

Polymerization-Induced Emission

Bin Liu,^{†ab} HaoKe Zhang,^{†c} ShunJie Liu,^c JingZhi Sun,^a XingHong Zhang^{*a} and Ben Zhong Tang^{*acd}

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Unorthodox luminescent polymers without large π -conjugated structure, as a kind of promising soft luminescent materials, recently received considerable attention owing to their easy preparation and good processability. These polymers generally have electron-rich moieties with the diversity of intermolecular and intramolecular interactions through delocalized electrons. Actually, polymerization itself is a way to realize fluorescence emission. Here, we propose the concept of polymer-induced emission (PIE), which is defined as the process of transforming non-luminescent small molecules into non-conjugated luminescent polymers (NCLPs). Correspondingly, PIE luminogens with luminescent cluster, proposed as the minimum group aggregates with critical size for emission, require further investigation for understanding the structure-emission relationship and related mechanism. Promisingly, the advanced polymerization methods have unlimited opportunities to the development of new soft luminescent polymers owing to the multi-level structures of polymers.

Introduction

The discovery and coined the concept of aggregation-induced emission (AIE) in 2001 by the Tang's group opened a new research field.¹ AIE, as it indicates, the emission comes from the molecular aggregates, which exhibits opposite feature to aggregation-caused quenching (ACQ).² A large number of studies have shown that the restriction of intramolecular motion (RIM) is the key reason for blocking the non-radiative pathways and simultaneously opening up the channel for radiative transition, and generating luminescence.³⁻⁶ Compared with traditional conjugated structure with ACQ effect, the conjugated groups of AIE luminogens (AIEgens, Fig. 1) are generally non-coplanar and have rotational groups.⁷ Thus, the fluorescence emission can be realized in the aggregate state due to the restriction of intramolecular rotation or vibration. Based on the RIM mechanism, a large number of AIEgens (Fig. 1A) have been derived and has evolved into the polymeric systems.^{8,9} Introducing AIEgens into the terminal, side or main chains of polymers (Fig. 1B) can enable them with AIE to aggregation-enhanced emission (AEE) features.¹⁰ A recent interesting example, reported by Tang and Liu *et al.*, demonstrated the monitoring of the reversible addition fragmentation chain transfer polymerization process using tetraphenylethylene (TPE)-containing initiator. The observed AEE phenomenon was correlated with the viscosity increasing and the realization of polymer chain entanglement.¹¹ In that case, polymerization is a powerful tool to realize and regulate the emission.

In this minireview, we will briefly summarize the types and the common characters of the previously reported luminescent polymers and propose polymerization-induced emission (PIE) with the aim of using polymerization as a tool for realizing and regulating emission and the related luminescent cluster. Promisingly, we expect our thinking can inspire more thoughts on the emission mechanism

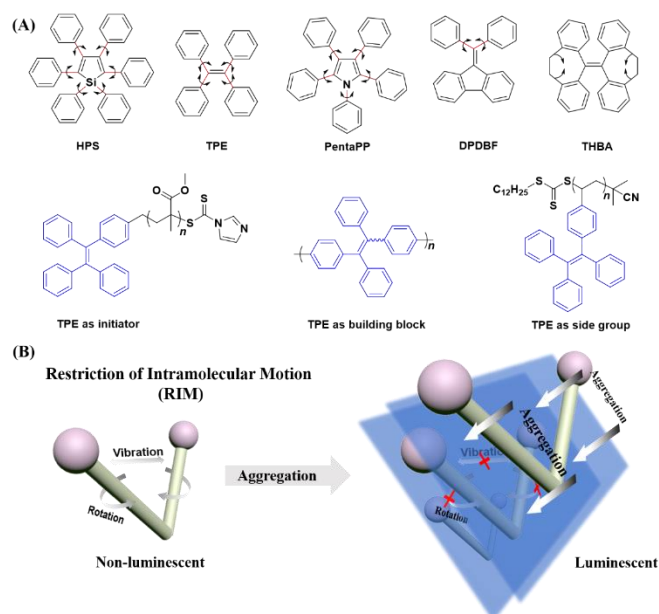


Fig. 1 (A) Representative examples of AIEgens and AIE-active polymers with AIEgens. (B) Schematic diagram of RIM.

of the non-conjugated polymers, as well as the new soft luminescent materials.

