UV-curable Thiol-ene Systems Composed of Dendritic Polyenes to Improve Photosensitivity

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Novel types of the dendritic polyenes with norborlene terminals (DNb\textsubscript{n}, \(n = 8, 16\)) were mixed with conventional six-armed polythiol (SH\textsubscript{6}) and photoinitiator (Ir-369) to obtain dendritic thiol-ene UV-curable materials in large scales. The photosensitivity of the norbornene-based dendritic resins was markedly improved by the activation of two types of polymerizations including thiol-ene polymerizations and radical-radical coupling.

Keywords: Dendrimer, Thiol-ene photopolymer, UV curing, Norbornene, intermolecular propagation, radical-radical coupling

1. Introduction

Dendrimers are monodispersed, spherical polymers with highly branched structures \[1,2\]. Faciely attacked by the surrounding molecules due to multiple terminals at the outermost positions, the polymers of these kinds exhibit specifically high reactivity. From the viewpoints, It can be expected that the photosensitivity of UV-curable resins is improved by the dendritic structuring of olefin compounds. However, due to difficulties in large-scale synthesis of dendrimers, most of the dendritic UV-curable materials so far reported have been focused on hyper-branched polymers (HBPs) with relative high molecular weight distributions, exampled by acrylate-based \[3-5\], methacrylate-based \[6-9\] and thiol-ene-based HBPs \[10-13\].

We have recently explored large-scale synthesis of polyol and polyacrylate dendrimers in 100 g scales based on the alternate multi-addition (AMA) process \[14,15\] to create novel types of photopolymers with high UV-curable performance \[16-19\]. In our previous works, it was revealed that the photosensitivity of thiol-ene UV-curable resins can be improved by using the polyallyl dendrimers (DAL\textsubscript{16}, Fig. 1) because of the acceleration of the addition of propagation 1 in Scheme 1 due to the activation of ene units involving dendritic structuring \[19\].

In this work, we synthesized dendritic polynorbornenes as ene compounds, aiming at further activation of the propagation reactions (propagation 2 as well as propagation 1 in scheme 1) coming from the distorted structures of norbornene radicals \[20, 21\]. We focus here on the UV-curing behaviors of the novel types of the norbornene-based dendritic thiol-ene resins and on their detailed mechanism of the photosensitivity enhancement.

2. Experimental

Dendritic polyenes (DAL\textsubscript{n} and DNB\textsubscript{n}, \(n = 16\): Fig. 1) were synthesized in large scales according to our previous literatures \[14,15\]. Spin-cast films were prepared onto PET films or silicon wafers (1000 rpm for 30s) from THF solutions containing the dendritic polyenes, conventional six-armed polythiol (SH\textsubscript{6}), photoinitiator (Ir-369) and stabilizer (cupferron). UV irradiation was conducted under ambient conditions using monochromatic UV light with a wavelength of 365 nm. The UV curing behaviors of each film were evaluated by measuring pencil hardness and FT-IR spectra.

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3. Results and discussion

Dendritic polyenes of DAL(n) or Nb(n) (n = 8, 16 in Fig. 1) were synthesized through terminal modifications of the polyacrylate or polyol dendrimers prepared in advance in large scales [14, 15]. The polydispersed index (PDI) of the obtained polyenes are in the range of 1.02 – 1.07, being confirmed their monodispersed structures.

The thiol-ene photopolymers composed of DAL(n) or Nb(n), SH6 and Ir-369 (Fig. 1) were initially in viscous states, while being hardened to exhibit HB - H in pencil hardness upon UV irradiation. Photosensitivity of each film was evaluated by measuring pencil hardness (Fig. 2 and Table 3) to be 140 mJ cm\(^{-2}\) for DAL8/SH6 and 70 mJ cm\(^{-2}\) for DAL16/SH6, whereas 2.1 mJ cm\(^{-2}\) for DNb8/SH6 and 1.5 mJ cm\(^{-2}\) for DNb16/SH6. The photosensitivity of the norbornene-based dendritic resins is 50 - 70 times higher compared with that of the allyl-based resins with the same number of the terminals. It is noteworthy that the effect of norbornenes in dendritic systems on thiol-ene reactivity is five- to seven-fold greater than that of typical non-dendritic systems reported thus far [20].

To deepen understanding the mechanism on the foregoing photosensitivity enhancement, the consumption behaviors of the SH and the C=C moieties of both DNb16- and AL16-based films during photopolymerization were monitored by measuring the areas of \(\nu_{\text{SH}}\) and \(\delta_{\text{C=C}}\) in FTIR spectra. The results are shown in Fig. 3. In the case of the DAL16/SH6 film, 35% consumption of C=C moieties was required for UV curing to begin, while the DNb16/SH6 film began to harden in only 5% consumption of C=C moieties. It is therefore expected that efficiently rapid intermolecular polymerization should occur by the dendritic structuring of the norbornene units. The

![Diagram of photopolymerization](image)

**Fig. 1.** Chemical structures of the dendritic polyenes of (DAL16 and DNb16), six-armed polythiol (SH6) and photoinitiator (Ir-369).

**Scheme 1.** Mechanism of thiol-ene photopolymerization.
consumed ratios of C=C moieties in a non-thiol-ene manner \( (R) \) were estimated from the difference in the normalized area of characteristic bands in FTIR spectra between \( \delta_{\text{C=C}} \) and \( \nu_{\text{SH}} \) and calculated as following equations:

\[
R \, \% = \left( \frac{A(C = C) - A(SH)}{A(C = C)} \right) \times 100 \tag{1}
\]

Where \( A \) stands for the normalized area of each band in FTIR spectra of the resins. The calculated results were also plotted in Fig. 3. It is noteworthy that the C=C moieties consumed in a non-thiol-ene manner increased significantly in \( \text{DNb}_{16}/\text{SH6} \) films, corresponding to 37-42% of total C=C consumption, whereas only 7-9% in the case of \( \text{DNb}_{16}/\text{SH6} \) films. When we irradiated UV light to the resins containing sole \( \text{DNb}_{16} \) and Ir-369 in the absence of polythiols (SH6), UV-curing was not observed at all. Accordingly, it is anticipated that the homogeneous polymerization among the terminal norbornene units does not take place. One of the most presumable mechanism is that ca. 40 % of norbornene units can be consumed due to the radical-radical coupling shown in Scheme 1 (termination). The termination due to the radical-radical coupling generally regards as unfavorable reaction to suppress the chain propagation in thiol-ene systems. However, in the dendritic thiol-ene systems, the intermolecular radical-radical coupling can also increase in the molecular weight of the polymeric products, reducing the fluidity of the resins.

In conclusion, it was found that the dendritic \( \text{DNb}_{16}/\text{SH6} \) resins can activate two types of addition reactions in thiol-ene polymerization, including the stepwise polymerizations \( (\text{propagation \, 1 \, and \, 2 in \, Scheme \, 1}) \) and the radical-radical coupling reaction (termination). Since each addition reaction can be effective for the UV-curing in the dendritic system, the \( \text{DNb}_{16}/\text{SH6} \) resins exhibit extraordinarily high photosensitivity to show five- to seven-fold greater than that of typical...
non-dendritic systems.

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