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Feature Article

Optical properties of amphiphilic copolymer-based self-assemblies

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ABSTRACT

As a promising technique for preparing polymeric materials with novel structures and properties, self-assembly is gaining increasing attentions. The applications of self-assemblies raise the claim of full expression of inherent functions and adequate stimuli-responsive features. Light is an excellent media for the realization of inherent functions, in favor of the communication with external environments. The aggregates self-assembled from polymers with optical functions can bring multifarious optical properties and promising applications. In the assemblies, the emission and fluorescence properties of polymers are dependent on both the aggregation type of the polymers and the aggregation-induced effects including planarization and specific intermolecular interactions. The aggregation-induced optical properties are influenced by external stimuli including pH and temperature, which confer various applications, such as in the areas of bioimaging and optical sensor. When photo-responsive groups with photochromism, photo-crosslink or photo-degradation properties are incorporated into polymers, self-assemblies are able to change their shape and inner structure under light irradiation. Such light triggered property is suitable in application for controllable release of loaded species from assemblies. We also discuss the challenges and developing directions regarding the studies and applications of self-assemblies from polymers with optical properties.

Contents

Abbreviations: AIEE, aggregation-induced emission enhancement; AIQ, aggregation-induced quenching; MCF-7, breast cancer cell; CLSM, confocal laser scanning microscopy; CPE, conjugated polyelectrolyte; NIH-3T3, fibroblast normal cell; FRET, fluorescence resonance energy transfer; FA, folic acid; LPL, linearly polarized light; MCTS, multicellular tumor spheroids; NIR, near infrared; NR, Nile Red; NLO, nonlinear optical; PL, photoluminescence; PDPA, poly(2-(diisopropylamino)ethyl methacrylate); PMPC, poly(2-(methacryloyloxy)ethyl phosphorylcholine; PFO, poly(9,9-dioctylfluorene); PAA, poly(acrylic acid); PEO, poly(ethylene oxide); PDMAEMA, poly(2-(dimethyl amino) ethyl methacrylate); PF-PE, poly(2,7-(9,9-dihexylfluorene)-alt-4,4′-phenylether); PMMAZO, poly(6-(4-methoxy-4′-oxy-azobenzene) hexyl methacrylate); PNIPAM, poly(*N*-isopropylacylamide); PF, polyfluorene; PS, polystyrene; PUNB, polyurethane containing nitrobenzyl group; RhB, Rhodamine B; R6GEM, rhodamine-based monomer; SEM, scanning electron microscope; sPCHD, sulfonated poly(1, 3-cyclohexadiene); TP, tetraphenylthiophene; TPE, tetraphenylethene; TEM, transmission electron microscope; 2PA, two-photon absorption; UCNPs, upconverting nanoparticles.

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1. Introduction

Self-assembly, a powerful bottom-up strategy for fabrication of nano-materials with diversified structures, has attracted extensive scientific interests since it is potential in building advanced functional materials for applications in electronics, optics, biotechnology and environmental technology [1–4]. The self-assemblies are formed by the non-covalent interactions, involving hydrogen bonds, electrostatic interactions, hydrophobic effects, metal–ligand coordination, and host–guest interactions [5]. Since the interactions are dynamic, reversible and controllable, self-assembly systems exhibit tunable structures and properties, which are in favor of the achievement of functional applications [6]. However, the functional applications of self-assembled aggregates raise the claim of full expression of inherent functions and stimuli-responsive features. Light, as green and neat energy, is an excellent media for the realization of inherent functions, in favor of the communication with external environments. In addition, the use of light as a trigger is particularly attractive since its characteristics can be remotely and accurately controlled, quickly switched and easily focused on specific areas [7].

Through various chemical techniques, optical groups with luminous or photo-sensitive properties can be introduced into polymers [2,8]. The polymers with inherent or introduced optical functions can be further copolymerized with other polymers to form amphiphilic copolymers. Under the balance of hydrophobic and hydrophilic effects, these copolymers with optical properties are able to self-assemble into diversified aggregates in solution, including micelles, vesicles, rings, and tubes [9–12]. The polymeric aggregates can behave enhanced optical properties as more than the summation of their building parts, even bring completely new types of properties for special interests and more applications [13]. In addition, assemblies of biocompatible optical polymers in solution exhibit unique advantages in the biomedical applications [14]. Given the presence of various unique optical properties from these biocompatible self-assemblies, it is possible to develop new tools for bioimaging, diagnostics, drug delivery, and therapy [15,16].

However, most of the current interests in optical self-assemblies are directed to the preparation of functional films. The situations of the self-assembled aggregates in solution are less documented [17,18]. In this feature article, we emphasize the properties of aggregates self-assembled from polymers owning optical functions. The article is divided into four parts. The first one makes a brief introduction of both the structure and property of polymers owning luminous or photo-sensitive properties, along with the self-assembly behavior of amphiphilic copolymers consisting of these polymers. In the second part, the optical properties of aggregates self-assembled from the amphiphilic copolymers with optical functions are featured. Both the aggregation-induced optical properties and photo-responsive properties are referred. The applications of these self-assembled aggregates in the fields of biomedicine and optical sensor are summarized in the third section. Lastly, conclusions and outlook are presented.

2. Self-assembling polymers with optical properties

2.1. Polymers with optical properties

A variety of polymers bearing optical groups are capable to self-assemble into nano-sized aggregates in solution. These optical polymers typically include photochromic polymers, conjugated polymers, photo-crosslink polymers, photo-cleavage polymers, and coordination polymers. The unique optical properties are derived from their elaborate molecular structures as described below.

Photochromic polymers functionalized by photochromic moieties are the most common class, which can introduce diverse photo-responsive properties to their self-assemblies [18,19]. Photochromism refers to the reversible transition of a chemical species between two isomeric forms with different absorption spectra. These reversible transition processes are usually triggered by the irradiation of ultraviolet (UV) or visible light (Vis), as depicted in Fig. 1. For example, UV irradiation induces photochromic reaction of azobenzene proceeded by the conversion of the planar *trans* isomer to the bent *cis* isomeric form via the isomerization of a —N=N— bond (Fig. 1a). The

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