

Kinetic Study on UV-curing of Hyperbranched Polysiloxane

Guo-Bin Zhang, Xiao-Dong Fan (✉), Jie Kong, Yu-Yang Liu

Department of Applied Chemistry, School of Science, Northwestern Polytechnical University, Xi'an, 710072, P. R. China
E-mail: xfang@126.com; Fax: +86 2988474139

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Summary

Ultraviolet (UV) curing kinetics of hyperbranched polysiloxane (HBP) initiated by 2-Hydroxy-2-methyl-1-[(4-isobutyl)phenyl]-1-propanone (Trade name: IHT-PI 185) was studied by using Differential Photo Calorimeter (DPC). The effects of photoinitiator concentration, UV irradiation intensity, environment temperature and atmosphere on curing behaviors were investigated. It was found that both curing rate (R) and ultimate vinyl conversion percentage (C) first increase and then tend to stabilize within 3 wt% of photoinitiator concentration. Higher UV irradiation intensity can lead to higher values of R and C. Particularly, R is proportional to the square root of irradiation intensity at initial stage. Although raising temperature could raise the values of R and C, the effect of temperature on R is not marked. Oxygen possesses a notable inhibition effect on curing, however, induction period can be reduced by enhancing irradiation intensity. Curing kinetics was studied using Ameliorated Autocatalytic Model attaching a diffusion term. It is found that the model is suitable to describe the autocatalysis effect at the initial stage and the termination stage controlled by diffusion process. The kinetic parameters including total apparent curing exponent and apparent activation energy calculated by model above are c.a. 6 and 13.15 KJ/mol, respectively.

Introduction

Since UV-curing was regarded as a “green” technology with characters of rapid reaction rate, energy saving and less environment pollution, the extensive applications in micromolding (UV LIGA), coatings, composite materials and dental restoration were carried out [1,2]. With the development of UV-curing technology, novel UV curable resins are needed to be designed and prepared which can be cured fast and work at high temperature or under corrosive environment [3]. Organosilicon polymers have high absorption in near-UV region, and could be fast UV curing via a simple chemical modification [4]. Meanwhile, the final cured products possess excellent heat and corrosion resistance due to their unique semi-organic compositions [5].

It was well known that UV-curable resin systems usually consist of oligomers, reactive diluents and photoinitiators. The oligomers can play an important role on the

properties of the cured products. And the reactive diluents are mainly used to adjust the system's viscosity, which can often cause unexpected damage not only on the curing process controlling but also on the final properties of cured products.

Highly branched polymers, including dendritic and hyperbranched polymers, have received much attentions over the past 15 years due to their unique structures and properties. These highly branched polymers with UV curable end groups can be cured fast even with no addition of reactive diluents due to their multifunctionality and low viscosity. In our previous work, we have synthesized a hyperbranched polysiloxane containing large amount of methylacyl groups which can be fast cured under UV irradiation [6]. We also systematically characterized the fine molecular structure of this polymer. In order to further understand its UV-curing behaviors and determine its curing kinetic parameters, we decided to continue studying this polymer, especially focusing on its UV-curing behavior and kinetics.

Based on the fundamental theory of photo-initiated reactions [1], UV-curing behaviors of multifunctional resins should possess the following characters: (1) autoacceleration and gelation at initial stage; (2) diffusion controlled termination process; (3) free volume effect. Armed with these understandings we studied UV curing kinetics for hyperbranched polysiloxane via Differential Photo Calorimeter (DPC). Firstly, the effects of the external factors including photoinitiator concentration, irradiation intensity, temperature and atmosphere on polymer's curing behaviors were examined. Secondly, curing kinetic parameters were analyzed using the Ameliorated Auto-catalytic Model attaching a diffusion term.

