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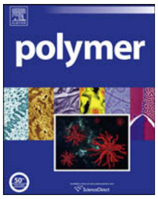

Self-initiated photopolymerization of hyperbranched acrylates

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ABSTRACT

Self-initiated photopolymerization of hyperbranched acrylates (HBAs) has been investigated. The photopolymerization progress was monitored by differential photo-calorimetry (DPC). It was shown that HBAs were able to self-initiate photopolymerization rapidly under the irradiation of medium-pressure mercury lamp. This behavior was explained by the longer wavelength absorption ($\sim$286 nm) of HBAs, which results from the overlapping of π-conjugated orbitals of acrylate groups. Autoacceleration effect was observed. The autocatalytic model was used to analyze the photopolymerization kinetics and found to well match the experimental data. It was found that acceleration stage ended at low conversion ($\alpha_{Rm} < 0.11$), and the final conversion α_f was lower than 40% in most cases. This was attributed to the poorer ability of HBAs to generate primary radicals and thus the insufficiency of free radicals in polymerization. Factors in favor of generating primary radicals extended the autoacceleration stage to higher conversion and gave higher final conversion. The values of activation energy were calculated to be in the range of 5.7–7.5 kJ mol^{-1}, analogous to those for the free radical photopolymerization of acrylate monomers in the presence of photoinitiator.

1. Introduction

Photopolymerization or photocuring technology has received great attention in the fields of academic research and industry applications due to the increasing concern for health and environmental safety [1–9]. Photopolymerization normally requires the addition of photoinitiators which absorbs the incident light and generate sufficient initial species to start polymerization reaction. However, the addition of photoinitiators leads to several problems in applications. Many photoinitiators cause yellowing which is harmful for clear coats. The migration of photolysis fragments out of the coating may cause unpleasant odor which should be avoided in some applications such as food packaging and cosmetic bottle. Therefore, one of the current trends of UV curing formulation is towards direct photopolymerization reactions without the addition of conventional photoinitiators. Various approaches have been reported in the literatures concentrated on self-initiated photopolymerization systems, including thiol-ene systems [1,10,11], electron donor-acceptor systems [12–14] and self-initiated photografting [15–17]. Monomers with specific structure, such as vinyl acrylates [18] and brominated acrylates [7], were found to be able to photopolymerize in the absence of photoinitiator. However, these approaches more or less suffer from certain limitations such as health or cost aspects, or only suit for specific applications such as surface photografting.

It was reported that acrylates can undergo photopolymerization without photoinitiators by irradiation with short-wavelength UV (222 nm) [19,20]. The normal acrylate monomers or oligomers can be cured as thin layers with monochromatic excimer lamps in UV-C or VUV region. Due to the high extinction coefficients of acrylate monomers at the wavelength of incident light, the thickness of the polymerization is limited to less than 1.5 μm [20]. On account of the requirement of short-wavelength UV source and the thickness limitation, self-initiation in this manner is very limited in application.

Recently, we have studied the photopolymerization kinetics of hyperbranched acrylates (HBA), and found that these hyperbranched acrylates can proceed photopolymerization quickly in the absence of photoinitiator under the irradiation of medium-pressure mercury lamps, the most common light source in UV curing with main emission bands longer than 250 nm. Hyperbranched (meth)acrylates are characterized by highly branched, tree-like structure and a large number of acrylate or methacrylate end-groups. The advantages such as high solubility, very rapid cure rate, low shrinkage and low viscosity compared to conventional acrylates of similar molecular weight [21] make them very suitable for UV curing applications. A considerable amount of research has been done on the synthesis and application of hyperbranched (meth)-acrylates [22–25]. To the best of our knowledge, however, there is no report concerning the self-initiated photopolymerization of

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Table 1
Characteristics of Boltorn hyperbranched polyester (data from supplier).

Sample	Generation number	Theoretical functionality	M_w (g mol^{-1}) by GPC	Polydispersity M_w/M_n	Hydroxyl value (mmol g^{-1})
H20	2	16	2100	1.3	9.14
H30	3	32	3500	1.5	8.87
H40	4	64	5100	1.8	8.66

hyperbranched (meth)acrylates. In this paper, we have synthesized series of hyperbranched acrylates with different functionality by modifying commercial available hyperbranched polyesters with acrylic acid and propionic acid at different feed ratio. The self-initiated photopolymerization behaviors of these hyperbranched acrylates under the irradiation of medium-pressure mercury lamps have been studied.

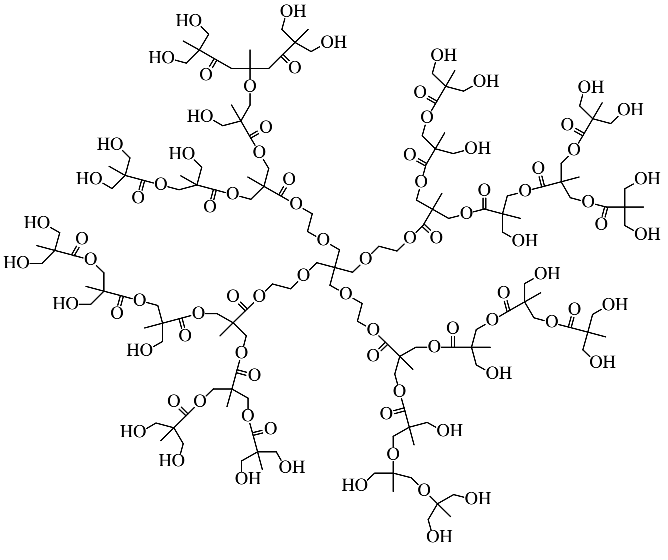
2. Experimental

2.1. Materials

Hyperbranched polyesters (Boltorn H20, H30, H40) were kindly supplied by Perstorp AB (Sweden) and used as-received. The Characteristics and typical structure of these materials are presented in Table 1 and Scheme 1 (taking H30 as example). Acrylic acid and propionic acid were purchased from Guanghua Chemical Co. Ltd. (Guangzhou, China) and purified by distilling under reduced pressure. All other chemicals used were analytical grade and used without further purification.

