Synthesis of Novel Macrophotoinitiator for the Photopolymerization of Acrylate

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ABSTRACT: A new kind of macrophotoinitiator (MPI) was synthesized through the copolymerization of acrylic monomers and the polymerizable photoinitiator monomer 2959-AA. Monomer 2959-AA was obtained by an esterification reaction between acrylic acid (AA) and the water-soluble photoinitiator Irgacure 2959 [2-hydroxy-4-(2-hydroxyethoxy)-2-methylpropiophenone]. By adjusting the monomer proportions in the MPIs, two series of MPIs with different 2959-AA contents and different glass transition temperatures were obtained. The molecular structure of 2959-AA was characterized by Fourier-transform infrared spectroscopy, nuclear magnetic spectrometry, and mass spectrometry. Polymerization of 1, 6-hexanediol diacrylate was initiated using Irgacure 2959 and 2959-AA, and two series of MPIs to be polymerized were studied with a photo-DSC test. Results showed that 2959-AA had higher chemical reactivity than Irgacure 2959 because of the higher solubility of the former. It was evident from the experiments that 2959-AA content in the MPI progressively increased the polymerization rate and monomer conversion when the glass transition temperatures of MPIs were similar. At the same 2959-AA content, the polymerization rate slightly slowed down with increased glass transition temperature. However, the radical lifetime and polymerization time were prolonged. © 2014 Wiley Periodicals, Inc. J. Appl. Polym. Sci. **2014**, *131*, 40352.

INTRODUCTION

Ultraviolet (UV)-visible (vis) photopolymerization is increasingly being used because of its advantages[1–5] of fast polymerization and flexible reaction equipment. Traditional small-molecule initiators are an important component of a polymerization reaction. However, these initiators have the disadvantages[6–9] of poor compatibility with UV-cured resin, slow migration toward the surface, generation of toxic free radicals, and yellowing of polymers. These disadvantages limit the use of UV-cured resins in various fields, including food and cosmetic industries. As a result, macrophotoinitiators (MPIs) are gradually receiving attention.[10–12] MPIs can overcome the disadvantages of small-molecule initiators, including poor resin compatibility, slow surface migration, and production of toxic end products.[6,13,14] The macromolecular chains of MPIs contain multiple active groups that can increase the concentration of free radicals and the utilization rate of light, which overcomes the disadvantage of oxygen inhibition during polymerization. One of the most frequently used methods of synthesizing macromolecular initiators is the introduction of double polymerizable groups to low-molecular-weight photoinitiators to synthesize a kind of polymeric initiator monomer, followed by copolymerization with different monomers depending on the desired properties.[15–18] Irgacure 2959 [2-hydroxy-4-(2-hydroxyethoxy)-2-methylpropiophenone], a commercially available CIBA photoinitiator, is a highly efficient radical photoinitiator for UV curing systems that is suitable for use in water-borne systems. Irgacure 2959 is also widely used in various fields because of its low toxicity, odor, volatility, and yellowing.[19] However, the solubility of Irgacure 2959 both in oil and water is not very ideal, thereby limiting the scope of its applications.

Esterification reaction between Irgacure 2959 and acrylic acid (AA) over methylsulphonic acid catalyst reportedly produces the polymeric photoinitiator monomer 2959-AA, which can generate free radicals under UV irradiation. The solubility of 2959-AA in the oil phase is also found to be markedly higher than that of Irgacure 2959. In the present study, the molecular structure of 2959-AA was characterized by infrared spectroscopy, nuclear magnetic resonance imaging, and mass spectrometry. Characterization results proved the successful synthesis of 2959-AA monomer. UV absorption spectrum results showed that the UV absorption peak position of 2959-AA was the same as that of Irgacure 2959. Upon UV irradiation, the infrared spectrum of 2959-AA monomer showed that it can generate free radicals

Table I. Synthesis Formulas of MPIs

Sample	2959-AA (g)	MMA (g)	BA (g)	AIBN (g)
P-1	2.00	14.68	8.32	0.75
P-2	1.00	15.67	8.33	0.75
P-3	3.00	13.69	8.81	0.75
P-4	2.00	4.53	18.47	0.75
P-5	2.00	10.06	12.94	0.75

and undergo polymerization. The polymerization behavior of 1,6-hexanediol diacrylate (HDDA) initiated by 2959-AA and Irgacure 2959 monomers were studied and compared using photo-DSC, and results showed that 2959-AA better induced polymerization. In addition, 2959-AA was found to be significantly more soluble in the oil phase than Irgacure 2959. Copolymerization of 2959-AA with MMA and BA produced MPIs. By adjusting the monomer proportions in the MPIs, two series of new MPIs with different content 2959-AA and glass transition temperature (T_g) were produced. In series I, the 2959-AA content of MPIs was gradually increased and T_g was similar. In another series of MPIs (series II), the content 2959-AA was same and T_g was gradually increased. The effects of active group contents and T_g's of the MPIs on polymerization behaviors with HDDA initiated by the two series of MPIs were studied using photo-DSC test. Results showed that in series I, at constant T_g, increased 2959-AA content of MPI increased the polymerization rate and the monomer conversion rate. In series II, at constant 2959-AA, increased T_g resulted in slower polymerization rate and lower monomer conversion.

