

Preparation and properties of photosensitive polymers based on hyperbranched aromatic polyamides

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1. Introduction

UV curable resins are increasingly used for many application fields, such as coating industry, microelectronics, and dental restoration. Dramatic difference in properties, caused by crosslinking reactions, can be achieved after the UV irradiation. The introduction of multi functionalized monomers to the crosslinking system increases crosslinking density of the cured resins, which often results in the increase in hardness. Tri and tetra functionalized monomers are often used as a multi-functionalized monomer. Recently, dendritic polymers have received considerable attention due to the unique architecture and properties. One of the characteristic features of dendritic polymers is multi-functionality. The number of the functional groups is essentially the same as that of the repeating unit when the dendritic polymer is composed of an AB₂ type branching unit. Therefore, enormously functionalized molecules can be prepared by chemical modification of the end functional groups. From the viewpoint for the application as a bulk material, hyperbranched polymers are attractive due to the ease of preparation, in comparison with dendrimers prepared through multi-step reactions. Preparation of hyperbranched aliphatic polyesters having vinyl groups and their photopolymerizations have already been reported in literatures [1-4]. Recently, photopolymerization kinetics was investigated by using photo-DSC measurements [2,4,5]. However, the thermal stability of cured materials is generally low since the repeating units are composed of aliphatic ester chains.

We have recently reported the synthesis and properties of hyperbranched aromatic polyamides [6]. It is found that properties of the polymers are highly dependent on the nature of end functional groups. New UV-curable and thermally stable resins could be produced by the introduction of crosslinkable groups to the end functional groups. In this paper, UV-curable double bonds were introduced to the end amino groups of the hyperbranched polyamide. Photopolymerization kinetics of the functionalized hyperbranched polymers was investigated by Photo-DSC.

2. Experiment

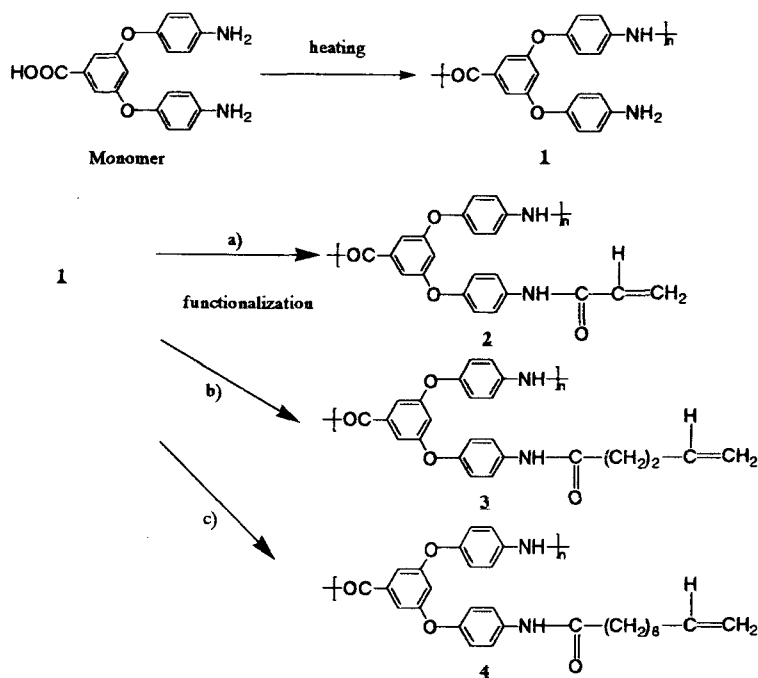
2.1. Synthesis of hyperbranched polyamide

A separable flask with 5.5 g of 3,5-bis(4-aminophenoxy)benzoic acid was set under reduced pressure to remove water and then flushed with nitrogen. The flask was heated at 235 °C for 5 min under reduced pressure. After the temperature was lowered down to room temperature, a transparent glasslike product was obtained. A white powdery polymer was precipitated from DMF solution of the product into methanol containing 0.1% lithium chloride. The precipitate was collected by filtration, washed with methanol, and dried in a vacuum at 90 °C to constant weight (polymer **1a**).

The low molecular weight part of the hyperbranched polyamide (**1b**) was precipitated by adding water (1 L) to the filtrate (2 L). The precipitate was collected by filtration and dried in a vacuum at 100 °C to constant weight.