2.2. Preparation of hyperbranched acrylates (HBAs)

Acrylic acid (10.31 g, 0.1431 mol) and Boltron H30 (16.03 g, 0.1431 mol hydroxyl end groups) were put into a three-necked flask equipped with reflux condenser and water separator, with 20 ml toluene as water-carrying reagent to accelerate the esterification, 1.54 g (3 wt%) 4-methyl benzene sulfonic acid as catalyst, and 0.264 g (0.6 wt%) *p*-methyl hydroquinone as inhibitor. The reaction was performed at 120 °C for 8 h, and then toluene and unreacted acid were removed under vacuum. To remove the catalyst and residual acid, the obtained solution was added into ethyl acetate, followed by washing with 10% Na_2CO_3, 1M HCl, and distilled water. Then the organic layer was dried over $MgSO_4$ and filtered, and ethyl acetate was finally removed by vacuum. The product obtained was yellowish viscous liquid, and named HBA2-a. ^{1}H NMR ($CDCl_3$): δ (ppm) = 6.34–6.45 (br, cis,–CH=CH_2), 6.09–6.15 (br,–C*H*=CH_2), 5.85–5.92 (br, trans,–C*H*=CH_2), δ = 4.0–4.3 (br,–CH_2–O–C(O)–), 1.13–1.40 (br,–CH_3–). FTIR spectrum (KBr, cm^{-1}): 1731(carbonyl), 1635 and 809(acrylate unsaturation). The ^{1}H NMR spectrum is shown in Fig. 1.



Scheme 1. Typical structure of H30.

The synthesis procedure is illustrated in Scheme 2. Other samples with different generation number (GN) were prepared by the same procedure based on different hyperbranched polyester precursors (H20, H30 and H40). Functionality of the hyperbranched acrylate was adjusted by changing the feed mole ratio of acrylic acid and propionic acid (*x*:*y*). Designation of the products, as well as the related parameters, is summarized in Table 2.

2.3. Characterization of products

The molecular weight and polydispersity were determined by Waters 1515 GPC instrument with tetrahydrofuran as the mobile phase. The flow rate of tetrahydrofuran was 1.0 mL/min. Narrow distribution linear polystyrenes were used as the standard to calibrate the apparatus, the molecular weight of the synthesized resins was measured using universal calibration.

Degree of esterification (D_E) of the products was calculated based on the acid value measured by titration.

The content of carbon double bonds in the products (*C*) was tested by titration based on Michael addition of acrylate with morpholine. The value obtained was then multiplied by weight average molecular weight (M_w) of the products to obtain the functionality (*F*), i.e. the average number of acrylate groups in a hyperbranched polyester molecule. The results of *C* and *F* are listed in Table 2. It is noticed that the value of functionality tested by titration of carbon double bonds and GPC should be lower than the actual value. This is because the hyperbranched polymer possesses highly compact molecular architecture in solution in comparison with the linear polymer, resulting in smaller hydrodynamic radius than that of its linear counterpart with the same molar weight. As a consequence, the average molecular weight of HBA determined by GPC which is calibrated with linear polystyrene is lower than its actual value, and thereby lower value of functionality is obtained.

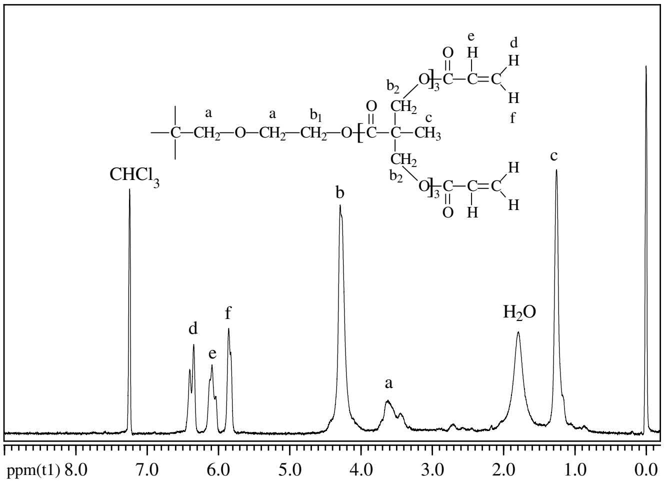
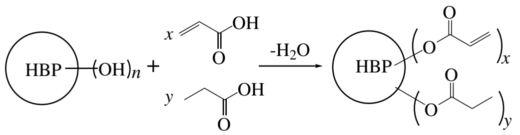


Fig. 1. ^{1}H NMR spectrum of HBA3-a.



Scheme 2. Illustrative procedure for the preparation of hyperbranched acrylates.

2.4. Differential photo-calorimetry (DPC) for the kinetics of the photopolymerization

The polymerization progress is monitored by means of differential photo-calorimetry (DPC). A modified CDR-1 DSC (Shanghai Balance Instrument Plant, Shanghai, China) equipped with RW-UVAΦ200U UV spot curing system (Runwing Co., Ltd, Shenzhen, China) was employed to measure the exothermal rates of irradiated samples. The UV source in the spot curing system is a 200 W medium-pressure mercury lamp with main UV emission bands in the region of 253.7–366.3 nm [26]. The thermal radiation was filtered in the optical system of UV spot curing machine. Both sample and reference were irradiated. The light intensity was measured by a UV-radiometer (type UV-A, Photoelectric Instrument Factory, Beijing Normal University, China), which is sensitive in the wavelength range of 320–400 nm. The DSC was calibrated with an indium melting standard.

The heat flow (dH/dt) from the sample during irradiation is measured as the function of reaction time (t). The reaction rate was calculated from the reaction enthalpy by the following equation:

$$R_p = \frac{d\alpha}{dt} = \frac{d(H/H_\infty)}{dt} = \frac{dH/dt}{C \times H_0} \qquad (1)$$

where R_p is the polymerization rate, H_∞ ($=i \times H_0$) the total enthalpy, H_0 the molar enthalpy of C=C bonds in polymerization, and C the content of carbon double bond in the system (mmol g^{-1}). The value of ΔH_0 for acrylates is 80.2 kJ mol^{-1} [27]. Curves of conversion versus irradiation time can be obtained by integrating the curves of polymerization rate versus irradiation time.

