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Light-Enabled Access to Oxidative Polymerization: A Short Perspective on Bioinspired Oxidative Photopolymerization

Baris Kumru

Solar irradiation provides critical energy to conduct chemical reactions. Many light-sensitive materials, such as semiconductors, guide photoredox-induced chemical pathways to tailor favored chemical conversions. Polymer synthesis by light is popular, however mainly addressed by conducting radical-based polymerization strategies. Oxidative photopolymerization is an advanced method to form functional polymers that are otherwise formed through complicated reactions. Herein, infant-stage oxidative photopolymerization will be introduced with examples in the field.

1. Introduction

Light has been shaping the life on Earth for long time, so critical that initial nitrogen-rich biomolecules are speculated to be selectively formed via light irradiation.[1] Light is assumed to be an integral part of natural polymer synthesis, and lignin has been a subject of study for long time to estimate the importance of light in plant growth. Lignin is a natural cross-linked polyphenol found in cell walls.[2] Lignin regulates the growth of plants by providing structural support and delivers defense against pathogens.[3] Despite its nonuniform chemical structure, lignin is biosynthesized from guaiacyl, syringyl, and *p*-hydroxyphenyl monomer units.[4] Lignin biosynthesis is highly complex and initiated by enzymes (peroxidase or laccase) oxidizing monolignol units to induce polymerization.[5] In this oxidation process, many active aromatic intermediates with a variety of functional groups (alcohol, aldehyde, and carboxylic acid) are formed and connected to growing polymer chain.[6] Compared to synthetic polymer synthesis, lignin biosynthesis takes place over very long term and monomer infusion to growing chain remains unclear. As a summary, lignin biosynthesis relies on oxidative polymerization. Interestingly, the positive effect of light on lignin biosynthesis has been confirmed. In wheat growth experiments, irradiated samples are reported to result in stiffer and thicker cell walls due to enhanced lignin polymer production compared to samples in dark.[7] It was noted that light can alter the macromolecular structure of lignin (meaning it influences the chemical structure of propagating units) and can form more robust material. When light is involved, irradiation activates gibberellin and phytochrome into an active state which delays shadow response and grows cells effectively.[8] Orthogonal translation of light-induced changes into phenolic compound organization highlights the complexity of responses in natural systems. With the knowledge of solar irradiation effect on membrane ion transport,[9] one can conclude that light has a canonical role in plant growth and regulation. More interestingly, lignin can behave as a semiconductor under light irradiation which enables photocatalytic transformations as reported in recent studies[10,11]; hence, the involvement of light into lignin and plant structures might be bigger than ever depicted.

Photochemistry possesses a key importance for transition toward sustainable chemical reaction design.[12] In addition to small molecules that respond to light, semiconducting materials pave the way for photoredox chemistry.[13] Many appealing applications such as photovoltaic devices to generate energy,[14] photocatalytic reactions to conduct organic synthesis[15] and CO_2 reduction,[16] and solar hydrogen fuel production via water splitting[17] can be accessed, just to name a few. Synthetic polymer chemistry follows a similar trend, there is an urgent need for light-induced scalable polymer synthesis pathways. This section is dominated by the utilization of small organic molecules that undergo photolysis to yield stable radicals.[18,19] So-formed radicals are then employed for radical polymerization of vinyl-containing monomers.[20] Nevertheless, the influence of photoredox chemistry is expanding in polymer science to access more advanced mechanisms.[21,22] The power of solar irradiation was demonstrated not only for the synthesis of polymers but also for depolymerization. At this stage, readers can consult oxidative photocatalytic lignin[23,24] and commodity plastic[25,26] depolymerization articles for further reading. One can speculate about the possibility of orthogonal polymerization–depolymerization reactions simultaneously under photocatalytic conditions, yet reaction engineering based on additives (i.e., scavengers) and bandgap positions can channel this into a desired state so that either photoinduced polymerization or depolymerization can be triggered.

