Received: 12 April 2018

Revised: 11 May 2018

(wilevonlinelibrary.com) DOI 10.1002/pi.5636

Fluorescent thermostable crosslinked poly(dodecylmethacrylate) composites based on porous polyethylene and CdSe/ZnS quantum dots

Miron Bugakov,^{a*}[®] Natalia Boiko,^a Pavel Linkov,^b Pavel Samokhvalov,^b Alexander Efimov,^a Sergey Abramchuk^a and Valery Shibaev^a

Abstract

Hybrid fluorescent polymer-inorganic nanoparticle composites have a broad set of valuable properties that allow them to be considered promising materials for photonics and photovoltaics. The design and methods of preparation of these composites are among the most critical topics of modern materials science. In this work, we have developed an approach to the preparation of composite polymer films with bright fluorescence and high thermostability. These composite films are based on a porous polyethylene (PE) matrix, the pores of which are filled by crosslinked poly(dodecylmethacrylate) and CdSe/ZnS core/shell quantum dots (QDs). The composites obtained are transparent in the visible spectral region and are able to withstand heating to high temperature and a considerable mechanical stress without loss of this property. These QD–PE composite films contain QDs in a high concentration and display very bright fluorescence, while they retain the mechanical properties of the initial porous PE film. Thus, the developed approach makes it possible to obtain composite materials combining the advantageous properties of PE and QDs without appreciable loss of individual component characteristics. A novel approach to the preparation of fluorescence composite polymer films, which have transparency, dimensional thermostability and resistance to mechanical stress, has been developed.

© 2018 Society of Chemical Industry

Supporting information may be found in the online version of this article.

Keywords: polymer composites; quantum dot – polymer composites; nanoporous polyethylene; fluorescence

INTRODUCTION

Hybrid organic polymer composites containing fluorescent semiconductor nanocrystals, or quantum dots (QDs), are promising materials for both academic research and practical applications. In recent years remarkable attention has been focused on the fabrication and study of hybrid polymer materials exhibiting the properties of both polymer matrix and embedded plasmonic or excitonic nanoparticles (NPs). Such systems combine the mechanical properties of the polymer matrix and the functional properties of inorganic NPs. At the present time, particular attention has been paid to polymer composite materials containing QDs. These NPs, as a rule, consist of a fluorescent core made of cadmium or lead chalcogenides, e.g. CdSe, CdS, PbS etc., and a protective high band-gap semiconductor shell. QDs, due to their small size (about 1-10 nm), demonstrate unique optical and electronic properties, among which are a strong absorbance of UV and visible light in a broad spectral range, high photostability and size-tunable fluorescence with a large quantum yield and narrow emission linewidth.¹⁻⁵ It should be pointed out that the optical properties of QDs are strongly size and shape dependent, which allows materials to be obtained composed of a single chemical substance but with different optical properties. These features of QDs make them promising components for the development of fluorescent

hybrid polymer composites, which could serve as materials for potential application in displays, sensors, optical amplifiers and lasers. Therefore, such QD-polymer composite materials are of particular interest in such fields of technology and engineering as photonics,⁶⁻⁸ optoelectronics⁹⁻¹¹ and photovoltaics.¹²⁻¹⁴

A primary issue that should be taken into consideration in the course of the development of QD-polymer composites with efficient fluorescence is the compatibility of these NPs with organic polymer matrices. During their synthesis and after isolation of them from the reaction medium, QDs are coated with organic molecules, e.g. oleylamine, which act as surface ligands and protect the colloidal NPs from aggregation and oxidation. At present, the preparation of hybrid polymer composite materials with QDs can be realized by several approaches¹⁵ which are generally based

- a Department of Chemistry, Moscow State University, Moscow, Russia
- b Laboratory of Nano-Bioengineering, National Research Nuclear University MEPhI (Moscow Engineering Physics Institute), Moscow, Russia

Correspondence to: M Bugakov, Department of Chemistry, Moscow State University, Leninskie Gory, 119991 Moscow, Russia. E-mail: bugakov.miron@gmail.com

on either QD ligand exchange techniques^{16–19} or the use of a polymer that compatible with ligand molecules covering QDs.^{20–27}

The first approach involves the synthesis of specially designed low molecular weight or short chain polymer substances which can act as surface ligands for QDs. This method is a good fit between the QDs and the corresponding functionality of the polymer matrix but it can be very time consuming.

