Patterning and Alignment of CdSe quantum rods in polyacrylate films

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Cover: Colour images of films acquired with microscope in polarising mode
Abstract

In the development of nanotechnology a need is created for controlling systems with nanoscale features. Patterning of CdSe quantum rods using polymerisation-induced phase separation was studied. Polymerisation of ethylhexyl methacrylate was locally initiated with 1-hydroxy cyclohexyl phenyl ketone using a quasi-1D masks and UV-light. A time-study was carried out revealing that patterning started after 15 min and continued up to 2 hours of exposure. The maximum concentration fluorescence contrast measured was 4.6. Varying masks where applied showing that the contrast reaches a maximum at 1200 µm. Also, films where patterned close to the isotropic-anisotropic phase transition to induced orientation in the film. Some orientation was measured however no quantitative value could be determined to describe the order in the system.
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**Introduction**

**Nanoparticles**

In the last few decades the interest in the field of nanotechnology has grown tremendously. In nano-sized systems the relevant length-scales are bigger than single molecules but a lot smaller than in bulk materials - typical sizes are between 1 and 100nm. Since industry is interested in down-sizing exciting technologies, it has become increasingly import to study smaller and smaller systems.

Smaller systems are not only studied due to simple practical considerations. Hence one can not simply make existing devices increasingly smaller and faster, e.g. for computers, as many systems, on a smaller scale, they can also exhibit very different properties from their bulk material that can be interesting and beneficial. Two important properties are quantum effects and surface effects. The surface area increases exponentially with particle size. This means that nanometer sized particles have huge surface areas compared to bulk material. This for instance can increase catalytic activities of a catalytically active substance. Other interesting features of very small objects in the form of semi conducting nanocrystals are quantum effects that become important at this scale. Nanocrystals are crystals that at least have one of their size components on the order of nanometers. These species are usually stabilized by organic ligands or polymeric stabilizers. Quantum nanocrystals are semiconducting nanocrystals that are so small that their excitons, formed by electron-hole pairs, that quasi-particles semi conductors produce after absorbing a photon, are bigger than the particles themselves. Because of their size the exciton has to be described by quantum theory. Quantum nanocrystals are made in all kinds of shapes e.g. spheres (dots), rods, rice shaped, branched structures (e.g. tri pods and tetra pods) etc...The particles are of interest for biosensing\(^1\), biotags\(^2\), laser media\(^3\), voltovaic devices\(^4\) and they are even studied as building blocks for quantum computers\(^5\).

![Figure 1 CdSe Quantum rice (left)\(^1\) and tertapods (right)\(^6\)](image)

For example, semiconducting nanoparticles are a hot topic in solar cell technology. It is shown that semiconducting nanoparticles can release more than one exciton for each absorbed photon, where

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1 Dyadyusha,L ;Lin, H; Jaiswal, S et al Chem. Commun., 2005 3201
2 Ramadurai, D; Geerpuram, D et al Superlattices and Microstructures 2006, 40, 38
3 Kazes, M.; Lewis; D.Y.; Ebenstein, Y; Mokari, T; Banin, U, Adv. Mater., 2002, 14, 317
4 Zhong, H; Zhou, Y; Yang, Yang, C; Li,Y J. Phys. Chem. C 2007, 111, 5638
6 Yin, Y; Alivisatos, P Nature 2005 437 664
traditional silicon solar cells produce only a single exciton per photon even when the photon energy is several times higher than the exciton’s energy. If these particles could be implemented in solar cells it could entail a drastic increase in the efficiencies in photovoltaic devices. To implement these particles in a device it would be useful to be able to position or pattern them.

Quantum rods exhibit different properties compared to their spherical counter part, the quantum dots. For example, CdSe QRs, with an aspect ratio bigger than two, which are studied in thesis, have a transition dipole along their longitudinal axis. This makes it possible to study their orientation with polarised fluorescence light.\(^7,8\)

In general, there are two different approaches to synthesize nanocrystals by self-assembly. One is by using nano-templates or nano-cavities to grow the crystals in. The crystals will be allowed to grow in the cavities. The growth is then limited by the walls of the cavity and the shape will therefore be determined by the shape of the template. The templates are usually created by self-assembled surfactants. A problem with this method is that the fragile structures that surfactants form aren’t always stable at the high temperatures at which some nanocrystals are being forged.

