

Photopolymerization of 1-Adamantyl Acrylate Photoinitiated by Free Radical Photoinitiators

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ABSTRACT: 1-Adamantyl acrylate was synthesized by reacting of 1-adamantanol with acryloyl chloride in the presence of tertiary amine. The structure of monomer was characterized by FTIR and ¹H NMR spectroscopy. The influence of photoinitiator and monomer types on the photopolymerization kinetics of this monomer was investigated by real-time infrared spectroscopy (RTIR). In the UV curing system, the introduction of 1-adamantyl acrylate could significantly reduce the polymerization shrinkage.

Thermogravimetric analysis of 1-adamantyl acrylate indicated that 1-adamantyl acrylate polymer has higher thermal stability than that of general commercial products. The results indicated that the synthesized monomer has good curing performance. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 123: 26–31, 2012

Key words: adamantyl group; photopolymerization; real-time infrared spectroscopy (RTIR); TGA

INTRODUCTION

The photopolymerization process has many advantages such as high production rates, ease of control, space saving, controlled pollution, and product quality.¹ Photoresists are one kind of photochemical applications, which are widely used for the manufacture of microelectronics, printing, printed circuit boards, optical materials, liquid crystalline display, and so on.^{2–7} With the development of integrated circuits, photoresists have evolved from the G-line (436 nm) lithography, I-line (365 nm) lithography, to deep ultraviolet 248-nm lithography, and the current course of development of lithography 193 nm.⁸ Matrix resin is one of the most important components among photoresist.

The 193-nm resists require more functionalities grafted on the polymer backbone to achieve some the lithographic specifications.⁹ In considering materials for use in 193-nm photoresist applications, the

choice of functionalized monomers is therefore critical, as it is the interactions of these groups that determine the physical and chemical properties of the polymers. By the careful design, the choice of monomers can achieve the desired properties.¹⁰

Conventional phenolic resins cannot be used as a base polymer for the ArF excimer laser resist due to their strong absorption at 193 nm.¹¹ It has been reported that poly (4-hydroxystyrene) polymers could not be used owing to their absorption to 193 nm, and acrylate type was a candidate polymer for 193-nm photoresist.¹² However, the etch rate of acrylate type polymer was fast and could not be used as a mask for the etch step in chip production.¹¹ Therefore, much research has been focused on solving these problems. Recently, acrylate polymers containing alicyclic hydrocarbons, such as adamantyl, have been proposed for their high transparency and good dry-etching resistance.¹³

Adamantane has a highly symmetric tetracyclic ring structure with four cyclohexanes in chair conformation. Acrylate bearing adamantyl group has some excellent application properties, such as radioprotective activity,¹⁴ photo-chemical and thermal stability,^{15–18} besides the four bridgehead sites of adamantyl group are chemically reactive, and various functional groups can be introduced into the structure of molecule.¹⁹ It has been studied that the rate of polymerization of (meth)acrylate bearing adamantyl group, thermal stability, and glass transition temperature of the corresponding polymer were increased.²⁰

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Yusuke et al. investigated that novel polysiloxane derivative containing adamantyl group in the main chain has high T_g as well as good thermostability.²¹ It has been reported that poly (adamantyl methacrylate-methylurethane)s were prepared by functionalisation of adamantyl methacrylate vinyl isocyanate precursor polymer. The polymers showed high and very stable NLO response even at elevated temperatures.¹⁷ The UV-vis transparency of adamantane attracts much attention for incorporating into photocure materials for short wavelength microlithography.²⁰

In this study, 1-adamantyl acrylate was synthesized via the reaction between 1-adamantanol and acryloyl chloride in the presence of tertiary amine. The structure of 1-adamantyl acrylate was characterized by FTIR and ¹H-NMR. The photopolymerization properties of 1-adamantyl acrylate in the presence of photoinitiator were investigated by real-time infrared spectroscopy (RTIR). In the paper, the thermal stability and volumetric shrinkage of 1-adamantyl acrylate were also studied.

