Photocuring of Radically Polymerizable Hyperbranched Polymers Having Degradable Linkages

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Hyperbranched polymers having a number of reductive disulfide bonds and radically reactive vinyl groups were synthesized by the bulk radical homopolymerization of bis(2-methacryloyloxyethyl)disulfide (disulfide based dimethacrylate, DSDMA) as a divinyl monomer in the presence of methyl 2-(bromomethyl)acrylate as an addition-fragmentation chain transfer agent. The resulting hyperbranched polymers (HB-DSDMAs) were photocured by irradiated at 365 nm in the presence of 2,2-dimethoxy-2-phenylacetophenone as a photo radical initiator. The photocured HB-DSDMA exhibited high transparency in the visible region and good solvent resistance for various organic solvents. Reduction of the disulfide groups smoothly proceeded in the presence of tributylphosphine as a reductant, and the cured HB-DSDMAs were completely solubilized. HB-DSDMAs were also photocured by irradiation at 254 nm due to the homolysis of the disulfide groups with subsequent initiation of the radical polymerization.

Keywords: Hyperbranched polymer, Curable polymer, Degradable polymer, Photopolymerization, Photo cleavage, Reductive decomposition

1. Introduction

Curable liquid resins are useful materials as underfill, coatings, and adhesives because of their excellent wetting nature in a liquid state and satisfying properties including chemical, mechanical, and thermal resistance after curing. Thermoset and photocurable multi-functional monomers such as epoxy and acrylic derivatives are widely used as curable liquid resins [1-3]. However, such low molecular weight monomers are usually volatile, i.e., volatile organic compounds (VOCs), and the release of VOCs is not favorable because of environmental pollution, odor, irritation, and inflammation. Even after the curing process, a small amount of unreacted monomers brought about the aforementioned problems and deterioration of the properties of the resulting cured materials. To overcome the volatility problems, non-volatile oligomers having larger molecular weights have been used instead of volatile monomers [4]. Although an increase in the molecular weight is effective to reduce the release of VOCs, the viscosity of the liquid resins increases by the use of oligomers. This disturbs the wetting nature of the curable liquid resins. The use of branched oligomers (polymers) is useful to maintain the liquid-like nature because branched polymers generally show a lower viscosity than the linear polymers having a comparable degree of polymerization [5].

We recently reported the one-pot synthesis of the hyperbranched polymers by radical homopolymerization of divinyl monomers in the presence of an addition-fragmentation chain transfer (AFCT) agent [6]. The resulting hyperbranched polymers have a number of conjugated vinyl groups coming from the divinyl monomer, i.e., the pendant vinyl group, and from the AFCT agent, i.e., the vinyl group at the ω-end group (Fig. 1). Due to the dense conjugated vinyl groups, the hyperbranched polymers showed spontaneous polymerization behavior at around 110
The curable hyperbranched polymers are expected to be useful as additives and/or alternatives for curable liquid resins. Conventional cured materials have the drawback of difficulties in their removal from substrates without damaging. Degradable cured resins, which exhibit both satisfying properties as cured materials and degradability, have been attractive as reworkable cured materials. Thermally degradable epoxides and (meth)acrylates having tertiary esters and tertiary carbonates [7-9], thermally degradable polyperoxide-based cured resins [10,11], epoxides having thermally reversible Diels-Alder adduct moieties [12,13], and biodegradable epoxides [14], were reported. Cross-linking agents having degradable linkages such as a reductive disulfide bond [15,16], a hydrolytic acetal group [17] and \( \omega \)-acyloxime moiety [18] were also reported.

Polymerizable hyperbranched polymers incorporating dense degradable bonds will be promising curable resins to reduce VOC emissions and to give reworkability. In this study, radically polymerizable hyperbranched polymers having a number of disulfide bonds as degradable linkages were synthesized (Fig. 2) and their photocuring and reductive degradation behaviors were investigated in detail.

2. Experimental
2.1. Materials
Methyl 2-(bromomethyl)acrylate (MBMA) [19] and bis(2-methacryloyloxyethyl)disulfide (disulfide based dimethacrylate, DSDMA) [20] were prepared according to the methods described in the literature. 2,2-Dimethoxy-2-phenylacetophenone (DMPA) (Tokyo Chemical Industry Co., Ltd., > 98.0%), tributylphosphine (Bu3P) (Wako Pure Chemical Industries, Ltd., > 98%), dithiothreitol (DTT) (Nacalai Tesque, Inc., > 97%), and di-tert-butyl peroxide (TBP) (Kishida Chemical Co., Ltd., > 98%) were used as received. Ethylene glycol dimethacrylate (EGDMA) was distilled under reduced pressure. 2,2'-Azobis(isobutyronitrite) (AIBN) was recrystallized from methanol. Other reagents and solvents were used without further purification or purified according to conventional methods.