The second approach is based on the use of commercially available monomers or polymers with a high content of aliphatic groups that can interact with long alkyl chain QD surface ligands. Lee et al.20 synthesized optically clear polymer composites composed of densely crosslinked poly(dodecylmethacrylate) (PDMA) and CdSe/ZnS QDs having different sizes. To synthesize these OD-polymer composites, the ODs were dissolved in a mixture of dodecyl methacrylate (DMA) and crosslinking agent and then radical polymerization was carried out. The QDs incorporated into the PDMA matrix demonstrated similar values of fluorescence quantum yield as their dilute chloroform solution. Having applied a 'layered' geometry, in which QDs of different size were located in different polymer layers, the authors succeeded in obtaining composites exhibiting white light emission under UV irradiation. In addition, the application of these QD-polymer composites in a down-conversion light-emitting diode (LED) was demonstrated. In this device QD-polymer composites performed the conversion of a high-energy emission of blue or UV LED to a low-energy radiation of green and red light.

A similar application of QD–polymer composites as a converter of high-energy UV irradiation to visible light or as a UV blocking material has been demonstrated in another report.²⁷ Here, the QD/silica/polymer composites were prepared by melt-mixing of QDs encapsulated in mesoporous silica through a microemulsion technique with poly(ethylene-*co*-vinyl acetate) pellets using a twin-screw extruder. The concentration of NPs in the polymer composites was varied from 0.1% to 1%. According to Mumin *et al.*²⁷ encapsulation in mesoporous silica not only prevented the agglomeration of QDs but also improved the photostability, the quantum yield of QDs and the compatibility of NPs with the polymer matrix.

Recently, our group has developed a novel approach for the preparation of fluorescent QD-polymer composites based on stretched polyethylene (PE) or polypropylene (PP) porous films.^{28,29} The porous PE or PP films were obtained by a stretching and subsequent annealing technique³⁰ and were characterized by high porosity (40%–50%) and different degrees of orientation. The proposed approach involves the adsorption of QDs on the inner surface of the film pores followed by annealing of the composite above the melting point of the polymer matrix. Annealing of the samples leads to a collapse of the porous structure to yield an optically transparent film with encapsulated QDs. However, heating of the samples above the melting point of PE resulted in loss of uniaxial polymer chain orientation of the stretched PE film and deterioration of mechanical as well as optical properties of the composites.

In this work we propose a new method of creation of fluorescent polymer composites based on porous PE with a high content of CdSe/ZnS quantum dots, characterized by high thermostability above the PE melting point (T_m). Furthermore, our method allows the anisotropic optical properties of the composites to be preserved under mechanical stress and heating. To obtain this sort of QD–PE composites, we modified the approach described by Bobrovsky *et al.*^{28,29} and replaced the heat treatment during the annealing stage by photopolymerization of a mixture consisting of DMA monomer, a crosslinking agent and a radical photoinitiator directly incorporated into the pores of the PE film. The technique developed allowed us to fabricate QD–polymer composites based on porous stretched PE films having very bright fluorescence, a relatively uniform distribution of QDs in the PE films, good mechanical properties typical of pure porous PE and high transparency due to the matching of the refractive indices of the PE matrix and PDMA.

