Photoacid Generation by Stepwise Two-Photon Absorption: Photoinitiated Cationic Polymerization of Cyclohexene Oxide by Using Benzodioxinone in the Presence of Iodonium Salt

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Photoinitiated cationic polymerization1−4 is of great practical interest due to their applicability for the curing of coatings and printing inks and for resist technology. The major classes of photoinitiators which can successfully initiate cationic polymerization include diaryliodonium,5 triarylsulfonium,6 and alkoxy- pyridinium7,8 salts. Besides their direct activation (direct light absorption), several indirect sensitization methods are reported to extend photopolymerization sensitivity to longer wavelengths. This way practical application of the photoinitiated cationic polymerization can become acceptable since medium- and high-pressure mercury lamps that are frequently used as light sources provide emissions at 313 and 366 nm. Successfully employed indirect ways include oxidation of photochemically generated free radicals,9 electron-transfer reactions in the exciplexes,10−12 and charge-transfer complexes.13,14 Among these methods, free-radical-promoted cationic polymerization finds wider application because of availability of a wide range of free radical photoinitiators absorbing at different wavelengths. In addition to the cleavage type photoinitiators, hydrogen abstraction type photoinitiators15,16 were shown to generate oxidizable electron donor radicals.

It was recently reported17 that functionalized salicylate esters can be readily prepared by a photochemical acylation process by using benzodioxinones in the presence of alcohols and phenols (Scheme 1). We have recently shown18 that this process can also be used for the preparation of oligoesters when benzodioxinones are equipped with aliphatic hydroxyl groups. Upon irradiation of benzodioxinones, ketene and the corresponding ketone are formed concomitantly. The intermediate ketone readily reacts with the alcohol present in the solution to yield salicylate ester.

Moreover, we also showed that, when suitably structured, aromatic ketones, i.e., benzophenone, formed concomitantly can absorb light and act as hydrogen abstraction type photoinitiators in the presence of donors.19−21

Two-photon absorption processes provide the means to activate chemical and physical processes with high spatial resolution due to the nonlinearity of light absorption. Therefore, two-photon absorption processes are widely used for a variety of applications, such as photopolymerization,22 three-dimensional (3D) microfabrication,23−26 optical data storage,27 imaging,28 and the controlled release29 of biological systems. In these

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reported applications, simultaneous two-photon absorption is utilized, where two photons of lower energy are absorbed by the chromophore simultaneously to populate the excited state. However, nonlinearity of light absorption can also be achieved by stepwise two-photon absorption. In this process, the first photon is absorbed to generate a long-lived excited-state or reaction product. In the second step, a photon of the same or different wavelength is absorbed by the long-lived excited-state or reaction product to generate the final photoproduc. Likewise, to simultaneous two-photon absorption, stepwise two-photon absorption occurs with high spatial resolution.

In this study we test whether benzodioxinone and naphthaldioxinone (Chart 1) can act as caged sensitizers for diphenyl- iodonium salt to generate acids for initiation of cationic polymerization. The first absorbed photon should uncage the sensitizer. The released sensitizer absorbs the second photon to reduce the iodonium salt yielding in protonic acids for initiation of cationic polymerization.

Cyclohexene oxide (CHO) was selected as the cationically polymerizable monomer as it structurally represents epoxides, which are used in acid-sensitive, positive-tone, chemically amplified resist, designed for 3D microfabrication and readily undergoes polymerization with cationic species and is inert to free radicals. The latter issue is particularly important as the process involves photochemical generation of electron-donating radicals. An iodonium salt, namely diphenyliodonium hexafluorophosphate, was used as the oxidizing agent in the process. Notably, reduction potentials of the onium salts must be relatively low. The other widely used onium salts such as sulfonium and N-alkoxy pyridinium salts are expected to exhibit lower efficiency due to their less favorable redox potentials (E1/2 red = −1.02 and −0.7 V (SCE), respectively) compare to the iodonium salts (E1/2 red = −0.2 V). Figure 1 shows optical absorption spectra of photoacid generators (PAG) benzodioxinone and naphthaldioxinone, structurally related compounds benzophenone and naphthalene, and oxidizing agent. Since
iodonium salt does not absorb light above 320 nm, all irradia-
tions were performed at $\lambda = 320 - 500$ nm.

