Synthesis and UV curing kinetics of rapidly UV-curable hyperbranched polycarbosiloxanes

Sheng-Jie Wang, Xin Liu, Jie Kong, Wei Tian, Xiao-Dong Fan, Hai Xu and Jian-Ren Lu

Abstract

Hyperbranched polycarbosiloxanes with peripheral photo-crosslinkable groups were synthesized through controllable hydrosilylation reaction from A2-type and CB3-type monomers. The polymerization of the monomer pairs was monitored using Fourier transform infrared spectroscopy, from which it was found that vinyl silane and methacrylate groups reacted with hydride silane from the beginning of the reaction. The results thus suggest a step-by-step polymerization rather than a two-step process for this system. The polycarbosiloxanes could be cured rapidly in either nitrogen or air atmosphere, this feature making them attractive for potential application as precursors of advanced ceramic devices with complex structures. The effects of light intensity, reaction temperature and atmosphere on the UV curing rate (Rp) and conversion (α) of the photo-crosslinkable groups were characterized carefully, and the curing kinetics was also investigated systematically. The results show that Rp and α increased with an increase of light intensity or temperature, and that the inhibiting effect of oxygen in air could be suppressed by enhancing the irradiation intensity.© 2010 Society of Chemical Industry

Keywords: hyperbranched; polycarbosiloxane; A2 + CB3 approach; UV curing kinetics

INTRODUCTION

Hyperbranched polymers have been the subject of much development over the past 20 years due to their unique physical and chemical properties and their ease of preparation. Many of them show attractive benefits in coatings, additives, catalysts, drug and gene delivery, nanotechnology and supramolecular science. However, a major drawback for hyperbranched polymers from ABn monomers is the lack of control over molecular weight and degree of branching, which in turn limits their value in certain applications. Fortunately, recently developed synthetic approaches including couple monomer methodology (CMM) and core resolution/slow addition techniques have been successfully employed to control molecular weight and reduce polydispersity. In particular, the CMM approach, including A2 + B′Bx, A2 + CBx (x ≥ 2), AA′ + B3 and other related techniques, is advantageous over traditional ABn monomer methods, such as facile preparation of monomers and control of molecular weights of the resultant polymers. Many hyperbranched polymers, such as poly(sulfone amine), poly(ester amine), poly(urea urethane)s, poly(amine ester)s and polyesters, and hyperbranched copolymers have been obtained through the CMM approach. However, so far, only limited investigations of hyperbranched organosilicon polymers obtained via this controllable approach have been reported. Preparation of high-performance ceramics via the pyrolysis of organosilicon precursors including polysilazane, polycarbosilazane and polycarbosilane is a powerful approach. Compared with commonly used linear organosilicon precursors, their hyperbranched analogues seem to be more promising, due to their low viscosity, excellent solubility and penetrability, and numerous active end groups (that allow further functionalization). We have recently synthesized hyperbranched organosilicon precursors with vinyl silane or allyl silane end groups. Furthermore, in those studies, we examined their UV curing properties, and explored their potential in ceramic devices with complex structures via the combination of UV curing coupled with open molding techniques. Interestingly, the results showed that even with high concentrations of photoinitiator or curing at high temperature, the photo-crosslinking rates of these precursors were evidently lower than those of other typical UV-curable polymers, such as polyacrylates and polymethacrylates. Introducing active diluents into these polymers is an effective way to improve their UV curing rates. However, these systems are inhomogeneous at the molecular level and the ceramic yields decrease with increasing concentrations of active diluents. We have thus continued our efforts through extensive exploration of the curing conditions under UV irradiation and, more importantly, kept the systems homogeneous by...
introducing new designed hyperbranched organosilicon polymers with functional curing groups.

