

The Role of Glucose Oxidase in Free Radical Polymerization

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Abstract: Enzymes are biological catalyst that are essential for living organisms. Enzymes have been extensively employed in many industrial applications including medicine, cosmetics, pharmaceuticals, dairy, baking, beverage, animal feed, paper, leather, and etc. In addition, enzymes have been widely utilized in polymer industry and chemistry. Herein, roles of the enzymes in free radical polymerization are reviewed. Enzymes are usually utilized in free radical polymerization for deoxygenation of polymerization medium or generation of free radicals in a cascade reaction. One of the primary challenges in radical polymerization revolves around oxygen inhibition. Various strategies have been devised to address this issue. These include employing inert gases, applying coatings, increasing initiator concentration, incorporating additives such as amines, thiols, boranes, and silanes, as well as utilizing enzymes for deoxygenation. Prof. Yagci significantly advanced this field with groundbreaking research. Yagci and colleagues introduced a pioneering photopolymerization system that utilized glucose oxidase (GOx) and sugar to eliminate oxygen from the polymerization environment. This innovative approach served as inspiration for others to develop controlled/living polymerization techniques utilizing enzyme-mediated deoxygenation.

Keywords: Free radical polymerization, oxygen inhibition, enzyme.

Glukoz Oksidazın Serbest Radikal Polimerizasyondaki Rolü

Özet: Enzimler, yaşayan organizmalar için hayati olan biyolojik katalizörlerdir. Enzimler, tıp, kozmetik, ilaç, süt ürünleri, fırıncılık, içecekler, hayvan yemi, kağıt, deri ve benzeri birçok endüstriyel uygulamada yaygın olarak kullanılmaktadırlar. Ayrıca, enzimler polimer endüstrisinde ve kimyasında da geniş ölçüde yer almaktadır. Bu çalışmada, serbest radikal polimerizasyon esnasında enzimlerin alabileceği roller araştırılmış ve derlenmiştir. Enzimler, genellikle serbest radikal polimerizasyonunda, polimerizasyon ortamının oksijeninin giderilmesi veya serbest radikallerin kademeli bir tepkime ile oluşturulması için kullanılır. Radikal polimerizasyondaki temel zorluklardan biri oksijen inhibisyonudur. Bu sorunu aşılması için çeşitli stratejiler geliştirilmiştir. Bunlar; inert gazların kullanımı, kaplama uygulamaları, başlatıcı konsantrasyonunun artırılması, aminler, tiyoller, boranlar ve silanlar gibi katkı maddelerinin eklenmesi ve deoksijenasyon için enzimlerin kullanılması gibi yöntemleri içerir. Prof. Yagci, çığır açan araştırmasıyla bu alanda önemli bir ilerleme kaydetmiştir. Yagci ve meslektaşları, glukoz oksidaz (GOx) ve şeker kullanarak polimerizasyon ortamındaki oksijeni gideren öncü bir fotopolimerizasyon sistemi geliştirmişlerdir. Bu yenilikçi yaklaşım, diğer bilim insanlarına enzim aracılı deoksijenasyon kullanarak kontrol edilen/yaşayan polimerizasyon teknikleri geliştirmesi için ilham kaynağı olmuştur.

Anahtar Kelimeler: Serbest radikal polimerizasyonu, oksijen inhibisyonu, enzim.

REVIEW PAPER

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1. Introduction

Chain-growth polymerizations are elegant tools for production of wide variety of materials; thus, they are extensively employed by industry and academics. Chain polymerizations rely on principally three distinct mechanisms; cationic, anionic, and free radical. Free radical polymerizations are much more widely employed due to their advantages over ionic polymerizations. Free radical polymerizations are suitable for a wide array of monomers and solvents, tolerant to many functional groups and impurities such as water, nucleophiles or electrophiles. Therefore, the experimental or large-scale setups of radical polymerization are much easier

compared to those of ionic polymerizations and friendly with many industrial applications.

Free radical polymerizations, commonly also known as free radical chain addition polymerization, was first discovered in 1920s. Hermann Staudinger described the generation of high molecular mass molecules by repeated addition a large number of small molecules (monomers) very first time in 1920. Thus, he coined the term “Makromolekül” in his paper titled “Über Polymerisation” (Staudinger, 1920). After this time, free radical polymerization is considered as a powerful and practical technique for synthesis/production of polymers employed across a diverse range

of applications. These fields encompass, but are not limited to, commodity materials, coatings, electronics, lithography, medicine, drug delivery, tissue engineering, sensors, and various other domains.