Experimental

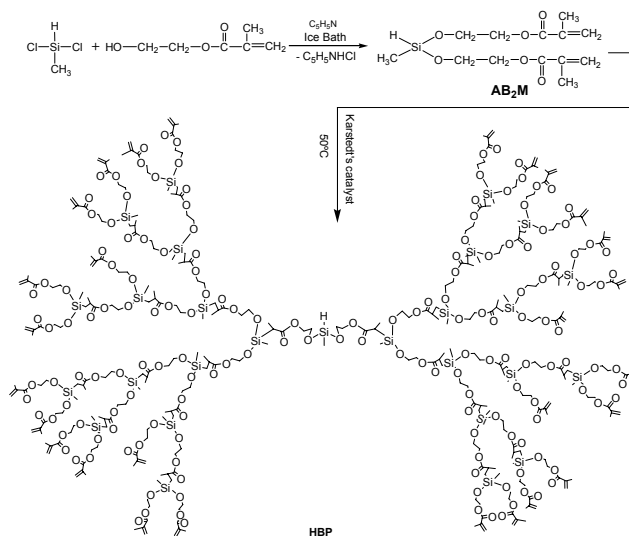
Materials and instruments

Methyldichlorosilane ($\text{CH}_3\text{HSiCl}_2$) was purchased from Xin'an Chemical Ltd. (Zhejiang Province, China) and was distilled before use. 2-Hydroxyethylmethacrylate ($\text{HOCH}_2\text{CH}_2\text{OCOC}(\text{CH}_3)\text{CH}_2$, AR) was supplied by Tangcheng Chemical Ltd. (Shanghai, China) and was used without further purification. Pyridine (AR) and hexane (AR) were purchased from Haijing Agent Plant (Tianjin city, China) and were used as received. $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ was purchased from Kaida Chemical Ltd. (Shaanxi province, China) and was transformed to Karstedt's catalyst following the reference [7]. Tetrahydrofuran (THF, HPLC grade) was purchased from Dikma Ltd. (USA). 2-Hydroxy-2-methyl-1-[(4-isobutyl)phenyl]-1-propanone (Trade name: IHT-PI 185), used as the radical photoinitiator with a purity of 91.78%, was purchased from Insight High Technology Co., Ltd, Beijing.

Differential Photocalorimeter (DPC) analysis: UV-curing enthalpy of HBP was recorded by DPC system, which consists of a Differential Scanning Calorimeter instrument (MDSC2910, Waters-TA Co., USA) and a Photo Calorimeter Accessory (PCA, Waters-TA Co., USA). UV light was transmitted from high pressure mercury lamp to the DSC furnace by dual light guides and was filtered by a broadband filter and a pair of neutral density filters (1% or 10%) to reach a desired irradiation intensity with wavelenghtes in the range of 320~500 nm. The irradiation intensity was measured at the end of the dual light guides; and the real irradiation intensity on the sample was roughly 1/10th of that recorded for diffusion through the 20 mm gap between the light guide and the sample. [8]

Preparation of hyperbranched polysiloxane (HBP)

Synthesis of hyperbranched polysiloxane (HBP) has been published in our previous work [6]. Its synthetic routes and molecular structure are shown in **Scheme 1**.



Scheme 1 Synthetic routes and molecular structures of AB₂M and HBP

Study on UV-curing behaviors of HBP

1.00 g of HBP and certain amount of photoinitiator, IHT-PI 185, were mixed and stored in dark cell for test. UV-curing curves of sample were recorded using DPC system under certain irradiation intensity in air or nitrogen atmosphere. Experimental procedures were set up as follows: first, the sample was held isothermally for 3 minutes, and then was exposed under UV irradiation for 10 minutes. After finishing the irradiation, the sample was again held isothermally for another one minute. Each sample was subjected to the same exposure procedure above for two times. The final DPC curve was obtained by subtraction of the second curve from the first one so as to eliminate the baseline shift due to a differential absorption between sample and reference. Enthalpies for samples were automatically integrated in the final DPC curve using TA Universal Analysis software.

Calculation of theoretical enthalpy, reaction rate and conversion percentage

For calculating the curing rate (R) and conversion percentage (C) from heat flow (dH/dt), the theoretical enthalpy (H_∞) which is the total enthalpy representing the consumption of all vinyl bonds should be determined first. H_∞ of AB₂M is equal to two times of quotient of theoretical molar enthalpy of methacryl groups (54.8 KJ/mol) divided by its molecular weight (302 g/mol), i.e., 363.0 J/g [10]. Because half of groups B were consumed when AB₂M was polymerized into HBP, which can be confirmed by ¹H-NMR quantitative analysis, so H_∞ of HBP is equal to the half of H_∞ of AB₂M, i.e., 181.5 J/g.