2.2. Measurements
The gel yield was determined after swelling polymers in chloroform for 24 h at room temperature. The number- and weight-average molecular weights \( (M_n \text{ and } M_w) \) were determined by gel permeation chromatography (GPC) with tetrahydrofuran (THF) as the eluent using a Tosoh CCPD RE-8020 system and calibration with standard polystyrenes. The \(^1\)H NMR spectra were recorded using a Bruker AN300N (300 MHz) spectrometer. The thermogravimetric and differential thermal analyses (TG/DTA) were performed using a Seiko EXSTAR6000 at the heating rate of 10 °C/min in a nitrogen stream at the flow rate of 200 mL/min. The differential scanning calorimetric (DSC) analysis was performed using a Seiko EXSTAR6000 at the heating rate of 10 °C/min. Transmittances of polymer films were recorded by a Shimadzu UV-2400 UV/Vis spectrometer.

2.3. Photoreaction
Photoreaction was carried out under atmospheric conditions by light irradiation from a high pressure mercury lamp (Toshiba SHL-100UVQ-2) passing through a poly(ethylene terephthalate) (PET) film (50 μm thickness) to cut \( \lambda < \text{ca. } 300 \text{ nm} \). The light intensity of 0.73 mW/cm\(^2\) was measured by a UV power meter (USHIO, UIT-101) equipped with a UVD-365PD optical receiver (330-390 nm). A high-pressure mercury lamp (Moritex MSU-6) was also used, and the light intensity was 10 mW/cm\(^2\) and 9 mW/cm\(^2\) without and with a glass filter, respectively.
3. Results and discussion
3.1. Synthesis of hyperbranched polymers
A typical polymerization procedure was as follows. In a Pyrex glass tube, the mixture of DSDMA, MBMA, and radical initiator was placed and sealed under vacuum after three times freeze-thaw cycles. The structures of chemicals are shown in Fig. 3. The polymerization carried out in the preheated aluminum block and quenched by cooling at −78 °C. The products were purified by reprecipitation in hexane and the precipitates were dried under vacuum for 24 h in the ice bath. The formation of hyperbranched polymer was confirmed by combined analysis of 1H NMR and GPC as described in our previous report [6]. The values of $M_n$, $M_w/M_n$, and glass transition temperature ($T_g$) of the representative hyperbranched polymer (HB-DSDMA) prepared under the conditions of [DSDMA]/[MBMA]/[TBP] = 1/1/1x10$^{-3}$, which shows the ratio of molar concentration of reagents, at 117 °C for 24 h were 1.2 x 10$^3$, 1.7, and −27 °C, respectively. HB-DSDMA used in this study were all applicable on solid substrates such as glass and stainless steel without dilution by solvents, i.e., in the bulk state.

3.2. Degradation behavior
HB-DSDMA ([DSDMA]/[MBMA]/[TBP] = 1/1/1x10$^{-3}$ at 117 °C for 24 h, 30 mg) was dissolved in the 5 mL of tetrahydrofuran (THF) solution containing Bu$_3$P (56 mmol/L) as a reductant and the mixture was stirred at room temperature for 6 h. The GPC elution curve of the reaction mixture is shown in Fig. 4 together with that of the original HB-DSDMA. The main broad peak shifted toward the longer retention time, i.e., lower molecular weight side, after 6 h. The result clearly shows that the reduction of the disulfide bonds proceeded and the molecular weight of HB-DSDMA was decreased. In order to confirm that the reductive decomposition of the disulfide bonds proceeds even after the curing reaction, the cross-linked DSDMA during the polymerization due to less MBMA ([DSDMA]/[MBMA]/[TBP] = 8/1/8 x 10$^{-3}$ in bulk at 117 °C for 11 h, 30 mg) was likewise immersed in the 5 mL of Bu$_3$P solution. After 30 min, the cross-linked DSDMA was almost dissolved in the THF solution by visual observation (Fig. 5). The GPC elution curves of the solutions after 30 min and 3 days are shown in Fig. 6. The GPC elution curve after 30-min immersion existed at lower molecular weight region than that for HB-DSDMA obtained before cross-linking. Furthermore, the molecular weight distribution after 3 days consists of larger amount of the lower molecular weight fraction than that after 30 min. Taking into account the GPC results with the visual observation, it is considered that the cross-linked DSDMA was solubilized in 30 min and further...
reductive decomposition proceeded. These results show that cross-linked DSDMA can be solubilized by the reductive decomposition of the disulfide bonds using Bu₃P.

DTT is also known to be a reductant for disulfide bonds [21]. However, the decomposition of HB-DSDMA did not proceed under the current experimental conditions, i.e., 30 mg of HB-DSDMA was immersed in 5 mL of THF solution containing DTT for 20 h. This is because DTT is more susceptible to autoxidation and less affinity to disulfide bonds [22]. Furthermore, it is noted that the rate of the reductive decomposition of polymers containing a disulfide bond is affected by the polarity and composition of the reaction mixture, nature of the polymer backbone, and so on [22]. Although precise adjustments of experimental conditions would enable decomposition by DTT, it is clear that Bu₃P is more facile and effective reductant for HB-DSDMAs.

