Biodegradable Polymer-based Long Persistent Luminescent Materials: Recent Advances in PLA, PCL and PHB Systems, Mechanisms, and Emerging Applications

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Abstract

Biodegradable polymer-based long persistent luminescent (LPL) materials have emerged as a new class of sustainable optical materials that combine environmentally friendly degradation behavior with ultralong afterglow emission. Unlike traditional inorganic persistent phosphors relying on defect traps in crystalline lattices, biodegradable polymer systems achieve room-temperature phosphorescence (RTP) and long-lived luminescence through molecular confinement, oxygen shielding, and triplet state stabilization within polymer matrices such as polylactic acid (PLA), polycaprolactone (PCL), and polyhydroxyalkanoates (PHAs, including PHB). Over the past decade, significant progress has been made in molecular design strategies, donor–acceptor exciplex engineering, crystallization control, and nanostructuring techniques such as electrospinning and 3D printing. This review systematically summarizes recent advances in biodegradable polymer-based LPL systems, focusing on mechanisms, structure-property relationships, and representative material platforms based on PLA, PCL, and PHB. Finally, emerging applications in bioimaging, anti-counterfeiting, smart packaging, and transient electronics are discussed, along with current challenges and future perspectives.

Keywords

Biodegradable polymers, Long persistent luminescence, Room-temperature phosphorescence, Afterglow, Sustainable optical materials

Introduction

Long persistent luminescence (LPL), also known as persistent phosphorescence or afterglow emission, refers to a luminescent phenomenon in which materials continue to emit visible light for seconds to hours after the removal of excitation. This unusual optical behavior arises from the storage and delayed release of charge carriers or excitons through defect or trap-mediated processes, enabling time-dependent photon emission without continuous excitation [1]. Traditional LPL materials are predominantly inorganic systems, such as $SrAl_2O_4$: Eu^{2+}, Dy^{3+} and related aluminates, which rely on deep trap states formed by crystal defects and dopant ions to store excitation energy. Although these materials exhibit high brightness and long persistence, their intrinsic non-degradability, high-temperature synthesis requirements, and poor biocompatibility significantly limit their applicability in biomedical imaging, wearable devices, and transient electronics [2]. In recent years, organic room-temperature phosphorescence (RTP) and polymer-based LPL systems have emerged as promising alternatives due to their structural tunability, low toxicity, and solution processability [3]. Compared with rigid inorganic hosts, polymer matrices can effectively regulate molecular motion, suppress nonradiative decay, and provide a protective microenvironment for triplet excitons, thereby enhancing afterglow performance [4]. More importantly, biodegradable polymers such as polylactic acid (PLA), polycaprolactone (PCL), and polyhydroxybutyrate (PHB) have recently been introduced as functional hosts for LPL systems, enabling the integration of luminescent functionality with environmental sustainability [5]. These degradable polymer materials exhibit broad application prospects in various fields, including anti-counterfeiting, dynamic display, information storage, intelligent sensing, and biological imaging [6-17].

Mechanism of polymer-based long persistent luminescence

The LPL behavior in biodegradable polymer systems primarily originates from efficient stabilization of triplet excitons and effective suppression of non-radiative decay pathways. Upon photoexcitation, singlet excitons are generated and subsequently undergo intersystem crossing (ISC) to form triplet excited states, which are typically spin-forbidden and therefore exhibit negligible radiative decay in fluid environments [18-20]. However, when embedded in rigid polymer matrices, molecular motions are significantly restricted, leading to suppressed vibrational and rotational relaxation, which in turn enhances radiative phosphorescence emission [21]. In addition, oxygen plays a crucial role as an external quencher of triplet excitons via energy transfer to ground-state triplet oxygen. Therefore, dense polymer packing, semicrystalline domains, or tightly aggregated structures in biodegradable polymers such as PLA and PHB can effectively inhibit oxygen diffusion and significantly prolong emission lifetime [22].

Beyond physical confinement, molecular-level electronic interactions also contribute to enhanced LPL performance. In donor-acceptor exciplex systems, long-lived charge-separated states can be formed, acting as energy reservoirs that enable trap-mediated delayed recombination and ultralong afterglow emission [23]. Moreover, recent studies have demonstrated that hydrogen-bonding networks, carbonyl-rich microenvironments, and heteroatom-containing biodegradable polymers can enhance spin-orbit coupling (SOC) via through-space n→π* interactions, thereby facilitating ISC efficiency and promoting both phosphorescence intensity and persistence duration [24]. These synergistic effects collectively establish biodegradable polymers as highly effective platforms for constructing environmentally friendly LPL materials.