Oxidative polymerization holds a great potential to tailor advanced materials for energy applications. In this short

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perspective, the power of solar irradiation to sculpt bioinspired oxidative photopolymerization mechanisms for the synthesis of conjugated polymers will be explained.

2. Synthetic Oxidative Photopolymerization

Conjugated polymers are integral materials in energy devices,[27] however they are made via complex synthetic routes. Monomers such as thiophene, aniline, pyrrole, and carbazole are quite inert by means of polymerizable moiety. Yet, synthetic polymer chemistry provided alternative polymerization routes. Such polymers can be formed electrochemically on electroactive surfaces.[28] Yet, polymers are obtained solely on surfaces which hinders modularity. Most common synthetic route to obtain conducting polymers is through cross-coupling reactions. Bishalogen substituted monomers can undergo cross-coupling reactions through metal-mediated reactions (i.e., Suzuki and Stille).[29,30] Multifunctional substitution results in conjugated microporous polymer synthesis.[31] Alternatively, oxidative polymerization by using strong oxidizing agents yields conjugated polymers as well.[32] Utilization of strong oxidizing agents (i.e., concentrated sulphuric and nitric acid, $KMnO_4$) triggers oxidative polymerization, however, strong ions attach to polymer structures by means of doping. It requires harsh synthetic conditions and waste problems. Generally, negative counterions from salt accompany propagating polymer chains to afford doped conducting polymer materials.[33] All of these methods have certain drawbacks such as toxicity, lack of sustainability, formation of undesired wastes, and complicated reaction setups.

2.1. Conjugated Polymers

Inspired from the biobased oxidative polymerization of aromatic molecules, oxidative photopolymerization is an infant-stage strategy to obtain conjugated polymers. By harnessing the power of light, advanced conjugated polymeric materials can be architected.[34] As an example, Yagci and colleagues introduced light-mediated step-growth polymerization of *N*-ethyl carbazole via electron transfer and coupling reactions using iodonium salts.[35] Oxidizing diphenyl iodonium hexafluorophosphate ($Ph_2I^+PF_6^-$) produces radical cation on *N*-ethyl carbazole which results in the coupling of active species to form a doped polymer. It is important to note that in this synthetic strategy the amount of iodonium salt was molar double of the monomer. Similarly, onium salt-induced photooxidative polymerization was demonstrated for thiophene[36] and thieno[3,4-b] thiophene[37] as well. Catalyst-free oxidative photopolymerization of phenyl azides to afford poly(1,2-azepine)s was reported in 1988.[38] Authors elucidated in-situ formation of azacycloheptatetraene intermediate from phenyl azide under light illumination, and light enables structural architecting so that patterned films were obtained. Authors underlined that doping poly(1,2-azepine)s with I_2 or AsF_5 constructs conductive material. Solid phase photopolymerization of pyrrole with poly(vinyl chloride) (PVC) under UV light has been investigated.[39] In this example, authors used ferrocene since it produces donor–acceptor structures in halogenated structures. It was noted that the chlorine radicals were formed from PVC under UV irradiation, which attacks pyrrole units to afford halogenated polypyrrole. Due to halogenation low conductivities were observed and the final structure was doped with $FeCl_4^-$ ions.

Semiconductors and photoredox mechanisms can assist conjugated polymer synthesis via oxidative photopolymerization. Using mesoporous TiO_2 can assist the formation of polypyrrole.[40] Photoredox pathway permits sufficient oxidating power to polymerize pyrrole. The addition of methyl viologen as an electron scavenger facilitates polymerization reaction. Authors exhibited the formation of polypyrrole in mesopores of TiO_2 to afford a composite material. Similar reaction was conducted for conductive interpenetrating network formation.[41] Methyl methacrylate-pyrrole mixture was photoactivated with iodonium salt *p*-(octyloxyphenyl)phenyliodonium hexafluoroantimonate (Ph_2ISbF_6) in combination with 2,2-dimethoxy-2-phenylacetophenone (DMPA) and 2-methoxy-2-phenylacetophenone (BZME) (**Figure 1**a). Orthogonal polymerization takes place since methyl methacrylate is polymerized via free radicals (formed via photoredox intermediates), whereas pyrrole is polymerized through oxidative polymerization. Simultaneous polymerization forms a homogenous mechanically robust conducting interpenetrating network evidenced by the absence of phase separation.