EXPERIMENTAL

Materials

1-Adamantanol (Luzhou Wanlian Chemical CO. Ltd., Luzhou, Sichuan, China), tertiary amine (Yong Da Chemical Agent Development Center, Tianjin, China), acryloyl chloride (Sanshengtengda Science and Technology Co., Beijing, China), 1,6-hexanedioldiacrylate (HDDA), tetrahydrofurfurylacrylate (SR285), trimethylolpropane triacrylate (TMPTA), Tri(propylene glycol) diacrylate (TPGDA), 2-(2-Ethoxyethoxy) Ethylacrylate (EOEOEA) were obtained from Sartomer Company (Warrington, PA). 2-Hydroxy-2-methylphenyl-propane-1-one (1173) and benzophenone (BP) were obtained from Runtec Chemical Co. Ltd. (Changzhou, China). Ethyl-4-dimethylaminobenzoate (EDAB, Sinopharm Group Chemical Reagent Co.) was used as received.

Synthesis of 1-adamantyl acrylate

Totally, 10 g of 1-adamantanol and 10 g of tertiary amine, dissolved in 400 mL of benzene were added into a three-necked flask in an ice water bath. Under magnetic stirring, 9 g of acryloyl chloride dissolved in 50 mL of benzene were added dropwise over a 3 h time period. Then the mixture was allowed to stand overnight, and the precipitate was filtered off. The liquid phase was washed three times with 1 mol/L HCl solution and 1 mol/L NaHCO₃ solution and deionized water, respectively. Then, the liquid was dried with sodium sulfate and was evaporated under vacuum to remove the solvent. The final product was clear yellow liquid (yield 75%).

Real-time infrared spectroscopy

Real-time infrared spectroscopy (RTIR) was recorded on a Nicolet 5700 instrument (Thermo Electron Corp., Waltham, MA). The mixture of monomer, initiator was placed in a mold made from glass slides and spacers with 15 ± 1 mm in diameter and 1.2 ± 0.1 mm in thickness and irradiated with UV radiation by UV spot light source (EFOS Lite, 50-W miniature arc lamp, with 5-mm crystal optical fiber, Canada) at room temperature. The double bond conversion of the mixture was monitored by using near IR spectroscopy with the resolution of 4 cm^{-1} . The light irradiance on the surface of samples was 50 mW/cm^2 . The absorbance change of the =C—H peak area from 6100.7 to 6222.5 cm^{-1} was correlated to the extent of polymerization.²² The conversion of the functional groups could be calculated by measuring the peak area at each time of the reaction and determined as following:

$$\text{DC}(\%) = \frac{A_0 - A_t}{A_0} \times 100$$

where DC is the degree of double bond conversion at t time, A_0 is the initial peak area before irradiation, and A_t is the peak area of the double bonds at t time.

Instrumentation

¹H NMR spectra were recorded on a Bruker AV500 unity spectrometer by using CDCl₃ as the solvent with TMS as an internal reference.

FTIR were recorded on a Nicolet Avatar 370 instrument (Nicolet Instrument, Thermo Company, USA).

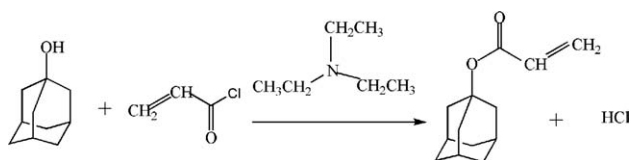
The light intensity was detected by UV Radiometer (Beijing Normal University, China).

Thermogravimetric analysis (TGA) was conducted in a pure N₂ atmosphere on a Netzsch TG 209C at a heating rate of $10^\circ\text{C}/\text{min}$.

