Polymer 42 (2001) 7575–7582

polymer

www.elsevier.nl/locate/polymer

Studies on the near infrared laser induced photopolymerization employing a cyanine dye–borate complex as the photoinitiator

Shihai Zhang, Bin Li, Liming Tang, Xiaogong Wang, Deshan Liu, Qixiang Zhou*

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

Received 17 October 2000; received in revised form 22 February 2001; accepted 8 March 2001

Abstract

Laser diodes are small, cheap and easy to operate, so the near infrared laser diode induced photopolymerization has potential applications in computer-to-plates, erasable computer compact discs and photolithography technology. In this paper, a novel cyanine dye–borate complex (CBC), 1,3,3,1′,3′,3′-hexamethyl-11-chloro-10,12-propylene-tricarbocyanine triphenylbutyl borate, was employed as the photoinitiator, and a near infrared laser diode emitting at 796 nm was used as the irradiation source of photopolymerization. The influence of various irradiation parameters, such as the CBC content, light intensity and sample thickness, on the photopolymerization kinetics of different acrylate monomers, with or without a binder, was investigated in detail by real-time FTIR. The maximum photopolymerization quantum yield was about 21.2 mol einstein^{-1} for TMPTA with a sample thickness of 20 μm and a CBC content of 2.0 wt% under 0.5 mW cm^{-2} laser irradiation. It was found that CBC was indeed capable of initiating the polymerization of acrylate monomers under the irradiation of a 796 nm laser. However, the dependence of polymerization rate R_p on the light intensity in the infrared laser induced process was not as pronounced as that induced by conventional UV/Vis light. Moreover, neat TMPTA gave a double bond conversion compared with the system including a solid binder under the same irradiation conditions. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Near infrared laser; Photopolymerization; Cyanine dye–borate complex

1. Introduction

Photopolymerization has found wide applications in imaging and radiation curing technologies, e.g. photoresists, photolithography, photocurable coatings and inks, etc. [1] Compared with conventional ultraviolet or visible lamps, lasers have distinct advantages as irradiation sources for industrial applications. The laser beam can be focused down to a micron-sized spot, which not only provides a high output energy density, but also greatly improves the image resolution of photoresists [2,3]. Moreover, the well-defined emitting wavelength of the laser can effectively reduce the undesirable secondary reactions induced by polychromatic radiation. Thus, the laser-induced polymerization has potential applications in the computer-to-plates (CTPs) or laser direct imaging (LDI) technology, in which high-resolution relief images stored in a computer can be directly transferred to photocurable plates without the use of a mask, and consequently the processing cost can be greatly decreased [2,4]. Photopolymerizations induced by UV and Visible lasers have received considerable attention in recent years [2–8].

Compared with conventional UV/Vis lasers, e.g. Argon-ion, He/Ne, and Krypto ion lasers, etc. laser diodes are cheap, compact and easy to operate. A QW1000 near infrared laser diode (Semiconductor Institute, Chinese Academy of Sciences) costs no more than 130 US dollars, and is approximately one cubic centimeter in size, while its performance, with an output power of 1 W at 796 nm, is satisfactory. Moreover, it has no rigorous requirements on the working environment (e.g. consuming inert gas, low temperature, etc.) for stable operation. These characters, especially its small volume, lend the laser diode to be a competitive candidate as the light source in applications such as CTPs technology and erasable compact discs in personal computers [4].

However, while photoinitiators sensitive to UV/Vis light are commercially available, studies on those sensitive to near infrared light, especially with wavelengths above 700 nm, can only be found in some patents [9–17]. Cyanine dye–borate complexes (CBCs) have been regarded as promising photoinitiators in the visible region since Chatterjee's

---

* Corresponding author. Address: Department of Materials Science and Engineering, The Pennsylvania State University, 312, Steidle Building, State College, PA 16802-5005, USA. Tel.: +1-814-862-8783; fax: +1-814-865-2917.

E-mail address: sqz100@psu.edu (S. Zhang).

0032-3861/01/$ - see front matter © 2001 Elsevier Science Ltd. All rights reserved.
PII: S0032-3861(01)00233-6

first report in 1988 [18]. Its sensitizing wavelength can be finely tuned by changing the number of conjugated double bonds in the cyanine dye. Two double bonds in the cyanine bridge chain gave a maximum absorbance wavelength ($\lambda_{\max}$) of about 550 nm [18–20], and it shifted to ca. 660 nm after one more double bond was introduced [21,22]. We have synthesized a cyanine dye–borate complex, 1,3,3,1′,3′,3′-hexamethyl-11-chloro-10,12-propylene-tricarbocyanine triphenylbutyl borate, which has four conjugated double bonds in the cyanine bridge chain and its $\lambda_{\max}$ red-shifted to 780 nm (in butanone) [23]. This CBC is able to discharge *n*-butyl radicals under the irradiation of near infrared light [24]. Most of the previous papers [18,19,21,22] were focused on the photodecomposition and intra-ion-pair electron transfer mechanisms of those CBCs and their photopolymerization behaviors have not got enough attention [20]. In this paper, the near infrared laser induced photopolymerization kinetics is investigated with CBC as the photoinitiator.