3.3. Photocuring and degradation

Photochemical reaction behavior of HB-DSDMA, which has dense disulfide bonds and radically reactive vinyl groups, was investigated. A disulfide bond undergoes photo cleavage upon irradiation at 254 nm and generates thiyl radicals [23]. Thiyl radicals exhibit a low sensitivity to oxygen due to a reversible nature and are useful to initiate radical polymerization of vinyl monomers [24]. In the case of HB-DSDMA, the homolysis of the disulfide bonds in the polymer main-chain and side-chain, i.e., degradation, and photopolymerization of the vinyl groups, i.e., cross-linking, are expected to proceed in a competitive manner by the irradiation at 254 nm.

In order to evaluate the effect of the two competitive reactions on polymer properties, HB-DSDMA was irradiated in the absence of a photo radical initiator by a high-pressure mercury lump with and without the glass filter to cut shorter wavelengths than ca. 300 nm (Table 1). HB-DSDMA irradiated without the filter, i.e., irradiation at ca. 254 nm, turned into insoluble in THF, whereas HB-DSDMA irradiated with the filter remained completely soluble in THF. The results clearly show that thiyl radicals generated by the photo cleavage of the disulfide bonds initiate polymerization of the vinyl groups and the extent of polymerization (cross-linking) exceed that of degradation. DSDMA also gave the same result as the case of HB-DSDMA. On the other hand, in the case of EGDMA not containing a disulfide bond, irradiation with and without the filter provided soluble materials in THF. This reference experiments further proved that the photo cleavage of the disulfide bond initiates the polymerization. The photocured HB-DSDMA was not solubilized by immersing in the THF solution of Bu₃P for 1 day. This is rationalized by the fact that reductive disulfide bonds were already consumed during the photocuring process.

![Fig. 6. GPC elution curves of HB-DSDMA obtained before gelation ([DSDMA]/[MBMA]/[TBP] = 8/1/8 x 10⁻³, at 117 °C for 9 h) (gray solid line), cross-linked HB-DSDMA ([DSDMA]/[MBMA]/[TBP] = 8/1/8 x 10⁻³, at 117 °C for 11 h) after immersing in the THF solution containing Bu₃P (56 mmol/L) for 30 min (black solid line) and 3 days at room temperature (black dashed line).](image-url)

Table 1. Results of photoirradiation in the absence of photo radical initiator.

|           | filter | solubility |
|-----------|--------|------------|
| HB-DSDMA  | +      | soluble    |
| DSDMA     | +      | soluble    |
| EGDMA     | +      | soluble    |

|           | filter | solubility |
|-----------|--------|------------|
| HB-DSDMA  | −      | insoluble  |
| DSDMA     | −      | insoluble  |

*Photoirradiation by a high-pressure mercury lamp, Moritex MSU-6, for 2 min. b+ with the glass filter, − without any filter.

In order to photo-chemically cure HB-DSDMA without consuming disulfide bonds, a photo radical initiator, DMPA, was used. DMPA was selected because of its absorption at around 350 nm, which is not blocked by the absorption of methacrylic polymers, and its transparency at visible region [24, 25]. The cast films of HB-DSDMA containing 1 wt% of DMPA were prepared and subjected to the photoirradiation, where shorter wavelength than ca.
300 nm was cut by the PET filter. The relationship between photoirradiation time and gel yield is shown in Fig. 7. With increasing the photoirradiation time, the gel yield gradually increased and reached 100% after 60-min irradiation. The cast film was highly transparent in the visible region and the transparency remained after curing for 60 min (Fig. 8). The transmittances of the cast films (70-μm thickness) at 700 nm were 98% both before and after the photocuring. The cured film by 60-min photoirradiation showed the good resistance for various organic solvents including acetone, THF, and chloroform. All the cured cast films were successfully solubilized by immersing in the THF solution containing Bu₃P as a reductant. This is due to the existence of the reductive disulfide bonds even after the photocuring process in the presence of DMPA, in contrast to the photocuring using photo cleavage of the disulfide bonds.

4. Conclusion

Free radical homopolymerization of DSDMA in the presence of MBMA yielded hyperbranched polymers incorporating a number of disulfide groups and pendant ω-end vinyl groups. The hyperbranched polymers were photocured by irradiation at 254 nm in the absence of photo initiators and irradiation at 365 nm in the presence of DMPA as a photo radical initiator. The cured materials by the irradiation at 365 nm underwent reduction by Bu₃P and were completely solubilized, whereas the cured materials obtained by the irradiation at 254 nm were not solubilized due to the consumption of disulfide bonds during the photocuring process. The hyperbranched polymers based on DSDMA are promising as chemically reworkable sealant, coating, and adhesives.

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