However, such powerful technique significantly suffers from oxygen inhibition (Davidson, 1998; Fouassier, 1995; Gauthier et al., 2005; Pappas, 1985; Yagci et al., 2010). Basically, oxygen inhibition is a phenomenon in which reactive species including excited photoinitiators, initiating or propagating free radicals are quenched by molecular oxygen (O_2) leading to prevention of any possible free radical polymerization. As most of the radical photopolymerizations are performed under air atmosphere radical, oxygen inhibition is unavoidable and the most challenging drawback of this valuable technique. (Davidson, 1998; Fouassier, 1995; Pappas, 1985) Therefore, countless efforts to eliminate oxygen inhibition have been made and reported as patents, research articles, reviews and technical reports (Fimia et al., 1993; Gauthier et al., 2005; Husár et al., 2014; Ligon et al., 2014; Yeow et al., 2018).

2. Mechanism of Free Radical Polymerization

Radical polymerizations involve free radicals as the active species for polymerization of mostly vinyl monomers. The polymerization mechanism involves four consecutive stages; initiation, propagation, chain transfer, and termination (Fig. 1) (Nesvadba, 2012).

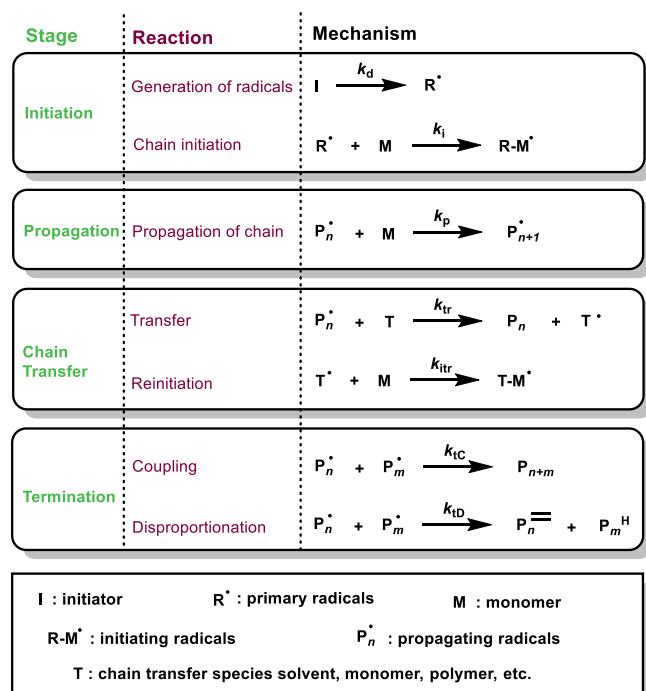


Fig. 1. The mechanism of free radical polymerization.

In the initial phase, known as “initiation”, free radicals (R^\bullet) are generated through thermal, photochemical, redox reactions, or ionizing radiation originating from initiators (I). In the following stage, initiating radicals react with vinyl-type monomers (M) to form propagating carbon-centered radicals (P_n^\bullet). The polymerization process primarily advances as these propagating radicals add to the monomers, resulting in the formation of polymer chains (propagation). Nevertheless, under certain circumstances, either initiating radicals or propagating radicals may abstract an atom (usually H), undergo addition to an unsaturated bond, followed by fragmentation, and participate in homolytic substitution. In such cases, the radical center is transferred to another molecule (which could be a solvent, monomer, impurity, or polymer chain, denoted as T), and polymerization proceeds from this newly formed radical center (T-M[•]). This predominantly undesirable and inevitable

occurrence is referred to as “chain transfer”. In traditional radical polymerization, another unavoidable stage is “termination”. This marks the concluding phase of polymerization, entailing the interaction between two radicals, either propagating or initiating radicals, leading to the formation of unreactive molecules. Termination in polymerization can occur through two distinct routes: “combination” and “disproportionation”. In the combination pathway, two radicals (P_n^\bullet , P_m^\bullet) join together to create a single molecule (P_{n+m}). On the other hand, disproportionation involves β -hydrogen abstraction from one radical (P_m^\bullet) by another radical (P_n^\bullet), resulting in the formation of two unreactive molecules. As evident from the mechanism, every step in radical polymerization incorporates radical species, making it vulnerable to oxygen inhibition. Especially, photo-initiated radical polymerizations are more susceptible to oxygen inhibition because photopolymerizations are usually performed in media open to air. Moreover, in addition to inhibition through radicals, excited photoinitiators can be also quenched by oxygen in photopolymerizations.