The characterization method employed in this study is real-time FTIR (RTFTIR), which can follow the photopolymerization process at the molecular level and easily detect the amount of residual monomer without any damage to the sample. The influence of laser irradiation conditions, such as the light intensity, irradiation time, sample thickness, photoinitiator content and post-polymerization, on the polymerization kinetics can be conveniently investigated by this method [7,25–33]. To our knowledge, this is the first report on systematic studies of the near infrared laser induced photopolymerization.

2. Experimental

2.1. Materials

CBC was synthesized by our known procedure [23] and was used as the photoinitiator. Multifunctional acrylate monomers employed here were trimethylolpropanetriacrylate (TMPTA, Eternal Chemical Co., LTD, Taiwan), phthalic diglycol diacrylate (PDDA, Dongfang Chemical Co., LTD, China), and a polyester (tetra)acrylate (CN920, Sartomer). All monomers were used as received. A copolymer of acrylic acid, methyl methylacrylate, styrene and butyl acrylate (AA/MMA/St/BA, 20/45/10/25, feed ratio in weight) was synthesized in our laboratory and used as the binder, which is an important component in CTPs to improve the mechanical properties of the resulting film.

2.2. Sample preparation

To prepare a typical TMPTA/CBC/binder sample, 0.1 g TMPTA and 0.1 g binder were dissolved in 0.3 g butanone and then different amount of CBC was added. The content of CBC is defined as the weight ratio of CBC to the monomer. For neat monomer/CBC systems, CBC was introduced into the 20% monomer/butanone solution in 5.0 wt% content and no binder was used. The solution was dropped on a NaCl plate, without removal of the solvent, and was covered with another NaCl plate with controlled thickness of 20–60 μm.

2.3. Instruments

The sample was placed in the sample compartment of a NICOLET 560 FTIR spectrometer and was irradiated by a QW1000 near infrared laser diode (emitting wavelength: 796 nm; Institute of Semiconductors, Chinese Academy of Sciences) through an optical fiber. FTIR spectra were collected simultaneously and continuously with the scan speed of one spectrum per second. Light intensity of the near infrared laser diode was measured by a LPE-1 energometor (Institute of Physics, Chinese Academy of Sciences). Electron extinction absorption spectra of the sample were collected with a Perkin–Elmer Lambda Bio 40UV/Vis spectrometer. Electron spin resonance (ESR) experiments were performed on a Bruker ER 200D-SRC spectrometer with 2-methyl-2-nitroso-propane (MNP) as the radical capturing agent. CBC and MNP were dissolved in toluene and the solution was purged with nitrogen for 10 min to get rid of the oxygen. It was then irradiated under the near infrared laser for 5 min. ESR spectra were collected immediately after the irradiation.

2.4. Determination of photopolymerization parameters

The degree of cure was characterized by double bond conversion, γ, of the monomer, which could be determined from the peak area drop of the unsaturation absorption bands (1620 and 1635 cm^{-1}, C=C stretching) in FTIR spectra of different irradiation time. Photopolymerization rate, R_p, was calculated according to the following equation [26]

$$R_p(\mathrm{mol\,l^{-1}\,s^{-1}}) = [M]_0(\mathrm{mol\,l^{-1}})\frac{A_{t1}-A_{t2}}{A_0}\,\frac{1}{t_2(\mathrm{s})-t_1(\mathrm{s})}, \tag{1}$$

where $[M]_0$ is the initial concentration of the double bond, A_{t1} and A_{t2} FTIR peak areas of the double bond at irradiation time t_1 and t_2, respectively, and A_0 the corresponding initial peak area before irradiation. R_p was only determined at the initial photopolymerization stage, where a nearly linear increase of conversion was observed.

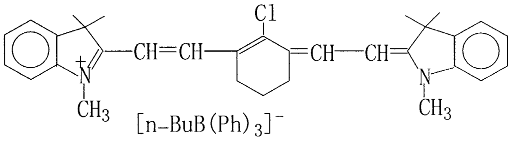
The quantum yield of photopolymerization Φ_p is defined as the number of polymerized double bonds per absorbed photon [33] and was determined from Eq. (2)

$$\Phi_p(\mathrm{mol\ einstein^{-1}}) = \frac{R_p(\mathrm{mol\,l^{-1}\,s^{-1}})e(\mu\mathrm{m})}{10^7 f\, I_0(\mathrm{einstein\,s^{-1}\,cm^{-2}})}, \tag{2}$$

where e is the sample thickness, f the absorption efficiency to the near infrared laser beam (f is approximately 100% for the employed CBC system due to its high molar extinction efficiency ϵ), and I_0 the incident light intensity.

