Sugar Overcomes Oxygen Inhibition in Photoinitiated Free Radical Polymerization

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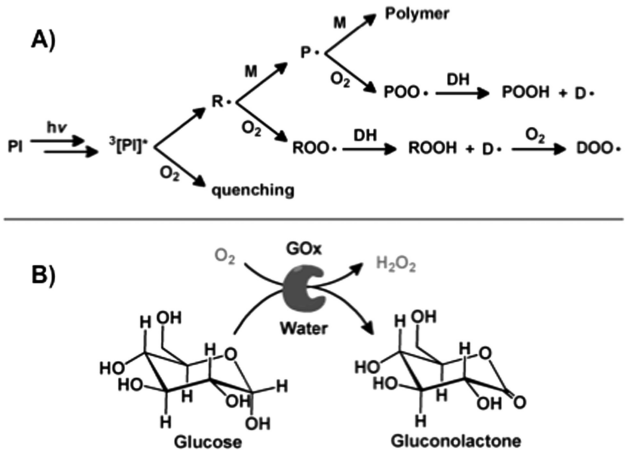
INTRODUCTION Free radical polymerization methods have played an enormous role in the materials engineering and science. Particularly, photo-initiated mode of radical polymerization has become a key method in countless number of industrial applications such as protective coatings, dental resins, printing inks, lithography, adhesives, varnishes, support materials, and composites.[1–5] In these applications, quenching of free radicals by molecular oxygen (O_2) is one of the most challenging problems. As this important technique is generally carried out under air atmosphere, it suffers noticeably from O_2 inhibition.[6–8] Principally, formation of initiating radicals is prevented in the presence of O_2 because excited states of photoinitiators,[9,10] especially *Type II* initiators, are strongly quenched by O_2. Moreover, O_2 scavenges both initiating radicals produced from photolysis of photoinitiators and propagating macroradicals, and transforms them to stable peroxyl radicals that barely participate in further corresponding reactions (Scheme 1A).[11] Newly formed peroxy radicals generally abstract hydrogen atoms from the polymer backbone to generate hydroperoxides. Such drawbacks cause premature polymerization and formation of wet and sticky surfaces as a consequence of long inhibition time, and decrease in both polymerization rate and final conversion ratio.[12]

Several attempts including addition of O_2 scavengers[12,13] or producing additional active species,[14–16] use of reactive photoinitiators,[17,18] performing polymerization under inert atmosphere (Ar, N_2, CO_2, etc.),[11] using wax barrier coats or performing the UV exposure under water have been made in the past to overcome this difficulty.[11] In addition, intense illumination or using an excess amount of photoinitiator is an alternative way to overwhelm oxygen inhibition by consuming O_2 dissolved in the resin for preventing, especially for thin films in contact with air.[10]. However, all these strategies either require supplementary processes with additional cost or are limited in their available specially designed photoinitiators.

Inspired by nature, (polymer) chemists have begun to take advantage of the properties of biomolecules toward diverse applications. For instance, the integration of biomolecules with synthetic materials or processes is a rapidly progressing interdisciplinary research field for preparation of functional and smart materials widely employed in medicine,[19] drug delivery systems,[20] biochemistry, bio-sensing platforms,[21–23] and many other research activities and industrial applications. Certainly, one can recruit any biomolecule in production of a material for a specific purpose by providing suitable conditions. Unearthing the secret of how nature is able to use sugar (i.e., glucose) to generate power (energy) gives alternative way to eliminate oxygen from a medium. Particularly, glucose oxidase (GOx; β-D-glucose:oxygen 1-oxido-reductase, E.C. 1.1.3.4), extremely valuable enzyme from not only metabolic but also industrial point of view, is a potential candidate for the prevention of oxygen inhibition. It is widely employed in the determination of free glucose amount in blood and body fluids, foods, drinks and agricultural products. It catalyzes specifically the oxidation of β-D-glucose (G) to D-glucono-δ-lactone in the presence of O_2 in aqueous solution (Scheme 1B).[24,25] Thus, the process has been employed several water-born applications.

In a typical application of this redox process, we have previously designed[26] a fluorescent probe for G sensing by combination of GOx with poly(vinyl alcohol)-pyrene matrix (PVA-Py) prepared by "Click" chemistry.[26] The PVA-Py matrix appeared to be very attractive, because it possesses both



SCHEME 1 Main pathways in oxygen inhibition of free radical photopolymerization (A). Oxidation of β-D-glucose to D-glucono-δ-lactone in the presence of molecular oxygen (B).

light absorbing chromophoric and oxidizing sites in the structure and does not require additional molecules. Moreover, it provides enhanced stability compared to the systems in which active sites are composed in the independent molecules. Recently, GOx was used in the presence of Fe^{2+} to produce free radicals for generation of biologically active hydrogels.[27,28]

Here, we take advantage of these features to develop a UV curing system based on free radical polymerization and consumption of O_2 by GOx in its usual enzymatic pathway. Thus, in this approach the polymerization system contains GOx and G in addition to usual components—monomer and initiator. Specifically, UV-curable aqueous formulations containing poly(ethylene glycol) diacrylate (PEG-DA) or acrylamide (AAm)/*N*,*N*'-methylenebisacrylamide (BAAm) as monomers, and *Type I* or *Type II* photoinitiators in the presence and absence of GOx and G were irradiated and polymerizations were monitored by photo-DSC.