EXPERIMENTAL

Materials

Irgacure 2959 was supplied by Jindun Chemicals Company Limited, Lanzhou, China. Methyl methacrylate (MMA), butyl acrylate (BA), and HDDA were purchased from Shanghai Chemical Reagents Company, Shanghai, China. Methylsulphonic acid, azodiisobutyronitrile (AIBN), 4-methoxyphenol (HQMME), sodium hydrogen carbonate, anhydrous sodium sulfate, ethyl acetate, and toluene were purchased from Tianjin Chemical Reagent Company, Tianjin, China. MMA and BA were vacuum distilled to remove trace inhibitors before use. Other reagents were used as received.

Synthesis of 2959-AA

A mixture of 22.43 g (0.1 mol) of Irgacure 2959, 7.92 g (0.11 mol) of AA, and 0.05 g (0.6 wt % with respect to AA) HQMME were mixed with 60 g of toluene in a 150 mL four-neck flask with a mechanical stirrer, thermometer, water segregator, and condenser pipe. The resulting mixture was stirred and heated to 65°C until Irgacure 2959 was completely dissolved. The mixture was instilled with 0.12 g (0.5 wt % with respect to reactants) methylsulphonic acid and heated and maintained at 95–100°C for 6 h. The water yield was 1.8 g. Toluene was removed by vacuum distillation. The crude product was diluted with 60 mL of CH_2Cl_2 and then washed with saturated aqueous $NaHCO_3$ (5 × 100 mL) and distilled water

(3 × 100 mL). The organic phase was dried with anhydrous Na_2SO_4 overnight, filtered, and distilled. The final product named 2959-AA was obtained as a yellowish liquid (90% yield). All steps were performed in the dark.

^{1}H NMR (400 MHz, CDCl$_3$): δ (ppm) 8.039–8.061 (—CH=CH—C—CO—), 6.916–6.945 (—O—C—CH=CH—), 6.395–6.442 (CH$_2$=CH—COO—), 6.095–6.165 (CH$_2$=CH—COO—), 5.827–5.857 (CH$_2$=CH—COO—), 4.495–4.519 (—COO—CH$_2$—CH$_2$—), 4.250–4.273 (—COO—CH$_2$—), 1.588 (CH$_3$—C—CH$_3$).

^{13}C NMR (400 MHz, CDCl3): δ (ppm) 202,165 (C=O), 162,132,127,114 (aromatic ring), 126,131 (C=C—), 65, 62 (—O—C—C—O—), 75 (—C—OH), 28 (—CH$_3$).

Fourier-transform infrared (FTIR; KCl plate, cm^{-1}): 3600-3100 (—OH), 1724 (C=O of ester group), 1666 (C=O abutted on the aromatic ring), 1600 (C=C of the aromatic ring), 1640 (C=C abutted on the ester group).

EIMS (70 eV) m/e: 279 (reactive hydrogen exchanged by deuterium).

Synthesis of MPIs

All MPIs were synthesized by thermal radical polymerization using AIBN as initiator and ethyl acetate as solvent. Ethyl acetate (35 g) was poured into a 150 mL four-neck flask with a mechanical stirrer, thermometer, and condenser pipe. The mixture was stirred and heated to reflux, after which 3.0 wt % AIBN (w/w) with respect to the monomers was added dropwise to the mixture. After 1.5 h of distribution droplets, the reaction was continued for 1.5 h. The temperature through the reaction process was controlled in 70–75°C. The formulas for the mixed monomers are shown in Table I. P-1, P-2, and P-3 (series I) were designed to have the same T_g but various contents of initiator group. P-1, P-4, and P-5 (series II) were designed to have the same content of initiator group but different T_g's.

Measurements

^{1}H NMR and ^{13}C NMR spectra were recorded on a Mercury Plus 400 MHz spectrometer with CDCl$_3$ as solvent.

FTIR measurements (Impact 400, Nicolet, Waltham, MA) were carried out using the KBr pellet method from 4000 to 400 cm^{-1}. The UV source used to irradiate the samples in FTIR measurements was a 1000 W high-pressure mercury lamp and the light intensity was 20 mW/cm^2. Mass spectra were recorded on a HP5989A mass spectrometer at 70 eV. UV-vis spectra were recorded in chloroform solution with a PerkinElmer Lambda 20 UV-vis spectrophotometer. Molecular weights were determined by gel permeation chromatography (GPC) in THF solution on a PerkinElmer Series 200 apparatus. Monodisperse polystyrene samples were used as calibration standards. T_g of the MPIs were measured using a DSC Q2000 V24.10 Build 122. The following parameters were used: N$_2$ flow rate, 100 mL/min; heating rate, 10°C/min; and temperature range, −90–110°C.