PLA-based long persistent luminescent materials

Recent studies have demonstrated that PLA is an effective biodegradable platform for constructing room-temperature phosphorescence (RTP) and LPL systems due to its rigidity, crystallinity, and biocompatibility. Zhang et al. reported PLA-based phosphorescent nanoparticles prepared by encapsulating organic emitters within a PLA matrix, where restricted molecular motion enabled persistent emission for bioimaging applications [25]. Ma et al. further developed stereo complex PLA (sc-PLA) systems by blending Poly(L-lactide) (PLLA) and Poly(D-lactide) (PDLA), showing that enhanced chain packing and crystallinity significantly improve triplet exciton stabilization and enable ultralong RTP in 3D-printable luminescent materials [26]. In addition, Wang et al. constructed biodegradable PLA-based RTP systems through crystallinity tuning and host-guest molecular confinement, achieving improved intersystem crossing efficiency and prolonged afterglow emission [27]. These results collectively confirm that PLA is not merely an inert host but a structurally active matrix in regulating triplet-state dynamics. Current PLA-based LPL strategies mainly rely on nanoparticle confinement, stereo complex crystallization, and molecular doping, enabling promising applications in bioimaging, anti-counterfeiting, and transient optical devices [28].

PCL-based flexible long persistent luminescent systems

PCL, a flexible and biodegradable aliphatic polyester, has recently been explored as a soft polymer matrix in organic RTP and LPL systems. Unlike semicrystalline polymers such as PLA, PCL possesses a predominantly amorphous and highly mobile chain structure at room temperature, which is generally unfavorable for stabilizing triplet excitons [29]. Therefore, efficient afterglow emission in PCL-based systems typically relies on external structural confinement strategies, including hydrogen-bonding networks, ultraviolet (UV)-curable crosslinked matrices, or physical immobilization of phosphorescent dopants. Recent studies have demonstrated that PCL can participate in multicolor and time-dependent afterglow systems when integrated into polymer networks or electrospun nanofibers. For example, UV-cured polyurethane systems incorporating PCL prepolymers have been shown to exhibit dual fluorescence/phosphorescence emission with time-dependent color evolution, attributed to the coexistence of aggregated and dispersed emissive states of doped phosphors within the polymer matrix [30].

In addition, electrospun PCL-based fibrous materials

provide nanoscale confinement and reduced oxygen diffusion, which further stabilizes triplet states and enables mechanically flexible luminescent textiles suitable for wearable sensing applications [31]. Overall, although PCL does not intrinsically support long persistent luminescence, its excellent flexibility, low glass transition temperature, and biodegradability make it a valuable component for constructing stretchable and transient luminescent systems.

PHB and other PHA-based LPL systems

PHB, a microbial-derived biodegradable polyester belonging to the PHA family, has attracted increasing attention as a sustainable matrix for luminescent functional materials due to its high crystallinity, strong intermolecular packing, and excellent oxygen-barrier properties [32]. Although PHB is not an intrinsic LPL emitter, recent studies have demonstrated its important role as a rigid host matrix in photoluminescent composite systems, where the semicrystalline domains of PHB can effectively suppress molecular motion and reduce oxygen-induced quenching of excited states. In reported PHB-based luminescent systems, emission is typically achieved by incorporating organic fluorophores or metal complexes into the polymer matrix. The rigid PHB environment stabilizes excited states through physical confinement, thereby improving photoluminescence efficiency and environmental stability compared with amorphous polymer hosts. In addition, the high crystallinity of PHB contributes to reduced gas permeability, which is beneficial for maintaining emission stability under ambient conditions. From an application perspective, PHB-based luminescent composites have been explored mainly in the fields of sustainable packaging, anti-counterfeiting coatings, and smart biodegradable films [33]. However, compared with PLA-based systems, PHB remains less developed in terms of room-temperature phosphorescence and long persistent luminescence performance. This is largely due to its intrinsic brittleness and limited tunability of molecular packing.

Conclusion

Biodegradable polymer-based long persistent luminescent materials represent an emerging intersection between sustainable polymers and advanced photonic technologies. Unlike conventional inorganic persistent phosphors, these systems achieve long-lived emission through molecular confinement, oxygen shielding, crystallization regulation, and charge-transfer-mediated energy storage. PLA, PHB, and PCL provide complementary platforms: PLA offers excellent transparency and crystallization control; PHB provides strong biodegradability and oxygen barrier properties; PCL enables flexible and transient applications. Through molecular engineering and structural optimization, biodegradable LPL materials have demonstrated promising applications in bioimaging, anti-counterfeiting, smart packaging, and transient electronics.

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Conflicts of Interest

The authors declare no conflict of interest.

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