In a model application, free radical photopolymerization of PEGDA using a *Type I* photoinitiator, 2,2-dimethoxy-2-phenyl acetophenone (DMPA), is enhanced by the presence of the redox components, GOx and G. The biological activity of GOx obviously leads to increase in the rate of the polymerization and monomer conversion (see curves A and B in Fig. 1). The action of the additives must be related to the consumption of O_2 during oxidation of G, thus the initiating and propagating radicals readily react with monomers without forming inefficient peroxy radicals. As a consequence of this effect, shorter induction periods are observed in such formulations. Full mechanisms for the polymerizations in air in the absence and presence of GOx and G are proposed in Figure 2. The proposed mechanism of the photopolymerization depends on prevention of photochemically formed radicals from molecular oxygen presenting in the close proximity. Complimentary polymerizations under nitrogen were also performed (curve C in Fig. 1). It is noted that the addition of GOx and G gave higher rates but similar conversion values to those obtained with the polymerizations conducted with nitrogen saturation. Efficiency of a *Type II* initiating system consisting of benzophenone (BP) and *N*,*N*-dimethyl aniline (DMA) was also investigated in photo-crosslinking of PEGDA. The effect of the GOx/G was the same for also this system (Run 4 and 5, Table 1).

Efficiency of this new system was also evaluated for acrylamide-based formulations. UV curing behavior of AAm/BAAm monomer pair initiated by BP/DMA is very similar, although the conversion changes as function of time for both systems vary somewhat.

Because the polymerization is slower in the acrylamide system, oxygen affects the process more significantly (Fig. 3, Curve B). Interestingly, the enzymatic route exhibits ability to prevent oxygen inhibition even better than deaeration with nitrogen. Analogous with results from *Type II* photoinitiator, comparable improvement in the rate and final conversion was attained by employing GOx/G in the formulations containing *Type I* photoinitiator (DMPA) (Run 9 and 10, Table 1).

To describe all these effects quantitatively, we performed polymerizations using different combinations of monomers and initiating systems (Table 1). In all cases, substantial increase in the rate and conversion of polymerization were achieved upon addition of redox components. Moreover, the time required to reach maximum rate (t_{max}) was much shorter in the presence of the GOx and G.

In summary, we developed a new method to overwhelm O_2 inhibition in photoinitiated free radical polymerization which is of considerable technical and commercial importance. The use

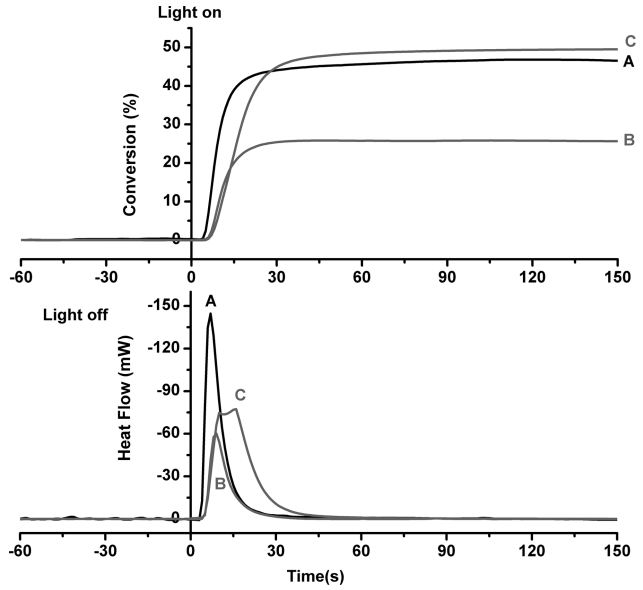


FIGURE 1 Conversion and heat flow profile during the UV curing of PEGDA (52 wt %) initiated by a *Type I* photoinitiator (DMPA, 1 wt %) in the presence (A) and absence (B) of glucose (1 wt %) and GOx (0.06 wt %) in aqueous solution under air atmosphere. Similar UV curing was performed without GOx and G under nitrogen atmosphere (C).

