Control of Photopolymerization of BITh Thin Films with Plasmonic Metal/Dielectric Substrates

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Abstract: We studied effects of metal-dielectric substrates on photopolymerization of BITh monomer. We found that the rate of photopolymerization is getting higher if the monomer film is deposited on top of silver, gold, and lamellar structures. © 2023 The Author(s)

The research field of nanophotonics is aimed at the study of light-matter interaction at nanoscale. While control of incident light is one of the most common directions of the nanophotonics research, the other areas include energy transfer, van der Waals interactions, and chemical reactions [1]. In this study, we ask the question whether the proximity to metallic and metal/dielectric substrates can control solid state photopolymerization, a chemical reaction of fundamental and practical importance, and compare the experimental results with the predictions of the developed theoretical model.

Photopolymerization is of importance in chemistry, physics, and materials science because it enables a wide range of advanced applications. Commonly, photopolymerization employs monomers that can be polymerized, *via* radical or ionic mechanisms, in presence of photoinitistors, upon exposure to UV, visible or NIR light [2]. One way to study the effect of metallic and metal/dielectric substrates on photopolymerization, is to deposit a thin monomer film onto a substrate, photo-expose it causing polymerization, and monitor the reaction by measuring spectroscopic properties or optical responses, which evolve in the course of the experiment. To this end, topochemical polymerization reaction of conjugated dye molecules based on 3,3’-dihydroxy-1H,1’H-[2,2’-biindene]-1,1’-dione (BIT) is an ideal system for the study [3]. [2,2'-Bi-1H-indene]-1,1'-dione-3,3'-diyl diheptanoate (BITh) is one of thoroughly studied systems that polymerize upon UV-visible light illumination in the solid state.

The polymerization mechanism of BITh is believed to be similar to that reported for the diene compounds. Thin film of BITh can be prepared by spin-coating from its chloroform solution. It has an absorption band ranging from ≈350 nm to ≈530 nm, with the maximum at ≈480 nm, and orange coloration. After UV or visible light illumination, the coloration and the ≈480 nm absorption band disappear and a colorless polymeric PBITh thin film is attained. Therefore, one can easily monitor the polymerization process of BITh using absorption and reflection spectroscopy.
The ≈480 nm spectral band is due to the π-electron delocalization ($\pi \rightarrow \pi^*$) and intramolecular donor-acceptor interactions ($n \rightarrow \pi^*$). The monomer BITh was synthesized, with modification, according to the procedure described by Dou et.al [3] and Gabriel [4], by functionalizing BIT with heptanoate on the hydroxyl groups in the 3 and 3’ positions.

Experimentally, we have fabricated and studied BITh monomer thin films (23 - 90 nm) deposited on (1) glass, (2) MgF_2 on top of glass, (3) Ag on top of glass, (4) MgF_2 on top of Ag deposited on glass, (5) lamellar Ag/MgF_2 structure deposited on glass (with MgF_2 as the top layer), and (6) Au on top of glass. The samples were illuminated with the Xe lamp.

The samples were photoexposed over one-to-thirty minutes, and the integral photoexposure time ranged between one and seventy minutes. After each photoexposure, the sample’s transmission spectra (on top of transparent substrates) or reflection spectra (on top of metal-based substrates) were taken. The transmission and reflection spectra showed the dips centered at λ~480 nm, which were due to the monomer’s absorption. With increase of the photoexposure, the dips became more shallow, manifesting photopolymerization of the monomer, Fig. 1a. When the strengths of the corresponding absorption bands were plotted against the photoexposure time, the resultant polymerization kinetics could, in the first approximation, be described with the exponential functions, Fig. 1b.

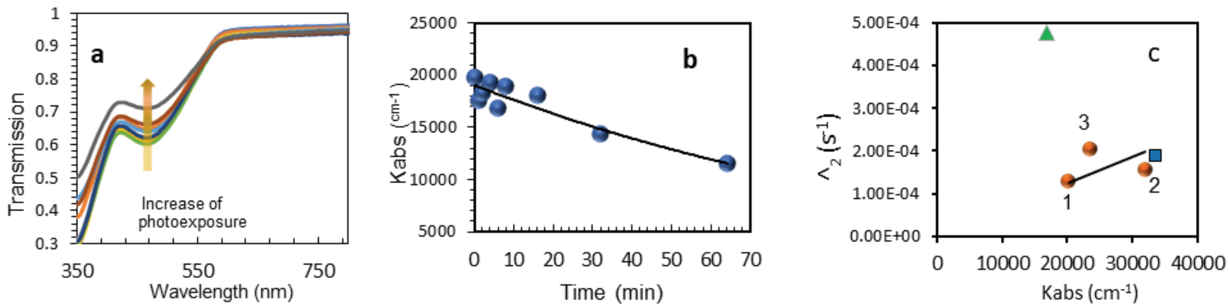

Figure. 1. (a) Transmission spectra of the BITh film after photoexposures ranging from 0 min to 64 min. (b) Decay kinetics. Characters: Kinetics of the maximal absorption coefficients in the photoexposed BITh film. Solid line: fit with the exponential function. (c) The photopolymerization rate Λ_2 plotted against the absorption coefficient K_{abs}. Circle 1: glass/MgF_2/BITh; circle 2: glass/Ag/MgF_2/BITh; and circle 3: glass/Ag-MgF_2 lamellar structure/BITh. Triangle – BITh deposited on Ag. Square – BITh deposited on Au.

In the two experimental samples, (i) glass/Ag/MgF_2/BITh and (ii) glass/Ag-MgF_2 lamellar structure/BITh, the monomer was separated from Ag by a thin insulating MgF_2 layer. In these samples (circles 2 and 3 in Fig. 1c), the data points (rate and Kabs) were reasonably close to the corresponding data point in the glass/MgF_2/BITh metal-free sample, circle 1 in Fig. 1c. Furthermore, the three circle character data points (two in the samples with metal and one in the sample without metal) formed a straight line, although with a notable data scatter, Fig. 1c. This suggests that the slope (rate and Kabs) was practically not affected by Ag separated from BITh molecules with a thin insulating MgF_2 film. At the same time, the values (rate and Kabs) in the Ag based samples (circles 2 and 3) were marginally larger than the corresponding point (rate and Kabs) in the metal-free MgF2 sample, circle 1 in Fig. 1c. This effect can be explained by a partial constructive interference of incident and reflected light waves in Ag-based samples, increasing both the effective absorption and the decay rate. However, the latter interference is not the only decisive factor determined the rate of photo-polymerization, as many spectroscopic parameters are known to be affected by the vicinity of metal/dielectric interfaces [1].

At the same time, in the glass/Ag/BITh samples, in which monomer molecules were not separated from Ag by an insulating layer, the decay rate was nearly threefold higher than that in the samples with MgF_2 layer. A similar effect, observed in Ref [5] photodegradation of the semiconducting polymer P3HT, was tentatively explained by a metal-polymer charge transfer (chemical catalysis).

Lastly, note that the Au substrate caused modest (~50%) enhancement of both monomer film absorption K_{abs} and the decay *rate* Λ_2, in comparison to BITh on top of MgF_2 without metal, Fig. 1c. The detailed study of the effect of Au-based substrates on photopolymerization of BIT is the subject of a separate study to be published elsewhere. More details of experiments and modeling will be presented at the conference.

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