RESULTS AND DISCUSSION

Ftir analysis

The synthesis route of 1-adamantyl acrylate was represented in Scheme 1. The structure of 1-adamantanol and 1-adamantyl acrylate was analyzed by FTIR spectra in Figure 1. The OH absorption at 3288 cm^{-1} of 1-adamantanol disappeared during reaction. The C—H absorption at 2910 and 2850 cm^{-1} of adamantyl group have no obvious change during the reaction.²³ Characteristic absorbance bands of 1-adamantyl acrylate were assumed as following: 1720 cm^{-1} characteristic absorbance bands was attributed to the stretching vibration of the ester carbonyl group,²⁴



Scheme 1 The synthesis route of 1-adamantyl acrylate.

the absorption band at 1634 and 801 cm^{-1} were assigned to the stretching vibration of the $\text{C}=\text{CH}_2$ ²⁵ and the out-of-plane bending vibration of $\text{C}-\text{H}$. The information observed from FTIR spectra indicated that 1-adamantanol reacted with acryloyl chloride generated 1-adamantyl acrylate.

¹H NMR analysis

The ¹H NMR spectra of 1-adamantanol and 1-adamantyl acrylate in CDCl_3 were shown in Figure 2. The spectra data was agreement with the expected structures. The signals around δ 1.5–2.2 ppm were assigned to the backbone of adamantyl group.²⁶ The hydroxyl group signal of 1-adamantanol, which was shown at δ 3.9 ppm, disappeared with the reaction in progressing, and the peaks in the region among 5.7, 6.2, and 6.4 ppm should be assigned to the acrylic groups of 1-adamantyl acrylate. The results indicated the successfully synthesis of 1-adamantyl acrylate.

The photopolymerization of 1-adamantyl acrylate

The 1-adamantyl acrylate solution containing 1wt % 1173 was exposed to UV light. A transition from a liquid precursor to a solid substance was observed visually. Results were presented the Figure 3. It could be seen from Figure 3(a) that the mixture of

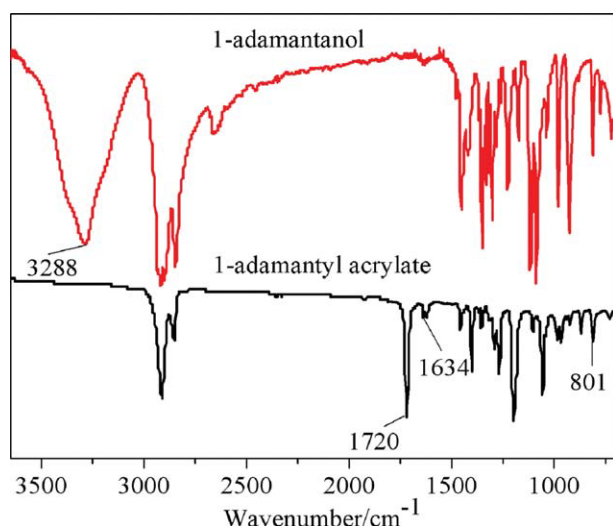


Figure 1 FTIR of 1-adamantanol and 1-adamantyl acrylate. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](#).]

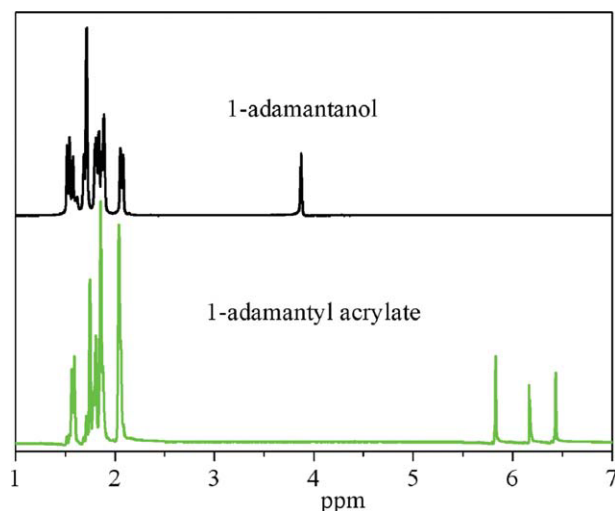


Figure 2 ¹H NMR spectra of 1-adamantanol and 1-adamantyl acrylate in CDCl_3 . [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](#).]