3. Result and discussion

3.1. Photopolymerization behavior of HBAs in the absent of photoinitiator

The hyperbranched acrylates with different functionality were irradiated with medium-pressure mercury lamp in the absence of photoinitiator. DPC curves obtained are shown in Fig. 2. The profile of the curves is analogous to those for the photopolymerization of multifunctional monomers with photoinitiator, suggesting that HBAs are able to self-initiate photopolymerization under the irradiation of medium-pressure mercury lamp.

Table 2
Designation of the products and related parameters.

Sample name	Boltron precursor	GN	x:y	Esterification degree (%)	$M_w \times 10^3$ (g mol^{-1})	C (mmol g^{-1})	F
HBA2-a	H20	2	1.0:0	83.41	2.67	4.21	11.24
HBA2-b	H20	2	0.7:0.3	80.42	2.83	2.94	8.32
HBA2-c	H20	2	0.5:0.5	79.30	2.43	2.01	4.88
HBA3-a	H30	3	1.0:0	85.43	5.00	4.85	24.25
HBA3-b	H30	3	0.7:0.3	78.85	4.50	3.76	16.92
HBA3-c	H30	3	0.5:0.5	81.76	5.35	2.70	14.45
HBA4-a	H40	4	1.0:0	82.00	6.78	5.06	34.31
HBA4-b	H40	4	0.7:0.3	86.00	6.44	3.55	22.86
HBA4-c	H40	4	0.5:0.5	80.80	6.42	2.42	15.54

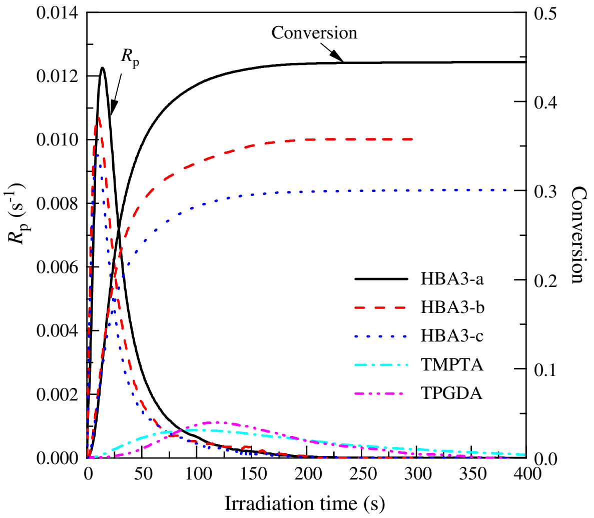


Fig. 2. Reaction rate and conversion as a function of irradiation time for the self-initiated photopolymerization of HBA3s, TMPTA and TPGDA. Reaction condition: 25 °C, light intensity 15 mW/cm^2, nitrogen atmosphere.

The mechanism of self-initiated photopolymerization of acrylates with long-wavelength UV radiation is not very clear. The normal acrylate monomers such as trimethylolpropane triacrylate (TMPTA) and tripropylene glycol diacrylate (TPGDA) have strong absorption at 230 nm which is assigned to π–π* transition of acrylate groups, but lack of absorption at longer wavelength (Fig. 3). For this reason, the investigations on self-initiated photopolymerization of acrylate monomers were mainly based on short-wavelength UV radiation, 222 nm typically [19,20,28]. Acrylates can be excited by short-wavelength UV radiation to form a triplet state which is highly localized at the vinyl bond [19]. This triplet state can undergo hydrogen abstraction from the –CH_2– group next to

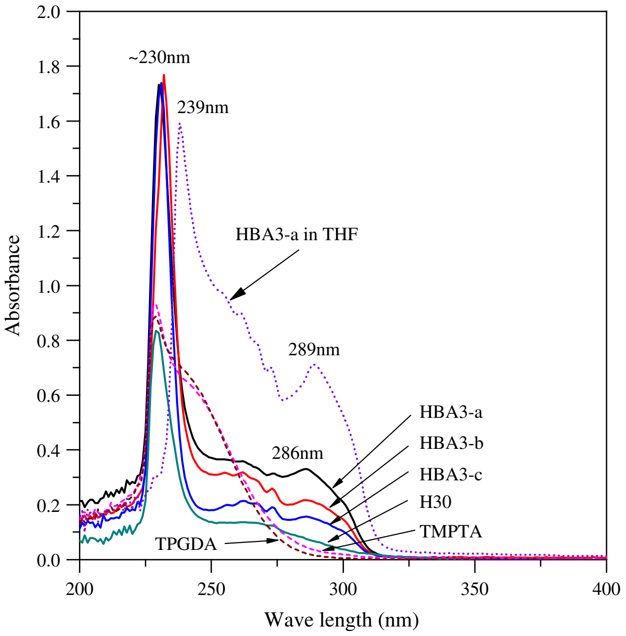


Fig. 3. UV absorption spectra of HBA3-n (n = a, b, c), H30, TMPTA and TPGDA in CH_2Cl_2.

oxygen, as well as the direct addition to acrylate double bonds at ground state, forming primary free radicals to initiate polymerization. Medium-pressure mercury lamp is not an efficient UV source to excite acrylates due to the lack of short-wavelength radiation. The efficiency of self-initiated photopolymerization of normal acrylate monomers such as TMPTA and TPGDA under the irradiation of medium-pressure mercury lamps is very poor, as shown in Fig. 2.

