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# 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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Received October 24, 2007

Revised Manuscript Received December 5, 2007

Photoinitiated cationic polymerization<sup>1–4</sup> 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,<sup>5</sup> triarylsulfonium,<sup>6</sup> and alkoxy-pyridinium<sup>7,8</sup> 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,<sup>9</sup> electron-transfer reactions in the exciplexes,<sup>10–12</sup> and charge-transfer complexes.<sup>13,14</sup> 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 photoinitiators<sup>15,16</sup> were shown to generate oxidizable electron donor radicals.

It was recently reported<sup>17</sup> 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 shown<sup>18</sup> 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 ketene 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.<sup>19–21</sup>

Two-photon absorption<sup>22</sup> 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,<sup>22</sup> three-dimensional (3D) microfabrication,<sup>23–26</sup> optical data storage,<sup>27</sup> imaging,<sup>28</sup> and the controlled release<sup>29</sup> of biological systems. In these

Scheme 1. Synthesis of Salicylate Esters by Photoinduced Acylation Using Benzodioxinone

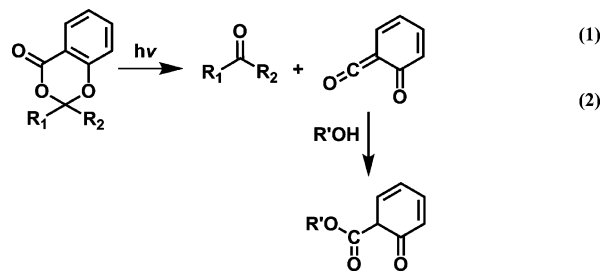
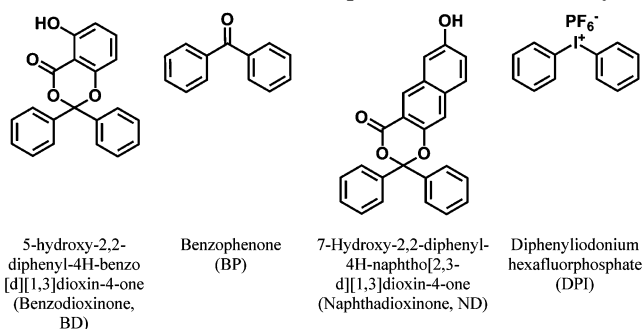


Chart 1. Structures of the Compounds Used in This Study



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 photoproduct. Likewise, to simultaneous two-photon absorption, stepwise two-photon absorption occurs with high spatial resolution.

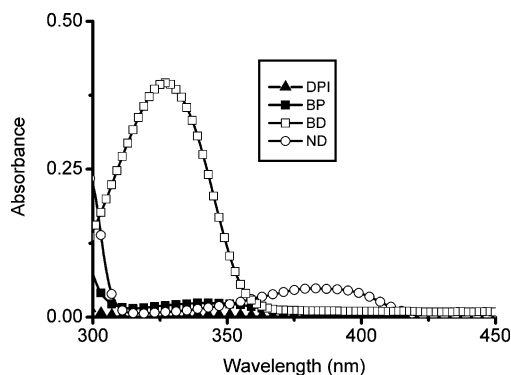
In this study we test whether benzodioxinone and naphthadioxinone (Chart 1) can act as caged sensitizers for diphenyliodonium salt to generate acids for initiation of cationic polymerization. The first absorbed photon should uncage the sensitizer. The released sensitizer absorbs the second photon to 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*-alkoxypyridinium salts are expected to exhibit lower efficiency due to their less favorable redox potentials ( $E_{1/2}^{\text{red}}$  are  $-1.02$  and  $-0.7$  V (SCE), respectively) compare to the iodonium salts ( $E_{1/2}^{\text{red}} = -0.2$  V). Figure 1 shows optical absorption spectra of photoacid generators (PAG) benzodioxinone and naphthadioxinone, structurally related compounds benzophenone and naphthalene, and oxidizing agent. Since

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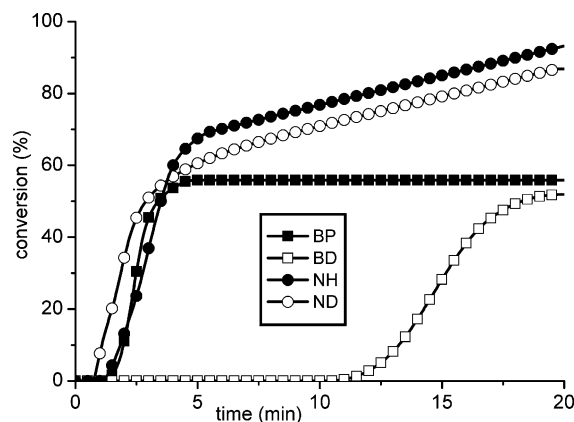
<sup>‡</sup> Columbia University.