2.2. Terminal functionalized polymers

In a 50 ml three-neck flask, 0.5 g of polymer **1a** ($M_w = 11000$) was dissolved in 10 ml of NMP. The flask was frozen using a dry ice acetone bath, and then 0.78 ml (9.56 mmol) of acryloyl chloride was added to the flask. The reaction was conducted at 0 °C for 2 h and then stirred at room temperature for 4 h. After the reaction mixture was poured into methanol, the precipitate was collected by filtration and dried in vacuum at 25 °C overnight to give polymer **2a**. $^1\text{H-NMR}$ (DMSO- d_6 , ppm): 10.30 (amide), 10.19 (amide), 7.72, 7.29, 7.08, 6.74 (aromatic), 6.40, 6.26, 5.74 (vinyl).



a) acryloyl chloride b) 4-pentenoyl chloride c) 10-undecenoyl chloride

Scheme 1.

Experimental conditions and procedures for the preparation of polymer **2b** from **1b** and acryloyl chloride are the same as those for **2a** except using methanol/water =1/2 (vol%) as a precipitant for **2b**.

Polymer **3a** and **3b** were prepared from 4-pentenoyl chloride and **1a** or **1b**, respectively, by the same procedure as for the preparation of **2a** or **2b**.

Polymer **4a** and **4b** were prepared from 10-undecenoyl chloride and **1a** or **1b**, respectively, by the same procedure as for the preparation of **2a** or **2b**.

2.3. Photo-DSC measurements for the functionalized polymers

The accurately weighed polymers (ca. 5 mg) were crosslinked using a photo initiator in open pans. The initiator, Irgacure 184, was applied at a concentration of 30 mol% to terminal vinyl groups of the polymers. Photopolymerization was carried out under nitrogen. The incident light intensity at the sample pan was measured to be $0.31 \text{ mW cm}^{-2} \text{ s}^{-1}$. The UV-cured products obtained after Photo-DSC measurements were baked at $130 \text{ }^\circ\text{C}$ for 10 min, and then T_g s of the cured samples were determined by DSC measurements.

3. Results and discussion

3.1. Preparation of terminal functionalized hyperbranched polymers

Hyperbranched aromatic polyamides were prepared by thermal polymerization of the AB₂ monomer, 3,5-bis(4-aminophenoxy)benzoic acid, as reported in our previous works [6]. The crude product was fractionated into two portions: methanol insoluble (**1a**) and soluble part (**1b**). Molecular weights (M_w s) of the hyperbranched polyamides determined by GPC were 11000 (**1a**) and 2600 (**1b**), respectively. The structure of the resulting hyperbranched polyamides was confirmed by spectroscopic measurements. Especially, the presence of end amino groups was confirmed by IR and ¹H NMR measurements. As shown in scheme 1, the terminal functionalized hyperbranched aromatic polyamides **2-4** were prepared by the reaction of **1** with acryloyl chloride, 4-pentenoyl chloride and 10-undecenoyl chloride. In ¹H NMR, the broad peak attributed to the amino protons disappeared after the functionalization. The conversion of the functionalization, calculated by the integration ratio of the peaks attributed to vinyl and aromatic protons, were in the range 96-99 %. Glass transition temperatures (T_g s) of the hyperbranched aromatic polyamides were influenced by the chemical structure of the terminal groups. T_g s of **1a** and **1b** were 175 and 158 $^\circ\text{C}$, respectively. As the alkyl chain between the vinyl group and the amide bond became longer, T_g s of the polymers decreased. All hyperbranched polymers are soluble in polar solvents, such as DMAc, DMSO, and *m*-cresol. Lower molecular weight polymers, **1b-4b**, showed good solubility even in THF.

3.2. Photopolymerization of functionalized hyperbranched aromatic polyamides

Photopolymerization kinetics was investigated by Photo-DSC measurements. The polymerization rate (R_p) was calculated by equation of $(dH/dt) / \Delta H_0$, where dH/dt is the decline of the reaction enthalpy. The enthalpy of polymerization, $\Delta H_0=81.5 \text{ J mmol}^{-1}$ (for polymer **2**) or $\Delta H_0=77.5 \text{ J mmol}^{-1}$ (for polymer **3** and **4**), were used for the calculation of the R_p . Figure 1 shows the influence of the terminal groups of the hyperbranched polyamides on R_p s of the crosslinking reactions. Acryl amide (**2a**) and allyl groups (**3a** and **4a**) were used as terminal groups. The length of alkyl spacer could influence the reactivity of allyl group. The maximum R_p (R_{pmax}) of **2a** was much larger than that of **3a** and **4a**. The induction period to reach the maximum is also short. It is clear that the photopolymerization of **2a** proceeded faster in comparison with that of **3a** and **4a**. The R_{pmax} of **3a** was slightly larger than that of **4a**. The difference might be caused by the increased entanglement of the terminal groups as compared with **3a**. Figure 2 shows the influence of the terminal groups on the conversion of the double-bond (P). The P was calculated by the following equation: $P=H_t / H_{\infty}$, where H_t is the reaction enthalpy within t second, H_{∞} is the reaction enthalpy for 100 % conversion of the double bond. H_{∞} was calculated by equation of $\{[\text{terminal vinyl group}] \times \Delta H_0 / \text{sample weight}\}$. Again, **2a** showed higher P , compared with other polymers. Both of R_p and P data suggested the high photo-reactivity of acryl amide terminal functional groups. On the other hand, P s for **3a** and **4a** were low, which implies the low photo-reactivity of allyl groups.