3. Results and discussions

CBC is a complex of cationic cyanine dye and anionic triphenylbutyl borate with the following structure:



Its maximum extinction efficiency $\epsilon_{\max}$ is $2.66 \times 10^5\ \mathrm{l\ mol^{-1}\ cm^{-1}}$ at 780 nm with a half peak width of 51 nm (in butanone). ϵ still remains at a relatively high value, $1.7 \times 10^5\ \mathrm{l\ mol^{-1}\ cm^{-1}}$, at 796 nm, the emitting wavelength of the adopted near infrared laser diode.

3.1. Intra-ion-pair electron transfer

As has been already mentioned, Chatterjee et al. [18] studied the photodecomposition mechanism of several similar CBCs in the visible region. Under irradiation of visible light, the cationic cyanine dye absorbs a photon and is excited; an electron is then transferred from the borate to the cyanine, which results in an unstable borate radical. The *n*-butyl radical released from the borate radical is capable of initiating radical polymerization of acrylate monomers. The mechanism is illustrated in Fig. 1.

The most important difference between our CBC and those reported by Chatterjee et al. [18] is that the former has more conjugated double bonds and is therefore sensitive to longer wavelengths of light. It is thus logical to assume that CBC will also undergo the same intra-ion-pair electron transfer process. Several resonance peaks were found in the ESR spectrum after CBC was irradiated by the 796 nm near infrared laser (Fig. 2), which indicates that *n*-butyl radicals had been released.

Furthermore, it was found that after irradiation, the CBC/TMPTA could not be dissolved in butanone, an excellent solvent of CBC, TMPTA and the binder. This means that a polymer network had been formed and that CBC is indeed capable of initiating the photopolymerization of acrylate monomers upon the irradiation by a near infrared laser.

3.2. Photopolymerization of TMPTA/CBC/binder system

Photopolymerization of the TMPTA/CBC/binder system was investigated in detail because it is close to the real CTPs compositions.

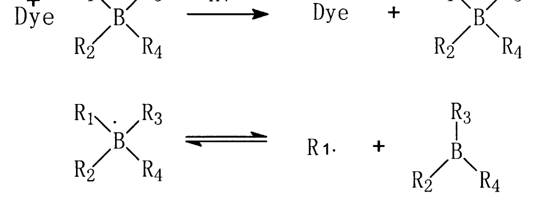


Fig. 1. Schematic illustration of the photoinitiating mechanism of cyanine dye–borate complex.

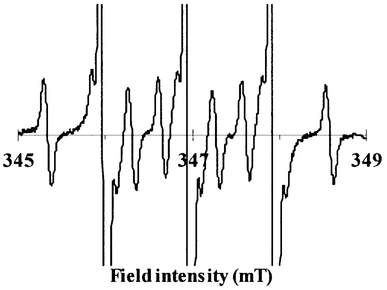


Fig. 2. ESR spectrum of CBC after irradiated by a near infrared laser.

3.2.1. Effects of the CBC content

The photoinitiator content plays a key role in the photopolymerization. In the conventional UV/Vis photopolymerization, R_p increases when more initiator is used, but it decreases rapidly if too much is added, which is attributed to the 'filter effect' [33]. This effect becomes more significant for photoinitiators with high molar extinction efficiency. CBC can have a ϵ as large as $1.78 \times 10^5\ \mathrm{l\ mol^{-1}\ cm^{-1}}$ at 796 nm, which is very large compared with that of normal UV photoinitiators, therefore the near infrared laser induced photopolymerization follows a similar trend. For TMPTA/CBC/binder system, the highest R_p and highest final γ were achieved at a CBC content of 2.0 wt% for a 20 μm thick film (Fig. 3). The reduction of photopolymerization rate can be easily understood if we consider the decrease in penetration depth of the laser beam as a result of the exceedingly high CBC content.

The photodecomposition of CBC is a relatively slow process (Fig. 4), i.e. less than a 30% drop in absorbance was observed after 120 s of irradiation ($17.0\ \mathrm{mW\ cm^{-2}}$, 10.0 wt% CBC content). Thus, the filter effect will prevail for a relatively long period. It was also found that the photodecomposition rate for samples with lower CBC content was higher than that with higher CBC content. This observation