EXPERIMENTAL

Materials

Porous PE films were prepared from commercially available linear PE ($M_{\rm w} \approx 1.4 \times 10^5$, $M_{\rm w}/M_{\rm n} \approx 6-8$, $T_{\rm m} \approx 130$ °C) by sequential extrusion with a subsequent annealing, uniaxial extension and thermal fixation.³⁰ Stretched porous PE films are characterized by the presence of large pores between stacks of lamellae with a size about 1000 nm (Fig. 1, SEM image, and Fig. S1). Pore size distribution was measured by the filtration porometry method; the porous PE films were characterized by asymmetric pore sizes of ca 50-500 nm³⁰ and a film thickness of ca 10 µm. DMA and dipentaerythritol hexaacrylate (a crosslinker) were acquired from Aldrich (Germany). DMA was purified by passing through a column filled with neutral alumina oxide to remove the polymerization inhibitor. All the other reagents were commercially available and were used without further purification (Aldrich, China). CdSe/ZnS core/shell QDs approximately 4 nm in diameter containing hydrophobic oleylamine surfactant on their surface were synthesized according to a previously reported procedure.31

Instrumental measurements

Spectral measurements were performed using a Unicam UV-500 UV-Vis spectrophotometer. Fluorescence spectra were recorded using an M266 automated monochromator/spectrograph (SOLAR Laser Systems, Belarus) equipped with a CCD U2C-16H7317 (Ormins, Belarus), a homemade light-collecting inverted system using a 100×/0.80 MPLAPON lens (Olympus, Japan) and a homemade confocal unit with two 100-mm objective lenses. Exciting light was cut off by Semrock 488-nm RazorEdge[®] ultrastep long-pass edge filters (Semrock, USA). Fluorescence of the QDs was excited by a KLM-473/h-150 laser (Plazma, Russia) operating at 473 nm. The incident light intensity was equal to 50 mW cm⁻² as measured with a LaserMate-Q (coherent) intensity meter.

Polarizing optical microscopy investigations were performed using a LOMO P-112 polarizing microscope equipped with a Mettler TA-400 heating stage.

For TEM studies, thin cut films of samples (80-100 nm) in the transverse direction to their surface were prepared at a cutting rate of 1 mm s^{-1} using an ultramicrotome (Reichert-Gung) with a diamond knife (Diatome). These films were studied using an LEO 912 AB Omega transmission electron microscope (Carl Zeiss) operating at an accelerating voltage of 100 kV.

Uniaxial tensile deformation was carried out using an Instron machine (model 4301) equipped with 1 kN load cell. Dumbbell-shaped specimens having 20 and 6 mm in gauge length were strained at a constant crosshead speed of 5 mm min⁻¹. Young's modulus (*E*), elongation at break ($\varepsilon_{\rm b}$) and tensile strength ($\sigma_{\rm b}$) were assessed. All tests were performed at room temperature.

The contraction of the PE films on heating in a free state was calculated from the change in dimensions of the specimen:

contraction = $\left[\left(I_0 - I_{\text{contracted}} \right) / I_0 \right] \times 100\%$



Figure 1. Preparation route of QD-containing polymer composites based on porous stretched PE films.

where I_0 is the initial specimen length and $I_{\text{contracted}}$ is the specimen length after contraction.

RESULT AND DISCUSSION

Preparation of QD-PE composites

First, we consider successive stages of QD–PE composite preparation. The PE films used in this work had an oriented pore structure with pore size about 50–500 nm and polymer fibrils aligned along the stretching direction (see SEM images, Figs 1 and S1). The initial films were strongly turbid due to light scattering at pore walls. However, the PE films can be made transparent if their pores are filled with a substance having refractive index equal to the refractive index of the PE film. It is well known that low molecular weight compounds can easily penetrate inside a film with a porous structure. At the same time, high molecular weight compounds, as a rule, lose this advantage due to the extremely high viscosity of their melts that does not allow polymer molecules to squeeze into film pores. However, this problem can be overcome if the polymer is being synthesized directly in the interior of the pores.