3. Oxygen Inhibition in Radical Polymerizations

Oxygen inhibition is a phenomenon in which reactive species including initiating or propagating free radicals, and excited state photoinitiators are quenched/terminated by molecular oxygen (O_2) stopping any possible free radical polymerization. As most of the radical photopolymerizations are performed under aerial atmosphere, oxygen inhibition is unavoidable and the most challenging drawback of this valuable technique (Davidson, 1998; Fouassier, 1995; Pappas, 1985).

Radical polymerizations under air shows an induction or inhibition period before the onset of polymerization because of dissolved O_2 (10^{-3} M). The concentration of dissolved O_2 should be minimal ($\sim 10^{-6}$ M), to ensure a successful polymerization (Cramer et al., 2006). Oxygen inhibition can occur at different levels of the polymerization. As shown in Fig. 2, firstly, generation of initiating radicals can be prevented because excited states of photoinitiators are strongly quenched by molecular O_2 .

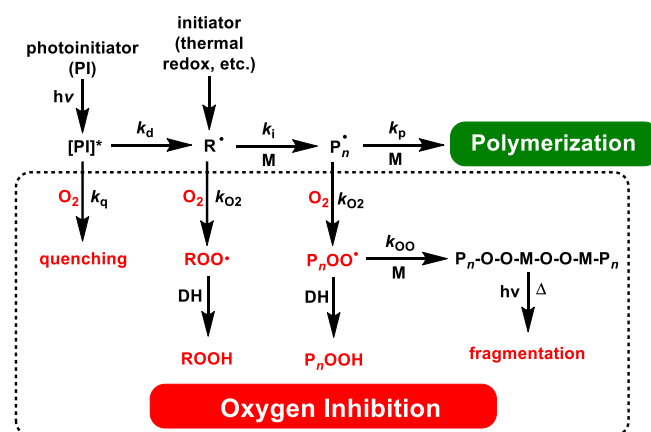


Fig. 2. Oxygen inhibition in free radical polymerizations.

For instance, the deactivation rate constant ($k_q = 0.7-7 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$) of excited state benzophenone derivatives by O_2 is higher than the charge transfer rate constant ($k_e = 0.07-2 \times 10^9 \text{ M}^{-1}\text{s}^{-1}$) of those (Fouassier et al., 1995). That means quenching of excited state photoinitiators by O_2 is more favorable than formation of initiating species. Secondly and more importantly, O_2 molecule with biradical ground state character reacts with carbon-centered radicals to give peroxy radicals that are not favorable in initiating further polymerization. Compared to the rate of typical rate of propagation ($k_p = \sim 10^2-10^4 \text{ M}^{-1}\text{s}^{-1}$), the rate of formation of peroxy radicals ($k_{O_2} = \sim 10^8-10^9 \text{ M}^{-1}\text{s}^{-1}$) is much higher. The concentration of dissolved

O_2 is typically around 10^{-3} M, while monomer concentrations are usually kept in the range of 0.1-10 M (Nesvadba, 2012). Under these conditions, most of the radicals in air-saturated monomers are transformed to peroxy radicals. Thus, O_2 scavenges both initiating radicals produced from photolysis of photoinitiators and propagating macro-radicals, and transforms them into peroxy radicals (Studer et al., 2003). The peroxy radicals add to monomers very slowly ($k_{OO} = \sim 0.1-3 \text{ M}^{-1}\text{s}^{-1}$) yielding new carbon centered radicals. Once more, these radicals can react favorably with O_2 resulting in a kind of copolymer of monomer and O_2 ($P_r-O-O-M-O-O-M-P_n$). Since peroxides are thermally and photochemically unstable, such polymer chains with peroxide impair the properties of the final product (Nesvadba, 2012). Furthermore, peroxy radicals can abstract hydrogen atoms from any molecule including the polymer backbone to generate unreactive hydroperoxides.