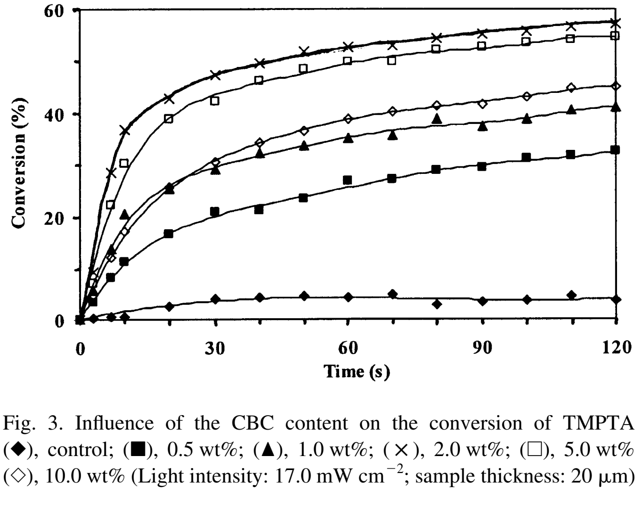


Fig. 3. Influence of the CBC content on the conversion of TMPTA: (◆), control; (■), 0.5 wt%; (▲), 1.0 wt%; (×), 2.0 wt%; (□), 5.0 wt%; (◇), 10.0 wt% (Light intensity: $17.0\ \mathrm{mW\ cm^{-2}}$; sample thickness: 20 μm).

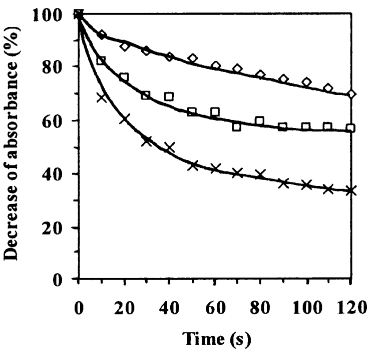


Fig. 4. Decrease in absorbance of CBC under the near infrared laser irradiation: (×), 2.0 wt%; (□), 5.0 wt%; (◇), 10.0 wt% (Irradiation intensity: 17.0 mW cm^{-2}; sample thickness: 20 μm).

gave further proof to the existence of filter effect. Moreover, the residual absorbance was relatively high and approached a constant value after a long time, which indicates that the photodecomposition products of CBC might still have absorbance at 796 nm, i.e. it is not photobleachable. Then the products will continuously prevent the laser beam from penetrating into the deeper layer of the sample and further photopolymerization is thus retarded. This soundly explains why the conversions approached different values for different CBC contents even after long periods of irradiation time.

3.2.2. *Effects of the light intensity*

In general, higher light intensity results in higher free radical concentration, and consequently faster curing (Fig. 5). As expected, the double bond conversion of TMPTA increased from 16% at laser power of 0.5 mW cm^{-2} to 37% at 17.0 mW cm^{-2} after 10 s irradiation. However, this influence is not as pronounced as that of the CBC content. At the end of 120 s exposure, only a 10% gap in the double bond conversion was observed when the light intensity increased from 0.5 to 17.0 mW cm^{-2}. It is well known in conventional photopolymerization systems, whether induced by UV or Vis light, that crosslinking remarkably influences the reaction process. Slight crosslinking, or a rapid increase of the viscosity resulting from the initial polymerization, will first limit the mobility of propagating polymer radicals, and bimolecule termination is consequently inhibited. This leads to the so-called ‘auto-acceleration’ (discussed later). A further increase in crosslinking density will restrict the diffusion ability of monomers and primary radicals, and the photopolymerization approaches a diffusion control stage, i.e. R_p decreases rapidly and light intensity will have no significant influence in the curing profile. Just like other monomers used in conventional UV/Vis photopolymerization(or more strictly, photocuring), TMPTA is a multifunctional acrylate monomer with three double bonds per molecule, so it is very easy to crosslink. Moreover, for CBC with a relatively slow intra-ion-pair electron transfer rate, the discharge of primary radicals is a competitive process. The *n*-butyl radical has a chance to recombine with the dye radical to produce an inactive molecule before it can escape the CBC cage to initiate possible polymerizations. In the diffusion control stage, high crosslinking makes the cage escape process more difficult so that R_p is further decreased. Although the enhancement of irradiation can surely increase the photodecomposition rate of CBC, it cannot necessarily increase the *n*-butyl radical concentration proportionally. Thus, higher laser power cannot promote the photopolymerization at an expected magnitude during the diffusion control stage. However, operating at a higher laser power is still of interest for increasing the initial photopolymerization rate so as to shorten the irradiation time [1].

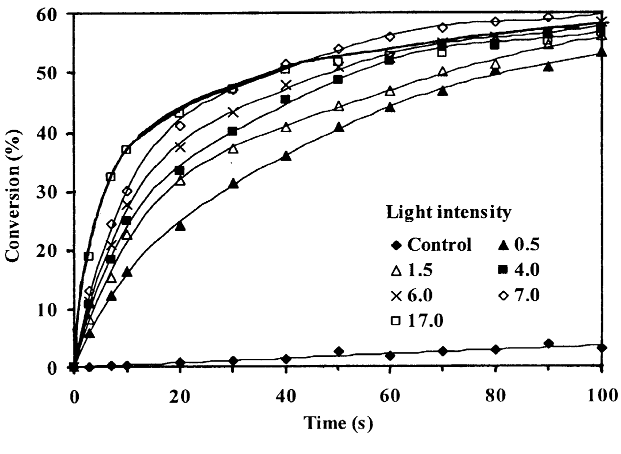


Fig. 5. Influence of the light intensity on the conversion of TMPTA (CBC content: 2.0 wt%; sample thickness: 20 μm).