In the work reported in this paper, we designed and synthesized CB3-type monomers, and then prepared hyperbranched polycarbosiloxanes via the hydrosilylation of A2- and CB3-type monomers, where A is a hydride silane, B represents methacrylate or acrylate and C represents vinyl silane groups. Owing to their peripheral methacrylate groups, these new hyperbranched polymers can be cured rapidly in either nitrogen or air atmosphere, without the need to add any active diluents. The effects of reaction temperature, atmosphere and light intensity on the curing behavior were also examined in order to optimize the experimental conditions. The information gained from this study forms a useful basis for the generation of high-performance ceramics, particularly towards developing complex ceramic devices using the combination of UV curing and the open molding process.

EXPERIMENTAL

Materials

Vinyltrichlorosilane (>99%) was obtained from the Research Center of New Silicone Materials of Wuhan University, China. 2-Hydroxyethyl acrylate and 2-hydroxyethyl methacrylate were purchased from Xi’an Organic Chemical Reagents Corporation, China. Chloroplatinic acid (39 wt% platinum) was provided by Shanghai KaiDa Chemical Ltd, China. 4-Dimethylaminopyridine was obtained from Zhejiang Jintan Chemical Plant, China. Pyridine (AR grade), tetrahydrofuran (AR grade), hexane (AR grade) and other solvents were obtained from Tianjin Kermel Chemical Reagents Co., Ltd, China. Butylated hydroxytoluene (IHT-PI 185) was received from Insight Materials Center of New Silicone Materials of Wuhan University, China. Pyridine (AR grade), tetrahydrofuran (AR grade), hexane (AR grade) and other solvents were obtained from Tianjin Kermel Chemical Reagents Development Center in China. 2-Hydroxy-2-methyl-1-(4-tert-butyl)phenylpropane-1-one (IHT-PI 185) was received from Insight Materials Center of New Silicone Materials of Wuhan University, China. All solvents and silane monomers were distilled and dried with 4 Å molecular sieves before use.

Instrumentation

Fourier transform infrared (FTIR) spectra were recorded with a WQF-310 model, Ruili Co., Beijing, China, using KBr as the sample holder and substrate. The scanning range was set from 4000 to 400 cm⁻¹.

Synthesis

Synthesis of M4

2-Hydroxyethyl methacrylate (41.64 g, 0.32 mol), pyridine (25.31 g, 0.32 mol), 4-dimethylaminopyridine (0.15 g) and hexane (100 mL) were charged into a three-necked flask equipped with an addition funnel, a mechanical stirrer and a nitrogen inlet. The flask was then cooled in an ice bath. A mixture of vinyltrichlorosilane (12.8 mL, 0.10 mol) and hexane (25 mL) was added into the flask at a rate of 15 drops per minute, and then the reaction was kept for 30 min at 0 °C, followed by stirring for 6 h at 15 °C. The precipitate was filtered and the filtrate was washed with water four times. The organic phase was dried with anhydrous magnesium sulfate overnight, followed by solvent evaporation. The resulting monomer M4 (vinylsilanilatriris(oxy)(oxy)(ethane-2,1-diyl) trimethacrylate) was obtained as a colorless liquid (M = 442.53 g mol⁻¹, yield = 53%).

FTIR (KBr; cm⁻¹): 3106, 3061 (ν(CH–CH=CH2–), 2955 (ν(CH3–CH2–), 2886 (ν(CH2–CH2–), 1725 (ν(C=C, methacrylate), 1639 (ν(C=O, vinyl), 1300 (ν(C–O–COO). 1H NMR (CDC3: δ, ppm): 6.13, 5.58 (CH2=CH(CH3)–COO–, 6H), 5.86–6.01 (CH2=CH–Si–3H), 4.24 (–COOCH2CH2–O–Si–3H), 4.01 (–COOCH2CH2–O–Si–3H), 1.94 (CH2=CH(CH3)–COO–, 9H). GC-MS (EI): purity >95%, m/z 441.7 (M – H)⁺. Element analysis: calc'd for C20H30SiO9: C 54.28%, H 6.83%; found: C 54.37%, H 6.80%.