To obtain the composite films we chose methacrylic monomer DMA with a long aliphatic chain that has the same refractive index as that of the PE film. Moreover, DMA can dissolve a rather large amount of QDs (up to 25 wt%). It should be noted that the glass transition temperature of polymer on the basis of DMA is considerably below room temperature (ca - 60 °C), which provides an enhanced mobility of macromolecules inside the porous PE matrix. On the other hand, in order to improve the mechanical properties of such films (tensile strength and moduli) a small amount of a crosslinking agent (dipentaerythritol hexaacrylate) was added to the photopolymerizable mixture deposited on the porous PE films. A UV photoinitiator (Irgacure 651) was also included in the photopolymerizable mixture to initiate polymerization of the monomers. The chemical structure of all components and the composition of the photopolymerizable mixture are shown in Table 1. A scheme demonstrating the sequence of preparation steps of QD-PE composite films is given in Fig. 1.

The first stage consisted in filling PE film pores with a concentrated (20 wt%) solution of QDs in octadecene. The octadecene solution easily penetrates inside the pores of the PE film driven by capillary forces, and the transparency of the film is dramatically increased due to matching of the refractive indices of octadecene and the PE film. Figure 1 (the first stage) schematically shows the coloured PE film containing the solution of QDs in octadecene arranged inside the pores. This film is rather transparent and displays birefringence.

At the second stage, the PE film was washed with acetone. After drying the sample in vacuum at ambient temperature, the turbidity of the film was recovered (Fig. 1, the second stage). Since QDs are insoluble in acetone and octadecene and acetone are completely miscible, the QDs were precipitated directly inside the pores of the PE film while the octadecene solvent was extracted with an excess of acetone. Thus, the initial porosity of the PE film was restored and QDs were adsorbed on the inner surface of the film pores, i.e. on the pore walls.

At the third stage, the porous PE film containing QDs was dipped into the photopolymerizable mixture (Table 1) until all pores were impregnated with the mixture. Then the film was drawn off from the photopolymerizable mixture and excess of the mixture was removed by wiping with filter paper. In order to induce photopolymerization, the film was placed in a special quartz cell; the inner space of the cell was filled with glycerin. The quartz cell was exposed to UV illumination ($\lambda = 365$ nm, I = 1 mW cm⁻²) for 20 min (Fig. 1, the third stage).



The initial PE films are highly opaque and scatter the light due to the porous structure with submicron and micron pore dimensions. On the other hand, the final QD–PE composite films are transparent due to the close refractive indices of PE and crosslinked PDMA and coloured due to the presence of QDs (Fig. 2(a)). The weight fraction of QDs in the QD–PE composite films was measured by gravimetry and was 18 wt%.

It is well known that the QDs have a tendency to form aggregates when they are displaced from their native medium. In order to check if QD aggregation occurred and to reveal the distribution of QDs within the composite films TEM measurements were carried out. As is clearly seen from Fig. 2(a), the final QD–PE composite film contained both individual QDs and QD aggregates. The latter consisted of hundreds of NPs (Fig. 3(a)). However, the dimensions of the aggregates are rather less than the wavelength of visible light (the size of the aggregates was less than 200 nm). In other words, the aggregates have an insignificant effect on such optical properties of the composite films as transmittance, light scattering etc. Moreover, oleylamine molecules, which cover the surface of the QDs, prevent coalescence of the NPs.

We have assumed that the most likely explanation of QD aggregate formation is connected with the washing process of the films with acetone at the second stage of composite preparation (Fig. 1). To clarify the reason for aggregate formation two additional samples of QD-containing composites were investigated (see Fig. 1, right-hand side). The first test sample (test sample 1) was prepared by filling the pores of the film with QD octadecene solution and subsequent extraction of octadecene with acetone. In other words, only the precipitation of QDs from octadecene solution by acetone directly in the film pores was realized. In comparison with



Stretching direction

Figure 2. Photographs of the final QD–PE composite films before (a) and after (b) mechanical stretching up to fracture. The dashed arrow indicates the initial stretching direction of the porous PE film. The solid arrow indicates the stretching direction under tensile drawing. The letters (text) are printed on paper and are used for demonstrating the transparency of the composite films.

the preparation route of the final QD-PE composite film (Fig. 1), the third stage of preparation was excluded for test sample 1.

