



Feature Article

Ordered photo- and electroactive thin polymer layers

Karol Wolski, Michał Szuwarzyński, Maciej Kopeć¹, Szczepan Zapotoczny*

Faculty of Chemistry, Jagiellonian University, Ingardena 3, 30-060 Krakow, Poland

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ABSTRACT

Photo- and electroactive nanometer scale thin films are of growing importance in applications related to solar energy conversion. Properly ordered surface-tethered polymer layers may mimic performance of natural photosynthetic systems serving as platforms for light harvesting, directional energy and electron transfer in confined environments. Herein we review selected polymer photo- and electroactive systems and propose novel approaches for obtaining polymer layers with spatially ordered arrays of chromophores and/or electroactive chains. Specifically, the use of amphiphilic polyelectrolyte micelles in layer-by-layer (LbL) electrostatic self-assembly was shown as an efficient way to incorporate non-aggregated dyes into the multilayer films. The synthesis of conjugated polymer brushes via self-templating surface-initiated polymerization (ST-SIP) was demonstrated as a versatile route toward ordered 1D molecular wires. Such ordered structures realized in LbL films or polymer brushes would be beneficial for applications requiring directional transport of excitation energy and electrons on macromolecular scale that should be realized in ultimate devices for solar energy conversion.

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* Corresponding author. Tel.: +48 12 6632254.

E-mail address: zapotocz@chemia.uj.edu.pl (S. Zapotoczny).¹ Current address: Department of Chemistry, Carnegie Mellon University, 4400 Fifth Avenue, Pittsburgh, PA 15213, USA.

1. Introduction

One of the main challenge which has to be addressed by chemistry and materials science of XXI century is related to the problems with obtaining environmentally clean and cheap energy [1]. Sun is the most powerful source of clean energy but the current usage of solar light in artificial conversion systems is still limited (less than 1% of entire energy requirements) [2]. However, nature realizes conversion of solar to chemical energy on a massive scale in photochemical process known as photosynthesis, which is essential for life on our planet. The process is mastered in green parts of plants with exceptional efficiency and precision. It starts with the absorption of light by appropriate chromophores resulting in their electronic excitation. The excitation energy migrates along the precisely arranged chromophores in photosynthetic antennas and it is trapped in the so-called reaction center where the photoinduced electron transfer (PET) occurs. Then, the charges are separated thanks to multiple electron transfer events occurring between species with the redox potential gradient. The proper molecular engineering of the photosynthetic systems is crucial for efficient harvesting of light, funneling of the electronic excitation energy and final separation of the charges. The separated charged species drive subsequent reactions proceeding in confined and ordered environments that finally lead to water splitting and production of highly energetic chemical compounds.

The photosynthetic systems provide inspiration for development of artificial energy conversion devices that rely on photoinduced charge separation as fundamental processes realized in both natural and artificial systems are the same. Unfortunately, construction of such multi-component ordered molecular architectures that would mimic the natural systems is very challenging with regard to synthetic organic and supramolecular chemistry and inaccessible using current “top-down” fabrication methods which do not reach the molecular level. Even so, the ultimate efficiency of manmade system for solar energy utilization may need to have some of the features of the natural one [3].

Directional migration/transfer of electronic excitation energy along the cascade of properly aligned chromophores and flow of electrons along the molecular wires or redox potential (polarity) gradients are the most striking challenges for photo- and electroactive macromolecular systems. Importantly, mechanisms of these processes taking place in such confined polymer environments often cannot be described using classical theories and still require more fundamental studies. Only recently, description using quantum coherence has been proposed for explanation of exceptionally high efficiency of electronic energy transfer (EET) and energy migration in the photosynthetic systems that could not be explained using the well-established Förster and Dexter theories of energy transfer [4]. While the number of theoretical works regarding such spatially confined processes has been growing [5] their experimental verification is limited, mostly due to the lack of simple and versatile synthetic strategy for fabrication of relevant organized systems.

In this paper we focus on selected types of polymer thin layers enabling formation of ordered nanostructures that are prerequisites for desired electrical and photophysical properties.

2. Multilayer polymer films

Electrostatically driven self-assembly of charged polymers often referred to as layer-by-layer (LbL) approach is a straightforward and robust way to fabricate nanocomposite materials of a desired structure [6]. Introduced by Decher [7] c.a. 20 years ago, it is based on alternating adsorption of polyanions and polycations on charged surfaces that leads to the formation of ultrathin polyelectrolyte multilayers (PEMs) [8,9]. Although the detailed mechanism of PEMs formation is still under discussion [10–12], the LbL method has attracted enormous attention due to its versatility and simplicity. It has been successfully extended to wide variety of other charged nanoobjects (e.g., nanoparticles, dyes, and dendrimers) and virtually to any flat or curved surfaces. For example, PEMs may be deposited on colloidal template and after its removal hollow capsules of nano- or micrometer size can be formed [13,14]. A number of recent reviews cover the studies on films and capsules obtained by the LbL technique from synthetic and natural polymers that find numerous applications e.g., in catalysis, separation/filtration, sensing, coatings, and biomedicine [15–19].

Due to the excellent control over the film buildup as well as the thickness of a single layer in a few nanometers range, which is the length scale relevant for EET or PET, the LbL technique should be an ideal method for preparation of nanostructured films to study photophysical and photochemical processes. Well-ordered stratified films would be of special interest for performing efficient EET and PET.

2.1. Photoactive PEMs

The most serious limitation of PEMs, especially for the abovementioned applications, is their internal structure which is not stratified across the surface normal due to interdiffusion of the neighboring layers [20,21]. Layer formation is driven by the entropy gain from complexation of two oppositely charged polyelectrolytes with a release of small counterions to the solution. However, some segments do not form complexes, diffusing into the film or forming ‘loops’ that dangle into solution and provide charge overcompensation [22,23]. For some specific polyelectrolyte pairs or deposition conditions, interdiffusion is rapid enough so it allows entire chains to diffuse into the structure of already adsorbed film and to diffuse out during consecutive deposition step leading to exponential film buildup with thicknesses reaching the range of micrometers [24]. Interdiffusion is much less pronounced in linearly growing PEMs and is reflected by ‘fuzzy’ internal structure with polyelectrolyte chains of a ‘nominal’ layer interpenetrating into a few adjacent layers [7,25]. While some attempts have been undertaken [26], no really stratified solely organic ultrathin films have been obtained so far, although it is possible to achieve at least partial

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