Non-conjugated luminescent polymers

It is very common phenomenon for natural macromolecules to have photoluminescence. For example, the cellulose, starch (e.g. rice) and protein can emit blue light under the irradiation of the ultraviolet (UV) light. These natural macromolecules have non-conjugated structures. However, because of complex components and possible impurities in these natural polymers, the luminescence mechanism is ambiguous and still in debate. In fact, scientists have observed that many synthetic polymers without conjugated structure can also emit fluorescence. Fig. 2 shows the representative luminescent polymers with the groups of isolated benzene ring, carbonyl, carbamate, cyano, thioether, thioamide and so on.

As early as in 1963, Bovey and coworkers¹² reported the fluorescence of styrene homopolymers and copolymers in solution and proposed the excimer emission of polystyrene, which is a good example of configuration-caused emission. However, the

^a MOE Key Laboratory of Macromolecular Synthesis and Functionalization, Department of Polymer Science and Engineering, Zhejiang University, Hangzhou 310027, China. E-mail: xhzhang@zju.edu.cn

^b School of Energy and Power Engineering, North University of China, Taiyuan 030051, China

^c Department of Chemistry, Hong Kong Branch of Chinese National Engineering Research Centre for Tissue Restoration and Reconstruction, Institute for Advanced Study, and Department of Chemical and Biological Engineering, The Hong Kong University of Science & Technology, Clear Water Bay, Kowloon, Hong Kong, China. E-mail: tangbenz@ust.hk

^d Center for Aggregation-Induced Emission, SCUT-HKUST Joint Research Institute, State Key Laboratory of Luminescent Materials and Devices, South China University of Technology, Guangzhou 510640, China

[†] These authors contributed equally.

fluorescence emission was in the ultraviolet region, which makes it impossible to observe with the naked eye. Soon afterwards, Hirayama *et al.* studied the fluorescence of a variety of diphenyl and triphenyl alkanes and proposed that formation intramolecular excimer was the cause of red-shift of emission wavelength.¹³ Kasha *et al.* held the idea that the excimer originated from the splitting of the monomer excited states due to the interactions.¹⁴ Poly(ethylene terephthalate), a kind of commercial polyester, was reported to have fluorescence and phosphorescence dual emission phenomena.¹⁵⁻¹⁷ The longer emission wavelength and intense phosphorescence was attributed to the conformation rigidification induced by crystallization. In 2012, Hong and co-workers synthesized blue-emitting polymers from acrylate monomers initiated by RAFT initiator containing benzene ring, and finally confirmed that π - π interactions of phenyl units and neighboring carbonyl units resulted in photoluminescence.¹⁸ Polymerization shortened the distance between benzene ring and carbonyl group from 3.25 to 3.20 Å as the degree of polymerization increased from 2 to 4, thus leading to the fluorescence emission from π - π interactions. Recently, Tang and co-workers prepared azetidine-containing polymers with excitation-dependent emission characteristic, and proposed that the multiple through-space electronic interactions between the lone pairs induced the fluorescence emission.¹⁹ Like the crystallization of AIEgens,²⁰⁻²² the chain growth facilitate the chain entanglement, intra/interchain interactions and conformational rigidification that induces the emission.

Studies have shown that some polymers without any aromatic structure also have photoluminescence phenomenon, which is closely related to the n - π interactions among the groups. Poly(amidoamine) (PAMAM) dendrimer is one of the most reported non-traditional luminescent polymers owing to the strong blue fluorescence.^{23, 24} Moreover, a large number of studies have shown that even small molecules with tertiary amine structure have similar phenomenon,^{25, 26} and the luminescence mechanism was attributed to the formation of “exciplex” or the oxidation of a tertiary amine.²⁷ Tang and co-workers firstly discovered that oligo(maleic anhydride)s and poly[(maleic anhydride)-*alt*-(vinyl acetate)] with multiple carbonyl moieties could emit the blue fluorescence and proposed that the fluorescence originated from the clustering of the locked carbonyl groups (Fig. 2B).²⁸⁻³⁰ Neither maleic anhydride nor vinyl