As can be seen from Figure 2, CHO was polymerized quite
efficiently with benzophenone, benzodioxinone, and naphtha-
dioxinone in the presence of iodonium salt. A short induction
period ($> 1$ min) observed in all cases may be due to adventitious
impurities present in the polymerization system and response
time of the photo-DSC system. Upon absorption of light, benz-
odioxinone is photolyzed according to reaction 3 in Scheme 2.
The second photon absorbed by benzophenone leads to the
formation of triplet benzophenone after intersystem crossing
which readily abstracts hydrogen from solvent or monomer
(reaction 4). Laser flash photolysis experiments were performed
to demonstrate that reaction 4 occurs under our experimental
conditions. A bimolecular rate constant of $k_q = 1.2 \times 10^6$ M$^{-1}$
s$^{-1}$ was observed for hydrogen abstraction by benzophenone
triplet states from (see Supporting Information). In this process,
diphenylketyl radicals are generated, which are known to be
powerful reducing agents ($E_{1/2}^{ox} \sim -0.7$ V (SCE)). Diphen-
ylketox radicals are reported to be able to reduce iodonium salts
(reaction 5). Back-electron-transfer reaction can be disre-
garded because the oxocarbenium ion decomposes into acid and
benzophenone ($E_{1/2}^{ox} \sim -0.7$ V (SCE)).

Figure 2 compares the polymerization rates of CHO by
benzophenone (BP) and the caged benzophenone (BD). It is
interesting to note that a relatively long induction period was
observed in the case of benzodioxinone (BD), which clearly
indicates the two-photonic nature of the process. The photo-
initiation occurs only after a sufficient amount of benzophenone
is released by the photolysis of benzodioxinone. Because the
extinction coefficient of benzodioxinone is $\sim 1$ order of mag-
nitude higher than for benzophenone (Figure 1), the majority
of benzodioxinone needs to be decomposed before the released
benzophenone can compete for the excitation light. A different
situation is encountered when naphthadioxinone (ND) is used.
Rapid polymerization with a negligible induction period gives
evidence for the participation of the naphthalene moiety, which
provides an additional initiation pathway. A similar polymer-
ization trend observed with naphthalene (NH) itself also
confirms this behavior. It is known that excited polynuclear
aromatic compounds undergo electron-transfer reactions within
the exciplex formed with the ground-state iodonium salt. As

Scheme 2. Photoinitiated Cationic Polymerization of Cyclohexene Oxide (CHO) by Consecutive Two-Photon Absorption Process

Figure 1. UV/vis spectra of diphenyliodonium hexafluorophosphate (DPI), benzophenone (BP), benzodioxinone (BD), and naphthadioxinone (ND) in CH$_2$Cl$_2$. The concentrations of all compounds are $6 \times 10^{-5}$ M.

Figure 2. Time vs conversion for polymerization of CHO for benzophenone (BP), benzodioxinone (BD), naphthalene (NH), and naphthadioxinone (ND) systems, cured at 30 °C by UV light with an intensity of 18.4 mW cm$^{-2}$. (The iodonium salt and photoinitiator concentrations are 0.02 M in terms of the benzophenone moieties.)
Scheme 3. Photoinduced Acid Generation from Naphthalene Moiety

![Scheme 3](image)

depicted in Scheme 3, the naphthalene radical cations (reaction 9) and/or protonic acids (reaction 10) produced initiate the polymerization in a manner that described for anthracene photosensitization.\(^{15,16}\)

In conclusion, from the results described above it is inferred that cyclic ethers can readily be polymerized by the photolysis of benzodioxinones in the presence of suitable oxidants such as iodonium salts. The process is based on two-photon absorption in which benzophenone is released by the photolysis of benzodioxinone. Subsequent absorption of the benzophenone thus formed eventually produces protonic acids capable of initiating cationic polymerization by successive hydrogen abstraction and redox processes. Mechanistic details by using laser flash photolysis studies. This material is available free of charge via the Internet at http://pubs.acs.org.

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**Supporting Information Available:** Experimental details and laser flash photolysis studies. This material is available free of charge via the Internet at http://pubs.acs.org.

**References and Notes**


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