Different from the normal acrylate monomers, the hyperbranched acrylates exhibit obvious absorption at around 286 nm, as shown in Fig. 3. This absorption band weakens as acrylate functionality decreases, and disappears for H30 which does not contain any acrylate group, suggesting that this new absorption band is correlated to the acrylate groups in HBAs. It is also found that increasing the polar of solvent results in red-shift of both absorption bands, from 230 nm and 286 nm in dichloromethane to 239 nm and 289 nm in tetrahydrofuran (Fig. 3). This implies that the transition type of the new absorption band is the same as that of the band at 230 nm, that is, π–π^* transition, for n–π^* transition absorption shifts to the opposite direction to π–π^* transition absorption as the polar of solvent is changed. The difference of HBAs from the normal monomers on UV absorption may be attributed to the unique structural character of the hyperbranched molecules. The hyperbranched acrylate molecule structurally consists of a polyester core and a shell rich in acrylate groups. This makes some acrylate groups very close to each other, causing the overlapping of π-conjugated orbitals of the adjacent acrylate groups. It is reported that the overlapping of π-orbitals leads to red-shift of UV–Vis absorption [29]. So it is likely that the new absorption band results from the red-shift of π–π^* transition absorption of some acrylate groups due to the overlapping of π-conjugated orbitals. It is noticed that this new absorption band is very weak relative to the normal π–π^* transition absorption. This may be attributed to the imperfect structure of the hyperbranched polyesters. As shown in Scheme 1, the functional end groups do not always locate at the outer layer, some of them are embedded in the core. It also increases the distance between the acrylate groups at outer layer. As a result, only a limited amount of acrylate groups can overlap and cause absorption at longer wavelength.

The longer absorption wavelength makes HBAs sensitive to the irradiation of medium-pressure mercury lamp. As shown in Fig. 4, the absorption band at 286 nm declines steadily with increasing irradiation time. This may be the cause of the self-initiation of HBAs under the irradiation of medium-pressure mercury lamp.

3.2. Kinetics

Fig. 2 shows that the reaction rate increases sharply at the beginning of UV irradiation and reaches a maximum ($R_p^{\max}$) in a few seconds, and then drops quickly. Accordingly, the conversion shows a sharp rise at the beginning, followed by a gentle increase, and finally trends to a constant value (final conversion α_f). This is a typical feature of polymerization with autoacceleration effect which is caused by reduction of the termination rate due to restricted diffusion of the reactive chain ends connected to the network being formed [30]. The shape of the rate curves is analogous to that for the autocatalytic reaction such as the curing process for epoxy-amine thermoset resins which is autocatalysed by hydroxyl groups formed. And the network formed in polymerization can be regarded as a catalyst which accelerates the polymerization via reducing the termination rate. Thus, the kinetics of the photopolymerization process can be treated with an autocatalytic model phenomenologically, and expressed as the following equation [2,31]:

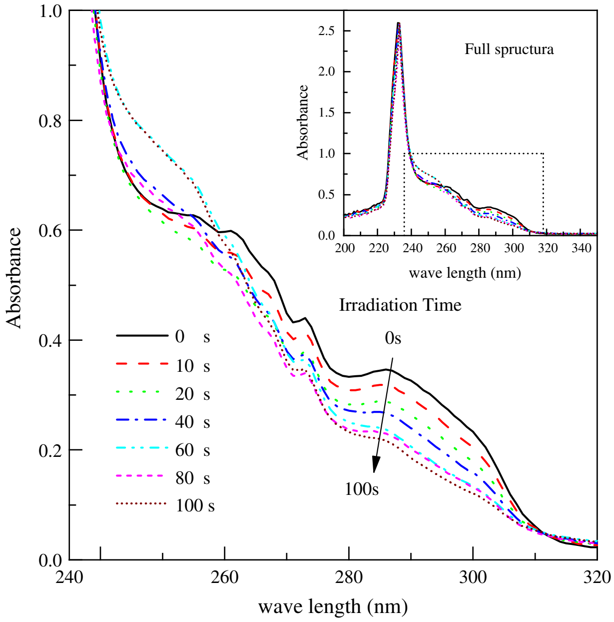


Fig. 4. UV absorption spectra of HBA3-a at different UV irradiation time.

$$\frac{d\alpha}{dt} = k\left(\frac{\alpha}{\alpha_f}\right)^m\left(1-\frac{\alpha}{\alpha_f}\right)^n \tag{2}$$

where α is the conversion of double bond, α_f the final conversion, k the rate constant, m the autocatalytic exponent, n the reaction order. Fig. 5 shows the curves of polymerization rate versus conversion from DPC results. The fitting curves based on Eq. (2) are obtained by non-linear regression analysis in OriginPro 8.0 (OriginLab Corporation, USA) and also shown in the figure. It is found that the fitting curves well match the experimental data in the whole conversion range. The kinetic parameters are obtained and summarized in Table 3, where α_{Rm} represents the conversion at which reaction rate reaches maximum.

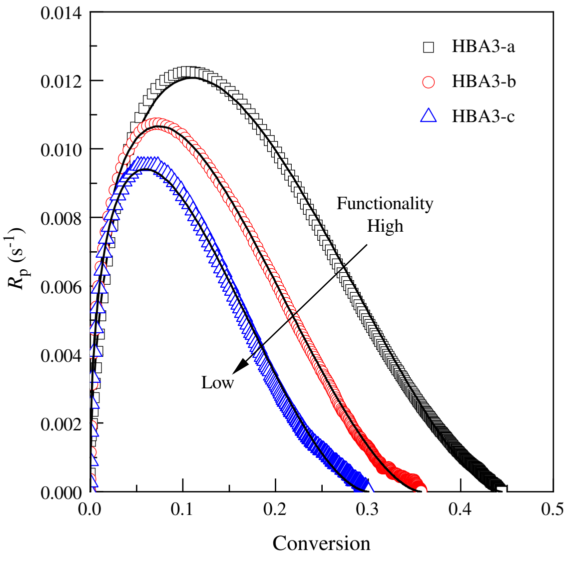


Fig. 5. Plots of reaction rate versus conversion for the self-initiated photopolymerization of hyperbranched acrylates (HBA3s) with different acrylate functionality. The solid curves are fitting curves based on autocatalytic model. Reaction condition: 25 °C, light intensity 15 mW/cm^2, nitrogen atmosphere.

Table 3
Kinetic parameters and correlated data for self-initiated photopolymerization of HBA.