Semiconductor-electron acceptor mixtures can be employed for oxidative photopolymerization of aniline.[42] In that study, aniline was employed with tris(2,2′-bipyridyl)ruthenium complex and methylviologen, and the effect of pH in photopolymerization was investigated. As reactive species (semiconductor and propagating aniline chain) are charged, their interaction through the ionic strength of media determines polymerization behavior. Authors stated that lower pH triggers electrostatic repulsion which hinders polymerization. The role of anion presence in the photopolymerization of aniline was a topic of investigation.[43] It was demonstrated by authors that the presence of nitrate (NO_3^-) ions promotes aniline polymerization via the formation of active intermediates. UV light decomposes nitrate ion into $^{\bullet}O^-$ which generates hydroxyl radical from water. Hydroxyl radical (oxidizing agent) attacks aniline molecule to form a radical cation, which subsequently initiates polymerization. In the presence of silver ions (Ag^+), silver ions are reduced by aniline dimers and trimers to afford Ag^0 as well as aniline polymer structures. The importance of long-range charges in aniline dimer propagation was proven by adding negatively charged Ionite H clay in photopolymerization media.[44] Thus, eventhough photoredox pathway eventuates via radical cations, charge interactions must be considered for molecular weight evolution.

3,4-Ethylenedioxythiophene (EDOT)-based monomers are attractive choices for semiconductor-catalyzed oxidative photopolymerization. Cesium lead iodide perovskite quantum dots ($CsPbI_3$ QDs) were utilized as colloidal photocatalysts to promote polymerization of EDOT derivative 2,2′,5′,2″-ter-3,4-ethylenedioxythiophene under visible light illumination (Figure 1b).[45] Significant darkening was reported as polymer evolution takes place, and it was noted that molecular oxygen and 4-benzoquinone improve polymerization due to electron acceptor character. QDs are embedded in a polymer network with adjustable QD morphology based on reaction conditions. Gold nanoparticle-coated TiO_2 assists nanopolymerization based