Synthesis of M5

Monomer M5 (vinylsilanilatriris(oxy)(oxo)(ethane-2,1-diyl) triacrylate) was synthesized as a colorless liquid from 2-hydroxyethyl acrylate and vinyltrichlorosilane using a similar route to that of M4 (M = 400.46 g mol⁻¹, yield = 48%).

FTIR (KBr; cm⁻¹): 3108, 3064, 3039 (ν(CH–CH=CH2–), 2954 (ν(CH3–CH2–), 2887 (ν(CH2–CH2–), 1729 (ν(C=C, acrylic), 1638 (ν(C=O, vinyl), 1601 (ν(C=C, vinyl), 1300 (ν(C–O–COO). 1H NMR (CDC3: δ, ppm): 6.26–6.32, 5.70–5.73 (CH2=CH–COO–, 6H), 6.01–6.06 (CH2=CH–COO–, 3H), 5.75–6.00 (CH2=CH–COO–, 3H), 4.13–4.16 (–COOCH2CH2–O–Si–3H), 3.87–3.90 (–COOCH2CH2–O–Si–3H), GC-MS (EI): purity >96%, m/z 399.6 (M – H)⁺. Element analysis: calc'd for C21H34SiO9: C 50.99%, H 6.04%; found: C 51.07%, H 6.09%.

Synthesis of A2

1,1,3,3-Tetramethyldisiloxane (A2) was synthesized as a colorless liquid (b.p. 70 °C at atmospheric pressure) from the hydrolysis of dimethyldichlorosilane.

FTIR (KBr; cm⁻¹): 2957 (νas(CH3–), 2136 (νs–Si–H), 1261 (δs–Si–CH2–), 1080 (νs–Si–O–Si–). 1H NMR (CDC3: δ, ppm): 4.73–4.75 (–Si–H, 2H), 0.22–0.25 (–Si–CH3, 12H). 13C NMR (CDC3: δ, ppm): 78.21 (Si–CH3, 4C). 29Si NMR (CDC3: δ, ppm): –4.74. GC-MS (EI): purity >97%, m/z 133 (M – H)⁺. Element analysis: calc'd for C2H4Si2O: C 35.82%, H 10.45%; found: C 35.86%, H 10.41%.

Synthesis of P5

A2 (1.34 g, 0.01 mol), M4 (4.43 g, 0.01 mol) and 5 mg of Karstedt catalyst (a platinum–divinyltetramethyldisiloxane complex, which
was prepared according to a previous description\textsuperscript{23} were charged into a 50 mL flask under vigorous stirring. The reaction was conducted at 35 °C in air atmosphere, and monitored using FTIR spectroscopy. The reaction was stopped after no Si–H absorption was detected from FTIR spectra (about 7 h). The product was dissolved in 5 mL of ether and purified three times via methanol precipitation, followed by solvent evaporation. Finally, the hyperbranched polycarbosiloxane P\textsubscript{a} was obtained as a viscous liquid (yield = 56%).