Photopolymerization behavior analysis was carried out on a modified CDR-1 DSC apparatus (Shanghai Balance Instrument Co., China) with a UV spot cure system BHG-250 (Mejiro Precision Co., Japan). The intensity of incident light at the sample pan was measured to be 25 mW/cm^2 using a UV power meter.
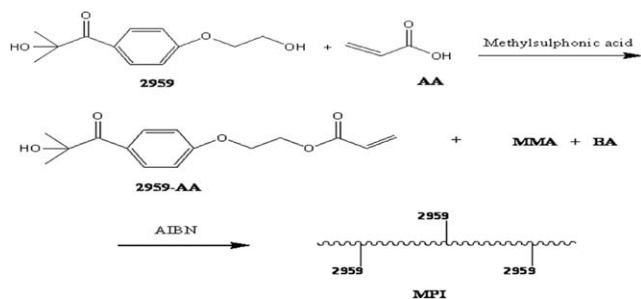
Scheme 1. Synthesis route of macrophotoinitiators.

The final unsaturation conversion (P^f) was calculated using the following formula:

$$P^f = H_t / H_\infty$$

where H_t is the heat effect within t seconds and H_∞ is the heat effect for 100% unsaturation conversion. The DSC curve was unified by the weight of sample (g). The polymerization rate was defined by J/g/s, that is, the heat of polymerization per second per one gram of sample. The value of polymerization heat $\Delta H_0 = 86$ J/mmol per acrylic double bond was used to calculate unsaturation conversion.[16]

RESULTS AND DISCUSSION

Synthesis and Characterization

The synthesis route of MPIs is shown in Scheme 1. The polymeric initiator monomer 2959-AA was initially synthesized by an esterification reaction between AA and Irgacure 2959. MPI was then obtained by the thermal radical copolymerization of MMA, BA, and 2959-AA using AIBN as initiator.

Figure 1 shows the ^{1}H NMR and ^{13}C NMR spectra of 2959-AA. In the ^{13}C NMR spectrum [Figure 1(a)], all carbon-corresponding peaks are very distinct. Figure 1(b) shows peaks at 8.039–8.061 ppm assigned to the two protons of the aromatic ring near the C=O group. The peaks at 6.916–6.945 ppm correspond to the other two protons of the aromatic ring. The peaks at 5.827–6.642 ppm can be assigned to the three protons in the double bond. The peaks at 4.496–4.519 ppm correspond to the protons of CH$_2$ near the aromatic ring, and the single peaks at 1.588 ppm are assigned to the six methyl hydrogens. The peaks of the protons of another CH$_2$ group and an oxhydryl group were considered together and represented by peaks at 4.250–4.273 ppm. For demonstration, a small amount of deuterium oxide was dropped onto the sample, and the integral area of peaks in similar positions was reduced by 1 in Figure 1(c) compared with Figure 1(b). The ^{1}H NMR and ^{13}C NMR spectra indicate that the unsaturated double bond is grafted onto Irgacure 2959, and 2959-AA is successfully synthesized.

The UV-Vis spectra of Irgacure 2959 and 2959-AA are shown in Figure 2. The two molecules have similar absorbance spectra, but 2959-AA has a smaller molar extinction coefficient than Irgacure 2959. These results indicate that 2959-AA can initiate photopolymerization of acrylate systems, but the absorbance is

lower due to the lower molar concentration of the chromophore moiety.

