Visible Light-induced Cationic Polymerization of Epoxides Sensitized by Benzoquinonylsulfanyl Derivatives

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On irradiation with visible light, cationic polymerization of epoxides by a photoacid generator (PAG) was sensitized by benzoquinonylsulfanyl derivatives. Spectral analyses suggest that the reduction of the quinone derivatives on irradiation was the initial and essential step of the polymerization.

Recent trend in UV curing is focused on photo-initiated cationic polymerization because it is usually free from oxygen inhibition, and monomers such as vinyl ethers and epoxides are available even though they are not used in photo-initiated radical polymerization.[1] The cationic polymerization has been accomplished by photoacid generators (PAGs) that generate strong acids on irradiation. However, PAGs in the early generation absorbs only short wavelength of light such as deep UV. Therefore, one of recent requirements of the polymerization systems is to extend the sensitization window to the longer wavelength region than 360 nm. Such light source has advantage in pigment systems or dental use as expected in photo-initiated radical polymerization.[2] Crivello et al. reported that camphor quinone sensitized photo-induced cationic polymerization of epoxides in the presence of PAGs using visible light.[3]

Benzoquinonylsulfanyl derivatives have absorption maximum around 430 nm.[4] We have been studying the utilization of quinones as a visible light-sensitizer for photo-generation of pendant amino groups.[5] On the way of investigation, we have found that the derivatives are very effective sensitizers in photo-initiated cationic polymerizations.

In this communication, we describe sensitization behavior of the benzoquinonylsulfanyl derivatives in cationic polymerization of epoxides initiated by a sulfonium salt.

2-Benzylsulfanyl-1,4-benzoquinone (QBS), 2-dodecylsulfanyl-1,4-benzoquinone (QDS), and 2-phenylsulfanyl-1,4-benzoquinone (QPhS) were obtained from corresponding thiols and 1,4-benzoquinone as described in literature.[4,5] *S*-Octyl-*S*-methyl-*S*-phenacylsulfonium hexafluoroantimonate (DPS-C_1C_8) was prepared as described in literature:[6] mp = 68–70 °C. 3,4-Epoxycyclohexylmethyl 3′,4′-epoxycyclohexanecarboxylate (ERL-4221) was obtained from Union Carbide and used as received. Cyclohexene oxide (CHO) was distilled under reduced pressure.

Cyclohexanone solution containing a quinone, DPS-C_1C_8 as a PAG, and ERL-4221 was spin-coated on silicone wafers. Film thickness was measured by a Nanometrics Nanospec/AFT M3000 interferometer to be ca. 0.8 μm. The films were irradiated by a Hamamatsu Photonics Photocure 200 Hg-Xe lamp through a Toshiba UV39 cut-off filter (>370 nm) in air and post-exposure baked (PEB) on a hot-plate at 100 °C for 5 min. The light intensity was 9 mW/cm^2 around 435 nm, which was measured by an Orc UV-M02 photometer. Thickness changes were measured before and after soaking in tetrahydrofuran (THF) for 5 min at room temperature.

Polymerization of CHO was carried out in the presence of a quinone derivative (0.1 mol%) and DPS-C_1C_8 (0.1 mol% against CHO) in a Pyrex tube (O. D. = 12 mm$^{\phi}$) on irradiation with an Ushio UM102 medium pressure Hg lamp through a UV39 filter followed by PEB at 60 °C for 30 min. The light intensity was 3 mW/cm^2 around 436 nm. After irradiation, the mixture was poured into methanol, and precipitated polymer was dried in vacuum. The molecular weight was measured by gel permeation chromatography using THF as an eluent and polystyrene standards. For UV spectral measurement, the mixture was irradiated under N_2 in a Pyrex tube (O. D. = 18 mm$^{\phi}$) with a 10 mm × 10 mm side cell.

Figure 1 shows the insoluble fraction of coating films of ERL-4221 into THF on irradiation followed by PEB. Films became insoluble in the presence of QBS, which clearly shows that QBS worked as a visible light sensitizer of polymerization. However, the insolubilization did not occur in the presence of QDS and QPhS.

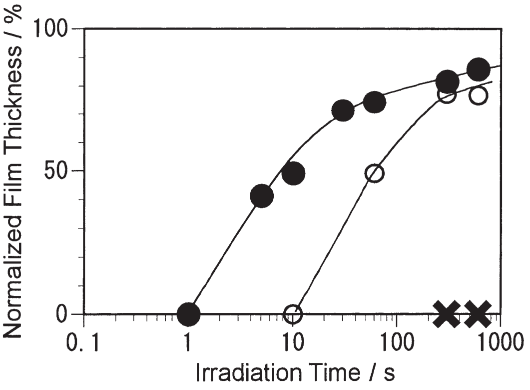


Figure 1. Insolubilization of QBS/DPS-C_1C_8/ERL-4221 mixture in THF on irradiation followed by PEB. QBS : DPS-C_1C_8 : ERL-4221 (molar ratio) = (●) 4 : 1 : 100, (○) 1 : 1 : 100, and (✖) 0 : 1 : 100.