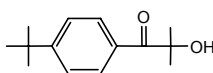
$$C = \frac{H}{H_{\infty}} \times 100\% \quad (1)$$

$$R = \frac{dC}{dt} = \frac{d \frac{H}{H_{\infty}}}{dt} = \frac{dH}{dt H_{\infty}} \quad (2)$$

where dH/dt is the value of heat flow at a certain time in the final DPC curves, H is integral value from DPC data at a certain time.

Results and Discussion

In our previous work, curing behaviors of HBP with IHT-PI 1173 have been studied. However the UV-curing rate initiated by 1173 was lower, so in this work, IHT-PI 185 was used as the photoinitiator to further study the photoinitiator's effect on system's curing rate due to its excellent initiation efficiency and good solubility. Its molecular structure is shown as **Scheme 2**.



Scheme 2 Molecular structure of photoinitiator IHT-PI 185

The typical curing curves and the corresponding integral curve are shown in **Figure 1**. With the data from the final DPC curves, the values of R and C under a fixed curing condition at any time can be calculated using equation (1) and equation (2).

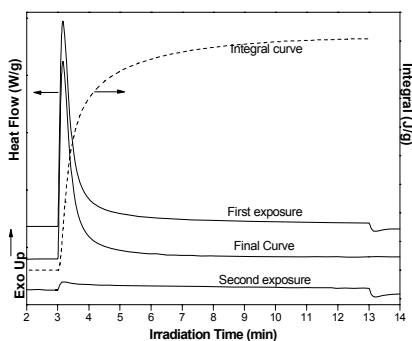


Figure 1 Typical curing curves and corresponding integral curve (HBP with 3 wt % of 185 under irradiation intensity of 41.60 mW/cm² in N₂ atmosphere at 25°C)

Effect of photoinitiator concentration

The effect of photoinitiator concentration on the values of R and C was studied using samples containing 1~7 wt% of photoinitiator and under irradiation intensity of 41.6 mW/cm² in N₂ atmosphere at 25°C. The results are shown in **Figure 2**.

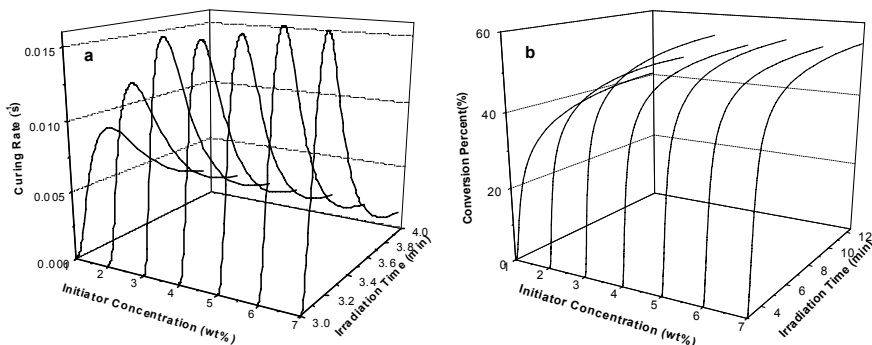


Figure 2 Effect of photoinitiator concentration on R (a) and C (b) in N₂ atmosphere

From **Figure 2**, it can be seen that both curing rate and ultimate conversion percentage increase with the increase in photoinitiator concentration up to 1~3wt%. However, with further increase in photoinitiator concentration of more than 3wt%, there exist almost no variations for both values. Classical expression for curing rate at initial stage (R_i) of multifunctional monomers can be described in equation (3) [11,12] with the steady-state assumption that initiation rate is higher than the rate of photoinitiator dissociation rate.

$$R_i = -\frac{d[M]}{dt} = \frac{k_p}{k_t^{0.5}}[M](\Phi \varepsilon I_0 [A]_0)^{0.5} \quad (3)$$

where k_p and k_t are propagation and termination reaction rate coefficients, respectively, $[M]$ is the concentration of vinyl bonds (mol/L), Φ is the quantum yield of photoinitiator, ε is the molar extinction coefficient of photoinitiator, I_0 is the incident UV irradiation intensity, $[A]_0$ is the photoinitiator concentration.