Figure 3 presents the FTIR spectra of 2959-AA (Curve 1) and 2959-AA after UV-irradiation (curve 2). The peaks at 1666 nm representing C=C and at 1410 nm representing C—H of C=C in curve 1 are obviously shortened in curve 2, indicating that the benzophenone groups of 2959-AA can decompose and
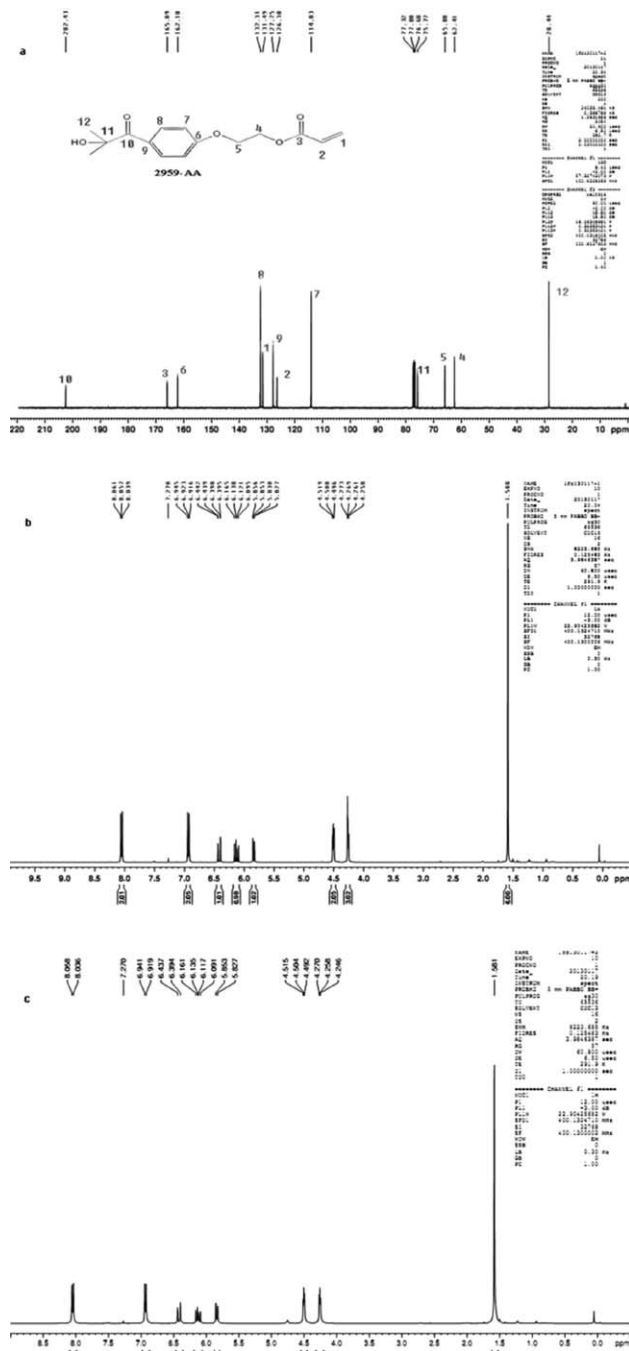

Figure 1. (a) ^{13}C NMR spectrum of 2959-AA in CDCl$_3$. (b) ^{1}H NMR spectrum of 2959-AA in CDCl$_3$. (c) ^{1}H NMR spectrum of 2959-AA in CDCl$_3$ with a small amount of D$_2$O.
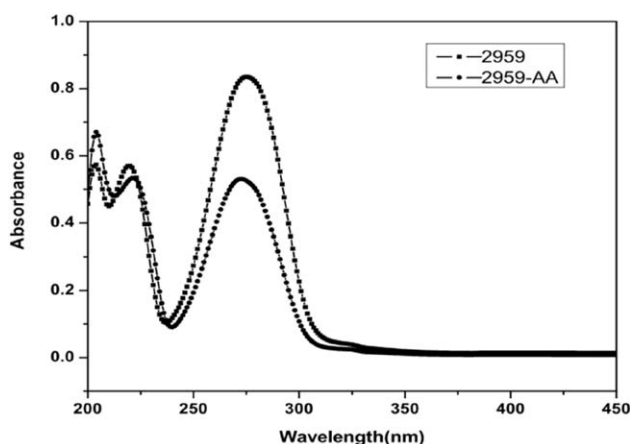
Figure 2. UV-vis spectra of Irgacure 2959 and 2959-AA (ethanol, 1.25 × 10^{-2} g/L).

produce radicals to initiate the polymerization of unsaturated bonds. FTIR analysis results further confirm that Irgacure 2959 still has good ability to initiate radicals in polymerization under UV light after being grafted onto unsaturated double bonds.

Figure 4 shows the FTIR spectra of MPI P-1. The characteristic absorption peak of C=C at 1666 nm and the peak at 1410 nm for shear vibration of C—H of C=C are not observed, indicating that all monomers are completely polymerized into MPI.

To minimize the effects of differences in molecular weights of MPIs on the polymerization reaction, the molecular weights of MPIs must be similar. Thus, all polymerizations reactions for the synthesis of MPIs were conducted under the same conditions. The results of molecular weight test by GPC are summarized in Table II. Considering that controlling the molecular weight in radical polymerization is very difficult, the results in Table II are acceptable.

To evaluate the effects of T_g on polymerization behavior, all T_g's of MPIs were tested using DSC. Figure 5 shows the DSC curves of P-1, P-2, P-3, P-4, and P-5. The T_g's and 2959-AA contents
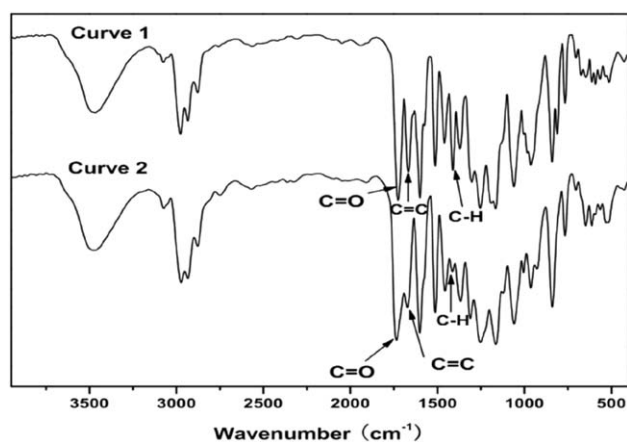