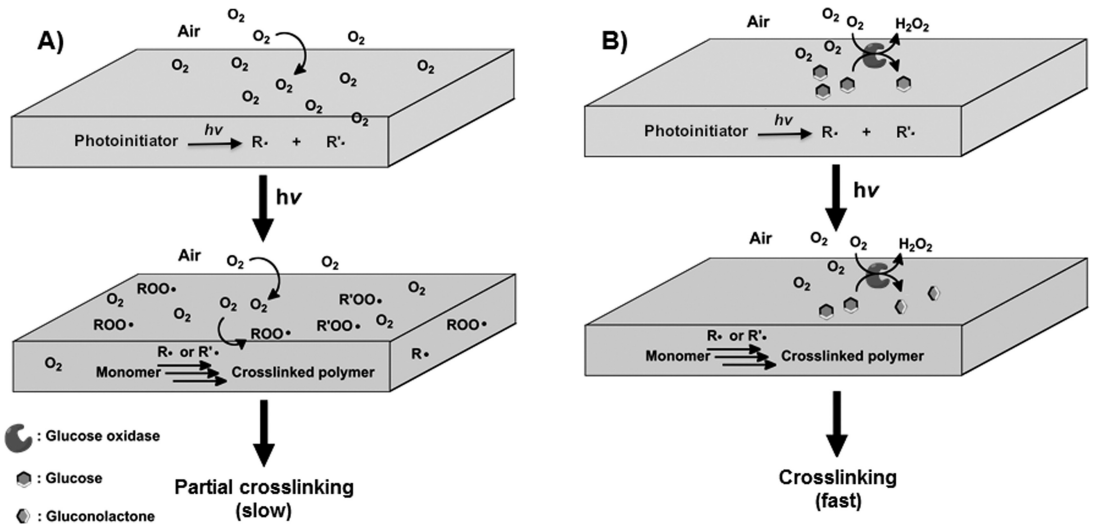


FIGURE 2 Photoinitiated free radical polymerization in air in the absence (A) and presence of GOx and G (B).

of GOx and G for consuming oxygen in photoinitiated free radical polymerization offers a very simple approach that is controlled by the redox process. Detailed photo-DSC investigations reveals that the enzymatic system enhances the efficiency of the free radical photopolymerization initiated with both *Type I* and *Type II* photoinitiators. The current limiting factor of the system is that it can only be applied to water-born coatings involving aqueous photo polymerizations. Because the redox components are insoluble in organic systems, facilitating their dissolution through structural modifications should lead to a much wider practical applications.

EXPERIMENTAL

Materials

The monomers, poly(ethyleneglycol) diacrylate (PEGDA) (Aldrich, M_n ~575 g/mol) and acrylamide (AAm) (Fluka); the crosslinker, BAAm (Merck); the initiators, 2,2-dimethoxy-2-phenylacetophenone (DMPA) (Ciba), BP (Acros, 99%); and the hydrogen donor, *N,N'*-dimethylaniline (DMA) (Fluka, 99.5%), were used as received. GOx (2.5 mg/mL) and D-glucose (G) were purchased from Sigma-Aldrich. Solvents were purified by conventional drying and distillation procedures.

Preparation of Photo-Curable Formulations

Photo-induced crosslinking of PEGDA or AAm/BAAm was carried out using 1 wt % of both *Type I* and *Type II* photoinitiating system (DMPA or BP/DMA) in presence or absence of GOx/G (0.06 wt %/1 wt %). All formulations are listed in Table 1. All components except GOx solution were put in an Eppendorf tube and dissolved. Then GOx solution was added into this mixture and immediately used in photopolymerizations. A typical photopolymerization performed on photo-differential scanning calorimetry (Photo-DSC) is as follows: 4.5 mg of *Type I* photoinitiator (DMPA, 1 wt %), 4.5 mg of G (1

TABLE 1 Photo-Induced Crosslinking Polymerization of Water Soluble Monomers the Presence or Absence of GOx/G Under Air Atmosphere at 20 °C

Run	Monomer[a]	PI[b]	[G] (wt %)	[GOx] (wt %)	t_{max} (s)[c]	Conv. (%)[d]
1	PEGDA	DMPA	1	0.06	7	47
2	PEGDA	DMPA	–	–	9	26
3[e]	PEGDA	DMPA	–	–	10	49
4	PEGDA	BP/DMA	1	0.06	12	45
5	PEGDA	BP/DMA	–	–	14	32
6	AAm/BAAm	BP/DMA	1	0.06	27	39
7	AAm/BAAm	BP/DMA	–	–	66	14
8[e]	AAm/BAAm	BP/DMA	–	–	28	32
9	AAm/BAAm	DMPA	1	0.06	8	24
10	AAm/BAAm	DMPA	–	–	10	22

[a] PEGDA: poly(ethylene glycol) diacrylate (52 wt %); AAm: acrylamide (49 wt %); BAAm: *N,N'*-methylenebisacrylamide (2 wt %).
[b] DMPA: 2,2-dimethoxy-2-phenyl acetophenone (1 wt %); BP: benzophenone (1 wt %); DMA: *N,N'*-dimethylaniline (1 wt %).
[c] t_{max} = The time required to reach maximum rate.
[d] Conversions (%) of double bonds were calculated from integral areas of heat flow values using heat of polymerization (ΔH_0) values for acrylate as 80 and 78 kJ mol^{-1}, respectively.
[e] Polymerizations were performed under nitrogen atmosphere.

