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Quantum dot–polymer composites based on nanoporous polypropylene films with different draw ratios

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ABSTRACT

Hybrid composites of polymers with fluorescent nanoparticles are unique materials combining good mechanical properties of the host polymer matrices and luminescent properties of the embedded nanoparticles. Here, we report on the optical characterization of novel inorganic–organic hybrid composites based on nanoporous polypropylene (PP) as a polymer matrix and quantum dots (QDs) as a fluorescent inorganic component. The first type of the composite films is prepared by absorption of CdSe/ZnS QDs onto the porous structure of the PP films, followed by annealing at 170 °C, i.e., above the melting point of the PP. The second type of the composite films is obtained by filling of porous QD–PP composites with a nematic liquid crystalline (LC) mixture. Both types of composites are characterized by low light scattering, which makes it possible to study their optical properties by absorbance and fluorescence spectroscopies. TEM and confocal fluorescence microscopy have been used to analyze the aggregation of QDs in composites of different types. It has been shown that introduction of QDs into PP with a low draw ratio decreases the degree of alignment of LC molecules embedded into the pores of QD–PP composite films.

1. Introduction

In recent years enormous efforts in both industrial and academic laboratories worldwide have been brought into development of new organic–inorganic hybrid optically active composites, in particular, polymer blends containing quantum dots (QDs). QDs possess unique properties and have a number of advantages over conventional organic fluorescent dyes, such as a high photostability, large quantum yield of fluorescence, size-dependent emission wavelength tunable in a broad spectral range, and narrow peak of fluorescence [1–8].

Noticeable efforts of many research groups are focused on the preparation of QD–polymer composites and investigation of their properties [5–24]. Incorporation of QDs into a polymer matrix results in highly fluorescent materials with good mechanical properties typical for polymeric systems that can be used to obtain stable films, coatings, fibers, and microparticles. Different aspects of the synthesis, characterization, and application of these systems in sensors [9–13], light emitting

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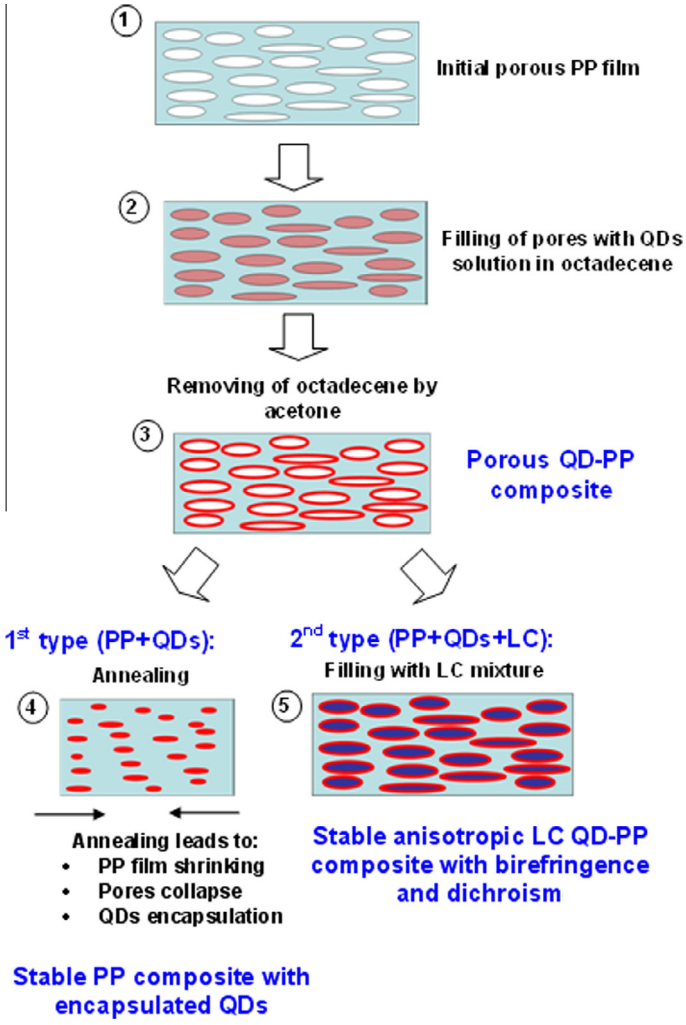
diodes [14–16], photovoltaic devices [19,20], various types of displays [19,20], and biological systems [21–24] have been reported recently.

It should be pointed out that, in most cases, methods of QDs incorporation into polymer matrix are rather complicated and time-consuming; in addition, they involve several stages of chemical modification of QDs [25–27]. For example, a recent paper [26] describes the surface modification of QDs with a functional silica shell and polymerizable groups. The polymerizable groups were covalently bound to a polymer matrix in order to prevent segregation of the components through polymerization and crosslinking. The resulting functionalized QDs were successfully used for fabrication of polymer structures with a complex architecture by two-photon polymerization. These 3D luminescent structures can be considered to be attractive candidates for the use in photonics and designing of metamaterials.

In our recent study [28], we developed a very simple method for preparation of fluorescent QD-containing composites. This method is based on filling nanoporous stretched polyethylene (PE) films with concentrated solutions of QDs in octadecene followed by extraction of octadecene with acetone. Since QDs are insoluble in acetone, they remained absorbed in the porous microstructure of PE films after the extraction procedure. Subsequent annealing of the films at temperatures near or above the PE melting point allows one to encapsulate QDs irreversibly inside the PE matrix and increase the optical transparency of the films. This method has been shown to be very simple and to allow obtaining highly fluorescent and flexible polymer films containing QDs at concentrations as high as several percent.

Here, we used a similar approach for the preparation of two types of polymer composites based on porous polypropylene (PP) films formed at different spin draw ratios, and, hence, characterized by different porosities and orientation degrees. The general procedure of preparation of the composite films is shown in Scheme 1.



Scheme 1. Schematic representation of the methods used for the preparation of two types of stable and optically clear fluorescent polymer composite films: annealed **PP** + **QDs** films (1st type) and **PP** + **QDs** + **LC** films (2nd type).