acetate as monomers have fluorescence in solution and solid. It is polymerization that induced the shortening of carbonyl distance (2.84–3.18 Å), the formation of carbonyl cluster and further the emission of fluorescence, that is, clustereoluminescence. Afterwards, Yuan and co-workers prepared non-conjugated poly(N-hydroxysuccinimide methacrylate)³¹ and polyacrylamide³² with carbonyl groups, polysulfoxide and polysulfone with S=O³³ and polyacrylonitrile with the cyano groups³⁴, and proposed clustering-triggered emission (CTE) mechanism (Fig. 2C). Even PEG and similar copolymer consisting of C–O–C moieties in the main chain skeleton also exhibited blue fluorescence in concentrated solution and solid,³⁵ which fully demonstrated that the transition can still be achieved by polymerization even without π -electrons. We have also found that poly(hydroxyurethane)s exhibited strong blue fluorescence both in solid and solution,³⁶ while the hydroxyurethane with carbamate and hydroxyl group had no luminescence. Meanwhile, the fluorescence intensity was exponentially related to the molecular weight, indicating that polymerization could enhance the interaction of the carbonyls. Very recently, Yan *et al.* proposed through-space conjugation to explain the luminescence mechanism of hyperbranched polysiloxane, which were also attributed to the polymerization of monomers.³⁷ Some other polymers, such as poly(amido amines), polyurea, polyethylenimine, poly(amido acid)s and poly(amino ester)s had the similar luminescent properties.³⁸⁻⁴⁰ Sulfur, which is in the same main group as oxygen, has the similar properties. Hu and Tang *et al.* prepared poly(thioamide) containing “heterodox clusters” through a facile multicomponent polymerization.⁴¹ The n - π interaction of thioamides between polymer intrachain and intermolecular chains is the reason of induced fluorescence. Clearly, these examples show that the monomers for synthesized polymers with fluorescent properties are often electron-rich, unsaturated carbon-heteroatom structures (e.g., O, N, S etc., Fig.2A).

Being different from the traditional aromatic molecules or extended π -conjugated systems having the excited state with intramolecularly delocalized π electrons, the above mentioned NCLPs have a distinct paradigm. They have group (moiety) aggregates or associates like cluster with delocalized n or π electrons that can also be excited to emit by UV light.⁴² For AIEgens, crystallization (one of the forms of aggregates) is the driving force to induce emission (Fig. 1). Of course, the polymerization of small AIEgens can also lead to the emission. In contrast, the photoluminescence of the non-conjugated polymers comes from the polymerization of non-emissive electron-rich monomers (Fig. 2). The emission essence of the NCLPs here is proposed by the aggregation of electron-rich group and restriction of motion that caused the delocalization of electrons.

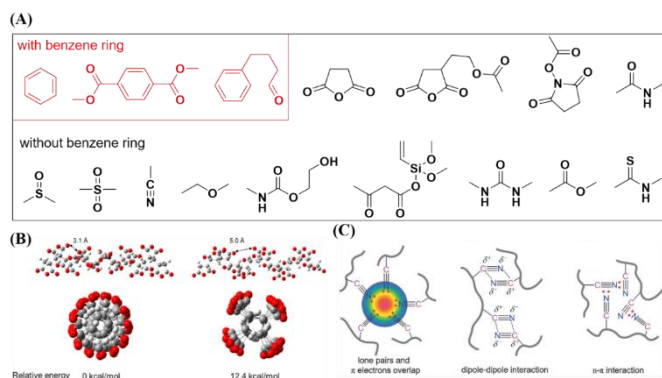


Fig. 2 (A) The typical examples of PIEgens.^{12-18, 28-41} Two typical CTE diagrams: (B) Optimized conformations of poly(maleic anhydride); (C) Possible intra- and intermolecular interactions of polyacrylonitrile within cyano clusters.

Polymerization-induced emission

Like crystallization for generating emission from aromatic AIEgens, polymerization is a powerful tool for generating emission from non-emissive electron-rich monomers. For example, high molecular weight vinyl polymers containing fluorescent 2,4,6-triphenylpyridine pendant groups with AIE characteristics exhibited very small emission difference in solution and solid, which achieved solution fluorescence.⁴³ In a very recent review paper,⁴² Tomalia *et al.* summarized four routes to emissive materials by the integration of