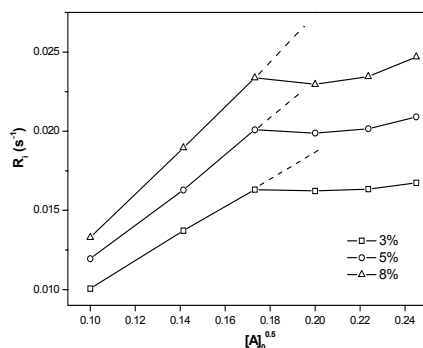


Figure 3 Curing rate versus $[A]_0^{0.5}$ in N₂ atmosphere (C=3, 5 and 8%)

Actual relationship between R_i and $[A]_0^{0.5}$ measured from the experiment is shown in **Figure 3** where the conversion percentages are equal to 3%, 5% and 8%, respectively. From **Figure 3**, it also can be seen that R_i is proportional to $[A]_0^{0.5}$ if photoinitiator concentration used is less than 3wt%, which is in accordance with equation (3). And the relationship drifts off the linearity if the initiator concentration is higher than 3wt%. These accorded well with the conclusions of other researchers including Lecamp [12], Wang [13] and Kou [14], etal.

Two factors may result in deviations from linearity if photoinitiator concentration used is more than 3wt%. One is that Φ will decrease with increasing photoinitiator concentration because Φ is reduced nonlinearly by coupling termination of initial radical A^* . The other is that increasing photoinitiator concentration can improve the reaction rate of the external layer but simultaneously can decrease the curing rate of the bottom layer. The result can be explained by free volume effect that ultimate vinyl conversion percentage varies in a similar way with the curing rate following the increase in photoinitiator concentration [11,15]. UV-curing process usually proceeds very fast, and therefore the curing system can't reach and maintain its volume equilibrium due to the lower volume shrinkage rate, which generates a temporary excess of free volume among the curing materials. The faster the curing rate is, the more free volume can be achieved. This free volume can greatly promote the mobility of reactive groups and enhance their activity. Consequently, ultimate vinyl conversion percentage first increase and then tend to stabilize within 3% of photoinitiator concentration.

Effect of irradiation intensity

Effect of irradiation intensity on the values of R and C was studied using the sample containing 3wt% of photoinitiator under irradiation intensity of 4.70 mW/cm², 9.98mW/cm², 19.40 mW/cm², 41.60 mW/cm², 61.01mW/cm², 80.42mW/cm² and 110.90mW/cm², at 25°C and in both N₂ and air atmosphere, respectively. Results are shown in **Figure 4**.