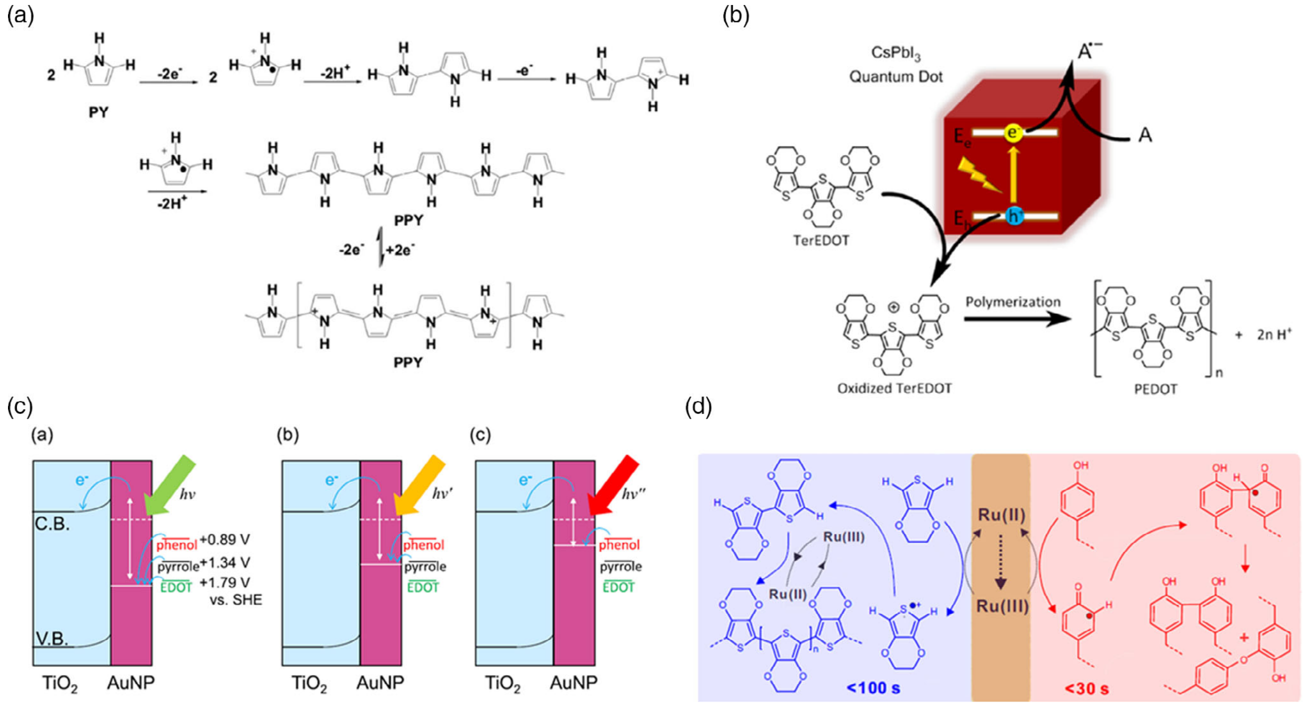

Figure 1. a) Polymerization mechanism of pyrrole initiated by solar irradiation using iodonium salt complexes and photosensitizer. Adapted with permission.[41] Copyright 2015, Elsevier. b) Photooxidative polymerization of EDOT trimer using perovskite nanocrystals. Adapted with permission.[45] Copyright 2017, American Chemical Society. c) Depiction of shift in Fermi level in semiconductor heterojunction by different wavelength which enables oxidation of monomers to initiate polymerization. Adapted with permission.[46] Copyright 2020, American Chemical Society. d) Oxidative photopolymerization of EDOT in printed composite sample using ruthenium complexes. Adapted under the terms of the CC BY 4.0 license.[49] Copyright 2021, the Authors. Published by Springer Nature.

on plasmon-induced charge separation.[46] Authors demonstrate site-specific polymerization of phenol and EDOT, which possess different oxidation potentials. Irradiation wavelength has a significant role in shifting Fermi levels, thus based on the applied wavelength monomer-specific site-tunable polymerizations can be attained (Figure 1c). Metal-free semiconductor graphitic carbon nitride (g-CN) can be employed for EDOT photopolymerization.[47] Our group depicted two reaction pathways based on the solid content of g-CN photocatalyst, when used in catalytic amount g-CN can be separated from polyEDOT. Brown liquid non-doped polyEDOT has a massive advantage in processability, which can be doped on coated surfaces within seconds. Excess g-CN results in surface polaron formation with polyEDOT which coats g-CN with polyEDOT and dopes polyEDOT with a negative surface charge of g-CN nanosheets. g-CN nanosheets have similar potential once they are in hydrogel networks.[48] Colloidal g-CN was employed as a photoinitiator to form a vinyl-based hydrogel network through radicals generated via photoredox chemistry. Subsequently, aniline was immersed in a so-formed hydrogel network and oxidative photopolymerization took place to obtain a hybrid network. A hybrid network was reported to possess good conductivity and photothermal effect. Oxidative photopolymerization in a network strategy was adopted to fabricate tough conductive hydrogels based on EDOT. Additive manufacturing was utilized to print tailored monomer composition, including EDOT and Ru(bpy)$_3$Cl$_2$.[49] Orthogonal chemistry enables the formation of polyvinyl alcohol-based hydrogel network and photopolymerization of EDOT in printed material (Figure 1d). Here, the ink recipe formulation plays a pivotal role. The major advantage of oxidative photopolymerization compared to oxidative polymerization via oxidizing agents rely on the absence of real charges. Oxidative photopolymerization affords reaction mechanism based on excited electrons and holes, thus neutral non-doped structures can be obtained. However, it is important to mention that every time a monomer is added to the growing chain, photophysical properties (i.e., bandgap) of recently formed polymer changes which eventually determines the molecular weight of polymers. It is important to choose a photocatalyst with suitable bandgap to ensure the propagation of polymer chain to afford larger molecular weights.

