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

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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
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).
The first type of the composite films is similar to the one described recently, based on porous PE [28]: absorption of CdSe/ZnS QDs onto the porous structure of the PP films (steps 1, 2, and 3 in Scheme 1) is followed by annealing of the composite at 170 °C, i.e., above the melting point of the PP (step 4). Annealing of the QD–PP composite results in collapse of nanoporous structure, leading to a decrease in light scattering (increase in films optical transparency) and irreversible encapsulation of nanoparticles.

The second type of the composite film is obtained by filling porous QD–PP composite with a liquid crystalline (LC) mixture, which forms a nematic mesophase (Scheme 1, step 5) and has a refractive index close to that of PP. Recently, porous films of PP and PE were proven to be good polymeric matrices for the introduction of liquid crystals [29–34]. It was shown that the LC molecules are highly oriented by the walls of the pores along the draw direction in these composites.

It is noteworthy that both types of the composites have a low light scattering and a good optical transparency, allowing us to study their optical properties using spectrophotometry and confocal fluorescent microscopy. Moreover, the obtained films combine good mechanical properties of PP with bright fluorescence of QDs, which offer various applications of these hybrid materials.

The goal of this study was to analyze the influence of the PP microstructure, which is predetermined by the spin draw ratio of the polymer matrix, on the optical properties of the QD–PP composites, such as absorbance and fluorescence spectra, optical anisotropy, and the degree of orientation of LC molecules.

2. Experimental

2.1. Preparation of nanoporous PP films

Porous PP films were prepared with the use of commercial-grade isotactic PP (PPG 1035–08, Stavroten, Russia) with Mw = 3.8 × 10^5, Mw/Mn = 4–5, and Tm = 172 °C. The porous structure was formed in a complex procedure consisting of the stages of melt extrusion, annealing, uniaxial extension (the pore formation stage), and thermal fixation of the prepared porous samples [35–37]. The first stage of the process was performed using a SCAMIA laboratory extruder at a temperature of 200 °C. The degree of the melt orientation was characterized by the spin draw ratio (Λ), calculated as the ratio of the film take-up speed to the melt flow rate. The extruded films were annealed at fixed ends of the sample (isometric annealing) for 1 h at Tann = 170 °C. The uniaxial extension of the annealed films was performed at room temperature at a rate of 200%/min; the total extension degree was 200%. To prevent film shrinkage after the release of the extending stress, the porous samples were thermally fixed under isometric conditions for 1 h at a temperature of 170 °C. In this study, the PP porous films prepared at spin draw ratios of 39 (PP-39) and 78 (PP-78) were used for the preparation of composites.

2.2. Synthesis of QDs

The procedure of the synthesis of CdSe/ZnS core/shell QDs is described in detail in the Supporting Information. CdSe cores with a diameter of ~2.9 nm were synthesized by the hot-injection method, using n-hexadecylphosphonic acid as a capping agent. After the isolation and purification, the CdSe cores were coated with a three-monolayer ZnS shell in an octadecene-octylphosphate solution, and the native surface capping ligands were further replaced by tri-n-octyl phosphate oxide (TOPO). The fluorescence quantum yield of the core/shell QDs was determined to be 68% using rhodamine 6G as a reference dye. Prior to introducing them into the PP matrix, the purified CdSe/ZnS QDs were dissolved in 1-octadecene (20 mg/mL).

2.3. Preparation of QD–polymer composites

Polymer PP-based QDs composites were prepared by coating of nanoporous PP films with concentrated QDs solution in octadecene (20 mg/mL). After complete filling of the films by solutions, that takes couple of seconds, excess of the solution was removed by filter paper. Then films were washed with excess of the acetone and dried in air.

2.4. Methods

The absorbance spectra of the composite films were recorded using a Unicam UV-500 UV–Vis spectrophotometer. The fluorescence spectra of the films and QDs solutions were measured by means of an M266 automated monochromator/spectrograph (SOLAR Laser Systems, Belarus) with a 532-nm diode laser as an excitation source. The fluorescence confocal images were recorded at the wavelength of QDs fluorescence maxima in the range of 579–585 nm for all samples. The fluorescence spectra were recorded using an M266 automated monochromator/spectrograph (SOLAR Laser Systems, Belarus) coupled with a CCD U2C-16H7317 (Ormins, Belarus), a homemade light-collecting inverted system using a 100X/0.80 MPLAPON lens (Olympus, Japan) and a homemade confocal unit with two 100-mm objective lenses, a 100-μm pinhole, and two Semrock 488-nm RazorEdge® ultrastep long-pass edge filters (Semrock, USA). An LGN-519M Ar⁺ laser (Plazma, Russia) operating at 488 nm was used for fluorescence excitation, providing an incident light intensity of 0.1 mW as measured with a LaserMate-Q (Coherent) intensity meter. The integration time of 0.3 s was used for the recording of confocal images.
For TEM studies, thin sections of the samples (80–100 nm) perpendicular to their surface were prepared using an ultramicrotome (Reichert-Gung) with a diamond knife (Diatome) at a cutting rate of 1 mm/s. The sections were studied using a Leo 912 AB Omega transmission electron microscope (Karl Zeiss) operating at an accelerating voltage of 100 kV.

