Synthesis of Polyallyl Dendrimers to Apply to Novel UV Curing Materials

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1. Introduction

Thiol-ene photopolymers are typically composed of photoinitiators, polythiols and multifunctional olefins called “ene compounds” such as norbonene, acrylate and allyl ether derivatives. Upon irradiation with actinic light to give a radical (In-) from a photoinitiator, key species of thyl radicals (R-S·) are generated by hydrogen abstraction. Subsequent chain transfer proceeds in two steps (Propagation 1 and 2 in scheme 1) until termination occurs by radical-radical coupling. [1]

The photopolymers of these kinds have attracted much interest in recent years for the application to UV curing materials, since the process is not inhibited by dissolved or ambient oxygen in a contrast to conventional acrylate/metacrylate systems.

Recent reports have focused on the synthesis of novel polyene derivatives [2] with a hyperbranched core aiming at peculiar physical properties such as lower viscosity and lower polymerization shrinkage. Assisted by such practical advantages, we have started to synthesize well-designed compounds of a series of novel “dendritic” polyallyl compounds having an almost uniform molecular weight. Our major interest is to investigate the relationship between the number of the terminated ene groups and the reactivity of photopolymerization. We describe here a novel clue and guideline to accomplish UV curing materials with high photosensitivity.

2. Method

Polyallyl dendrimers of AL16 and AL32 (Scheme 2) were synthesized through the Michael addition of diallylamine to the polycrylate dendritic precursors (Ac8 and Ac16) [3, 4]. Pentaerythritol tetraakis(thioglycolate) (PETG, Scheme 2) and Ir-369 were used as a polythiol and a photoinitiator, respectively.

Spin-cast films were prepared on silicon wafers or on PET substrates from THF solutions containing PETG and polyallyl dendrimer (AL16 or AL32) in a molar equivalent weight (0.8 M) and Ir-369 (0.08 M). The resultant films were heated at 75 °C for 1 minute and exposed to 365 nm light (30 mW cm\textsuperscript{-2}). Sensitivity curves were constructed by measuring pencil hardness.

3. Results and Discussion

Novel polyallyl dendrimers of AL16 and AL32 were conveniently synthesized by the addition of an excess amount of diallylamine to a THF solution of the polycrylate dendrimer having eight or sixteen
Scheme 2. Chemical structures of Ir-369, PETG, AL16 and AL32 used in this study.

acrylate units at the terminals of the molecules [3]. After stirring under the ambient and the following reflux conditions, the resultant solutions were sufficiently dried to remove the solvent and the excess diallylamine, giving viscous oils of AL16 and AL32 in quantitative yields.[4]

Spin-casted films composed of the polyallyl dendrimer (AL16 or AL32), PETG and Ir-369 were viscous (below 6H in pencil hardness) before UV irradiation. The films were storable without any change at least for two weeks in the dark. Such a favorable stability is probably due to N-nitroso-N-phenylhydroxylamine aluminium salt (cupferon) as a polymerization inhibitor [5], which was used for the synthesis of the dendritic acrylates (Ac8 and Ac16) [3].

UV irradiation of films resulted in increase in hardness, reaching 3H after the adequate exposure doses. From FT-IR measurements, the exposure processes were accompanied by the significant decrease in the intensity of the absorption bands at around 1650 and 2570 cm⁻¹ assigned to νC-C and νSiH, respectively, indicating that UV curing comes from the thiol-ene photopolymerization, as shown in scheme 1.

Photosensitivity of the AL32/PETG system was considerably higher than that of the AL16/PETG system, as shown in Fig. 1. The results suggest that the increase in the number of terminated allyl groups at the periphery positions of dendritic molecules leads to enhancing local concentrations of allyl units to improve the chain transfer reaction. We anticipate that performances of the present UV curing materials are improved by appropriate choice of dendritic backbones and polythiol compounds.

References and Notes
3. The polyacrylate dendritic precursors (Ac8 and Ac16) were synthesized from pentaerythritol tetraacrylate as a core, mercaptoethanol and 2-isocyanato-2-methylpropan-1,3-diol diacrylate by the alternate multi-additions (AMA) method.
4. H-NMR spectral data for AL16: δ (ppm, CDCl3): 1.39 (s, 12H, -CH3), 2.47-2.81 (m, 56H, -OCO-CH2, -S-CH2, N-CH2), 3.10 (d, J=6.0 Hz, 32H, N-CH3), 4.17-4.27 (m, 32H, -CH2-OCO-), 5.13-5.21 (m, 32H, allyl-H), 5.75-5.89 (m, 16H, allyl-H). AL32: δ (ppm, CDCl3): 1.40 (s, 36H, -CH3), 2.47-2.81 (m, 136H, -OCO-CH2, -S-CH2, N-CH2), 3.10 (d, J=6.0 Hz, 64H, N-CH3), 4.16-4.32 (m, 80H, -CH2-OCO-), 5.13-5.21 (m, 64H, allyl-H), 5.75-5.89 (m, 32H, allyl-H).