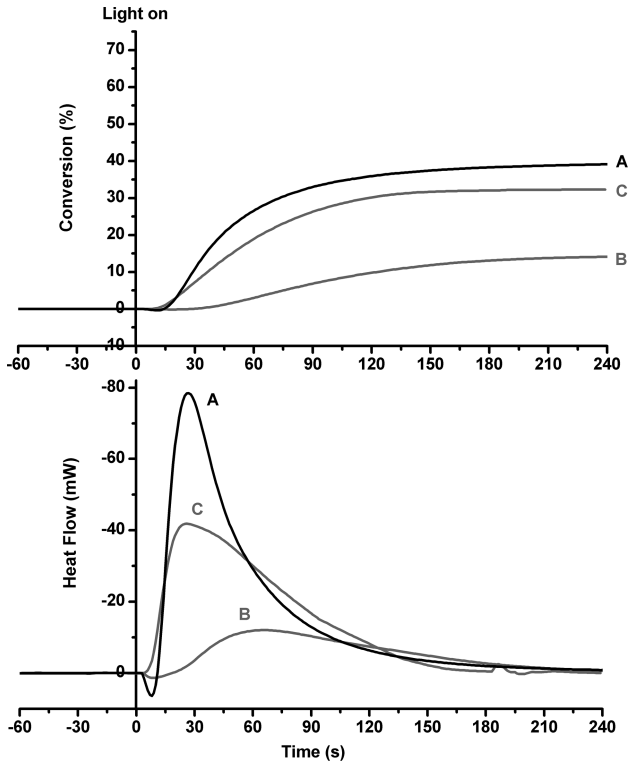


FIGURE 3 Conversion and heat flow profile during the UV curing of AAm (49 wt %)/BAAm (2 wt %) initiated by a *Type II* photoinitiating system in the presence (A) and absence (B) of glucose (1 wt %) and GOx (0.06 wt %) in aqueous solution under air. BP (1 wt %)/DMA (1 wt %) were used as the *Type II* initiating system. Similar UV curing was performed without GOx and G under nitrogen atmosphere (C).

wt %) was dissolved in PEGDA (0.2 mL, 52 wt %) and 0.1 mL of water. Just before irradiation, 0.1 mL of GOx solution (containing 0.25 mg of the enzyme) was added into the reaction solution (total volume: 0.4 mL). Then, 6–10 mg of the reaction solution was transferred to a DSC pan for liquid sample.

Photo-Differential Scanning Calorimetry

The photocuring of PEGDA and AAm/BAAm was studied by Photo-DSC at 20 °C under air or nitrogen atmosphere. The formulations prepared according to Table 1 were dropped (6–10 mg) onto an aluminum pan and the film samples were placed into the sample holder of photo-DSC instrument. The polymerizations were carried on a Perkin-Elmer Diamond DSC equipped with a UV–vis light source (Omnicure Series 2000 emitting light in the range of 320–500 nm). A uniform UV light intensity is delivered across the DSC cell to the sample and the reference pans. The measurements were carried out in an isothermal condition at 20 °C under air atmosphere. The DSC run was begun, but for the first 60 s, a shutter prevented irradiation of the sample to stabilize the light source and to establish the heat flow baseline. When the light was switched on, an exotherm was observed. Irradiation was continued after the exotherm peak until no change was observed in the heat flow. To remove the slight imbalance of the thermal heating effect on the sample and reference pans, the cured sample was again irradiated with the same conditions to produce a background which was subtracted from the data of the first run.

The reaction heat liberated from the polymerization was directly proportional to the number of acrylate or acrylamide groups reacted in the system. By integrating the area under the exothermic peak, the conversion of the vinyl groups (C) or the extent of the reaction was determined as follows:

$$C(\%) = (\Delta H_t / \Delta H_0^{\text{theory}}) \times 100$$

where ΔH_t is the reaction heat evolved at time t and $\Delta H_0{}^{\text{theory}}$ is the theoretical heat for complete conversion. $\Delta H_0{}^{\text{theory}}$ equals to 80 and 78 kJ mol^{-1} for an acrylic double bond and acrylamide, respectively.[29]

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