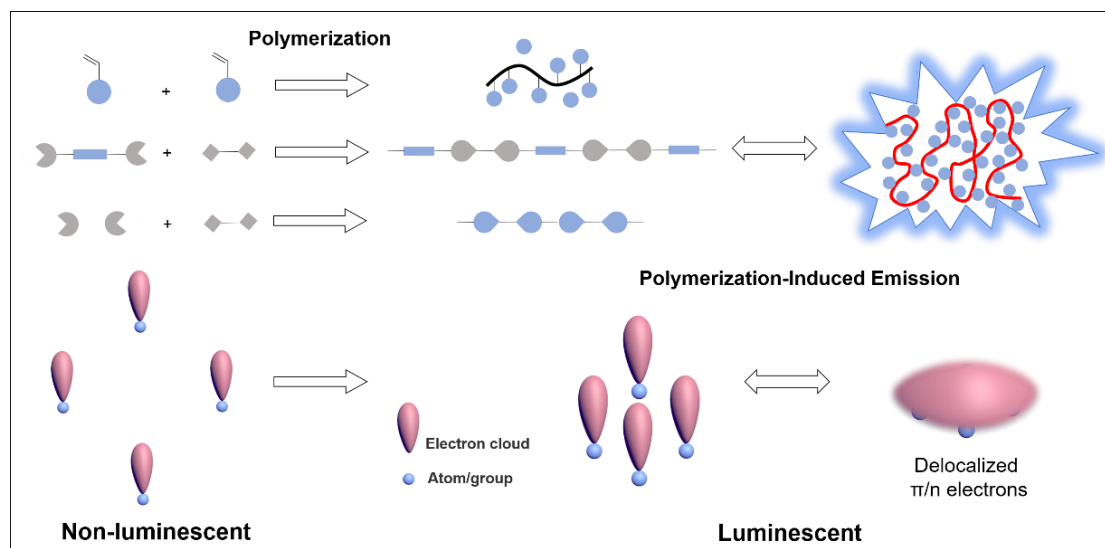


Fig. 3. The schematic diagram of PIE. Chain polymerization provides polymers with pendent groups that are closer, step polymerization can provide PIEgens or produce new PIEgens. The general character is the formation of luminescent cluster by polymerization.

the electron-rich molecules. Therefore, the architectural confinement can be carried out by polymerization and is a chemical route, which is one of the forms of proposed polymerization-induced emission (PIE). Note that, the polymerization process is generally an entropy reduction process, mostly accompanied with chain entanglement and intra/interchain interactions. Meanwhile, the process will prompt the electron-rich moieties close that clusters with delocalized n and/or π electrons produce, thus leading to the emission process. Such group aggregates can be named as PIEgens, i.e. chemically linked clusters. The schematic diagram of the polymerization method and emission mechanism of PIE is shown in Fig. 3.

There are two basic characters of PIE: 1) The emission of luminescence and its intensity basically depend on the degree of polymerization of NCLPs, which is the basic condition for the formation of cluster. In other words, clusters can only be formed at a certain degree of polymerization or molecular weight to further produce luminescence, and the emission intensity increases with the increasing degree of polymerization. 2) The diversity of polymer structure enriches the emission of luminescence. Polymers possess multi-level structures in different size level, including short-range structure such as the repeated unit, configuration (isotactic, syndiotactic, atactic, cis-trans isomer), architecture (linear, star, crosslinked, hyperbranched, dendritic), sequence (alternating, block), and long-range structure such as conformation and aggregation

As for the proposed cluster, many basic issues are waiting to answer: How to form luminescent clusters during polymerization of non-luminescent monomers; what about the structure, size of the clusters and the cluster distribution in polymer aggregates. These basic questions are directly related to the polymer structure and photophysical properties, and very rarely explored. Therefore, future works will focus on the fine characterization and analysis of cluster structure for understanding the relationship between cluster structure (composition, size and distribution) and function, the preparation of luminescent clusters with stable electronic structure and their regulation.

(crystalline and amorphous states), leading to unique emission. Therefore, it is a virgin land for man-made emission.

Many advanced polymerization methods have been developed in last two decades^{44, 45} and polymers with various microstructures and topologies can be produced even in large-scale manner, so it is very promising to use polymerization to generate and regulate emission, i.e., PIE. It means the monomers are chemically or covalently linked together, but the electron-rich moieties are still spatially separated. There is no directly linked covalent bond between the groups such as carbonyl, amide, anhydrate and so on.

Clusters in non-conjugated luminescent polymers

Traditionally, cluster in chemistry is defined as an ensemble of bound atoms or molecules that is intermediate in size between a molecule and a bulk solid.⁴⁶ Herein, the cluster refers to the aggregates or assemblies of the functional groups of polymers. It is the basic emission unit for the generation of delocalized n and/or π electrons in NCLPs and has the characteristics of polydispersity with the minimum size for producing luminescence. Therefore, such emission might be from the group aggregation with the size level from chain segment (*ca.* several repeated units) to chain/chain aggregates. In contrast with AIEgens, these non-conjugated polymers have enhanced emission owing to restricted intramolecular mobility.

Concluding remark

As discussed above, NCLPs can be realized by the polymerization of non-luminescent monomers, and a new term of PIE is proposed to categorize this unique kind of AIE materials. It represents a new class of luminescent materials without large π -conjugated group. Clusters, the basic emission units of NCLPs, are formed by the aggregation of electron-rich groups and result in the generation of delocalized electrons, and further induce the emission. A deeper understanding into the nature of the so-called cluster is still urgently needed in

order to prepare NCLPs with excellent properties. With such perspective, in the hope that this will accelerate the advancement of this promising class of materials as well as innovative high-tech applications.

Conflicts of interest

There are no conflicts to declare.

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