FTIR (KBr; cm\textsuperscript{-1}): 3106 (\textnu=C–H, methacrylate), 2957 (\textnu=CH=CH\textsubscript{2}), 2882 (\textnu=CH\textsubscript{2}=CH\textsubscript{2}), 2838 (\textnu=CH\textsubscript{2}=CH\textsubscript{2}), 1722 (\textnu=C=O), 1640 (\textnu=C=O), 1454 (\delta=CH\textsubscript{2}), 1255 (Si–CH\textsubscript{3}). \textsuperscript{1}H NMR (CDCl\textsubscript{3}; δ, ppm): 6.10, 5.54 (CH=CH\textsubscript{2}), 4.22 (COOCH\textsubscript{2}CH\textsubscript{2}–O–Si), 3.96 (–COOCH\textsubscript{2}CH\textsubscript{2}–O–Si), 2.53 (Si–CH\textsubscript{2}–CH(CH\textsubscript{3})–COO–, \beta-addition product), 1.89–1.91 (CH\textsubscript{2}=C(CH\textsubscript{3})–COO–, 1.12–1.17 (Si–CH\textsubscript{2}–CH(CH\textsubscript{3})–COO–, \alpha-addition product; Si–CH\textsubscript{2}–CH(CH\textsubscript{3})–COO–, \beta-addition product), 1.03–1.05 (Si–CH(CH\textsubscript{3})–, \alpha-addition product), 0.62–0.72 (Si–CH\textsubscript{2}–CH(CH\textsubscript{3})–COO–, \beta-addition product), 0.50–0.52 (Si–CH\textsubscript{2}–CH(CH\textsubscript{3})–COO–, \beta-addition product), 0.00–0.12 (Si–CH\textsubscript{3}). \textsuperscript{13}C NMR (CDCl\textsubscript{3}; δ, ppm): 166.78 (C=O), 135.98 (CH\textsubscript{2}=C(CH\textsubscript{3})–COO–), 125.27 (CH\textsubscript{2}=C(CH\textsubscript{3})–COO–), 65.18 (COOCH\textsubscript{2}CH\textsubscript{2}–O–Si), 60.81 (COOCH\textsubscript{2}CH\textsubscript{2}–O–Si), 34.65 (Si–CH\textsubscript{2}–C(CH\textsubscript{3})–COO–) 33.47 (Si–CH\textsubscript{2}–CH(CH\textsubscript{3})–COO–, 19.32 (Si–CH\textsubscript{2}–CH(CH\textsubscript{3})–COO–, 1.89–1.91 (CH\textsubscript{2}=C(CH\textsubscript{3})–COO–, 7.17 (Si–CH\textsubscript{2}–CH(CH\textsubscript{3})–COO–), –0.71 (Si–CH\textsubscript{3}).

Synthesis of P\textsubscript{b}

Similar to the synthesis of P\textsubscript{a}, the hyperbranched polycarbosiloxane P\textsubscript{b} was also synthesized using equal molar amounts of monomers of A\textsubscript{2} and M\textsubscript{b}.

FTIR (KBr; cm\textsuperscript{-1}): 3104 (\textnu=C–H, acrylate), 2959 (\textnu=CH\textsubscript{2}=CH\textsubscript{2}), 2882 (\textnu=CH\textsubscript{2}=CH\textsubscript{2}), 1717 (\textnu=C=O), 1639 (\textnu=C=O), 1454 (\delta=CH\textsubscript{2}), 1256 (Si–CH\textsubscript{3}). \textsuperscript{1}H NMR (CDCl\textsubscript{3}; δ, ppm): 6.03, 5.48 (CH\textsubscript{2}=CH–COO–), 5.76 (CH\textsubscript{2}=CH–COO–), 4.15 (COOCH\textsubscript{2}CH\textsubscript{2}–O–Si), 3.91 (COOCH\textsubscript{2}CH\textsubscript{2}–O–Si), 2.47 (Si–CH\textsubscript{2}–CH(CH\textsubscript{3})–COO–, \beta-addition product), 1.06–1.08 (Si–C(CH\textsubscript{3})–COO–, \alpha-addition product; Si–CH\textsubscript{2}–CH(CH\textsubscript{3})–COO–, \beta-addition product), 0.97–1.00 (Si–CH(CH\textsubscript{3})–, \alpha-addition product), 0.76 (Si–CH\textsubscript{2}–CH(CH\textsubscript{3})–COO–, \beta-addition product), 0.46 (Si–CH\textsubscript{2}–CH\textsubscript{2}, \beta-addition product), –0.06–0.02 (Si–CH\textsubscript{3}).

Thermal properties of hyperbranched polycarbosiloxanes

Samples for DSC tests were prepared according to the following procedure. An amount of 10 mg of hyperbranched polycarbosiloxane sample containing 4 wt% photoinitiator was added into an uncovered aluminium pan, and irradiated at 20 °C for 10 min with a light intensity of 39 mW cm\textsuperscript{-2}. The specimens were then kept at 150 °C for 3 min to eliminate the heat history, and then cooled. After equilibration at –60 °C, the specimens were heated to 150 °C at a heating rate of 15 °C min\textsuperscript{-1}, and thus DSC curves were obtained. Note that both UV curing and DSC testing were performed under nitrogen atmosphere. Samples for TGA were obtained using a similar procedure but without pre-heating treatment after UV curing.

