Local Concentration of Allyl Groups at Dendrimer Surface to Improve Photosensitivity of UV Curable Materials

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1. Introduction

Thiol-ene photopolymers comprised of polyene, polythiol and radical photoinitiator have attracted ever increasing attention as UV-curable materials because of the inertness to polymerization-inhibitory effect of ambient oxygen in contrast to conventional acrylate systems [1]. The photopolymerization is initiated by the generation of a thiyl radical ($R-S^{\bullet}$) to add to a $C=C$ bond to form a carbon radical species, which regenerates $R-S^{\bullet}$ to reiterate the radical addition. Because of the stepwise manner of the thiol-ene addition polymerization, highly photocrosslinked networks of thiol-ene systems rely on the multifunctionality of both monomers so that polyenes with branched structures have been so far devised. In this context, dendrimers bearing multiple ene residues at their termini are of great significance in thiol-ene UV curing due to the local concentration of their multifunctionality. We have developed recently the quantity preparation of dendritic polyacrylates starting from commercially available compounds [2]. We report here that dendritic acrylate residues at termini were converted into polyallyl groups, taking the poor storage stability of combinations of acrylates and polythiols into account, to formulate dendritic ene-thiol systems. Polyallyl dendrimers were readily prepared by the Michael addition of the corresponding polyacrylates with diallylamine to provide novel thiol-ene photopolymers demonstrating high UV-curability of their thin films even under aerobic conditions.

2. Method

Polyallyl dendrimers of **AL**(*n*) (*n* = 8 – 32, Scheme 1) were synthesized through the Michael

addition of diallylamine to the corresponding polyacrylate dendrimers (**Ac4**, **Ac8** and **Ac16**)[2b,2c]. Spin-cast films were prepared on PET substrates from THF solutions containing polythiol (**SH4**, Scheme 1), polyallyl dendrimer (**AL**(*n*)) and photoinitiator (**Ir-369**). The resultant films were

Scheme 1. Chemical structures of **SH4** and **AL**(*n*) (*n* = 8–32) used in this study.

Figure 1. Pencil hardness of thin films of **AL8/SH4** (+), **AL16/SH4** (x) and **AL32/SH4** (prepared from spin-casting solutions of $[AL] = [SH] = 0.8$ M), and of **AL32/SH4** (●, prepared from a spin-casting solution of $[AL32] = [SH4] = 0.25$ mM) as a function of exposure doses of 365 nm light.

dried at 75 °C for 1 min and exposed to 365 nm light (22 mW cm^{-2}). Sensitivity curves were constructed by measuring pencil hardness.

3. Results and Discussion

Dendritic polyenes having 8-, 16- and 32-terminated allyl units (**AL**(*n*), *n* = 8 - 32) were synthesized by the Michael addition of a stoichiometric amount of diallylamine to terminal acrylates of the corresponding dendrimers in THF solution in the presence of a catalytic amount of montmorillonite (clay) [3]. Note that the number of allyl groups is doubled relative to that of acrylate. The products were obtained without any purification process and characterized by $^1\text{H-NMR}$ and MALDI-TOF/MS measurements, revealing the validity of the molecular structures shown in Scheme 1.

A solution of a polyene dendrimer, **SH4** and **Ir-369** was spin-cast to give a viscous thin film. UV irradiation brought about the thiol-ene photopolymerization, which was traced by FTIR measurements. The hardening of UV-exposed films was monitored by recording pencil hardness. It was observed that the pencil hardness levels off at H ~ 2H for every film.

Figure 1 summarized the results for changes of

pencil hardness of mixtures of a dendritic polyene and **SH4** as a function of exposure doses of 365 nm light. In order to determine the effect of polyfunctionality, mixtures of **AL8/SH4**, **AL16/SH4** and **AL32/SH4** were formulated to equalize the molarities of allyl and thiol groups, notifying the stoichiometric addition reaction of the present system. As displayed in Figure 1, **AL32/SH4** reached H in pencil hardness at 350 mJ cm^{-2} whereas *ca.* 600 and 2400 mJ cm^{-2} doses were needed for the same hardness of **AL16/SH4** and **AL8/SH4**, respectively. It is likely that the difference reflects the concentration effect of allyl groups localized at a molecular surface of the dendrimer. When the **AL32/SH4** system was formulated in such a way that the molarities of both ingredients are equal, UV exposure doses needed for film hardening were reduced down to 230-370 mJ cm^{-2} . The results are probably due to the increase in the relative number of allyl groups attacked by the thiyl radicals as well as by the mobility of thiyl radicals in films.

In summary, UV-curing performances of thiol-ene photopolymers were enhanced by employing dendritic polyenes. Further improvement is anticipated by optimizing mixing ratios of ingredients.

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