Another sample of the QD–PE composite film (test sample 2) was prepared by solely filling the initial porous PE with the photopolymerizable mixture containing a small amount of dissolved QDs and photopolymerization under UV illumination (Fig. 1, test sample 2 preparation). Figure 3 shows TEM images of the final QD–PE composite film and all test samples obtained by the various ways.

The dimensions of the aggregates are considerably smaller in test sample 2 (Figs 3(c) and S2) compared with test sample 1 prepared by the two-stage method (Figs 3(b) and S3). On the other hand, test sample 1 contains aggregates with dimensions like the aggregates from the QD–PE composite film prepared by a complete three-stage routine (Figs 3(a) and S4). Thus, we can conclude that the formation of aggregates takes place predominantly in the second stage of the preparation route.

Thus, the distribution of QDs in the final QD-PE composite film is heterogeneous, which is caused by an uncontrollable precipitation of QDs in the second stage and the tendency of NPs to form aggregates due to the extremely high surface area of the QDs. On the other hand, the majority of QDs that were introduced in the third stage of preparation of the final QD-PE composites are distributed inside the composite in a non-aggregated manner. However, despite the presence of QD aggregates, their dimensions are predominantly less compared to visible wavelengths, which does not impair the transparency of the QD-PE composite films. It should be noted that test sample 2 (Fig. 1) contains only about 6 wt% of QDs which is three times smaller than in the final QD-PE composites obtained by the three-stage method.

We now consider the optical and mechanical properties of a sample of the final QD–PE composite obtained by the three-stage method and containing 18 wt% QDs.

Optical properties of QD-PE composites

As can be seen from Fig. 4, the transmittance spectrum of the QD–PE composite film has appreciable absorbance in the blue spectral region, rising with decreasing wavelength, with a pronounced peak with a maximum at 560 nm. This maximum corresponds to the first excitonic transition of the QDs. The same peak is observed in absorbance spectra of test sample 1 and 2 (Fig. S5). Absorbance in the blue region is primarily related to the absorbance of QDs. In addition, minor light scattering artefacts can be observed between 600 and 700 nm, probably occurring due to the existence of closed pores which are inaccessible for the photopolymerizable mixture.

www.soci.org



Figure 3. TEM images of (a) final QD-PE composite films (Fig. 1) obtained by the three-stage QD introduction method; (b) test sample 1 obtained by the two-stage method; and (c) test sample 2.



Figure 4. Transmittance and fluorescence spectra under blue light illumination ($\lambda_{ex} = 473$ nm) of the QD–PE composite film. The inset shows a photograph of the QD–PE composite film fluorescence.

Under blue light illumination ($\lambda = 473$ nm) the QD–PE composite films demonstrate a bright fluorescence with a peak maximum at 584 nm (Fig. 4). At the same time, the fluorescence peak of QDs dissolved in chloroform is observed at 575 nm (Fig. S6(a)). The noted slight shift of the peak may be associated with an aggregation of QDs^{32,33} Indeed, test sample 1 containing large QD aggregates has a peak maximum at 583 nm. At the same time, the peak maximum of test sample 2, which chiefly contains non-aggregated QDs, is similar to the solution of QDs (Fig. S7). Therefore, in the case of the final composite polymer films, the observed shift of the peak position is due to an aggregation of QDs. The inset in Fig. 4 shows a photograph of the QD-PE composite film under illumination by blue light. It should be pointed out that the composite films display homogeneous strong yellow fluorescence easily visible by the naked eye. These spectral features are typical for QDs and provide experimental proof of the presence of a high concentration of QDs in the composite films.