RESULTS AND DISCUSSION

Synthesis of monomers

The molecular structures of the monomers are shown in Scheme 1. Their syntheses are described above. The application of pyridine as HCl absorbent and 4-dimethylaminopyridine as catalyst can favor SiCl/–OH condensation due to their strong nucleophilicity and thereby decrease unwanted products.\textsuperscript{19,26} As alcoholysis is an exothermic reaction during the synthesis of CB\textsubscript{3}-type monomers, it is very necessary to control the reaction rate to prevent other side reactions from occurring. As shown in the FTIR spectrum of M\textsubscript{a} (Fig. 1), there are typical absorption peaks of methacrylate

\begin{scheme}
\centering
\includegraphics[width=0.8\textwidth]{Scheme1.png}
\caption{Polymerization mechanism of A\textsubscript{2}-type and CB\textsubscript{3}-type monomers.}
\end{scheme}
Figure 1. FTIR spectra of A2, M2 and Pa.

Figure 2. Conversions of reactive groups during the polymerization of A2 and M2.

Figure 3. $^{29}$Si NMR spectrum of Pa.

(1725 and 1639 cm$^{-1}$ for C=O and C–C, respectively), but no absorption of hydroxyl group over the range 3300–3600 cm$^{-1}$, indicating that there is no 2-hydroxyethyl methacrylate in the product. The chemical shift near 4.01 ppm (Si–O–CH$_2$OCO–) in the $^1$H NMR spectrum demonstrates that methacrylate groups are linked successfully to silicon atoms. Similarly, both M2 and A2 were also effectively synthesized, as manifested from the spectral analysis.

Polymerization of A2- and CB3-type monomers

In the presence of the Karstedt catalyst, the polymerization of A2- and CB3-type monomers was carried out via bulk polymerization and monitored using FTIR spectroscopy, from which the changes of double bonds in vinyl (1601 cm$^{-1}$), methacrylate (1639 cm$^{-1}$) and hydride silane (2136 cm$^{-1}$) groups can be observed. The spectra were normalized using the C=O band (1725 cm$^{-1}$) as an internal standard to offset variations in sample thickness. Therefore, the conversion of functional groups can be calculated according to

\[
\text{Conversion (\%)} = \frac{A_0 - f A_t}{A_0} \times 100
\]  

where $A_0$ is the area of the original absorption peak of the functional groups, $A_t$ is the peak area reacted over time period $t$ and $f$ is the correction factor that is in inverse proportion to the sample thickness.

The conversions of functional groups of hydride silane and the double bonds in vinyl and methacrylate groups against time for the reaction of equivalent A2 and M2 are shown in Fig. 2. Both vinyl and the double bonds in methacrylate groups can react with hydride silane from the beginning of the reaction until the vinyl silane groups are used up (ca 180 min). This observation is obviously different from previous reports, in which vinyl silane was completely reacted with hydride silane during the first 12 min prior to hydrosilylation of other functional groups.$^{14,27}$ As a result, we cannot picture the reaction in terms of the two-step reaction model proposed previously,$^{11}$ but presume a step-by-step mode (shown in Scheme 1) to describe the complex polymerization process of A2 and M2 in this reaction system. There are three methacrylates and just one vinyl group in the CB3-type monomers. The concentration of the vinyl groups is comparatively low. In contrast, there are seven atoms in the backbone of each methacrylate group, which not only increases the steric hindrance of the vinyl group but also increases the probability of entrapment in the cage of the methacrylate groups. These situations could reduce the reaction rates of vinyl silane and increase the rates of methacrylate group on a relative basis, reducing the gap of hydrosilylation rates between vinyl silane and methacrylate groups. This may well be the reason for the change of polyaddition mode. It should be noted, however, that the vinyl silanes still show higher hydrosilylation activity than the methacrylate groups, which might explain why the resultant product is a soluble polymer rather than a gel. In addition, a similar polymerization mode can be expected in the hydrosilylation reaction of another CB3-type monomer (M3) with A2.