Figure 3. FTIR spectra of 2959-AA (curve 1) and 2959-AA after UV irradiation (curve 2).
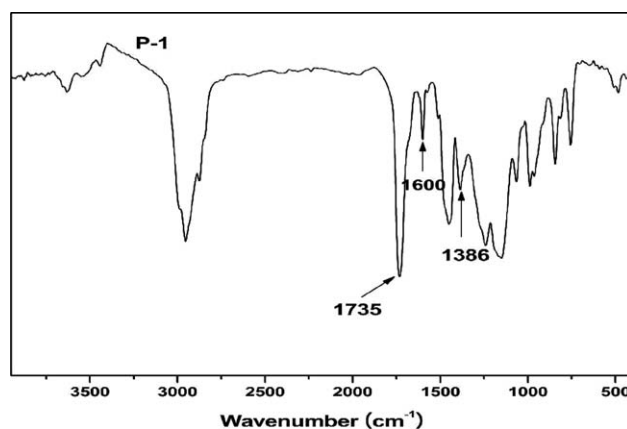

Figure 4. FTIR spectra of MPI P-1.

of the MPIs are summarized in Table III. The data indicate that P-1, P-2, and P-3 have similar T_g's with increased 2959-AA content, whereas P-4, P-1, and P-5 show an increasing T_g trend at the same 2959-AA content.

Photopolymerization Behaviors of HDDA Initiated by Irgacure 2959, 2959-AA, and MPIs

Figures 6 and 7 show the photo-DSC profiles of the photopolymerization rates and monomer conversions of HDDA initiated by Irgacure 2959 (full line) and the polymerizable photoinitiator 2959-AA (dotted line). The results verify that 2959-AA can efficiently initiate photopolymerization and exhibits more preferable polymerization behavior than Irgacure 2959. Evidently, 2959-AA takes less time to reach the maximum polymerization rate ($R_{p,\max}$). The final conversion of 2959-AA is similar to that of Irgacure 2959, but 2959-AA takes a shorter time to reach the reaction endpoint. In the conversion calculation, the heat released by the unsaturated bonds of 2959-AA is ignored because this portion of heat contributes very little to the total heat. The data of HDDA polymerization initiated by Irgacure 2959 and 2959-AA are listed in Table IV. The abovementioned advantages of 2959-AA can be attributed to the esterification of the primary hydroxyl group of Irgacure 2959 with AA that results in improved compatibility with HDDA. The initiator concentration in the reaction system becomes more homogeneous, and the production of radicals becomes more rapid under UV irradiation such that the monomers can more easily catch radicals. As a result, monomer conversion reaches a higher ratio in a shorter time.

In the polymerization reactions initiated by MPIs, different termination patterns of polymerization are obtained because half of the radicals are attached onto the chains of MPIs and numerous radicals exist on one chain of MPIs.