Polarizing optical microscopy reveals a birefringence of the QD–PE composite film that is associated with the crystalline structure of the initial stretched oriented PE film. In addition, orientation of PE chains in the QD–PE composite causes a transmittance change if this sample is observed in polarized light (Fig. 5). On the other hand, owing to extremely high light scattering, birefringence of the initial porous PE film cannot be directly observed using polarizing optical microscopy. Nevertheless, after filling the pores with a substance having the appropriate refractive index



Figure 5. Optical microscopy image between crossed polarizers (scale bar 100 μ m) of the QD–PE composite film before (a) and after (b) rotation at 45°. The blue arrows indicate the direction of the polarizers and the white arrow indicates the stretching direction.



Figure 6. Stress-strain curves of porous PE (curve 1) and QD-PE composite (curve 2) films (T = 20 °C).

(e.g. dimethylformamide), the film becomes transparent and birefringence can be clearly observed.

Mechanical properties and thermal stability of QD-PE composites

To study the possible influence of crosslinked polymer on the mechanical properties of the composite PE films we performed mechanical measurements of the QD–PE composite films and compared their properties with the same mechanical characteristics of the initial samples of the porous PE films.

Figure 6 presents stress-strain curves for samples of the initial porous PE film and its composite with QDs during axial drawing. The values of Young's modulus, elongation at break and ultimate strength, calculated from the typical stress-strain curves of these

O SCI

Table 2. Mechanical properties of porous PE samples and the QD – PE composite film			
Sample	Young's modulus (E), MPa	Elongation at break ($\varepsilon_{\rm b}$), %	Tensile strength ($\sigma_{ m b}$), MPa
Porous PE film	310 ± 10	66 ± 1	150 ± 10
QD-PE composite film	280 ± 14	82 ± 1	140 ± 10



Figure 7. Changes in linear size (along the stretching direction) of porous PE (curve 1) and QD–PE composite (curve 2) films upon annealing at various temperatures. To achieve the equilibrium state, the samples were annealed at each temperature for 20 min.

compounds, are given in Table 2. For the pure porous PE and the QD–PE composite films deformation proceeds in a homogeneous manner along the entire gauge length of the sample. These curves have the typical shape inherent to oriented crystalline polymers under deformation.^{34,35}

The initial pure porous PE and QD–PE composite films show similar mechanical properties in terms of Young's modulus, elongation at break and tensile strength as follows from Table 2 and as is clearly seen by comparing curves 1 and 2 in Fig. 6. It should be noted that, despite the high concentration of QDs in the composite films, the initial mechanical properties of PE are completely preserved. The QD–PE composite films have rather high values of elongation at break, 82%, and approximately the same values of tensile strength (140–150 MPa).

As described by Nwabunma and Thein³⁶ introducing inorganic NPs into unoriented polyolefins may lead to their embrittlement. Typically, the content of inorganic additive sufficient for composite embrittlement amounts to 20 wt% or less. On the other hand, the mechanical properties of QD–PE composite films obtained in this work are mainly determined by the initially oriented PE matrix and are independent of the presence of both QDs and crosslinked PDMA impregnated in PE pores.

It should be noted that QD-PE composite films do not change their transparency during the deformation (Fig. 2). This means that deformation of QD-PE composites is not accompanied by processes of cavity formation. Thus, QD-PE composite films can preserve good optical properties under mechanical load up to their break and can be used as optical media that undergo mechanical action.

The heating of porous PE films above the melting point of PE may lead to collapse of the pores which in turn would stimulate distortion of the geometrical shape of the polymer films. Figure 7 demonstrates the changes in linear size of the porous PE film



Figure 8. Optical microscopy image between crossed polarizers (scale division 10 μ m) of a QD–PE composite film annealed at 160 °C before (a) and after (b) rotation at 45°.

along the stretching axis after heating at various temperatures. A contraction by more than two times from the initial porous PE film was observed for these samples. In contrast, the QD–PE composite films in which pores were filled with crosslinked PDMA are characterized by low contraction, which was depressed about three times (Fig. 7). As can be seen in Figs 7 and S8, the geometrical shape and dimensions of the composite films have changed little after heating at 160 °C.