Characterization of hyperbranched polycarbosiloxanes

FTIR spectra of M2, A2 and their resultant polymer, P2, are shown in Fig. 1 for comparison. In the FTIR spectrum of the polymer, we still observe the absorption bands of the double bonds (1640 cm$^{-1}$) and the unsaturated hydrogen (3106 cm$^{-1}$) in methacrylate groups, while the absorption bands of hydride silicon groups (2136 cm$^{-1}$), double bonds (1601 cm$^{-1}$) and unsaturated hydrogen (3061 cm$^{-1}$) in vinyl groups are completely absent. Furthermore, from the $^1$H NMR and $^{13}$C NMR measurements, we can conclude that vinyl and hydride silane groups participated in the reaction and that polycarbosiloxanes with methacrylate end groups are finally obtained.

The $^{29}$Si NMR spectrum of P2 (Fig. 3) shows two chemical shifts centered at 7.97 and $-44.60$ ppm. According to work previously reported,$^{14,27,28}$ they can be assigned to the chemical shifts of silicon atoms bonded with one and three oxygens, resulting from the original monomers A2 and M2, respectively. The integration ratio of the two chemical shifts is 1:0.52, which is in agreement with the feeding ratio of silicon atoms in the two monomers (1:0.5). In
addition, there may be more than one structure for the chain unit of one silicon atom linked to the three oxygen atoms, containing three (terminal unit), two (linear unit), one (semi-dendritic unit) or zero (dendritic unit) methacrylate groups for the same silicon atom. However, their chemical shifts in the $^{29}$Si NMR spectrum are overlapped due to their very similar structures. Thus we cannot obtain the degree of branching of the polymer directly from its $^{29}$Si NMR spectrum in this case.

SEC-MALLS, refractive index and viscosity measurements were used to obtain the exact molecular weights and other molecular parameters of the hyperbranched polycarbosiloxanes. The refractive index increments (dn/dc) of the polymers were determined using refractive index detection, and $M_w$ was measured using MALLS. Other molecular parameters in solution, including intrinsic viscosity, hydrodynamic radius and Mark–Houwink (MH) parameters, were also obtained, and the results are listed in Table 1. Note that these parameters are just statistical averages because the polymers are composed of various sizes and structures.

The MH equation describes the relationship between intrinsic viscosity and molecular weight of a polymer, and can be used to characterize the hyperbranched polymers because the exponent $\alpha$ in the MH equation depends on their molecular structure.29–33 For a random coil, $\alpha = 0.5 – 0.7$; and $\alpha$ is greater than 1 for an elongated rod. In contrast, $\alpha < 0.5$ for hyperbranched polymers. From Table 1 it can be seen that the exponent $\alpha$ for the resultant polycarbosiloxanes is below 0.50, indicating rather dense molecular arrangements corresponding to the hyperbranched structures.

### UV curing behavior

The UV-curing characteristics of the hyperbranched polycarbosiloxanes were recorded using a differential scanning photo-calorimeter (DPC). In addition, blank experiments were performed under various curing conditions to eliminate the influence of temperature and light intensity. The differences of DPC signals between the sample and the blank were used to determine the cumulative reaction heat. Fig. 4. Reaction rate versus conversion of $P_a$ at various light intensities, at 20 °C, in nitrogen atmosphere.