Sample	$R_p^{max} \times 10^2$ (s^{-1})	α_f	α_{Rm}	$k \times 10^2$ (s^{-1})	m	n	F
Photopolymerization in N_2							
HBA2-a	1.12	0.37	0.09	3.57	0.49	1.69	11.24
HBA2-b	0.94	0.35	0.07	2.83	0.44	1.73	8.32
HBA2-c	0.83	0.30	0.05	2.41	0.42	1.84	4.88
HBA3-a	1.23	0.44	0.11	4.06	0.54	1.63	24.25
HBA3-b	1.07	0.36	0.07	3.16	0.45	1.69	16.92
HBA3-c	0.95	0.30	0.05	2.81	0.43	1.76	14.45
HBA4-a	0.95	0.35	0.08	3.49	0.56	1.85	34.31
HBA4-b	0.90	0.33	0.06	2.76	0.46	1.88	22.86
HBA4-c	0.82	0.28	0.05	2.52	0.43	1.91	15.54
Photopolymerization in air							
HBA3-a	1.05	0.38	0.09	3.79	0.57	1.80	24.25
HBA3-b	0.84	0.29	0.05	2.65	0.46	1.82	16.92
HBA3-c	0.80	0.22	0.04	2.31	0.42	1.86	14.45

Parameter k relates to the reactivity of the reactants, type and concentration of photoinitiator (if present), atmosphere, light intensity and temperature. Photoinitiator and light intensity are related to the number of primary free radicals formed. In the case of self-initiated photopolymerization, the primary free radicals are generated from the acrylate groups with overlapping π-conjugated orbitals. Higher functionality means a shorter distance between the acrylate groups which is in favor of the overlapping of π-conjugated orbitals and thus the formation of primary free radicals, resulting in higher reaction rate constant k, as shown in Table 3.

The value of m is correlated to the autoacceleration in polymerization. Higher autoacceleration effect contributes to a larger m value, and for a polymerization without autoacceleration, the value will be zero. Table 3 shows that m values increases with increasing functionality. Higher functionality induces faster formation of polymeric network and thus leads to a greater dependence of termination rate on conversion which causes the overall rate to increase faster with conversion. This gives rise to higher autoacceleration effect, resulting in greater m value.

Reaction order n reveals the dependency of polymerization rate on the concentration of unreacted double bonds. The theoretical value of n provided by Paul J. Flory is 1.5 for monomer initiated polymerization [32]. As shown in Table 3, the self-initiated photopolymerization of HBAs with different functionality give n values in the range of 1.63–1.91. The n value greater than 1.5 may be attributed to the primary radical termination. The increased viscosity during polymerization makes bimolecular termination between propagating radicals difficult, primary radical termination may become important or even the only mode of termination which causes a second order dependence on monomer concentration [33]. Table 3 also shows that n value reduces with increasing functionality. It is probably that higher functionality provides more carbon double bonds to react with the generated primary radicals, resulting in less chance of primary radical termination, gives lower n value.

Table 4
Calculated values of E_a, k_0 and b.

	E_a (kJ mol^{-1})	$k_0 \times 10^2$ (s^{-1})	b
HBA2-a	6.6	0.53	0.69
HBA3-a	5.7	0.70	0.65
HBA4-a	7.3	0.55	0.67
HBA3-b	6.9	0.42	0.74
HBA3-c	7.5	0.36	0.78

It is noticed that the autoacceleration effect ends at rather low conversion ($\alpha_{Rm} = 0.04$–0.11), and increasing functionality extends the acceleration stage to higher conversion. It is supposed that the deceleration should primarily result from the insufficient supply of free radicals, rather than monomer consumption or diffusion restriction related to gelation or vitrification. As mentioned above, the primary free radicals are generated from the acrylate groups with overlapping π-conjugated orbitals. Considering that the absorption at 286 nm is relatively weak, the amount of acrylate groups which can absorb UV irradiation and generate primary radicals will be limited, causing insufficient supply of free radicals. Factors in favor of generating free radicals, such as functionality, inert atmosphere (Table 3) and incident light intensity (Table 5), conduce to extend the autoacceleration stage to higher conversion. It also gives carbon double bonds more chance to react with free radicals, leading to higher final conversion.

3.3. Effect of generation number

The change of generation number leads to the changes of functionality and the mobility of molecules, both of which have influences on the kinetics of self-initiated photopolymerization of hyperbranched acrylates.

DPC curves for the fully acrylated hyperbranched polyesters with different generation number are shown in Fig. 6. The corresponding kinetic parameters are listed in Table 3. It is found that n value for HBA3 is slightly lower than that for HBA2 with similar degree of acrylation due to the higher functionality, as shown in Table 3. But it reverses and rises to a high value for HBA4. This can be attributed to the poorer mobility or higher viscosity of HBA with high generation number which is in favor of primary radical termination.

Autocatalytic exponent m always increases with increasing generation number. The reason is that both increase in functionality and decrease in the mobility of molecules are in favor of the autoacceleration effect.

Table 5
Kinetic parameters for self-initiated photopolymerization of HBAs at different light intensity.

I_0 (mW cm^{-2})	$R_p^{max} \times 10^2$ (s^{-1})	α_f	α_{Rm}	$k \times 10^2$ (s^{-1})	m	n
HBA2-a						
7.5	0.67	0.30	0.06	2.04	0.47	1.66
10	0.91	0.33	0.07	2.72	0.46	1.69
15	1.12	0.37	0.08	3.57	0.49	1.69
20	1.30	0.48	0.10	4.03	0.48	1.70
HBA3-a						
7.5	0.75	0.37	0.09	2.55	0.55	1.66
10	1.04	0.38	0.08	3.17	0.48	1.70
15	1.22	0.44	0.10	4.06	0.54	1.63
20	1.38	0.54	0.14	4.84	0.57	1.68
HBA4-a						
7.5	0.58	0.23	0.05	2.11	0.55	1.91
10	0.71	0.27	0.06	2.55	0.56	1.83
15	0.95	0.35	0.08	3.49	0.56	1.85
20	0.11	0.41	0.11	4.01	0.57	1.76
HBA3-b						
7.5	0.66	0.29	0.06	1.86	0.42	1.70
10	0.84	0.32	0.07	2.32	0.43	1.70
15	1.07	0.36	0.07	3.16	0.44	1.69
20	1.29	0.44	0.09	3.85	0.44	1.71
HBA3-c						
7.5	0.62	0.18	0.03	1.67	0.41	1.75
10	0.77	0.25	0.05	2.25	0.43	1.73
15	0.96	0.31	0.06	2.81	0.43	1.76
20	1.24	0.36	0.07	3.61	0.43	1.74