Oxygen inhibition causes long induction periods, premature polymerization, formation of wet and sticky surfaces, and poor mechanical properties in the final product as a consequence of long inhibition time, and decrease in both polymerization rate and final conversion ratio (Belon et al., 2010; Pynaert et al., 2013). Such shortcomings can be observed in most of the radical polymerizations, especially in photo-curing of thin films and coatings due to large surface area exposed to air (Nesvadba, 2012). Moreover, when the thickness of such films decreases the oxygen inhibition photopolymerization rate and yield decrease sharply (Fouassier, 1993).

3.1. Strategies to Overcome Oxygen Inhibition

Various strategies have been developed to eliminate the issue of oxygen inhibition in free radical polymerizations (Fimia et al., 1993; Gauthier et al., 2005; Husár et al., 2014; Ligon et al., 2014; Yeow et al., 2018). The strategies can be classified into three primary groups based on their mode of action: Physical approaches, chemical approaches, and intrinsically oxygen-tolerant approaches. Table 1 summarizes these approaches. Addition of certain enzymes to the polymerization media may prevent oxygen inhibition. Some enzymes such as oxidoreductases catalyze the oxidation reaction yielding radicals that may initiate polymerization. Such enzymatic reactions may also result in oxygen free medium since they mostly utilize oxygen for oxidation of their substrates.

Table 1 Overview of the methods for elimination of oxygen inhibition.

Strategy	Method
Physical approach	Inerting with gas
	Isolating polymerization from air by coating with a film, wax, or by lamination
	Increasing light intensity
Chemical approach	Using excess amount of initiator
	Adding additives such as amines, thiols, ethers, silanes, phosphines, boranes, etc.
	Using functional initiator or monomer
	Using singlet oxygen scavengers
Intrinsically oxygen-tolerant approach	Using enzymes
	Using semiconductor nanoparticles or polymerization through singlet oxygen

3.2. Roles of Enzymes in Free Radical Polymerization

3.2.1. Glucose Oxidase

Enzymes are proteins that efficiently catalyze a variety of chemical

reactions in living organisms with specificity. In this context, enzymes have been widely employed in the industry to accelerate numerous industrial processes and facilitate the production of valuable products (Zhu et al., 2011). An exceptional enzyme in this category is glucose oxidase (GOx) enzyme (EC number 1.1.3.4) which is utilized in numerous commercial applications. These applications include enhancing the color and taste of foods and beverages, food preservation, glucose removal from dried egg powder and oxygen elimination from various juices and beverages (Khatami et al.; Wong et al., 2008). GOx is an oxidoreductase that facilitates the oxidation of β -D-glucose to hydrogen peroxide and D-glucono- δ -lactone, leading to the eventual formation of gluconic acid in the presence of oxygen (Fig. 3) (Dinda et al., 2018; Huggett & Nixon, 1957).

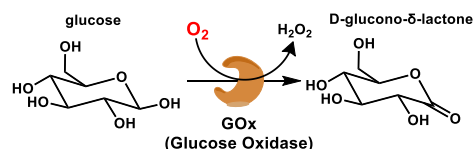


Fig. 3. Oxidation of glucose by glucose oxidase (GOx).