The sensitization by QBS was also applied to the bulk polymerization of mono-functional epoxide, CHO in the presence of DPS-C_1C_8. On irradiation of mixture for 2 min, a polymer was obtained after pouring in methanol though its amount was small. Additional heating at 60 °C for 30 min gave 30.3% yield of polymer having Mn = 7,400 and Mw/Mn = 2.10. No polymer precipitated after PEB in the absence of QBS or in the presence of QDS and QPhS in this condition. On irradiation for 3.5 h, QDS/DPS-C_1C_8/CHO mixture gave a polymer having Mn = 18,500 in

35.3% yield after PEB, while QPhS mixture did not. QBS/CHO mixture also gave a polymer on irradiation for 20 min followed by adding DPS-C_1C_8 and then heating for 30 min.

On irradiation of QBS in polystyrene matrix, new peaks appeared at 3100 ~ 3600 cm^{-1} and 315 nm in IR and UV spectra, respectively. These results show that QBS was transformed into a reduced form because 2-benzylsulfanyl-1,4-hydroquinone has a maximum peak at 314 nm in UV spectrum.

Figure 2 shows the UV-vis spectral changes of QBS/CHO mixture on irradiation. On irradiation, the peak at 425 nm decreased, and a new peak appeared at 317 nm (curve b). This result suggests that QBS was transformed into a reduced form. When DPS-C_1C_8 was added to the irradiated mixture, the peak around 430 nm increased again along with the decrease in the peak at 317 nm (curve c). This result suggests that a redox reaction[7] occurred between reduced QBS and DPS-C_1C_8.

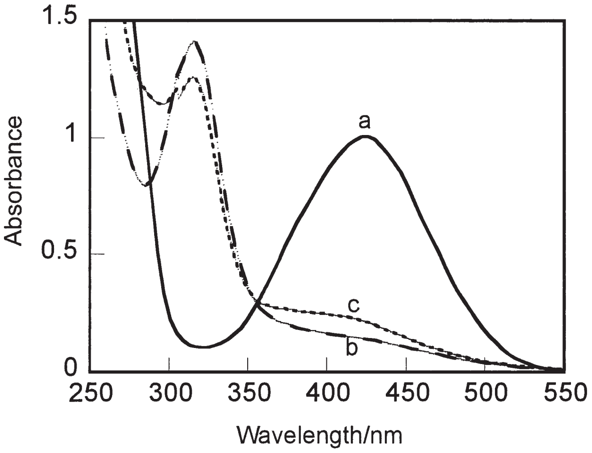
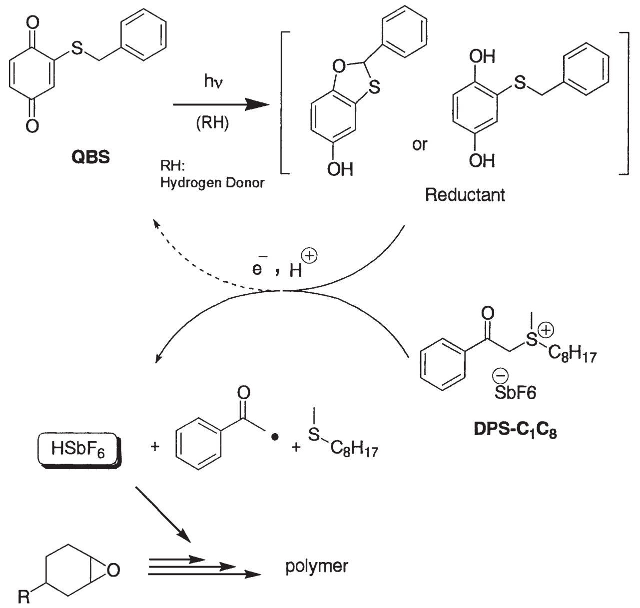


Figure 2. UV-vis spectra of QBS/CHO mixture (a) before and (b) after irradiation for 5 min, and (c) after addition of DPS-C_1C_8. QBS : DPS-C_1C_8 : CHO (molar ratio) = 4 : 4 : 100,000 (molar ratio).

The changes of UV/vis spectra for QDS and QPhS were very slow compared to QBS. These results indicate that the photoreduction of quinone derivative was a trigger of the polymerization. Intramolecular hydrogen abstraction would proceed preferentially, because both QBS and QDS have an α-hydrogen to sulfur atom. Plausible mechanism is illustrated in Scheme 1.

In conclusion, benzoquinonylsulfanyl derivatives worked as a photosensitizer for UV curing using visible light. QBS was the most effective in the polymerization of epoxides.



Scheme 1. Plausible mechanism of sensitization by QBS.

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References and Notes

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