3.2.3. *Effects of the sample thickness*

Fig. 6 depicts the dependence of the double bond conversion on the sample thickness. Based on the Beer–Lambert Law, for sample with 2.0 wt% CBC content (CBC/TMPTA = 2.0 wt%, the concentration of CBC in the butanone solution is approximately 0.005 mol l^{-1}) and 20 μm thick, the absorbance at 796 nm is 1.82 in theory and was found to be 1.98 in experiments (Fig. 7), i.e. 99% of the incident light will be absorbed by the sample. This means,

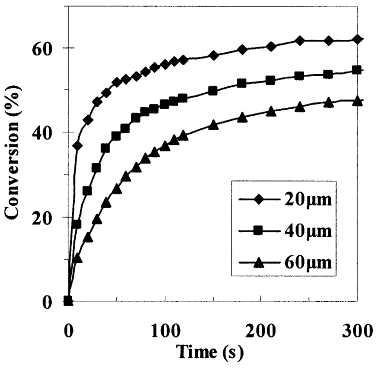


Fig. 6. Influence of the sample thickness on the conversion of TMPTA (Light intensity: 17.0 mW cm^{-2}; CBC content: 2.0 wt%).

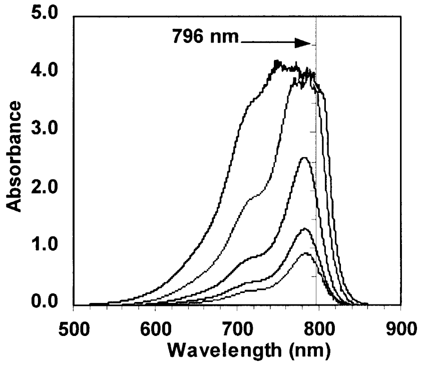


Fig. 7. Absorption spectra of TMPTA/CBC/binder with different sample thickness and CBC content, from top to bottom: 5.0 wt%, 20 μm; 2.0 wt%, 40 μm; 2.0 wt%, 20 μm; 1.0 wt%, 20 μm; 0.5 wt%, 20 μm.

for a thick sample, the top 20 μm layer will absorb most of the incident light and has a chance to be polymerized, whereas the bottom layer has few chances to absorb photons and to be polymerized. For this reason, the double bond conversion obtained from RTFTIR is 'apparent conversion' of both the polymerized top layer and the unpolymerized bottom layer. It is expected that the real conversion should be much higher in the top layer than in the bottom layer. For TMPTA with a CBC content of 2.0 wt%, the double bond conversion decreased dramatically when the sample thickness increased from 20 to 60 μm (Fig. 6). Fig. 7 shows the absorption spectra for samples with different CBC contents and thickness. The absorbance increases proportionally with the increase of CBC content or sample thickness. The significance of filter effect can be readily understood and predicted from the strong absorbance for the sample with high CBC content and thickness (Fig. 7).

3.2.4. *Quantum yield of photopolymerization (Φ_p)*

The quantum yield reflects the total photopolymerization efficiency of the system, including the ability of the photoinitiator to discharge radicals and the ability of the monomer to carry out polymerization. Values of the photopolymerization quantum yield of TMPTA at 10% double bond conversion are given in Table 1.

For the polymerization that follows the bimolecular termination mechanism, e.g. coupling or disproportionation, Φ_p decreases if the light intensity I_0 increases [29]

$$\Phi_p \propto I_0^{-0.5} \tag{3}$$

For those following the unimolecular termination mechanism, e.g. the propagating polymer radical is trapped by the crosslinked network, or is transferred to impurities, the light intensity I_0 will theoretically have no influence on Φ_p [33]

Table 1
Photopolymerization quantum yield of TMPTA/Binder/CBC system (CBC content: 2.0 wt%; *e*: 20 μm; $[M]_0$: 2.0 mol l^{-1}; calculated at 10% double bond conversion)

Laser power (mW cm^{-2})	0.5	1.5	4.0	6.0	7.0	17.0
I_0 (10^{-8} einstein s^{-1} cm^2)	0.33	1.00	2.67	4.00	4.67	11.30
R_p (10^{-2} mol l^{-1} s^{-1})	3.6	5.0	7.4	7.6	9.1	13.5
Φ_p (mol einstein^{-1})	21.2	10.0	5.6	3.8	3.9	2.4

$$\Phi_p \propto I_0^0 \tag{4}$$

Table 1 shows that Φ_p decreases rapidly, from 21.2 to 2.4 mol einstein^{-1}, when I_0 increases from 0.5 to 17.0 mW cm^{-2}. This indicates that the near infrared laser induced photopolymerization prefers bimolecular termination to unimolecular termination.