3.2.2. GOx-Mediated Initiation of Radical Polymerization

The capability of GOx in removing oxygen from the polymerization medium and generating initiating radicals has inspired numerous polymer chemists. For the first time, Iwata and coworkers achieved polymerization of 2-hydroxyethyl methacrylate (HEMA) under aerobic conditions taking advantage of this system (Iwata et al., 1991). In this groundbreaking research, the polymerization was initiated by introducing a solution of GOx to a mixture comprising HEMA, glucose, Fe^{2+} and cyclohexanone. In this study, the enzymatic reaction served two roles. Initially, it consumed the dissolved oxygen converting it into H_2O_2 , thereby creating an oxygen-free environment. Subsequently, initiating radicals, specifically $HO\cdot$, were generated through the Fenton redox reaction between H_2O_2 and Fe^{2+} . The flexibility and resilience of this emerging environmentally friendly synthetic approach have inspired numerous studies, encompassing areas such as hydrogel formation for cell encapsulation (Johnson et al., 2009), polymerization-based signal amplification in biodetection (Berron et al., 2011), interfacial radical polymerization (Shenoy & Bowman, 2012), fabrication of thermoresponsive microgels (Gau et al., 2018), formation of core-shell particles (Shenoy et al., 2013) and the preparation of layered hydrogels (Johnson et al., 2010; Zavada et al., 2016). In more recent studies, a comparable deoxygenation approach has been applied in diverse polymerization processes with varying initiation mechanisms. These include enzyme catalyzed redox (i.e. horseradish peroxidase, HRP or laccase) (Enciso, Fu, Lathwal, et al., 2018; Liao et al., 2015; Liu et al., 2017; Nieto et al., 2010; Uyama et al., 1997), $Cu(0)$ -mediated redox (Moreno & Sipponen, 2020), ascorbic acid mediated redox (Lv et al., 2017; Navarro et al., 2019) and thermal (Chapman et al., 2014; Chapman et al., 2016; Enciso, Fu, Russell, et al., 2018; Schneiderman et al., 2018) initiation (Fig. 4). Furthermore, this methodology was applied to an intriguing polymerization system known as blood-catalyzed RAFT polymerization (Reyhani et al., 2018). As indicated in this research, the iron ion (Fe^{2+}) naturally present in the hemoglobin of red blood cells, along with H_2O_2 produced by the oxidation of glucose by GOx, generated initiating radicals ($HO\cdot$) through the Fenton reaction. All these polymerizations facilitated by enzyme-degassing were initiated through a cascade reaction. Alternatively, these polymerizations can be initiated through a distinct mechanism by introducing a thermal initiator or photoinitiator.