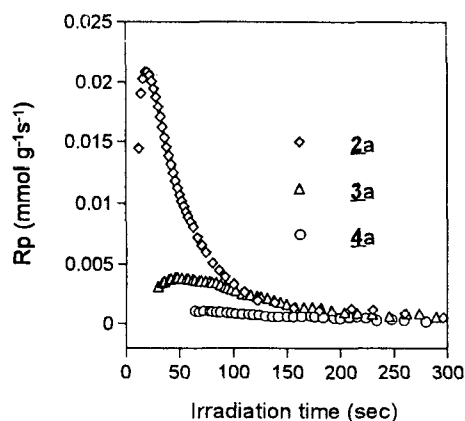


Figure 1. Polymerization rate of polymers with different chemical structures of terminal groups.

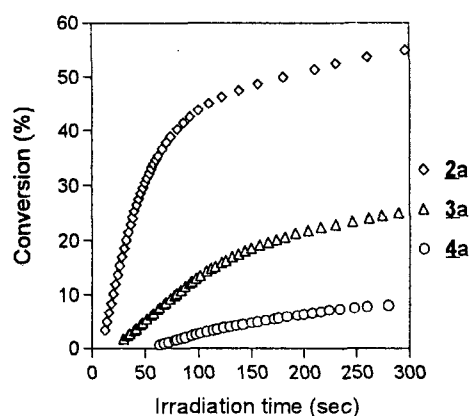


Figure 2. Conversion of the double bond in polymers with different chemical structures of terminal groups.

Influence of the molecular weight of hyperbranched aromatic polyamides on R_p is shown in figure 3. Hyperbranched polymer **2b** having lower molecular weight showed higher R_{pmax} in comparison with **2a**. The conversion, P , of **2b** was also larger than that of **2a**, as shown in figure 4. The same phenomena were also observed for all of other polymers (**3b** and **4b**). The results suggest that the mobility of the molecules is also an important factor to determine R_p and P .

As shown in table 1, T_g s of the hyperbranched polymers increased after the UV-curing. Dramatic increase in T_g s was observed for the polymers with a lower molecular weight.

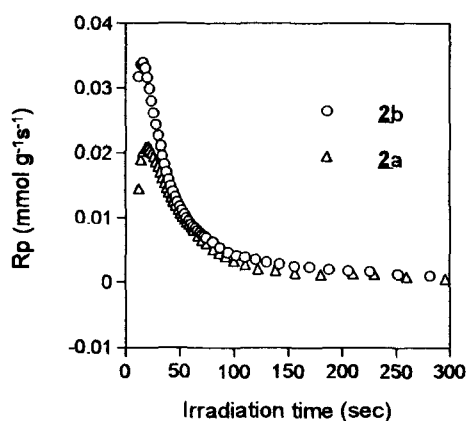


Figure 3. Polymerization rate of polymers with different molecular weights.

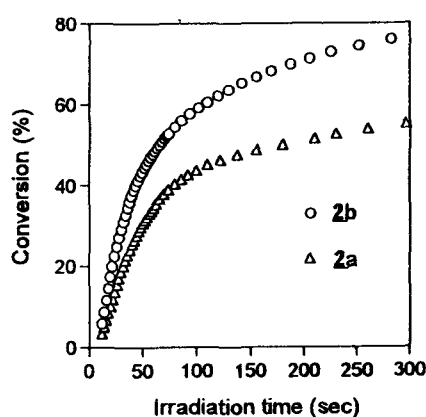


Figure 4. Conversion of the double bond in polymers with different molecular weights.

Table 1. Properties of the UV-cured products.

Entry	T_g bef. ^a (°C)	T_g af. ^b (°C)
2a	175	- ^c
3a	160	166
4a	127	156
2b	157	- ^c
3b	110	161
4b	96	159

^a T_g of the functionalized polymer before UV curing.

^b T_g of the functionalized polymer after UV curing.

^cNo discernible T_g s by DSC measurements at a heating rate of 10 °C min⁻¹ under nitrogen atmosphere.

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