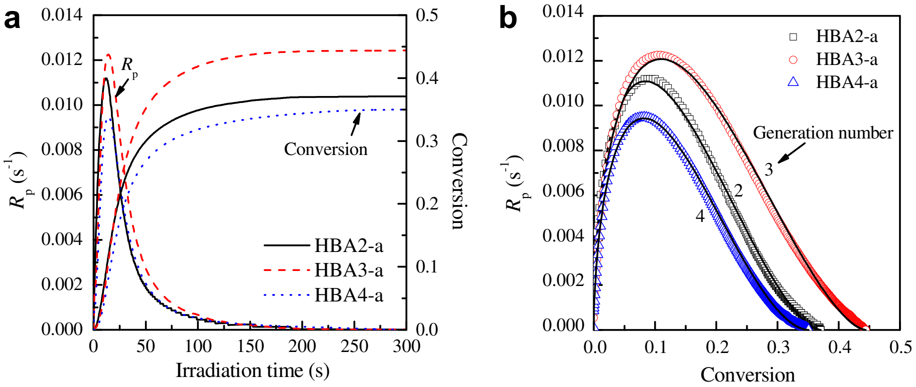


Fig. 6. Reaction rate and conversion as a function of irradiation time (a) and reaction rate as a function of conversion (b) for the self-initiated photopolymerization of hyperbranched acrylates with different generation number. The solid curves in (b) are fitting curves based on autocatalytic model. Reaction condition: 25 °C, light intensity 15 mW/cm^2, nitrogen atmosphere.

The lower rate constant k and lower final conversion α_f for HBA4 may be attributed to the higher irregularity on structure for HBA with higher generation number. As mentioned in Section 3.1, the structure of the hyperbranched polyesters is imperfect. Some functional end groups are embedded in the core. It becomes more obvious at higher generation number. The increasing polydispersity of molecular weight with increasing generation number (Table 1) also implies the higher irregularity at higher generation number. This is unfavorable to the formation of primary radicals and the propagation reaction, resulting in lower k and α_f.

3.4. *Effect of atmosphere*

The kinetic parameters for self-initiated photopolymerization of HBA3 in air atmosphere are listed in Table 3. The DPC curves of HBA3-a in N_2 and air are presented in Fig. 7 for comparison. It is found that both polymerization rate and final conversion decline in air, indicating the existence of oxygen inhibitory effect. Oxygen molecules inhibit free radical polymerizations by reacting with primary and growing chain end radicals to form peroxy radicals which are more stable and do not readily reinitiate polymerization [34]. Oxygen inhibition aggravates the insufficiency of free radicals, leading to the decrease of α_{Rm} and α_f.

The oxygen inhibitory effect is also manifested by the increase in the reaction order n (Table 3). In the presence of oxygen, the double bonds must compete with oxygen in the reaction with radicals. This increases the dependency of polymerization rate on the concentration of carbon double bonds, resulting in higher n values.

The influence of oxygen on autoacceleration effect is very limited because the oxygen inhibition does not affect polymer network mobility which is correlative to the autoacceleration effect. Thus, the m exponents for photopolymerization in air are close to those in N_2, as shown in Table 3.

In view of the lack of induction period and less reduction of final conversion, the oxygen inhibitory effect for the self-initiated photopolymerization of HBAs is not as obvious as that for the polymerization of normal monomer. Oxygen diffusion is limited due to the high starting viscosity of HBAs. High functionality is in favor of the double bonds to compete with oxygen in the reaction with radicals. High UV intensity can reduce oxygen inhibition [5]. These factors make the polymerization less sensitive to oxygen.

3.5. *Effect of temperature*

The self-initiated photopolymerization behaviors of the hyperbranched acrylates at different temperature have been tested by DPC. The results are shown in Fig. 8, taking HBA3-a as example. In all cases, both reaction rate and final conversion increase steadily as the temperature increases from 25 °C to 90 °C. The rise of temperature improves the translational diffusion of HBAs and segmental diffusion of pendant double bonds, resulting in lower dependency of reaction rate on reactant concentration, and thus

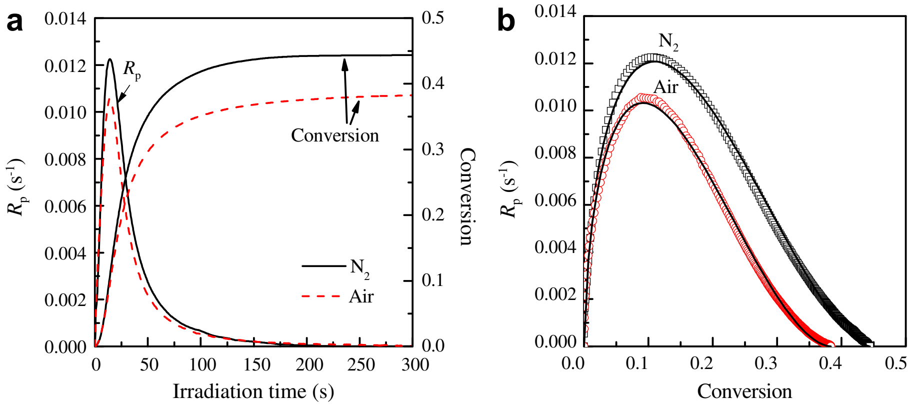


Fig. 7. Reaction rate and conversion as a function of irradiation time (a) and reaction rate as a function of conversion (b) for the self-initiated photopolymerization of HBA3-a in nitrogen or air. The solid curves in (b) are fitting curves based on autocatalytic model. Reaction condition: 25 °C, light intensity 15 mW/cm^2.