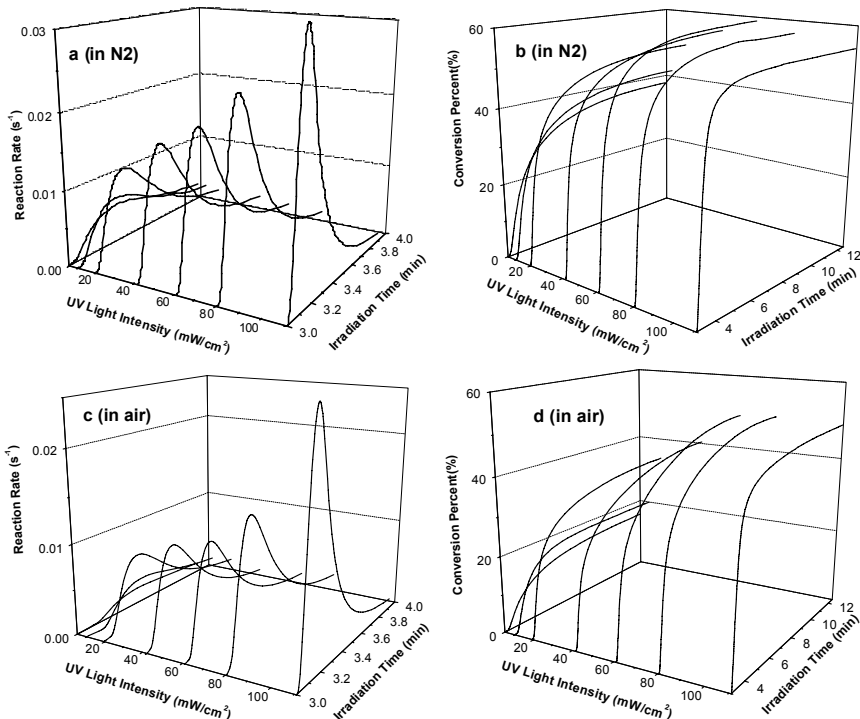


Figure 4 Effect of UV-irradiation intensity on R (a, c) and C (b, d) in both N₂ and air atmosphere

From **Figure 4**, it can be clearly seen that curing rate increases with increasing irradiation intensity up to 110.90 mW/cm^2 , while vinyl conversion percentage approaches a maximum value at irradiation intensity of 61.01 mW/cm^2 and then hardly varies. The results can be explained by the fact that UV-curing process is very sensitive to irradiation intensity, which controls the formation of primary radicals, and correspondingly dominates the curing rate. According to equation (3), the relationship between R_i and $I_0^{0.5}$ should be linear. Actual relationship between R_i and $I_0^{0.5}$ is shown in **Figure 5** where conversion percentages are reached to 3%, 5% and 8%. Obviously, R_i is proportional to $I_0^{0.5}$, which is in accordance with equation (3).

According to the free volume effect, the value of C should be improved with increase in irradiation intensity. But under intense UV irradiation ($>60.01 \text{ mW/cm}^2$), the value of C hardly varies, which should be further studied.

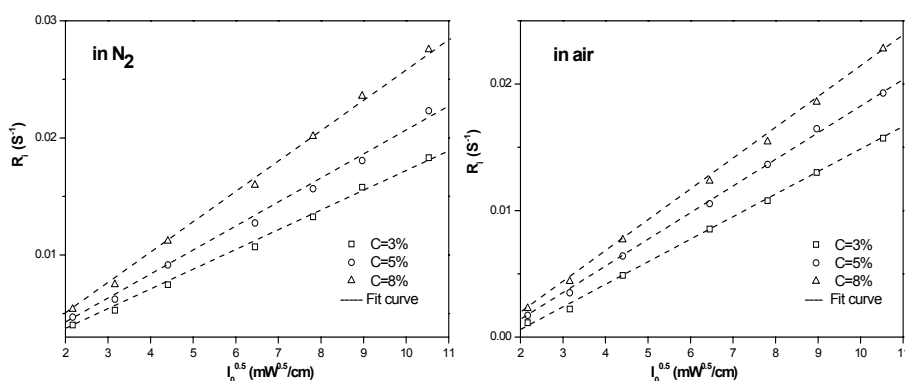


Figure 5 Curing rate versus $I_0^{0.5}$ in N_2 and in air atmosphere ($C=3, 5$ and 8%)

Effect of temperature

Effect of temperature on the values of R and C was studied using the sample containing 3 wt% of photoinitiator at 0°C , 25°C , 50°C and 75°C under irradiation intensity of 61.01 mW/cm^2 , in N_2 or air atmosphere, respectively. Results are shown in **Figure 6**.

From **Figure 6**, it can be seen that increasing temperature can simultaneously raise the values of R and C . Temperature mainly affects curing rate constant k and correspondingly affects curing rate, which can be confirmed by **Table 1**. Arrhenius type curing rate constant, k , can be expressed as equation (4).

$$k = A e^{-E_a/RT} \quad (4)$$

where A is preexponential factor, s^{-1} ; E_a is the apparent activation energy, KJ/mol ; R is the universal gas constant, $R=8.314 \text{ J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$.