Thus, filling the pores of PE composites by crosslinked PDMA has hampered contraction to a considerable degree and improved the thermal stability of QD–PE composite films. It is interesting to note that after thermal treatment of QD–PE composite films at 160 °C (above the melting point of PE) the optical anisotropy of the film is preserved but it becomes less pronounced (Fig. 8).

In addition, thermal treatment at 160 °C of QD–PE composite films increased the transmittance of the sample in the visible region (Fig. S6(b)). The light transmittance reached a value up to 70% in the visible region. This may be due to the collapse of pores that were not filled with PDMA on heating of the PE film above the melting point. It should be noted that annealing has slightly improved text readability through the QD-PE composite film (Fig. 7).

Annealing of the QD–PE composite films led to decreasing intensity of fluorescence as also clearly seen in Fig. S6(a). This phenomenon can be explained by the decrease in light scattering of the composite film that was shown above or by the change of aggregation state of the QDs.³⁷

CONCLUSION

A novel approach to the preparation of fluorescent composite polymer films based on porous PE film, crosslinked poly(dodecylmethacrylate) and CdSe/ZnS QDs has been developed. The composite films are characterized by a high content of QDs (*ca* 18 wt%) and a relatively uniform homogeneous distribution of NPs within the samples. The QD–PE composite films displayed very bright fluorescence in the visible region, high transparency and considerably higher thermal stability in comparison with the initial porous PE film even above the PE melting point.

It was found that the mechanical properties of the QD-PE composite films are similar to those of pure PE film and the tension of the QD-PE composite films leaves their optical properties unchanged. The QD-PE composite films obtained in this work can be used in photonics, optoelectronics, photovoltaics and as greenhouse coverings.

ACKNOWLEDGEMENTS

This study was financially supported by the Russian Science Foundation (grant no. 14-13-00379) – composite preparation, optical, thermal and mechanical measurements (M. Bugakov, N. Boiko, V. Shibaev). Part of this study dealing with the preparation of CdSe/ZnS quantum dots was supported by the Russian Foundation for Basic Research (grant no. 16-34-60253).

SUPPORTING INFORMATION

Supporting information may be found in the online version of this article.

REFERENCES

- 1 Jabbour GE and Sariciftci NS, *Electronic, Optical and Optoelectronic Polymers and Oligomers*. Cambridge University Press, Cambridge (2014).
- 2 Rogach A, Semiconductor Nanocrystal Quantum Dots: Synthesis, Assembly, Spectroscopy and Applications. Springer, Wien (2008).
- 3 Pietryga JM, Park Y-S, Lim J, Fidler AF, Bae WK, Brovelli S *et al.*, *Chem Rev* **116**:10513–10622 (2016).
- 4 Reiss P, Carrière M, Lincheneau C, Vaure L and Tamang S, Chem Rev 116:10731–10819 (2016).