However, further study found that the termination was not a strict bimolecular process. Plot of log R_p with log I_0 (Fig. 8) shows a slope of 0.37, not 0.5 (an essential character for bimolecular termination mechanism [34]). A possible explanation lies in the decrease of the primary radical discharging efficiency, f_d, of CBC with the increase of light intensity, and this argument is stated as follows.

For the photopolymerization in which one primary radical is produced for each absorbed photon and the bimolecular termination mechanism is followed, the initiation rate R_i and termination rate R_t are determined by Eqs. (5) and (6), respectively [35]

$$R_i = f_d k_d I_0 \tag{5}$$

$$R_t = 2k_t[M^*]^2 \tag{6}$$

where k_d and k_t are the initiation and termination constants, respectively, and $[M^*]$ the radical concentration.

With the steady-state assumption

$$[M^*] = \left[\frac{f_d k_d I_0}{2k_t}\right]^{0.5} \tag{7}$$

thus

$$R_p = k_p[M]_0[M^*] = K[f_d I_0]^{0.5} \tag{8}$$

where k_p is the propagation constant and K equals $[M]_0 k_p (k_d/2k_t)^{0.5}$.

If f_d is a constant, as in most radical UV/Vis photopolymerization processes, R_p will be approximately proportional to the square root of I_0. On the other hand, if f_d decreases

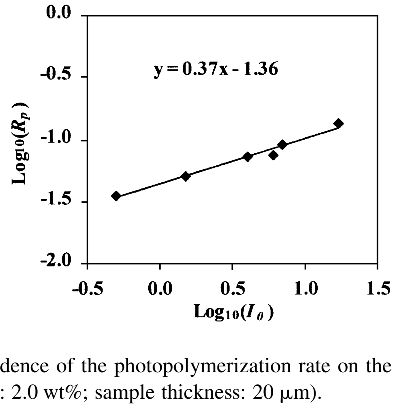


Fig. 8. Dependence of the photopolymerization rate on the light intensity (CBC content: 2.0 wt%; sample thickness: 20 μm).

with the increase of the light intensity, the slope of log R_p–log I_0 plot will be apparently smaller than 0.5. For the photopolymerization initiated by CBC, as discussed earlier, discharging of *n*-butyl radical involves a multi-step, intra-ion-pair electron transfer process. The primary radical has a chance to recombine with the cyanine radical, or to be quenched by other residual impurities in the sample during the slow CBC photodecomposition process. The possibility will become larger if I_0 increases, due to the consequently higher CBC decomposing rate and higher cyanine radical concentration. Furthermore, the ease of crosslinking for TMPTA, as aforementioned, makes this situation more serious. This leads to the decrease of f_d at higher I_0; and this is also part of the reason why the light intensity does not give the expected influence on the near infrared laser induced photopolymerization.

As explained before, with the proceeding of irradiation, a crosslinked network is formed and R_p decreases rapidly due to the diffusion control. So it can be easily understood that Φ_p will decrease significantly with the prolonged irradiation time.

3.3. Photopolymerization of neat monomers

Neat monomers also have similar photopolymerization kinetics to that of TMPTA/CBC/binder systems. The light intensity dependence of γ and R_p for neat TMPTA, PDDA and CN920 is shown in Figs. 9–11, respectively. Increase of

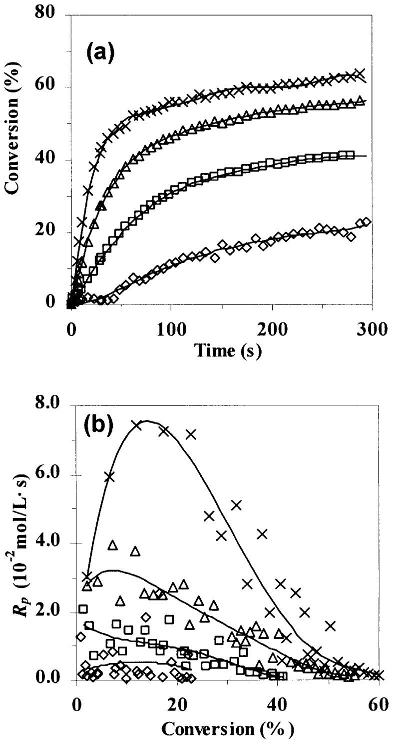


Fig. 10. Influence of the light intensity on the (a) conversion and (b) photopolymerization rate R_p of neat PDDA: (×), 0.5; (△), 6.0; (□), 11.0; (◇), 17.0 mW cm^{-2} (CBC content: 5.0 wt%; sample thickness: 20 μm).