Unlike heat-curing reaction, the effect of temperature on UV-curing rate is not marked. The maximum curing rate only increases by about onefold to twofold when curing temperature was raised from 0 to 75°C , as seen in **Figure 6**. This may be attributed to the fact that the decomposition rate of photoinitiator is not dependent on temperature, and the activation energy for UV-curing is relatively small [11]. The apparent activation energy of UV-curing for HBP is calculated as 13.15 KJ/mol (see

in section 3.6), so from equation (4), it can be concluded that k value for UV-cured system can increase a little but k value for heat-cured system can increase about 1~3 times if the temperature increases by 10°C.

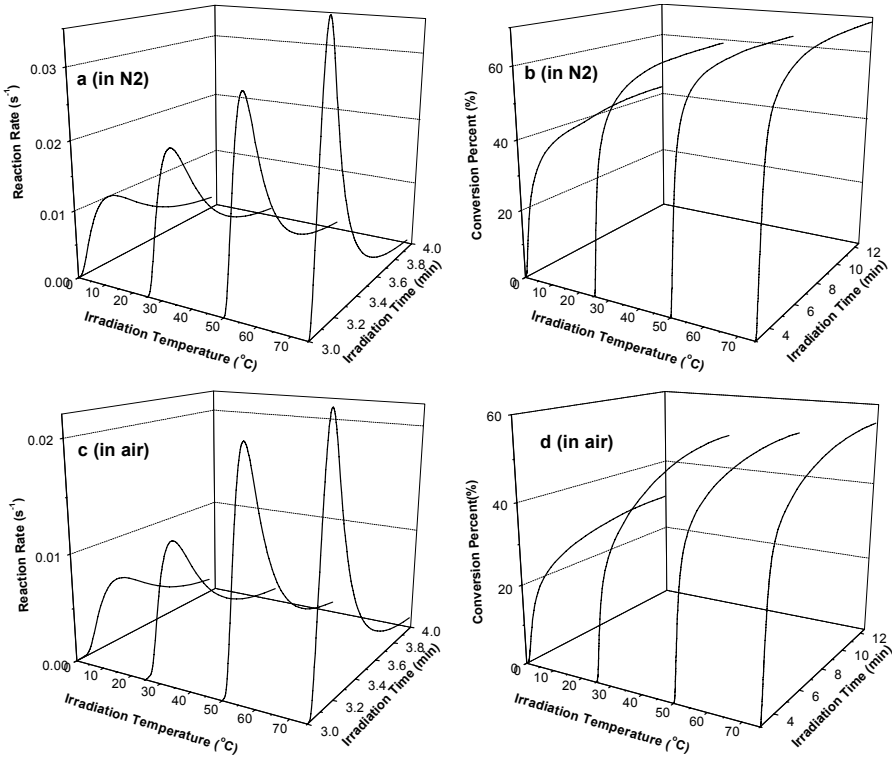


Figure 6 Effect of temperature on R (a, c) and C (b, d) in N₂ and air atmosphere

However, ultimate conversion percentage increases with the increase in temperature, this is mainly attributed to that higher temperature can reduce the system's viscosity and promote the mobility of vinyl groups and radicals, and correspondingly increases the ultimate air conversion percentage.

Effect of oxygen

Effect of oxygen on the values of R and C was also examined by comparing the results in N₂ and air atmosphere using the same sample under the same curing condition. A typical result is shown in **Figure 7**, and the tests were conducted at 25°C and with 3 wt% of photoinitiator under irradiation intensity of 19.4 mW/cm².

When curing in air, it was found that a very thin facial layer of the sample could not be cured even irradiating for 20 minutes. Obviously, there existed an apparent induction period for curing in air. Both the values of R and C were lower compared to that in N₂ atmosphere, as seen from **Figure 7**. This is because oxygen exerts a detrimental effect on production of free radicals. The oxygen can quench excited triplet states of photoinitiator to reduce their quantum yield. In addition, oxygen can

