDDA with 10 s of laser irradiation (Concentration of PDDA: 0.7 mol L^{-1} , laser power density: 17.0 mW cm^{-2} , sample thickness: $20 \mu\text{m}$).

Influence of Concentration of Photoinitiator

Figure 5 shows the polymerization curves of samples with different concentration of photoinitiator. The CBC content (the weight ratio of CBC *vs.* PDDA) in the polymeric mixture played a significant role for the polymerization rate and double bond conversion. As the concentration of CBC rose from 0.5% to 5%, the rate of polymerization increased greatly. However, further increasing concentration of photoinitiator did not improve Rp correspondingly. On the other hand, Rp decreased when the concentration of photoinitiator was above 5%. Figure 6 depicts the relationship between the double bond conversion at the end of 10 s of laser irradiation and concentration of CBC.

Such an unusual phenomenon may be attributed to the internal filter effect of the photoinitiator²⁰ which prevents the infrared light from penetrating into the deep part of the high absorbing layer. It's also possible that when the concentration of photoinitiator is so high that too many radicals are formed at the same time, the coupling of these radicals results in the decrease of initiation efficiency. So there is an optimum value for the concentration of photoinitiator in the polymerizing system.

Figure 7. Double bond conversion of samples under irradiation of different laser power density (Concentration of PDDA: 0.7 mol L^{-1} , CBC content: 5.0 wt%, sample thickness: $40 \mu\text{m}$, laser power density unit: mW cm^{-2}).

Influence of Laser Power

As what is depicted in Figure 7, Rp increased when the power of infrared laser was enhanced. The light intensity of the laser (I_0) was not measured directly in the experiments. But since light intensity was proportional to laser power density (W), it's reasonable to use the value of laser power density for the determination of polymerization kinetics. For typical photopolymerization in which the termination step is by di-radical termination mode, there is a kinetic relationship as eq 3.³⁰

$$R_p = k_p[M](\phi \epsilon I_0[\text{Ini}]/k_t)^{0.5} \quad (3)$$

where k_p and k_t are propagation rate constant and termination rate constant, respectively. $[M]$ and $[\text{Ini}]$ are the concentration of monomer and photoinitiator, respectively. Units: R_p , $\text{mol L}^{-1} \text{s}^{-1}$; $[M]$ and $[\text{Ini}]$, mol L^{-1} ; k_p and k_t , $\text{L mol}^{-1} \text{s}^{-1}$; ϵ , s^{-1} .

When the other parameters are set constant, R_p is proportional to the square root of light intensity, $I_0^{0.5}$, and so proportional to $W^{0.5}$. If the logarithm of both sides of eq 3 is taken and W is used, there should be

$$\log R_p \propto 0.5 \log W \quad (4)$$

So there must be a linear correlation between $\log R_p$ and $\log W$ with a slope of 0.5. To testify this equation, a figure of $\log R_p$ *vs.* $\log W$ is depicted in Figure 8. What we can see from this figure approves of it.

It can be seen that the ultimate double bond conversion of sample irradiated under higher laser power was also larger than that under lower laser power. For the sample irradiated with laser power density of 17.0 mW cm^{-2} , the double bond conversion of sample after irradiated for 10 min could reach 74%, while for that with laser power density of 0.5 mW cm^{-2} only 49%. This is also attributed to the internal filter effect of photoinitiator.

Influence of Thickness of the Samples

The FT-IR spectra of samples with different thickness were shown in Figure 9. As the thickness of the polymeric sample layer increased from $20 \mu\text{m}$ to $80 \mu\text{m}$, the

Figure 8. The relationship between $\log R_p$ and $\log W$ (Concentration of PDDA: 0.7 mol L^{-1} , CBC content: 5.0 wt%, sample thickness: $40 \mu\text{m}$).

Figure 9. Double bond conversion of samples with different thickness (Concentration of PDDA: 0.7 mol L^{-1} , laser power density: 17.0 mW cm^{-2} , CBC content: 5.0 wt%).

rate of polymerization fell significantly. According to Lambert-Beer Law, the light traversing through a layer of absorbing media weakens greatly along the direction of thickness. When thickness of the sample increases it is possible that the underside of the layer undergoes no light irradiation and so no polymerization occurs. But the FT-IR spectrum obtained is still for the whole layer. Then there must be a lower value for the conversion calculated (*apparent conversion*) compared with its actual value and it is the same case for the measurement of R_p (*apparent R_p*).

Also it's clear that the final double bond conversion for the thicker sample is lower than that of the thinner one, which shows the result of internal filter effect of the photoinitiator again.

CONCLUSION

A novel cationic cyanine dye-borate complex was prepared through ion-exchange reaction between cationic cyanine dye and tetramethylammonium *n*-butyltriphenylborate. Its absorbance matched the output wavelength of the infrared laser used in this article well and was employed as the photoinitiator for the infrared laser-induced photopolymerization. The photopolymerization of PDDA was successfully monitored

through Real Time FT-IR spectroscopy (RTFT-IR).

As the concentration of photoinitiator rose, the polymerization rate (R_p) and double bond conversion increased considerably. However, they decreased when the concentration of photoinitiator exceeded a critical value as a result of the internal filter effect of photoinitiator. The coupling of radicals at high concentration of photoinitiator, which results in decreasing of initiation efficiency, may also account for it.

R_p increased when the infrared laser power was enhanced. The ultimate double bond conversion of sample irradiated under higher laser power was larger than that under lower laser power. The relationship between R_p and laser power revealed that there was a correlation of R_p vs. square root of laser power.

As the thickness of the polymeric sample layer increased, R_p fell significantly. The final double bond conversion for the thicker sample is also lower than the thinner one, which may also be attributed to internal filter effect of the photoinitiator.

Acknowledgment. The authors of this paper appreciate the great help of Prof. Kunhua Wang of Tsinghua University in devising and adjusting the RTFT-IR setup.

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