2.2. Resins

Alternative starting materials can afford polymers via oxidative photopolymerization. Commercial liquid poly(disulfide) resin (Thioplast) was cross-linked rapidly thanks to oxidative photopolymerization mechanism.[50] Multifunctional thiol monomers were employed with photogenerated guanidine base in presence of air under UV light, which produces a step-growth mechanism through in-situ formed thiyl radicals. Eventually, the system results in disulfide crosslinks to form a resin that can be of high interest for aerospace applications.

2.3. Artificial Lignin-Like Polymers

As the last example, inspired by lignin biosynthesis, our group reported oxidative photopolymerization of guaiacol (one of the lignin monomers).[51] We employed tungsten single atom-doped g-CN as a semiconducting photocatalyst, and polymerization of guaiacol was conducted under visible light using hydrogen peroxide as an active oxidating agent. Once photocatalyst activates hydrogen peroxide (such as in enzymatic reactions), radical cations formed on guaiacol propagates. In 6 h, pale yellow liquid guaiacol was converted to lignin-like brown material after polymerization and purification. Relative molecular weights of 3500 Da were detected with significant shouldering in size exclusion chromatography. This is one of the first examples of bioinspired chemistries to form artificial lignin-like polymer materials via solar irradiation.

3. Conclusion and Perspective

Conjugated polymers and conducting polymers are integral parts of energy conversion and storage devices. While the majority of science focuses mainly on their application, elucidation of alternative synthetic methodologies to afford improved materials is a must. In this case, light irradiation has a massive impact on bioinspired oxidative polymerization. Polymerization in this case relies on photogeneration of monomeric radical cations which triggers polymerization. Soluble anions generally accompany so-formed polymers to attain a doped state. Semiconductors can be employed to activate polymerization through photoredox cycle. As no real anions are present, photoredox mechanism yields non-doped conjugated polymer structures. Furthermore, lignin monomer guaiacol can be oxidatively photopolymerized to synthesize artificial lignin-like polymers. Such polymers are characterized by conductivity, absorption, and molecular weight (if polymers are soluble in commercial solvents).

Eventhough the field is infant, it welcomes many opportunities. Photochemistry will enable optimized synthetic conditions with maximum efficiencies to architect conjugated molecules. Majority of articles stand on the UV range to initiate oxidative photopolymerization, and in the future employing visible light must be governed. As the processes here aim at mild reaction conditions, sustainability and processability of conjugated polymer synthesis will improve, and waste generated during synthesis will be minimized. As photovoltaics design relies on employing semiconductors in sandwich structures, oxidative photopolymerization to fabricate conjugated polymers directly on semiconductor surfaces could generate defect-free interfaces which can boost device performance. Thus, light irradiation might aid the generation of conjugated matter to be employed in highly efficient solar energy conversion devices in near future. Efforts to polymerize lignin monomers will lead to the synthesis of 'improved lignin' which can be used for wood engineering to attain mechanically superior wood-based composites. Forming polyphenolic materials (similar structures to Novolac resins) without using formaldehyde can be starting products to attain engineering thermoset materials for high-end applications such as forming fiber-epoxy composites for aerospace structures. In a similar fashion, such polyphenolic polymers can be investigated for agricultural delivery as well. Alternatively, redox rich nature of polyphenolic compounds obtained via oxidative photopolymerization could be considered for battery applications. As a summary, bioinspired oxidative photopolymerization will enrich literature to guide advanced polymer synthesis for solar-energy-mechanical-agricultural applications.

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Conflict of Interest

The author declares no conflict of interest.

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