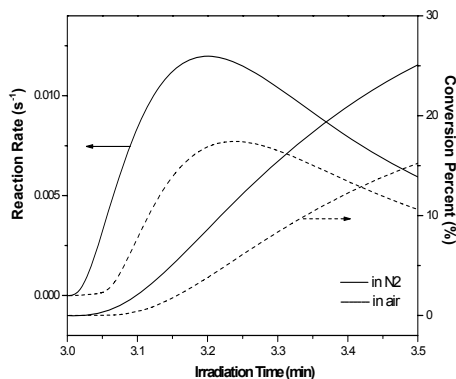


Figure 7 Comparison of curing behaviors in N_2 and air atmosphere

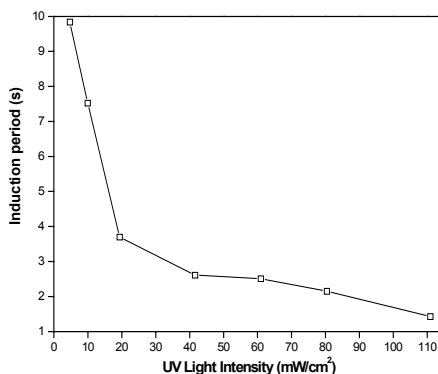


Figure 8 The curve of induction period versus I_0

also react with the carbon-based polymer radicals to form peroxy radicals whose reactivity is much less towards vinyl bonds. All these can effectively offset the efficiency of initiation of radicals [1]. However, the induction periods can be reduced drastically following increasing irradiation intensity up to 41.60 mW/cm^2 , and then tend to approach equilibrium, as seen in **Figure 8**. The result may be attributed to photoinitiator decomposing quickly under the intense UV irradiation.

Determination of kinetic parameters

Kinetic parameters were determined through the isothermal DPC data at different temperatures. Curves of R versus C in different temperatures under irradiation intensity of 61.01 mW/cm^2 in N_2 or air atmosphere are shown in **Figure 9**.

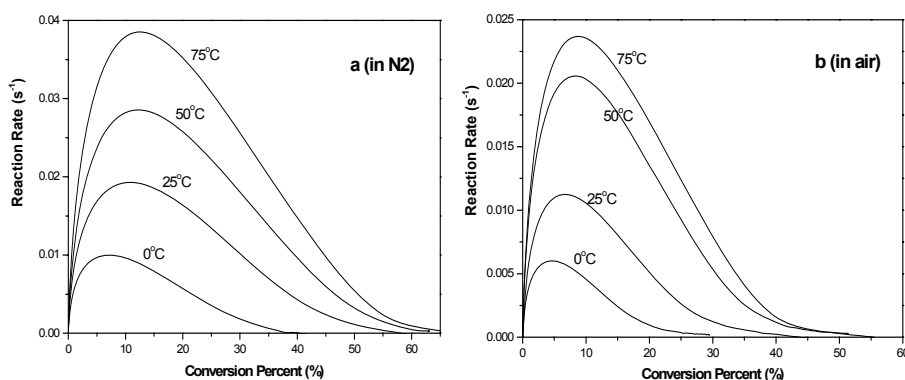


Figure 9 Curves of R versus C at different temperatures in N_2 (a) and air atmosphere (b)

From **Figure 9**, it can be seen that the maximum curing rate at the different temperature can be reached in the range of 8 to 15% of conversion percentage. All of them are similar to a typical autocatalytic reaction. And also clearly, all the UV curing processes are diffusion controlled at the last stage [16]. So, the autocatalytic kinetic

model attaching a diffusion term (see in equation (5)) can be employed to study the kinetics for this system [17].

$$R = \frac{dC}{dt} = kC^m(1-C)^n \frac{1}{1 + \exp[p(C-q)]} \tag{5}$$

where k is the Arrhenius type rate constant (see in equation (4)); n is the reaction order exponent and m is the autocatalytic exponent; α represents the total apparent curing exponent so α is equal to $n+m$; $1/\{1+\exp[p(C-q)]\}$ is the diffusion term, whose value is between 0.5 and 1.0 if $C < q$ and becomes zero if $C > q$.