Another approach is by using the kinetics of nucleation and growth. The growth of the crystals is controlled by the thermodynamics of the system and the concentrations of the precursors. The latter method seems to be best suited for semiconducting nanocrystals; this is because these particles are created at high temperatures and their shape can be controlled because of their different crystal surfaces that show to have different binding properties towards the precursors. Thus some of the lattice facets will grow faster than others resulting in a non spherical particle, whose shape is depended on the concentration of the precursors.\(^9\)

The synthesis of CdSe nanocrystals is extensively studied in several papers. High quality CdSe used to be synthesised by using the extremely toxic and unstable-at-room-temperature precursor CdCH\(_3\)\(^10\) which is also very sensitive toward oxidation. This made it possible for only about a dozen research groups to synthesize CdSe high quality nanocrystals. In recent studies, however, Peng et al. discovered an alternative route for the synthesis by using the less toxic and more stable CdO\(^11,12\). This method works by first starting with the nucleation of Cd-posphonic acid complexes (Octadocyl phosphonic acid or Tetradocyl phosphonic acid) and Se atoms that form so called “magic sized nanoparticles”. These particles are tetrahedrally shaped, about 3nm in size, and invisible for regular TEM. They are stabilized by their closed-shell structure. These magic sized nanocrystals can grow to various structures like quantum rise, quantum dots, quantum rods or branched structures depending on the concentration of the Cadmium and Selenide precursors. At high concentration of monomer the particle will grow from all

\(^7\) Chen, X; Nazzel, D; Goorskey; Xiao, M, Phys. Rev. B, 2001, 64, 245304
\(^8\) Hu, J; Li, L et al, science, 2001, 292, 2060
\(^10\) Peng, A; Peng, X, JACS, 2002, 124, 3343
\(^11\) Peng, A; Peng, X, JACS, 2001, 123, 1398
\(^12\) Peng, A; Peng, X, JACS, 2001, 123, 183
four corners resulting in tetrapods. At a bit lower concentrations only one of the corners is allowed to grow resulting in rod shaped structures.

Semiconducting quantum particles are sensitive towards oxidation and they also exhibit non-radiative decay processes\textsuperscript{13}. These properties reduce the fluorescence yield of quantum rods. To reduce these effects a shell of ZnS, that has a larger bandgap, can be deposited around the nanoparticles. This also prevents the surface from oxidising.

\textsuperscript{13} Hines, M. A.; Guyot-Sionnest, P. J. Phys. Chem, \textbf{1996} 100 468
Patterning nanorods

As previously mentioned, to make nanocrystals useful it is important to be able to position them and, in the case of anisotropic particles, even orient them. One way of patterning NC’s is using Polymerisation-induced phase separation (PIPS) in combination with light induced polymerisation and a shadow mask. This method was proposed by Kumacheva and Paquet\(^\text{14}\). They showed that quantum dots could be patterned in a polyacrylate film by inducing a controlled phase separation in the film. Certain areas in the film are exposed by UV light whereas other areas remain unexposed. At the exposed areas the film started polymerising resulting in a phase separation between the monomer phase and the polymer rich phase. The nanocrystals having a higher affinity for the monomer phase start to migrate towards to unexposed areas resulting in an inverse pattern of the mask. The important part of this process is that there is enough time between phase separation and solidification (divergence of viscosity) of the film. In this time interval the patterning takes place.

PIPS is a process where polymerisation is used to induce phase separation. This has been widely used in liquid crystal displays to make polymer dispersed liquid crystals (PDLC)\(^\text{15}\). For this purpose a mask is not necessarily used, because the aim to make PDLC size lies mainly on the control of the droplet size that, in turn, effect the optical properties. However, a very similar study to this one with liquid crystals has

\(\text{Figure 2 The process of the patterning technique.}\)

\(\text{Figure 3 Phase diagram for PIPS that change with polymer concentration\(^\text{17}\).}\)

\(^{14}\) Paquet, C; Kumacheva, E, Adv. Func. Mater. 2007 17 3105  
been carried out by Ren and Wu. Although PIPS is an extensively studied process it is not yet completely understood. Similar processes like solvent-induced phase (SIPS) and temperate-induced phase separation (TIPS) can be relatively easily described by Cahn-Hilliard theory. PIPS is more complicated due to the polymerisation that makes the phase diagram constantly change. Nevertheless several attempts have been made to model PIPS by combining Chan-Hilliard theory for phase separation with Flory-Higgins theory for polymerisation. In Figure 3 the dotted lines represent the spinodal and the solid lines the binodal lines, \( N_a \) is the degree of polymerisation, \( \chi \) is the Flory-Higgins interaction parameter and \( \phi \) the dimensionless concentration of polymer — with increasing polymer concentration the phase separation region grows with the critical point shifting as well.