In the present work we have developed a method enabling to obtain thin polymer slices at room temperature without preheating of the test films. The studied film is placed in a thin slit near the vertex of the pyramid of cured epoxy resin and mechanically pinched there, aided by a pronounced plasticity of cured epoxy resin under local loads. Then the top of the pyramid is corrected with a razor blade and then the procedure of slices preparation is carried out in a conventional manner at the highest possible cutting speed.

3. Results and discussion

Two PP films with different spin draw ratios ($\lambda = 39$ and 78) were used as polymer matrices for incorporation of QDs. The prepared porous films possess an orientated porous structure due to the extension strain induced at the stages of melt extrusion and pore formation. Annealing of the extruded films was also accompanied by an increase in the degree of orientation, because annealing under isometric conditions ensures preservation of tensile stresses in the sample. The increase in orientation degree during the film preparation led to growth of the number and sizes of the pores; as a result, flow-through channels appeared, making the films permeable to liquids. The PP films prepared at spin draw ratios of 39 and 78 contained a network of through pores with average sizes of 120 and 140 nm and had overall porosities of 40 and 45%, respectively.

The prepared PP nanoporous films were characterized by a well-developed relief-like surface, which provided a high adhesion to various low- and high-molecular-weight substances, which makes them suitable for using as supports or containers for embedding of active components and formation of composite systems. Initially transparent, annealed films became milk-white and nontransparent during the extension at the stage of pore formation due to light scattering at the pore walls. However, the films became transparent again when filled with organic liquids due to good wettability of PP by these substances. Optical transparency of such composites depends on the properties of the liquid introduced into the pores and

Fig. 1. SEM images (LEO 1550 FE, Carl Ziess) of two PP samples with different draw ratios ($\lambda$): (a) PP-39 ($\lambda = 39$), (b) PP-78, ($\lambda = 78$). The stretching direction is vertical.
the wettability and refractive index of the host polymer film. The LC mixture used in the present study provided a low light scattering and a high optical transparency of the composites, which made it possible to study their optical properties.

Fig. 1 shows SEM images of two PP films with completely different microstructures. The PP film with a high spin draw ratio ($\Lambda = 78$) is characterized by a large number of long fibrils strongly aligned along the stretching direction (Fig. 1b). In the case of PP film with a low spin draw ratio ($\Lambda = 39$), the fibrils are hardly seen in the SEM image (Fig. 1a).

After filling of both films with QDs and annealing of them, we have performed TEM analysis of the composite films obtained (Figs. S2 and S3). A common feature of the two samples based on PP films was a uniform distribution of QD clusters across the films.

Using the prepared composite porous PP films with absorbed QDs, we prepared the second type of the composite materials with high birefringence and dichroism. For this purpose, a nematic LC mixture based on MLC6816 (cyclohexane derivatives, Merck) was introduced into the porous structure of the PP$+\text{QDs}$ films.

Due to the good matching between the refractive indices of both components, these films became transparent, which allowed us to perform spectral investigations (measurements of the absorbance and fluorescence spectra) [32].

It is noteworthy that our experiments showed that PP and QDs are completely insoluble in the MLC6816 nematic mixture. In other words, introduction of the LC mixture into the PP$+\text{QDs}$ nanoporous composite films does not lead to swelling of PP or dissolution of QDs and their redistribution within the films.

![Fig. 2. The (a) absorbance and (b) fluorescence spectra of the composite films. Excitation wavelength, 532 nm.](image-url)
The obtained composite films are characterized by noticeable absorbance and fluorescence in visible spectral range (Fig. 2) determined by QDs. The positions of low-energy electronic transition peaks completely coincide in the films and QDs solution (557 nm) (Fig. 2a). Irradiation of the films with light of any wavelength below \( \lambda < 550 \text{ nm} \) excites very bright orange fluorescence with a maximum at \( \lambda \approx 580 \text{ nm} \). The position of the fluorescence maximum is slightly shifted to longer wavelengths (by 4 nm) for the annealed composite film based on PP-78, which may be related to stronger aggregation of QDs causing interparticle energy transfer [38].