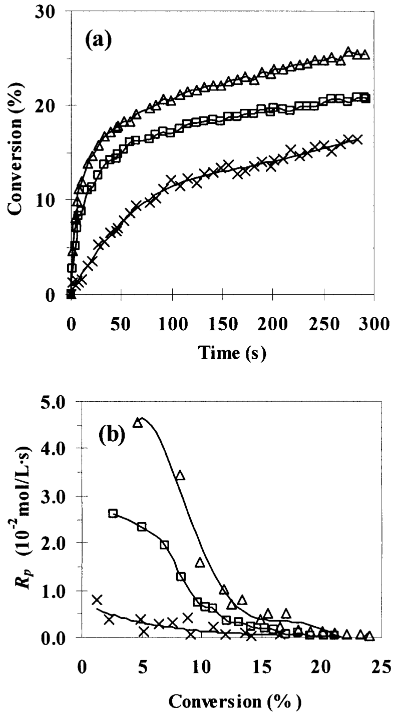


Fig. 9. Influence of the light intensity on the (a) conversion and (b) photopolymerization rate R_p of neat TMPTA: (×), 0.5; (□), 17.0; (△), 21.7 mW cm^{-2} (CBC content: 5.0 wt%; sample thickness: 20 μm).

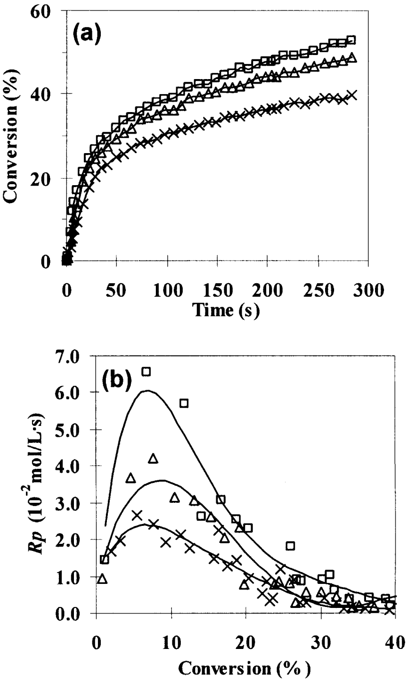


Fig. 11. Influence of the light intensity on the (a) conversion and (b) photopolymerization rate R_p of neat CN920: (×), 6.0; (△), 11.0; (□), 21.7 mW cm^{-2} (CBC content: 5.0 wt%; sample thickness: 20 μm).

γ and R_p with I_0 was clearly observed for all the three monomers.

PDDA has a relatively lower acrylate functionality, i.e. only two double bonds per molecule. Thus, a weaker crosslinking tendency at certain double bond conversions can be expected. It was found that PDDA actually gave a higher conversion compared with TMPTA at the same laser irradiation conditions. On the other hand, although CN920 has a higher functionality, four double bonds per monomer, it still gave a relatively high conversion because, as an oligomer, it has longer flexible chain spacers between the double bonds. Consequently, higher chain length between crosslinking points, or lower crosslinking density, can be expected for CN920 at the same conversion as TMPTA.

Comparison of the photopolymerization profiles of TMPTA/CBC/binder system and the corresponding TMPTA/CBC system gave an unexpected finding. The introduction of a solid binder to TMPTA led to a higher double bond conversion. For a 20 μm thick sample with 5.0 wt% CBC content and under 17.0 mW cm^{-2} light intensity, TMPTA/CBC/binder system reaches a conversion of more than 50% after 120 s, whereas less than 20% is achieved for that without a binder. We think the binder influences the polymerization process in two different ways. During the initial stage, i.e. double bond conversions of less than 10%, the inclusion of binder raises the sample viscosity considerably; therefore the autoacceleration effect occurs at a lower conversion and in a more remarkable situation. Higher initial R_p thus can be expected for the TMPTA/CBC/binder system [35]. During the second stage, i.e. γ higher than 20%, the binder can act as an effective special solid spacer to decrease the intramolecular reaction possibility, i.e. to sterically hinder the reaction between the polymer radical and the double bonds suspended to its own chain, and to promote its reaction with the double bonds in the free monomers. The crosslinking process is thus delayed and the crosslinking density will be lower in the TMPTA/CBC/binder system compared with that without a binder and at the same double bond conversion. This is beneficial to further polymerization because a higher final conversion can be readily achieved in the former system. It is worth noting that solvent cannot delay the crosslinking due to its liquid state.

As mentioned before, the auto-acceleration effect was found in all three neat monomers, which could be explained by the decrease of termination rate when the system is crosslinked, the same as that for conventional radical polymerization.