- 5 Samokhvalov P, Artemyev M and Nabiev I, Chem Eur J **19**:1534–1546 (2013).
- 6 Rodarte A, Cisneros F, Hein J, Ghosh S and Hirst L, *Photonics* **2**:855–864 (2015).
- 7 Generalova AN, Oleinikov VA, Sukhanova A, Artemyev MV, Zubov VP and Nabiev I, *Biosens Bioelectron* **39**:187–193 (2013).
- 8 Han S, Li X, Wang Y and Su C, Anal Methods 6:2855 (2014).
- 9 Min S-Y, Bang J, Park J, Lee C-L, Lee S, Park J-J *et al.*, *RSC Adv* **4**:11585 (2014).
- 10 Dabbousi BO, Bawendi MG, Onitsuka O and Rubner MF, Appl Phys Lett 66:1316–1318 (1995).
- 11 Kahmann S, Mura A, Protesescu L, Kovalenko MV, Brabec CJ and Loi MA, J Mater Chem C 3:5499–5505 (2015).
- 12 Palaniappan K, Hundt N, Sista P, Nguyen H, Hao J, Bhatt MP et al., J Polym Sci A Polym Chem 49:1802–1808 (2011).
- 13 Nozik AJ, Beard MC, Luther JM, Law M, Ellingson RJ and Johnson JC, Chem Rev 110:6873–6890 (2010).
- 14 Kamat PV, J Phys Chem C 112:18737-18753 (2008).
- 15 Tomczak N, Ja D, Han M and Vancso GJ, *Prog Polym Sci* **34**:393–430 (2009).
- 16 Kim S and Bawendi MG, J Am Chem Soc 125:14652-14653 (2003).
- 17 Cao X, Li CM, Bao H, Bao Q and Dong H, Chem Mater **19**:3773-3779 (2007).
- 18 Wang X, Dykstra TE, Salvador MR, Manners I, Scholes GD and Winnik MA, J Am Chem Soc **126**:7784–7785 (2004).
- 19 Hammer NI, Early KT, Sill K, Odoi MY, Emrick T and Barnes MD, *J Phys* Chem B **110**:14167–14171 (2006).
- 20 Lee J, Sundar VC, Heine JR, Bawendi MG and Jensen KF, Adv Mater 12:1102–1105 (2000).
- 21 Li Y, Yeung C, Pickett N, Skabara PJ, Cummins SS, Ryley S et al., J Mater Chem 15:1238–1243 (2005).
- 22 Woelfle C and Claus RO, Nanotechnology 18:25402 (2007).
- 23 Wood BV, Panzer MJ, Chen J, Bradley MS, Halpert JE, Bawendi MG et al., Adv Mater 21:2151–2155 (2009).
- 24 Song H and Lee S, Nanotechnology 18:55402 (2007).
- 25 Šajinović D, Šaponjić ZV, Cvjetićanin N, Marinović-Cincović M and Nedeljković JM, *Chem Phys Lett* **329**:168–172 (2000).
- 26 Choi S, Song H, Park IK, Yum J, Kim S, Lee S *et al.*, *J Photochem Photobiol* A Chem **179**:135–141 (2006).
- 27 Mumin MA, Xu WZ and Charpentier PA, *Nanotechnology* **26**:315702 (2015).
- 28 Bobrovsky A, Shibaev V, Elyashevitch G, Mochalov K and Oleynikov V, *Colloid Polym Sci* **293**:1545–1551 (2015).
- 29 Bobrovsky A, Shibaev V, Abramchuk S, Elyashevitch G, Samokhvalov P, Oleinikov V et al., Eur Polym J **82**:93–101 (2016).
- 30 Elyashevich GK, Kuryndin IŚ, Lavrentyev VK, Bobrovsky AY and Bukošek V, *Phys Solid State* **54**:1907–1916 (2012).
- 31 Bobrovsky A, Samokhvalov P and Shibaev V, Adv Opt Mater 2:1167–1172 (2014).
- 32 Gong X, Tang CY, Pan L, Hao Z, Tsui CP and Liu J, *Compos Part B Eng* **55**:234–239 (2013).
- 33 Gong X, Pan L, Tang CY, Chen L, Hao Z, Law W-C et al., Compos Part B Eng 66:494–499 (2014).
- 34 Hiss R, Hobeika S, Lynn C and Strobl G, *Macromolecules* **32**:4390–4403 (1999).
- 35 Zachariades AE, Mead WT and Porter RS, Chem Rev 80:351-364 (1980).
- 36 Nwabunma D and Thein K, Polyolefin Composites. Wiley-Interscience, Hoboken, NJ (2008).
- 37 Biju V, Makita Y, Sonoda A, Yokoyama H, Baba Y and Ishikawa M, J Phys Chem B 109:13899–13905 (2005).