monomer and initiator was flowing without irradiation by UV light. The sample after exposure by UV light for 5 min became to be a solid [Fig. 3(b)]. Depending on the mechanism of decomposition of the photoinitiator upon irradiation and the structure of the monomer, photopolymerization proceeds by a radical mechanism.²⁷ (1) Chain initiation: Under UV light irradiation, photoinitiator 1173 generates high reactivity of free radical. Addition reaction occurs to produce monomer radicals between the monomer and the free radical of photoinitiator 1173. (2) Chain propagation: the monomer radical with high activity, reacts with the monomer to produce polymer.²⁸ Benzoyl radical of photoinitiator 1173 which did not involve in the reaction generated benzaldehyde by hydrogen reaction and 2-hydroxy-1, 2-diphenyl-ethanone. Part of hydroxyl isopropyl radical which did

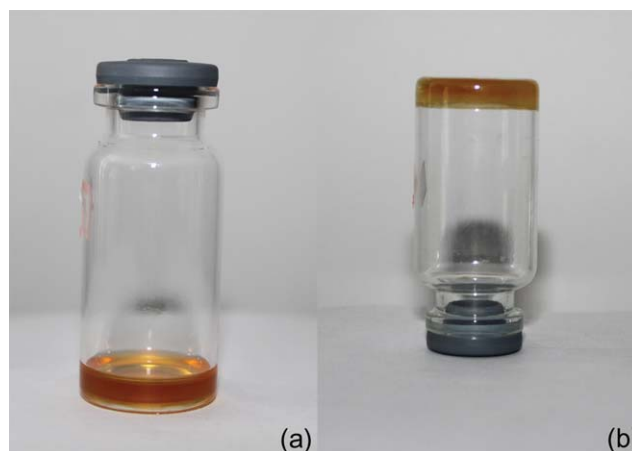


Figure 3 The photopolymerization of 1-adamantyl acrylate: (a) before photopolymerization; (b) after photopolymerization. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](#).]

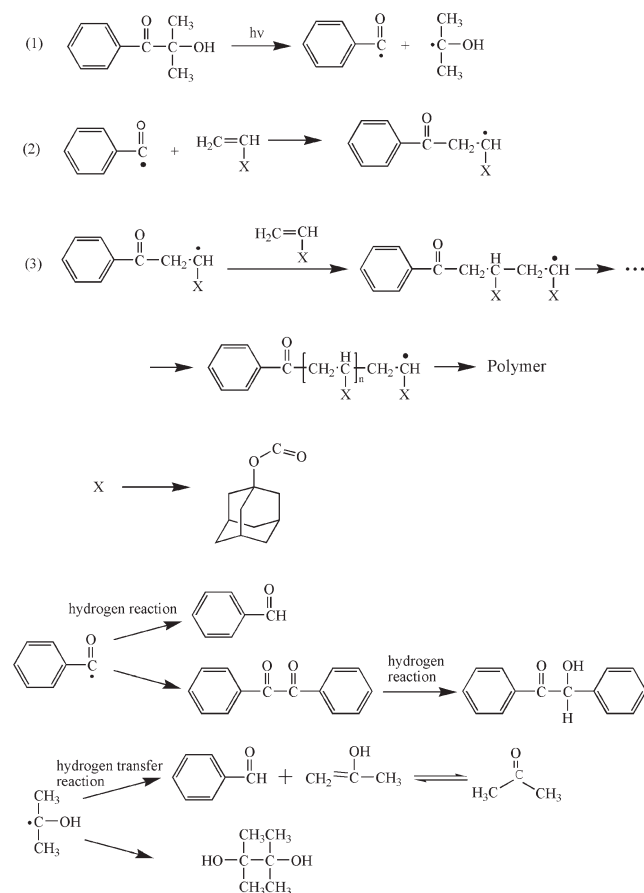


Figure 4 The photopolymerization process.

not participate in the reaction occurred to the coupling reaction. Besides, there were some of hydroxyl isopropyl radical to happening hydrogen transfer reaction generate to benzaldehyde and isopropyl enol. The photopolymerization process was shown in Figure 4. It was found that the monomer in the