The patterning as carried out in this study is illustrated in Figure 2. CdSe quantum rods and photo-initiator are dissolved in an ethylhexyl methacrylate film. Ethylhexyl methacrylate was chosen because this monomer gave the best patterning results according to Paquet and Kumacheva. A mask with vertical lines, creating a quasi 1D system, was applied to project a UV image on the film. In the next step, polymerisation and phase-separation starts. Subsequently, the CdSe rods start migrating resulting in a pattern. In the final step the mask is removed and the film is illuminated once more to polymerise the entire film.

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16 Ren, H; Wu, S, *Appl. Phys. Lett.* **2002** 81 3537

Alignment rods

Alignment of silver mesoparticles has previously been studied by the stretch-film method. With this method nano rods are aligned by stretching a film just above it glass transition temperature\textsuperscript{18}. According to Onsager rod shaped particles can also be aligned by confinement. Onsager was the first to predict that thin hard rod-shaped particles align themselves in solution above a certain concentration\textsuperscript{19}. Hard rod-shaped particles undergo an isotropic to nematic phase transition by losing entropy when increasing the concentration sufficiently. In the patterning techniques described in this report local concentration or quantum rods are increased. When the average concentration of the film is just below the phase transition orientation of the quantum rods would be expected after patterning by lifting the concentration just enough for the film to become anisotropic. However, Onsager assumed for his theory to describe these phase transitions a low concentration and high aspect ratio. The rods used in the experiments reported here have an aspect ratio of 7. Bolhuis and Frenkel\textsuperscript{20} calculated the entire phase diagram of hard spherocylindrical particles, giving a more accurate estimate of the phase diagram than Onsager (see Figure 4). Here the volume-density of the spherocylinders, volume rods divided by the total volume, are plotted against the diameter divided over the length. The rods used here have a ratio D/L of 1.7\textsuperscript{21}. There phase transitions are indicated by the blue lines in the phase diagram. Note that for Onsager’s theory D/L would go to 0 which would results in a significantly different phase diagram.

The phase transition from isotropic to anisotropic for 3nm wide and 60nm long CdSe nanorods stabilized by trioctylphosphine was already studied by Alivisatos et al\textsuperscript{22}. They showed to have a phase transition at 6.1% from isotropic to anisotropic at 9.9% from anisotropic to nematic, whereas Bolhuis et al calculated a respectively 19.2% and 21.5%. Alivitos concludes that attractive forces from the ligands seem to lower the concentrations of the phase transitions. Rods used in this paper have a D/L, the inverse shape anisotropy parameter, of 0.17 predicting phase transition by Bolhuis at respectively 39% and 41%. From this we can conclude that the phase transitions are below 39% and 41%. To determine the concentration in the films a 100% yield and the density of bulk CdSe were assumed.

From this their can be concluded that to align these rods in a film after migrating towards more concentrated areas it is a precondition to have a sufficient increase in concentration of nano rods. Another thing that has to be taken in account is that the rods must have enough time to change their

18 Fornasiero, D; Grieser, F Chem. Phys. Lett. 1987 139 103
20 Bolhuis, P; Frenkel, D J. Chem Phys 1998 106 666
21 D/L =D/(L_{rod}·D) where D is the diameter of the rod and L_{rod} is the length of the rod. D/L goes to infinity for an isotropic particle
22 Li, I;Marjanska, M; Park, G; Pines, A; Alivisatos, P, J. Chem. Phys. 2003 120 1149
orientation before the whole film is polymerised and that rods are no longer able to move for Alivisatos reported to equilibrate his system over months22. To optimise the system for obtaining maximal concentration differences different masks and different UV exposure times were used. The results from these experiments are described and discussed in the sub-section entitled ‘spatial distribution’. Birefringence in the films is discussed in the sub-section birefringence.
**Methods**

All chemicals were purchased at Sigma-Aldrich except for octadecyl phosphonic acid (ODPA) that was purchased at PCI synthesis.