Table II. Molecular Weights of MPIs

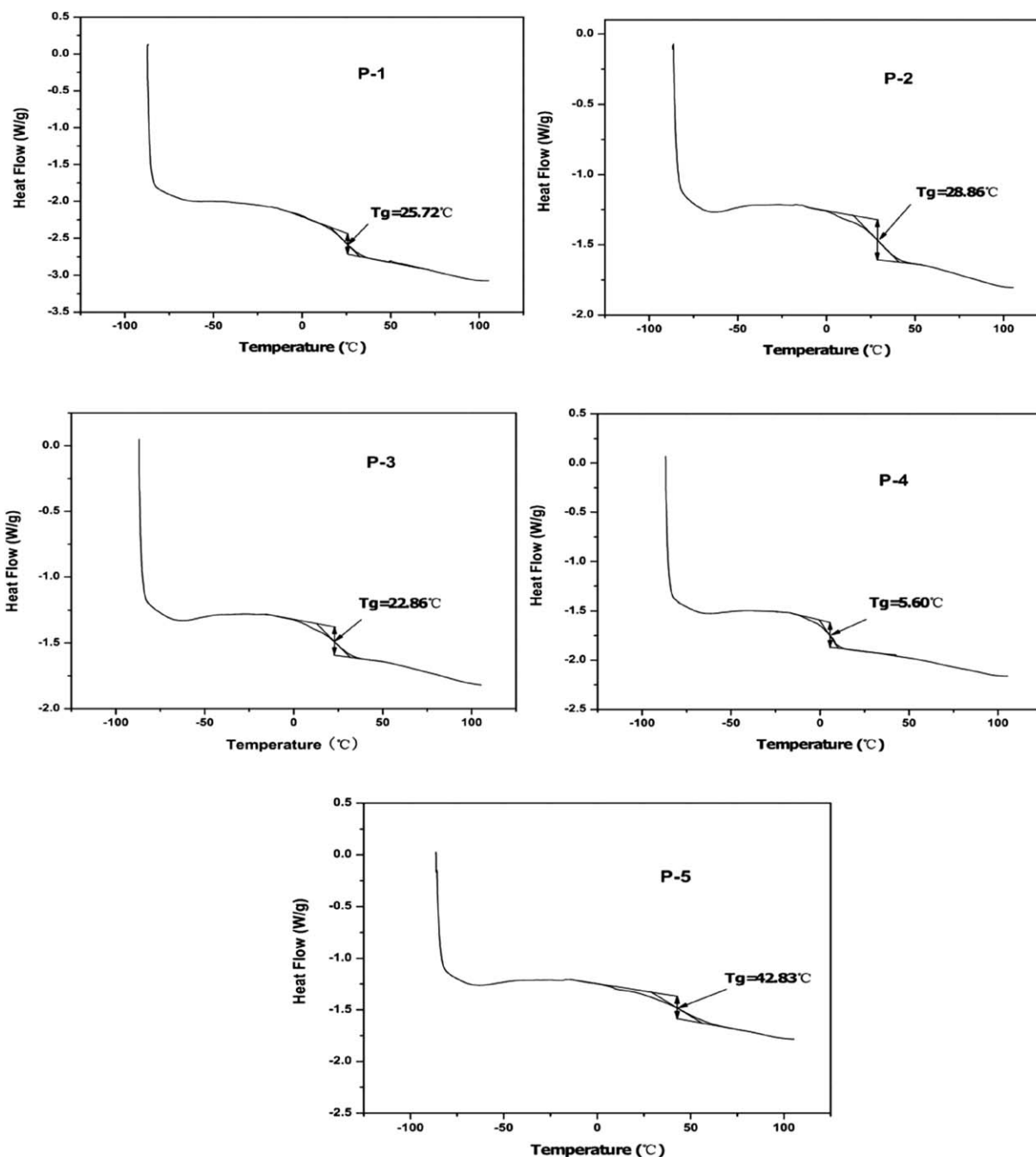| Sample	P-1	P-2	P-3	P-4	P-5
M_w	48868	38138	54334	53734	37163
M_n	20722	18458	20914	22748	17695
M_w/M_n	2.358	2.066	2.598	2.362	2.100

Figure 5. DSC curves of MPIs.

The mechanism of polymerization reaction initiated by MPIs is shown in Scheme 2. The resulting product is a crosslinked polymer. Figures 8 and 9 show the polymerization rates and conversions of polymerizations of HDDA as initiated by MPIs (series I). The samples are prepared with a fixed weight ratio of MPI to HDDA. Samples P-1, P-2, and P-3 have similar T_g's. The 2959-AA contents follow an increasing rising trend from P-2, P-1, to P-3 because of the different 2959-AA contents in the MPIs. Several conclusions can be drawn from the results. First, P-1, P-2, and P-3 can initiate polymerizations with high monomer conversion, and the final conversion increases with

increased amount of initiating groups in the MPIs. Second, the rates of polymerization become increasingly faster from P-2, P-1, to P-3. The time to reach $R_{p,\max}$ becomes shorter, and the

Table III. T_g's of MPIs

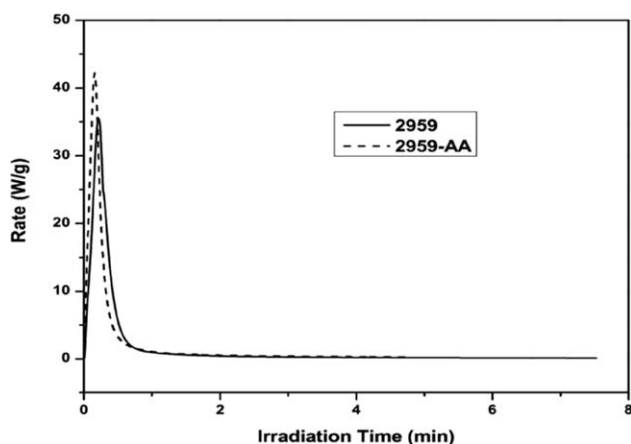| MPI	P-1	P-2	P-3	P-4	P-5
Percent of 2959-AA (%)	8	4	12	8	8
T_g (°C)	25.72	28.86	22.86	5.60	42.83