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

iodonium salt does not absorb light above 320 nm, all irradiations were performed at  $\lambda = 320\text{--}500$  nm.

As can be seen from Figure 2, CHO was polymerized quite efficiently with benzophenone, benzodioxinone, and naphthadioxinone 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, benzodioxinone 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  $k_q = 1.2 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$  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 ( $E_{1/2}^{\text{ox}} \sim -0.7 \text{ V (SCE)}$ ).<sup>30</sup> Diphenylketyl radicals are reported to be able to reduce iodonium salts (reaction 5).<sup>31–33</sup> Back-electron-transfer reaction can be disregarded because the oxocarbenium ion decomposes into acid and benzophenone<sup>34</sup> (reaction 6). The ensuing protonic acid is

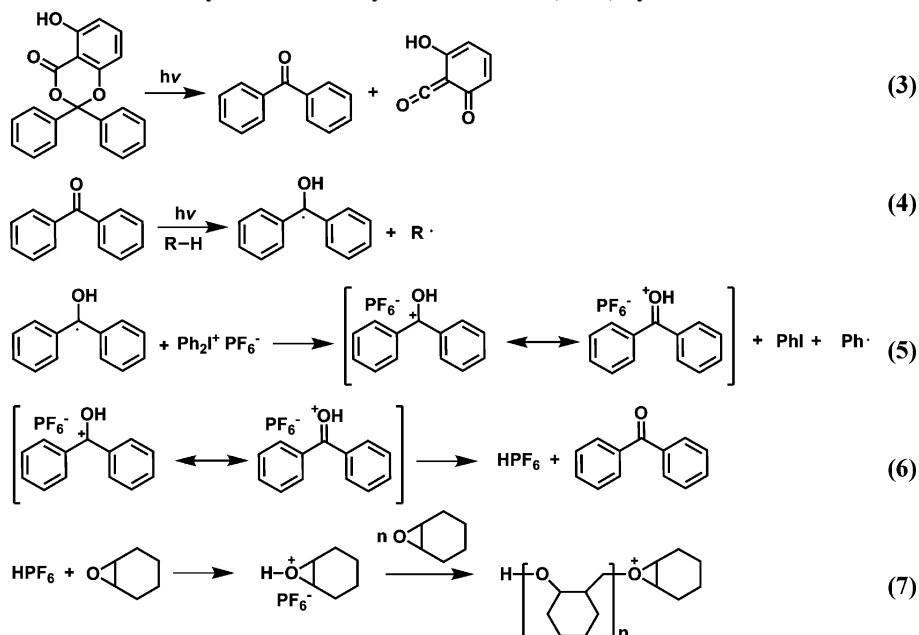


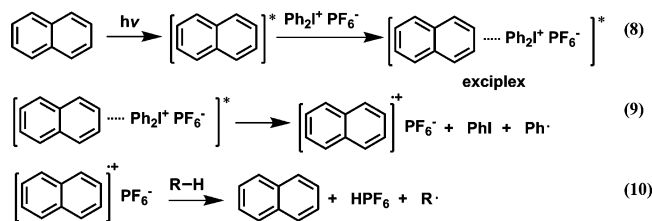
**Figure 2.** Time vs conversion for polymerization of CHO for benzophenone (BP), benzodioxinone (BD), naphthalene (NH), and naphthadioxinone (ND) systems, cured at  $30^\circ\text{C}$  by UV light with an intensity of  $18.4 \text{ mW cm}^{-2}$ . (The iodonium salt and photoinitiator concentrations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

capable of initiating cationic polymerization of CHO (reactions 7 and 8).

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-photon 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 magnitude 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 polymerization 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**



**Scheme 3. Photoinduced Acid Generation from Naphthalene Moiety**

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.<sup>15,16</sup>

In conclusion, from the results described above it is interfered 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 together with the application of the system to a positive-tone chemically amplified resist for the fabrication of microchannel structures are now in progress.

**Acknowledgment.** The authors thank Istanbul Technical University, Research Funds, for financial support. The authors at Columbia thank the National Science Foundation (Grant CHE-04-15516) and SEMATECH International for financial support.

**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>.

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MA7023649