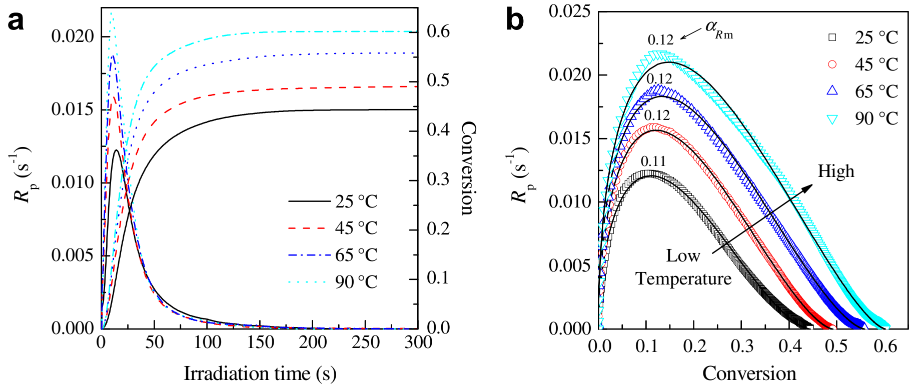


Fig. 8. Reaction rate and conversion as a function of irradiation time (a) and reaction rate as a function of conversion (b) for the self-initiated photopolymerization of HBA3-a at different temperature. The solid curves in (b) are fitting curves based on autocatalytic model. Reaction condition: light intensity 15 mW/cm^2, nitrogen atmosphere.

reduces the reaction order n, as shown in Fig. 9. The drop of reaction order n with rising temperature is the primary factor that leads to the increase in reaction rate. The increase in the diffusion of double bands with raising temperature enhances the chance of double bonds to react with free radicals, leading to higher final conversion.

Fig. 8(b) shows that the values of α_{Rm} are almost the same at different reaction temperature. This can be attributed to the insensitivity of the generation of primary radicals to temperature. In view of the sensitivity of gelation and vitrification to temperature, the result supports that the deceleration does not result from gelation or vitrification, as mentioned in (Section 3.2).

Fig. 9 also shows that the autocatalytic exponent m slightly decreases with increasing temperature. The improved diffusion of the reactive chain ends at higher temperature leads to the increase in the termination rate, resulting in less autoacceleration effect and thus lower m value. Although the decrease in m may depress the reaction rate, the effect is very limited since the change of m is inconspicuous.

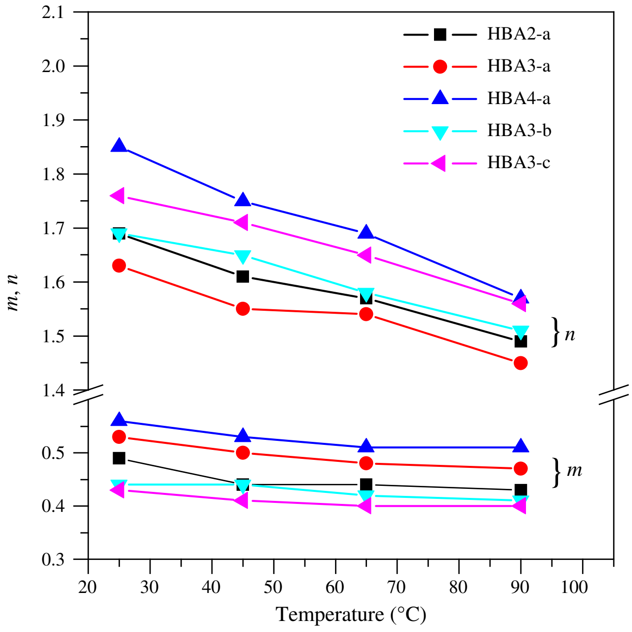


Fig. 9. Dependency of m and n on temperature for the self-initiated photopolymerization of the hyperbranched acrylates. Reaction condition: light intensity 15 mW/cm^2, nitrogen atmosphere.

The temperature dependence of rate constant k can be expressed as an Arrhenius relation:

$$k = Ae^{-E_a/RT} \tag{3}$$

where A is the pre-exponential factor, E_a the activation energy, R the gas constant and T the temperature. The activation energy can be obtained from the slope of $\ln k$ versus T^{-1} plot (Fig. 10), and the results are listed in Table 4. Values of E_a between 5.7 and 7.5 kJ mol^{-1} are found, analogous to those for the free radical photopolymerization of acrylate monomers in the presence of photoinitiator [30].

3.6. Effect of incident light intensity

The photo-induced generation of primary free radicals is relatively difficult in the absence of photoinitiator. This makes the self-initiated photopolymerization of acrylates highly depend upon the intensity of irradiation source. In most cases, light intensity up to 5 mW cm^{-2} is necessary for obtaining distinct DPC curves. We have tested the self-initiated photopolymerization behaviors of the hyperbranched acrylates by DPC, with light intensity from 7.5 to

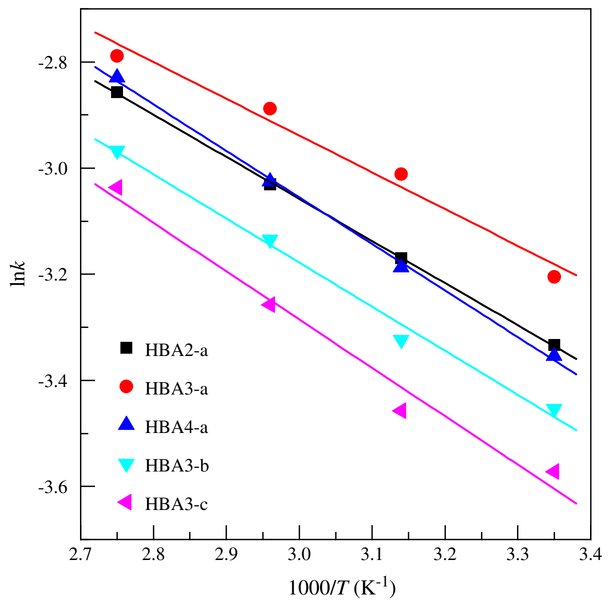


Fig. 10. Plots of ln k versus T^{-1} for the calculation of activation energy E_a.