Figure 6. Rates of polymerizations of HDDA initiated by Irgacure 2959 and 2959-AA.
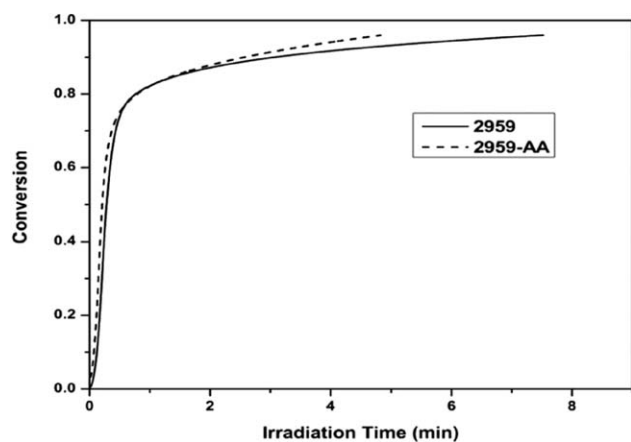

Figure 7. Conversions of HDDA initiated by Irgacure 2959 and 2959-AA.

values of $R_{p,max}$ increases. Third, the total reaction times increase, with P-1 taking the shortest time and P-3 taking the longest time. Data on the polymerization behaviors of series I are shown in Table V. The high monomer conversions can be explained by the good compatibility between HDDA and MPIs, and the variation in polymerization behaviors can be interpreted as being caused by the increase in radical concentrations during polymerization. Figures 8 and 9 clearly suggest that the main exothermic processes finish in a short time, consistent with the characteristics of a free radical reaction. The reaction rates and conversions are found to increase with increased radical concentration. However, considering that half of the radicals are attached onto the chains of MPIs, the mobility of radicals

Table IV. Data on Polymerization Behaviors of HDDA Initiated by Irgacure 2959 and 2959-AA

Sample	$R_{p,max}$ (W/g)	T_{max} (min)	Conversion (%)	$T_{endpoint}$ (min)
Irgacure 2959	35.483	0.214	96.0	7.525
2959-AA	42.178	0.156	95.9	4.828
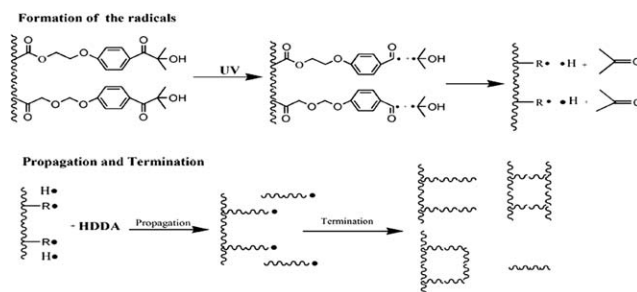
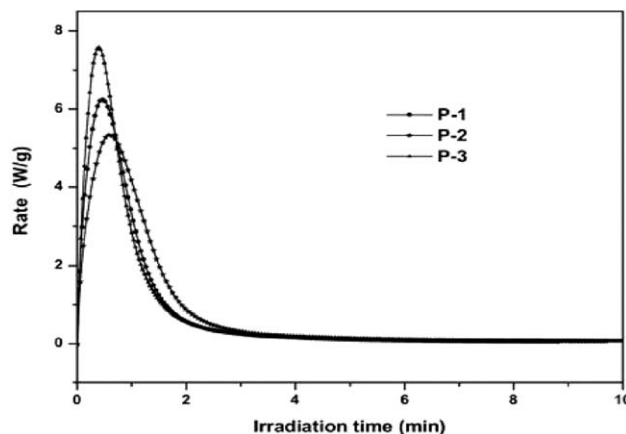**Scheme 2.** Mechanism of polymerization reaction initiated by MPIs.

Figure 8. Polymerization rates of polymerization with HDDA initiated by MPIs (series I).

and collision probability between free radicals are reduced, the lifetime of radicals increase, and the polymerization time also increases.