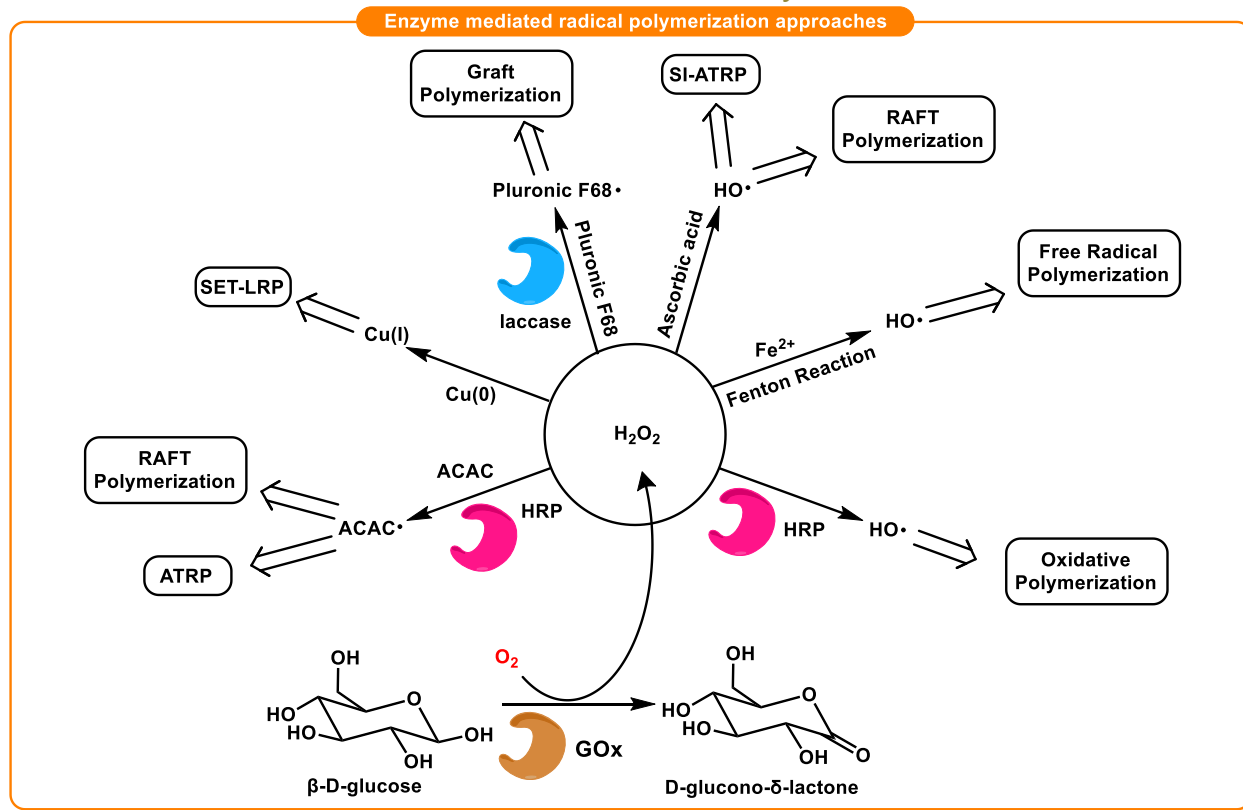


Fig. 4. Enzyme-mediated deoxygenation of polymerization medium and a cascade initiation.

3.2.3. GOx Overcoming Oxygen Inhibition

Motivated by the contributions mentioned earlier, Yagci and Kahveci developed a photopolymerization system incorporating GOx and sugar as agents for removing oxygen from the polymerization medium (Oytun et al., 2013). Similarly, the oxidation of glucose by GOx in the presence of oxygen was utilized to eliminate dissolved oxygen, while the initiation was accomplished through photoinitiation. In particular, acrylate and acrylamide derivatives were rapidly and effectively polymerized using both Type I and Type II photoinitiators under aerial conditions. Interestingly, the enzymatic approach demonstrated superior capability in overcoming oxygen inhibition, even outperforming inerting with nitrogen. This photopolymerization approach has been applied in numerous other studies (Fig. 5), encompassing the fabrication of double network gels for biomaterial applications (Mohammed et al., 2019), synthesis of polymer bioconjugates through photoinduced Atom Transfer Radical Polymerization (ATRP) (Fu et al., 2018), synthesis of block copolymers via Reversible Addition Fragmentation chain Transfer (RAFT) polymerization (Li & An, 2021), synthesis of surface-tethered polymer brushes based on PET-RAFT polymerization (Seo et al., 2020), creation of nanoscale reactors for miniaturized high-throughput synthesis (Rosenfeld et al., 2020; Tan et al., 2017), and photo-induced ATRP (Wang et al., 2019; Wang et al., 2018).

5. Conclusion

Enzymes are important class of biomolecules for not only organisms but also industrial applications such as dairy, beverage, animal feed, paper, leather, cosmetics, pharmaceuticals, etc. Moreover, enzymes have been utilized in polymer chemistry. In this study, the role of the enzymes in free radical polymerization is reviewed. Oxidoreductases, such as GOx, HRP, and laccase, have been successfully utilized in deoxygenation and initiation of radical polymerization. One of the most important issue in radical polymerization is oxygen inhibition. Prof. Yagci made a brilliant contribution to the field with a pioneering

work. Yagci and coworkers reported a photopolymerization system incorporating GOx and sugar as agents for removing oxygen from the polymerization medium. This novel system inspired others to developed controlled/living polymerization approaches deoxygenated with enzymes. Such approaches can be beneficial for UV curing performed in the air by enhancing polymerization in air atmosphere and leading to more effective polymerizations in the future.

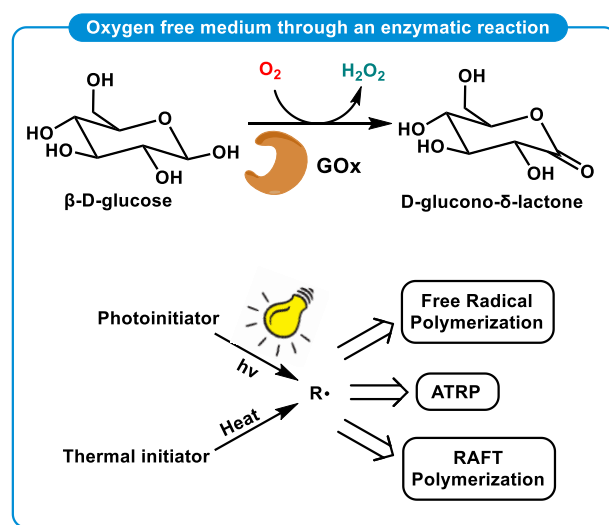


Fig. 5. Deoxygenation of polymerization medium via an enzymatic reaction.

Author Contributions

E.L.S.K.: Reviewing, writing/editing. M.U.K.: Supervision, conceptualization, reviewing, writing/editing.

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