Influence of light intensity

Keeping the temperature at 20 °C, the hyperbranched polycarbosiloxanes were irradiated under various light intensities. Polymerization rate $R_p$ as a function of conversion $\alpha$ is shown in Fig. 4. $R_p$ increases with increasing light intensity, and $\alpha$ shows a similar trend. It is well understood that the polymerization rate is proportional to the square root of the irradiation intensity37 and the effect of light intensity on the conversion can be interpreted as follows. Curing usually results in volume shrinkage. In the case of UV curing, the very rapid chemical reaction and relatively slow volume shrinkage result in greater free volume. Greater free volume readily increases mobility and diffusivity of the chain units with photo-crosslinkable groups, resulting in higher conversion. Similar results have been observed by Maffezzoli and Terzi.37

The DPC curves obtained in air are shown in Fig. 5, where it can be seen that the inhibition effect of oxygen cannot be neglected. $R_p$ and $\alpha$ values are lower than the corresponding ones under nitrogen atmosphere irradiated with the same light intensity. In particular, under low irradiation intensity, i.e. 8 mW cm$^{-2}$, the final conversion is only around 27%; $R_p$ and $\alpha$ then increase rapidly with increasing light intensity, suggesting that the inhibition effect of oxygen is reduced as the intensity increases.

Influence of reaction temperature

Figure 6 shows reaction rates versus conversion at various temperatures for a light intensity of 39 mW cm$^{-2}$. The effect of temperature on photopolymerization is similar to that of light

![Table 1. Molecular parameters of the polymers determined using SEC-MALLS](image)

<table>
<thead>
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<th>Sample</th>
<th>dn/dc</th>
<th>$M_w$ (g mol$^{-1}$)</th>
<th>$M_n/M_w$</th>
<th>$n_\eta$</th>
<th>$n_w$</th>
<th>$n_\zeta$</th>
<th>$R_\eta(n)$</th>
<th>$R_\eta(w)$</th>
<th>$R_\eta(\zeta)$</th>
<th>$\alpha$</th>
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intensity. Both $R_p$ and $\alpha$ increase with increasing temperature. Furthermore, the conversion at the maximum reaction rate increases with increasing temperature. As is widely known, during free radical polymerization, the reaction rate is proportional to the propagation reaction rate constant. Furthermore, according to the Arrhenius equation, the propagation rate constant also increases with increasing temperature as a result of positive activation energy (Table 2). Thus, the higher the temperature, the higher is the polymerization rate. As for the conversion, this may also be interpreted in terms of the 'free volume effect', as described in the previous section.

Figure 7 shows the isothermal DPC curves in air at various temperatures. $R_p$ and $\alpha$ show trends of increasing with increasing temperature until reaching maximum values at 40 °C, and then decrease abruptly with further increase in temperature. As described already, the propagation rate constant increases with increasing temperature, resulting in the increase of polymerization rate. However, the mobility of oxygen and the concentration of oxygen in the curing system increase with temperature because the viscosity of the curing system decreases with increasing temperature, resulting in a decrease of $R_p$. Oxygen inhibition will occur until polymerization increases the viscosity sufficiently to prevent the diffusion of oxygen into the sample. Therefore, the reaction rate is dependent on the particular predominant factor. Similarly, the conversion will decrease if more free radicals are exhausted by oxygen at a low conversion.

UV curing kinetics
As shown in Fig. 6, the polymerization rate increases rapidly at the beginning of the reaction, reaches its maximum at low conversion and then decreases to zero. It is a typical auto-accelerative reaction resulting from the different mobilizing ability of the reactive species during various reaction stages. Generally, UV curing kinetics like this can be expressed by the following empirical equation:

$$ R_p = \frac{d\alpha}{dt} = k\alpha^m(\alpha_f - \alpha)^n \quad (5) $$

where $n$ is the order of the reaction, $m$ is the auto-accelerative exponent, $k$ is the reaction rate constant and $\alpha_f$ is the final conversion rate, described as the ratio of the total exothermal heat to the theoretical enthalpy. Applying Eqn (5) to this system, kinetic parameters $k$, $m$ and $n$ can be obtained using a least-squares regression method to fit the experimental data to the model (using MatLab 7.1 software), as listed in Table 2. It is evident from Table 2 that both $m$ and $n$ are dependent on temperature and that they have the same trend of increasing with increasing temperature. The total orders of the UV curing reaction for the two hyperbranched polycarbosiloxanes are 2.1 obtained from the average values of $m + n$.