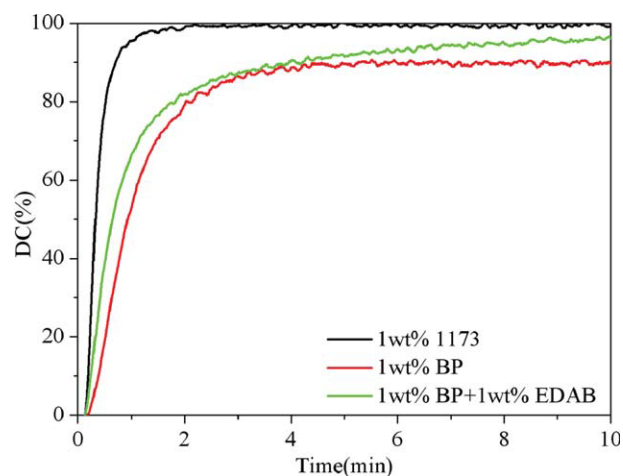


Figure 5 The double bond conversion versus irradiation time of 1-adamantyl acrylate initiated by different photoinitiator systems. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

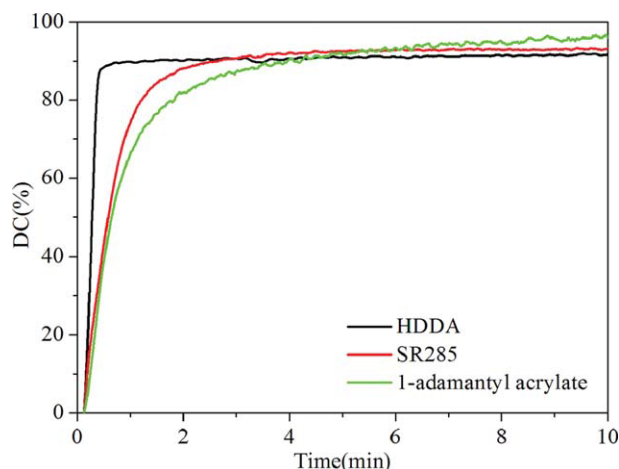


Figure 6 The double bond conversion versus irradiation time for different monomers ([BP] = [EDAB] = 1 wt %). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

presence of photoinitiator could polymerize and rapidly transform from liquid to solid. The result indicated that 1-adamantyl acrylate could be polymerized very fast.

Kinetics study of the polymerization of 1-adamantyl acrylate

The selection of a photoinitiator is of prime importance in the design of UV-curing systems, since the photoinitiator rate depends on the photoinitiator.²⁹ To further elucidate the effect of type of initiator on the photopolymerization of 1-adamantyl acrylate, the kinetics of the photopolymerization of 1-adamantyl acrylate initiated by different initiators was investigated and the results were shown in Figure 5. In this research work, 1173 and BP were used as photoinitiator, EDAB was the coinitiator for BP. Almost completed depletion of the double bond of the photopolymerization initiated by 1173 was observed. The double bond conversion was higher and induction period was lower when photopolymerization was initiated by BP in presence of coinitiator EDAB than when photopolymerization was initiated by BP alone. The result indicated that 1173 was more efficient than BP with amine.

The photopolymerization kinetics of three monomers initiated by BP using EDAB as coinitiator was studied and the results were given in Figure 6. Three monomers of 1-adamantyl acrylate, HDDA and SR285, were chosen for comparison, because they possessed similar molecular weight. It was seen that for the given conditions, the double bond conversion of 1-adamantyl acrylate (97%) was the highest among the tested monomers. As the functionality of monomer increased, the polymerization rate increased. At the beginning of polymerization, the

polymerization rate of HDDA was higher than that of 1-adamantyl acrylate, because HDDA was a diacrylate. However, the final conversion of 1-adamantyl acrylate was higher than that of HDDA. It was the reason that as the functionality of monomer increased, the viscosity of the resin increased, with the resulting gel-effect and the higher crosslink density, set a limit to the extent of the double bond conversion. The kinetics result was similar of 1-adamantyl acrylate and SR285, due to the principle that they were monofunctional monomers.