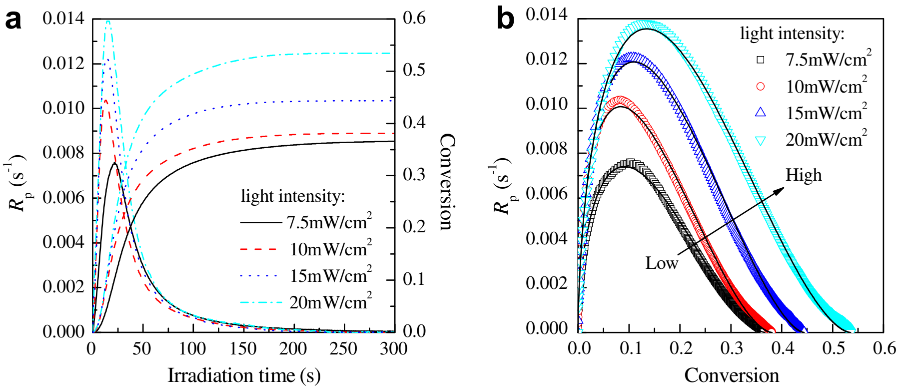


Fig. 11. Reaction rate and conversion as a function of irradiation time (a) and reaction rate as a function of conversion (b) for the self-initiated photopolymerization of HBA3-a at different light intensity. The solid curves in (b) are fitting curves based on autocatalytic model. Reaction condition: 25 °C, nitrogen atmosphere.

20 mW cm^{-2}. The results are shown in Fig. 11, taking HBA3-a as example. The related parameters are listed in Table 5. It shows that both maximum polymerization rate and final conversion enhance markedly with increasing light intensity. Rising light intensity leads to the increase in the concentration of primary radicals generated, and the direct consequence is the enhancement of polymerization rate. As mentioned in Section 3.2, the higher concentration of primary radicals extends the acceleration to higher conversion, gives carbon double bonds more chance to react with free radicals, resulting in higher final conversion.

Since the light intensity has no direct influence on the mobility of molecules and reactive species, the change of m and n with light intensity is unapparent, as shown in Table 5. In most cases, the differences of m and n at different light intensity are less than 5%. Thus, the enhancement of polymerization rate with rising light intensity is mainly the contribution of rate constant k. In consideration of the effect of light intensity on the photopolymerization of acrylates, rate constant k can be expressed as the following equation [2,31]:

$$k = k_0 I_0^b \tag{4}$$

where k_0 is a temperature dependent constant, I_0 the incident light intensity, b the light intensity exponent. The value of b is related to the termination mechanism, that is, 0.5 for bimolecular termination (second order reaction) and 1.0 for unimolecular termination (radical trapping, first order reaction). The experimental value of exponent b can be obtained from the slope of double logarithm plot of k versus I_0 (Fig. 12), and the results are listed in Table 4. Values in the range of 0.65–0.78 are obtained, suggesting that both unimolecular termination and bimolecular termination occurred in the self-initiated photopolymerization of the hyperbranched acrylates. Lower functionality gives less chance of bimolecular termination, resulting in larger value of b exponent. As a consequence, the b values are in the order HBA3-c > HBA3-b > HBA3-a.

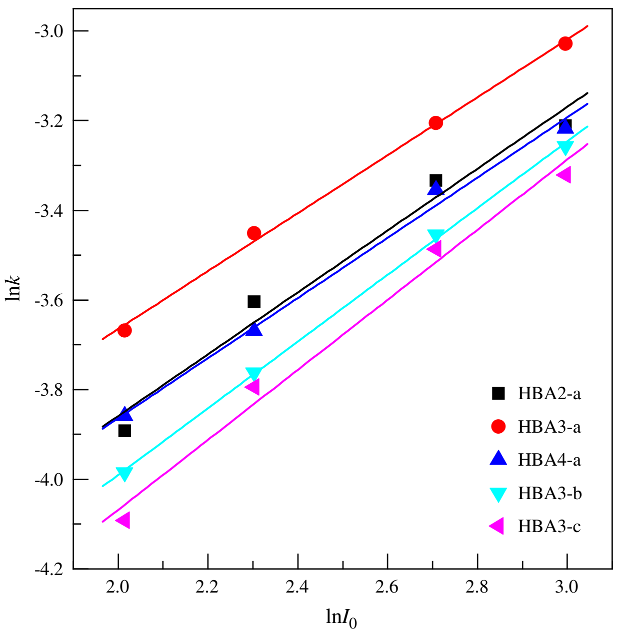


Fig. 12. Plots of ln k versus ln I_0 for the self-initiated photopolymerization of the hyperbranched acrylates.

4. Conclusions

The hyperbranched acrylates exist absorption at longer wavelength (~286 nm), which results from the overlapping of π-conjugated orbitals of acrylate groups. This makes HBAs sensitive to UV source with longer wavelength. They have exhibited the ability to self-initiate free radical photopolymerization under the irradiation of medium-pressure mercury lamps. The polymerization processes were successfully monitored by means of differential photo-calorimetry. The autocatalytic model was used to analyze the photopolymerization kinetics and found to well match the experimental data. Acceleration stage ends at low conversion ($\alpha_{Rm} < 0.11$), and the final conversion α_f is lower than 40% in most cases. This can be attributed to the poorer ability of HBAs to generate primary radicals and thus the insufficient supply of free radicals in polymerization. Factors in favor of generating primary radicals can extend the autoacceleration stage to higher conversion and give higher final conversion. The relatively high activity of hyperbranched acrylates in self-initiated photopolymerization provides a promise approach to develop photoinitiator-free photocuring system.

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