The propagation rate constant $k$ is assumed to follow the Arrhenius law, and the apparent energy of activation $E_a$ can be obtained from the slope of a plot of $\ln k$ versus $1/T$, as shown in Fig. 8. It can be seen that the experimental data are linear for the two polymers when the values of $1/T$ are below 0.0034 K$^{-1}$.
Table 2. UV curing kinetics parameters for the hyperbranched polycarbosiloxanes

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<tr>
<th>Sample</th>
<th>Temperature (°C)</th>
<th>k (s⁻¹)</th>
<th>m</th>
<th>n</th>
<th>Average of m+n</th>
<th>Eₐ (kJ mol⁻¹)</th>
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Figure 9. Comparison between experiment and the model for Pₐ.

(T > 20 °C). However, the experimental data deviate from the linear relation below 20 °C. This deviation may be associated with the glass transition of the cured polymers. The glass transition temperature of the cured polymers is near 20 °C, which may have an impact on the activation energy of the curing reactions. Eₐ can be obtained from the fittings above 20 °C, which are 18.1 and 23.9 kJ mol⁻¹ for polymers Pₐ and Pₐ, respectively. Figure 9 compares the experimental data of conversion and those obtained from the graph plotted using Eqn (5). It is observed that simulated and experimental conversions are in good agreement, suggesting that the model applied here is useful for describing the UV curing kinetics of the hyperbranched polycarbosiloxanes.

Thermal properties of UV-cured hyperbranched polycarbosiloxanes

Glass transition temperature (T_g)
The samples for DSC tests were heated to eliminate the thermal history. T_g values for the UV-cured hyperbranched polycarbosiloxanes were then obtained, as summarized in Table 3. The T_g values of Pₐ and Pₐ are 15.0 and 21.3 °C, respectively. It is well known that polymethacrylates normally have higher T_g values than polycarlylates because the methyl groups restrict C–C rotations in the backbone. T_g of the UV-cured Pₐ is lower than that of Pₐ in this study, suggesting that Pₐ has a lower crosslinking density.

Thermal degradation behavior
Thermal degradation parameters, i.e. initial degradation temperature T_i (temperature at 5% weight loss), maximum thermal decomposition temperature T_max, final decomposition temperature T_f and ceramic yield Y_c at 800 °C, are listed in Table 3. Both the UV-cured polymers exhibit similar pyrolysis behavior. Furthermore, the total weight losses are very high, suggesting that most of the carbon atoms are lost as volatiles. In order to provide mechanistic insight, the effects of molecular structure, crosslinking density, composition of volatile components, curing method and control of the atmosphere during pyrolysis on the ceramic structure and yield will be investigated in more depth during a subsequent study.

CONCLUSIONS

Hyperbranched polycarbosiloxanes were synthesized via a controllable ‘A₂ + CB₄’ approach. FTIR spectral monitoring of the reaction suggested a step-by-step polymerization process. SEC-MALLS measurements gave the exponent α in the Mark–Houwink equation as below 0.5, consistent with the dense structural arrangement of hyperbranched polymers. The hyperbranched polycarbosiloxanes could be cured rapidly under UV irradiation either in nitrogen or air atmosphere, and the reaction rate and conversion of unsaturated groups could be regulated by changing irradiation intensity, reaction temperature and environment. In addition, analysis of UV curing kinetics indicated that activation...
energy was 18.1 and 23.9 kJ mol\(^{-1}\) for \(P_a\) and \(P_b\), respectively. Moreover, TGA measurements suggested that the two cured polymers had similar ceramic yields.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge the support of the Natural Science Foundation of Shandong Province of China (no. ZR2009BQ014) and the Specialized Research Fund for the Doctoral Training Program of Higher Education (no. 200804251523). Start-up funding to young researchers from the China University of Petroleum (East China) (no. 2008CBB11) is gratefully acknowledged.

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