The properties of MPIs also affect the polymerization behaviors. In series II, the MPIs are designed with different T_g's and the same 2959-AA content. The polymerization behaviors of HDDA as initiated by the MPIs (series II) are shown in Figures 10 and 11. The samples are prepared with a fixed weight ratio of MPI to HDDA. The 2959-AA contents of samples P-1, P-4, and P-5 are similar, and the T_g's exhibit an increasing trend from P-4,
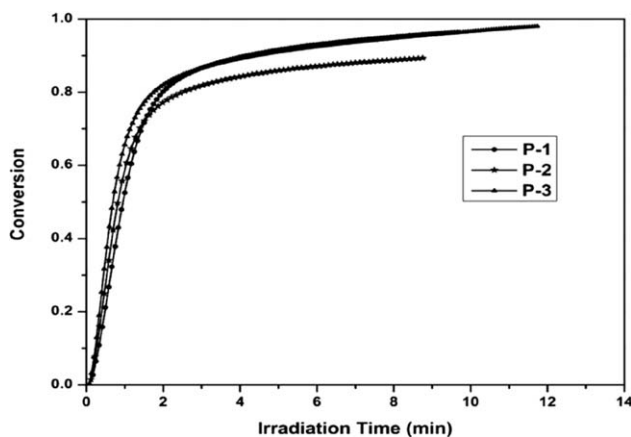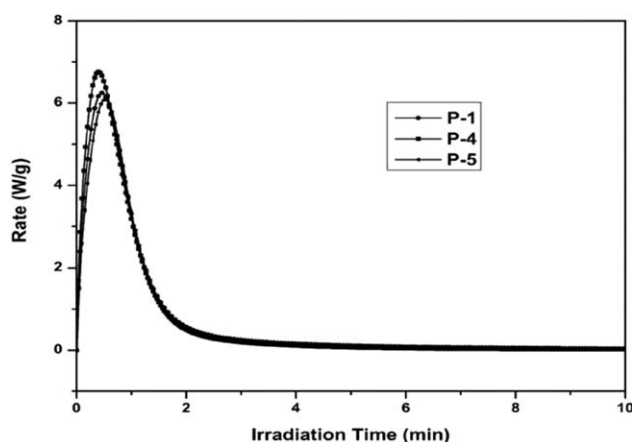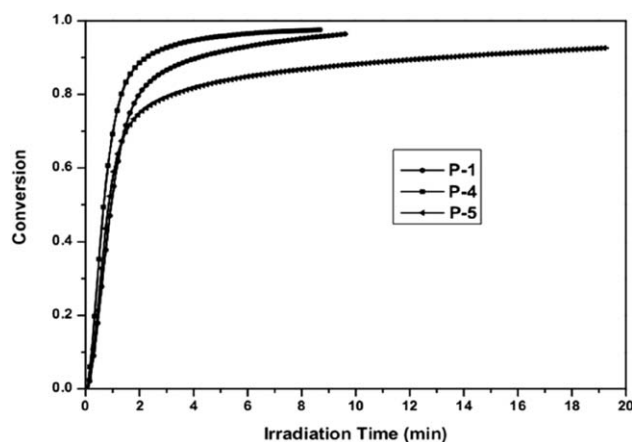

Figure 9. Conversions of polymerization with HDDA initiated by MPIs (series I).

Table V. Data on Polymerization Behaviors of Series I MPIs

Sample	$R_{p,max}$ (W/g)	T_{max} (min)	Conversion (%)	$T_{endpoint}$ (min)
P-2	5.329	0.592	89.4	8.828
P-1	6.243	0.449	96.5	9.688
P-3	7.582	0.385	98.1	11.788

Table VI. Data on the Polymerization Behaviors of Series II MPIs

Sample	$R_{p,max}$ (W/g)	T_{max} (min)	Conversion (%)	$T_{endpoint}$ (min)
P-4	6.763	0.403	97.6	8.738
P-1	6.243	0.449	96.5	9.688
P-5	6.086	0.525	92.6	19.338

Figure 10. Polymerization rates with HDDA initiated by MPIs (series II).

P-1, to P-5. Results show that the MPIs (series II) can also initiate polymerization with high monomer conversion. The rates of polymerization decrease, and the total reaction time of polymerization is prolonged with increased T_g. Data on the polymerization behaviors of series II are listed in Table VI, where $R_{p,max}$ appears later and values of $R_{p,max}$ become smaller with increase of T_g. Considering that all samples have the same active group concentration, variation in the polymerization behaviors can be solely attributed to the differences in MPIs. From P-4, P-1, to P-5, the T_g's of MPIs increase, which slows down the movement of chain segment although still in the monomer HDDA. Given the fact that half of the radicals are attached onto the chains of the MPIs, the $R_{p,max}$'s of the polymerizations are inevitably influenced by the speed of chain segments. Lower T_g's of MPIs

result in more flexible chain segments. Thus, double bonds more easily catch radicals, thereby increasing the polymerization rate. At the same time, slower chain segment movements reduce the collision probabilities of radicals such that termination reactions between radicals become less probable and total reaction times increase.

When HDDA is initiated in polymerization, the MPIs more slowly release heat, and longer reaction times are required to reach comparable monomer conversions than the low-molecular-weight initiators Irgacure 2959 and 2959-AA. The results may be explained by the lower active group concentrations in the MPI-HDDA systems, and the motions of radicals are impeded by macromolecular chains. Moreover, half of the radials are fettered onto the macromolecular chains.

CONCLUSIONS

The synthesis and polymerization behaviors of the polymerizable initiator 2959-AA and MPIs were reported. 2959-AA was obtained through an esterification reaction between AA and the water-soluble photoinitiator Irgacure 2959. Esterification reaction significantly improved the solubility of Irgacure 2959 in the oil phase. Two series of MPIs were obtained by a thermal radical copolymerization between 2959-AA and acrylic monomers. Photo-DSC tests showed that 2959-AA was more effective than Irgacure 2959 when HDDA was initiatored. Higher 2959-AA content and higher pliability of chain segments of MPIs were favorable for polymerization, and all the initiators reached ideal monomer conversions.

Figure 11. Conversions of polymerization with HDDA initiated by MPIs (series II).

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