Table 1 Kinetic parameters of UV curing of HBP using 3wt% IHT-PI 185 under irradiation intensity of 61.01 mW/cm²

Atmosphere	Temperature (°C)	K (s ⁻¹)	m	n	p	q	α	Average of α
In N ₂	0	0.0689	0.53	5.37	12.33	0.27	5.90	5.74
	25	0.1090	0.55	5.22	11.30	0.42	5.77	
	50	0.1620	0.57	4.96	12.25	0.49	5.53	
	75	0.2341	0.60	5.14	17.56	0.53	5.74	
In air	0	0.0498	0.51	5.48	17.30	0.12	5.99	5.76
	25	0.0795	0.53	5.39	12.17	0.21	5.92	
	50	0.1189	0.52	5.01	13.51	0.30	5.53	
	75	0.1825	0.60	4.98	9.95	0.30	5.58	

Kinetic parameters k , m , n , p and q were calculated using Software Matalab 7.1 via fitting the DPC data to equation (5), as shown in **Table 1**.

Curves of C versus irradiation time are presented in **Figure 10**. As can be seen, the experimental data and calculation curves are well fitted at different temperatures which indicates that the autocatalytic model is indeed suitable to describe the UV curing kinetics for this system.

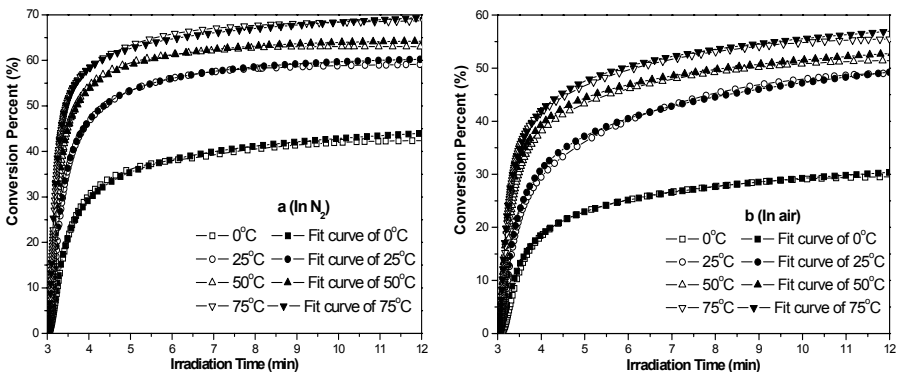


Figure 10 Curves of C versus time from kinetic equations and experimental in N₂ and air atmosphere

Apparent activation energy can be calculated through the relationship of k versus T . According to equation (5), $\ln k$ should be proportional to $1/T$, so curve of $\ln k$ versus

$1/T$ can be fitted into a straight line, whose slope and intercept are equal to $-E_a/R$ and $\ln A$, respectively (**Figure 11**). From **Figure 11**, fit equations are almost the same in both N_2 and air, which indicates that atmosphere may have no marked effect on values of E_a and A . So the average values in two atmospheres are taken as E_a and A for HBP of UV-curing, i.e., $E_a=13.15$ KJ/mol and $A=18.4$ s $^{-1}$.

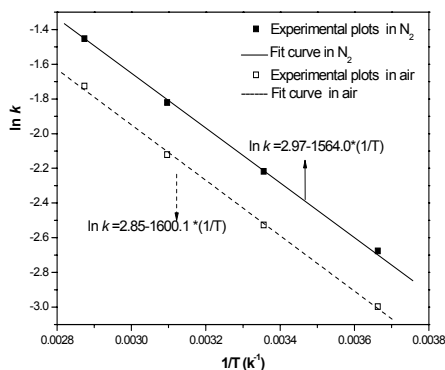


Figure 11 Relationship between $\ln k$ and $1/T$

Conclusions

UV curing behaviors and kinetics of hyperbranched polysiloxane with IHT-PI 185 as the photoinitiator were studied using a Differential Photo Calorimeter (DPC). It is found that both the value of R and C first increase and then tend to stabilize within 3 wt% of photoinitiator concentration. Raising UV irradiation intensity and temperature can lead to higher values of R and C . Oxygen possesses a notable inhibition effect on curing, however, induction period can be reduced by enhancing irradiation intensity. Kinetics were studied using an Ameliorated Autocatalytic Model attaching a diffusion term. The total apparent curing exponent α is calculated by the autocatalytic model to be about 6, and apparent activation energy is obtained to be 13.15 KJ/mol.

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