4. Conclusions

Near infrared laser induced photopolymerization of different acrylate monomers was investigated systematically by RTFTIR. We have shown that the CBC is able to initiate radical photoinitiator for acrylate monomers under the irradiation of a 796 nm laser diode. High light intensity, thin sample film and optimum CBC content are favorable conditions to achieve high final double bond conversion and photopolymerization rate. Unlike conventional UV/Vis photopolymerization, the light intensity has only a slight influence on that induced by the near infrared laser. Introduction of a solid binder is helpful to promote the polymerization process of TMPTA. However, further research, including the design of more effective photoinitiator, search for new monomers and optimization of irradiation parameters, is still necessary for the near infrared laser induced photopolymerization to compete with that induced by conventional UV light in the market.

Acknowledgements

The authors are indebted to Taiwan Eternal Chemical CO., LTD for their generous support of part of this project. Help on RTFTIR instrument preparation from Kunhua Wang (Tsinghua University) and on English writing from James Garrett (Pennsylvania State University) is also gratefully acknowledged.

References

[1] Dufour P. In: Fouassier JP, Rabek JF, editors. Radiation curing in polymer science and technology, vol. 1. London: Elsevier Applied Science, 1993 (chap. 1).
[2] Decker C, Elzaouk B. J Appl Polym Sci 1997;65:833.
[3] Decker C. J Polym Sci, Polym Chem Ed 1983;21:2451.
[4] Urano T, Nagasaka H, Shimizu M, Yamaoka T. J Imaging Sci Technol 1997;41(4):407.
[5] Decker C. Polym Photochem 1983;3(2):131.
[6] Chung CM, Kim JG, Choi JH. J Appl Polym Sci 2000;77:1802.
[7] Decker C, Moussa K. Makro Chem 1990;191:963.
[8] Decker C, Fouassier JP. In: Fouassier JP, Rabek JF, editors. Lasers in polymer science and technology, vol. 3. Boca Raton: CRC Press, 1989 (chap. 1).
[9] Yamamoto T, Otani K, Yoshida H, Shinohara N, Sugita, S., Kamata, H. JP 90 77 836.
[10] Liang RC, Davis P, Shanklin MS, Tsai YG. Eur Pat 0,408,227 A1.
[11] Gottschalk P, Neckers DC, Schuster GB. Eur Pat 0,23,587 A1.
[12] Kawabata M. Eur Pat 0,276,016.
[13] Haley NF, Corbiere SL. US Pat 5,466,557.
[14] Bonham JA, Rossman MA, Grant RJ. Eur Pat 0,359,430 A2.
[15] Iwai T, Okui T, Komano H. JP 09,244,236.
[16] Okamoto Y, Kondo S, Ukai T. US Pat 5,385,807.
[17] Kuroki T, Maehashi T, Matsumoto S, Fukumuro I. JP 9 197 668.
[18] Chatterjee S, Gottschalk P, Davis PD, Schuster GB. J Am Chem Soc 1988;110:2326.
[19] Chatterjee S, Davis PD, Gottschalk P, Kurz ME, Sauerwein B, Yang XQ, Schuster GB. J Am Chem Soc 1990;112:6329.
[20] Kabatc J, Jedrzejewska B, Paczkowski J. J Polym Sci, Part A: Polym Chem 2000;38:2365.
[21] Armitage B, Obrien DF. J Am Chem Soc 1992;114:7396.
[22] Armitage B, Retterer J, Obrien DF. J Am Chem Soc 1993;115:10,786.
[23] Li B, Zhang SH, Tang LM, Zhou, QX. Proceedings of '99 Polymerica Symposium of China (Shanghai), 1999. p. 103.
[24] Zhang SH, Li B, Tang LM, Zhou QX Acta Polym Sin 2001(1):114.
[25] Decker C, Moussa K. Makromol Chem 1988;189:2381.
[26] Decker C, Moussa K. Macromolecules 1989;22:4455.

[27] Allen NS, Hardy SJ, Jacobine AF, Glaser DM, Yang B, Wolf D. Eur Polym J 1990;26:1041.

[28] Udagawa A, Sakurai F, Takahashi T. J Appl Polym Sci 1991;42:1861.

[29] Decker C. J Polym Sci, Part A: Polym Chem 1992;30:913.

[30] Yang BD. J Polym Sci, Part A: Polym Chem 1993;31:199.

[31] Kaczmarek H, Decker C. J Appl Polym Sci 1994;54:2147.

[32] Chiou BS, Khan SA. Macromolecules 1997;30:7322.

[33] Decker C, Moussa K. J Appl Polym Sci 1987;34:1603.

[34] Selli E, Bellobono R. In: Fouassier JP, Rabek JF, editors. Radiation curing in polymer science and technology, vol. 3. Elsevier Applied Science: London, 1993 (chap. 1).

[35] Flory PJ. Principles of polymer chemistry. Ithaca, NY: Cornell University Press, 1967 (chap. IV).