Volumetric shrinkage

Although a high curing speed is highly desirable, it is a concern that a high curing speed could increase the degree of polymerization shrinkage with increasing of the functionality of monomer.³⁰ By incorporation of bulky substituents such as adamantyl group in the chain, it is possible to increase rigidity and intermolecular forces, resulting in decreasing the polymerization shrinkage.³¹ The polymerization shrinkage data of the commercial monomers and the mixed systems were shown in Table I. The polymerization shrinkage of TMPTA (16.8%) was significantly higher than the other monomers. However, the shrinkage obviously decreased due to incorporation of adamantyl group in copolymer. Besides, the polymerization shrinkage of the copolymer of TMPTA and 1-adamantyl acrylate decreased from 16.8% to 6.4%, with the increase of 1-adamantyl acrylate from 0 to 70%. The shrinkage of neat 1-adamantyl acrylate (5.6%) was obviously lower than the other monomers. It was attributed that the adamantyl group had a highly symmetrical and rigid tricyclic hydrocarbon consisting of used chair-form cyclohexane rings.

Thermogravimetric analyses

Thermogravimetric analyses (TGA) were carried out to evaluate the effect of the chemical modification

TABLE I
The Polymerization Shrinkage Data vs. the Content of 1-adamantyl acrylate

Monomer	Conc. of 1-adamantyl acrylate (%)	γ (%)
EOEOEA	0	8.3
EOEOEA	50	7.1
TPGDA	0	11.1
TPGDA	50	3.9
TMPTA	0	16.8
TMPTA	10	15.9
TMPTA	30	8.8
TMPTA	50	7.3
TMPTA	70	6.4
TMPTA	100	5.6

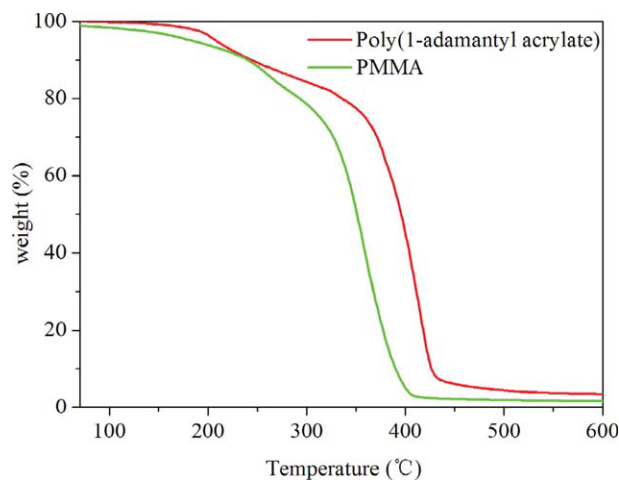


Figure 7 TGA thermograms of poly(1-adamantyl acrylate) and PMMA. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

on the thermal stability of poly (1-adamantyl acrylate). It started to decompose at about 237°C with a rapid drop beyond 365°C, and the decomposition process was almost completed at about 450°C. The degradation process undergone three steps: there was a weight loss observed in the curve before 300°C, which was due to the loss of the water; the degradation of polyacrylate initiated through depolymerization at about 325°C²⁸; an abrupt weight loss in the range 411–450°C indicated the decomposition of the backbone of the adamantyl group.³² Compared with poly (methyl methacrylate), poly (1-adamantyl acrylate) had higher decomposition temperature, thus better thermal stability.³³

CONCLUSIONS

1-Adamantyl acrylate was synthesized by acyl chlorination and confirmed by FTIR and ¹H NMR spectra. The photopolymerization kinetics results showed that 1-adamantyl acrylate could solidify in a short time and could reach 99% of double bond conversion in the presence of 1173 as photoinitiator. Compared with monomers HDDA and SR285, 1-adamantyl acrylate had the highest double bond conversion. The polymerization shrinkage obviously reduced, because of the introduction of 1-adamantyl acrylate, in the UV curing system. Compared with PMMA, poly (1-adamantyl acrylate) had higher thermal stability because of adding to adamantyl group.

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