The high optical transparency of both types of the composite films allowed us to perform detailed study of these films using confocal fluorescent microscopy. Fig. 3 shows the fluorescence intensity map of a PP + QDs composite film obtained by confocal microspectroscopy. As seen from Fig. 3, the intensity of PP-39 + QDs fluorescence was characterized by a high inhomogeneity (more than 20%). Annealing of the film did not lead to considerable flattening of the fluorescence intensity distribution, but it caused a twofold decrease in the lateral dimensions of inhomogeneities (Fig. 3a–c). This decrease in the lateral dimensions of the emitting zones may have been explained by partial dissipation of QDs aggregates upon annealing. In contrast, the distribution of PP-78 + QDs fluorescence intensity was homogeneous (deviations were less than 5%). After annealing, the overall intensity of the film fluorescence increased by a factor of two, which was accompanied by a rise of fluorescence inhomogeneity to 10% (Fig. 3d–f). Thus, this sample had considerably better fluorescence properties than the PP-39 + QDs films.

In order to study the influence of absorbed QDs on the degree of alignment of LC molecules in the composites films, the dichroic dye Disperse Red 1 (DR1) was dissolved in the MLC6816 LC mixture prior to its introduction into the porous structures.

![Disperse Red 1](image)

**Disperse Red 1, \( \lambda_{\text{max}} \approx 494 \text{ nm} \)**

**Fig. 3.** Map of the fluorescence intensities of QD–PP composite films measured by confocal microspectroscopy: (a) a PP-39 + QDs film filled with MLC6816; (b) an annealed PP-39 + QDs film; (c) the intensity diagonal cross-section for images (a) and (b); (d) a PP-78 + QDs film filled with MLC6816; (e) an annealed PP-78 + QDs film; (f) the intensity diagonal cross-section for images (d) and (e). The axis of PP stretching is vertical.
Fig. 4. (a) The spectra of absorbance of light polarized parallel and perpendicular to the LC-director (PP stretching axis) for a PP-78 film filled with the MLC6816 + DR1 mixture. (b) Polar plots of polarized light absorbance for different PP films filled with the MLC6816 + DR1 mixture.

Fig. 5. The values of dichroism at 494 nm for composite films based on PP with different draw ratios (Λ) filled with the MLC6816 + DR1 mixture and doped or not doped with QDs.
The polarized absorbance spectra of PP + QDs + LC composite films are shown in Figs. 4a and S4. Fig. 4b shows the corresponding angular distribution of the absorbance of polarized light. The considerable difference in the absorbances of light polarized along and perpendicular to the direction of PP film stretching was accounted for by a high degree of orientation of LC molecules along the PP film axis. The values of polarized absorbance at the maximum of Disperse Red 1 absorbance were used to calculate the peak dichroism (D) as

\[ D = \frac{A_\parallel - A_\perp}{A_\parallel + A_\perp}, \]

where \( A_\parallel \) and \( A_\perp \) are the absorbances of light polarized parallel and perpendicular to the preferred direction of azobenzene chromophore orientation, respectively.

The obtained values of dichroism are shown in Fig. 5. These values are much higher for the composite films based on PP-78, with a higher draw ratio, than for PP-39 films. The highly oriented fibrillar structure of these PP + QDs + LC films provides alignment of LC molecules similar to the alignment observed in conventional glass cells with polyimide coatings [32]. Moreover, introduction of QDs does not affect the values of dichroism in the case of PP-78 (Fig. 5). In the polymer matrix with a lower draw ratio (**A** = 39), the degree of LC molecule alignment is much lower, and introduction of QDs considerably decreases the value of D (Fig. 5). As seen in SEM images of PP matrices (Fig. 1), the porous structure of the PP-39 sample has pores of a very small size and lower anisometry, or even lacks any preferential orientation along the stretching direction. Most likely, adsorption of QDs leads to further decrease in the PP-39 pore anisometry and, hence, decrease in the degree of LC alignment in PP + QDs + LC films.

In conclusion, hybrid polymer composites based on porous PP as a polymer matrix and QDs as an inorganic component have been prepared. Investigations of their optical properties demonstrate a strong effect of the PP spin draw ratio on the optical properties of the composite films. In particular, spectral investigations of PP films filled with an LC mixture and doped with a dichroic dye reveal that an increase in the draw ratio of the polymer films during their formation improves the alignment of LC molecules within the films. On the other hand, introduction of QDs into PP films with a low spin draw ratio (**A** = 39) leads to a noticeable decrease in the dichroism of the resultant LC composite films.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.eurpolymj.2016.06.017.

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