**Synthesising CdSe nanorods in an one-pot synthesis**

3.2 gram; 8.3 mmol of trioctylphosphine oxide (TOPO) and 0.8 gram; 2.4mmol, ODPA and 0.13; 1mmol CdO was added to a three-necked round bottom flask. The flask was heated, while being stirred vigorously at 300°C obtaining a clear transparent solution. At this moment a solution of 60mgram; 0.75 mmol Se in 3.5mL TOP was added while the solution was kept between 280 and 300°C for 6 minutes. After the solution was allowed to cool to RT a dark brown/red fluorescing solution was obtained. The nanorods were precipitated by adding about 30% methanol. The solution was centrifuged and the pellet was redispersed in toluene. This cleaning method was repeated 3 times.

**Synthesising CdSe nanorods by multiple injection**

The synthesis of the CdSe nanorods by multiple injections was carried out according to the synthesis of CdSe nanorods described by Peng et al\(^\text{10}\). The procedure is written out in this report as well for clarity.

Cd-TDPA complexes were synthesised by heating CdO (0.6420 gram ; 5 mmol), Tridocyl phosphonic acid (ODPA 3.3447 gram ; 10 mmol) and Triocylphosphine oxide (TOPO 2.2 gram; 5.6 mmol) under argon for 5-7min at 270°C in a round-bottom flask. The clear solution was allowed to cool to RT and aged for 24h. The white opaque solid obtained was directly used for the synthesis of CdSe rods.

CdSe quantum rods were synthesised by adding 1.712 gram of the solid obtained from the Cd-ODPA complex synthesis to 2.287gram TOPO. This was heated under argon to 320°C. At this point 62.5mgram; mmol Selenium dissolved in a mixture of 187.5mgram; 0.23 mL tributyl phosphate (TOP) 1.447 gram trioctylphosphine (TOP) and 0.3 gram toluene was injected at once. After the injection the solution was allowed to cool to 250°C. Subsequently, every 20 minutes 0.35mL of the following solution was injected dropwise; Selenium dissolved in 2.68gram; 3.23mL TOP. After all of latter was injected the solution was kept at 250°C for 25min and only then it was allowed to cool to RT. 4-6mL Toluene was added. A dark red transparent solution was obtained. The solution was cleaned by precipitation of the nanorods by adding 30% (v/v) methanol and centrifuging. The supernatant was removed the rods where redispersed in 20mL toluene and the procedure was repeated once more. After cleaning the nanorods where kept in toluene.
**Core-shell synthesis**

For the core-shell synthesis the nanorods obtained by multiple injection nanorod synthesis were directly used. They were redispersed in hexanes. 12 grams of octadecylamine and 40 grams of octadecene were added. The hexanes where removed by rotavap evaporation. The remainder, a red emulsion, was kept under Argon atmosphere after degassing for a half an hour. The emulsion was heated in a three-necked round bottom flask to 110°C to remove the last bit of hexanes. After the solution stopped boiling it was heated further to 230°C. At this point, the solutions in Table 1 were dropwise injected subsequently every 10min. The Sulphur, Zinc and Cadmium solution from Table 1 were made by respectively dissolving 0.064 gram Sulphur in 39.4 gram octadecene at 100°C, 0.325 gram ZnO and 9.19 gram oleic acid in octadecene at 300°C and 0.103 CdO and 1.9 gram oleic acid in 13.7 gram at 200°C octadecene.

<table>
<thead>
<tr>
<th>Order</th>
<th>Solution(0.04M)</th>
<th>Amount in mL</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Cadmium</td>
<td>1.5</td>
</tr>
<tr>
<td>2</td>
<td>Sulphur</td>
<td>2.0</td>
</tr>
<tr>
<td>3</td>
<td>Cadmium</td>
<td>3</td>
</tr>
<tr>
<td>4</td>
<td>Sulphur</td>
<td>3.2</td>
</tr>
<tr>
<td>5</td>
<td>Cadmium</td>
<td>2.1+2.1</td>
</tr>
<tr>
<td>6</td>
<td>Sulphur</td>
<td>5.2</td>
</tr>
<tr>
<td>7</td>
<td>Cadmium + Zinc</td>
<td>2.7+2.7</td>
</tr>
<tr>
<td>8</td>
<td>Sulphur</td>
<td>5.8</td>
</tr>
<tr>
<td>9</td>
<td>Cadmium + Zinc</td>
<td>6.5</td>
</tr>
<tr>
<td>10</td>
<td>Sulphur</td>
<td>7.0</td>
</tr>
<tr>
<td>11</td>
<td>Zinc</td>
<td>8.0</td>
</tr>
<tr>
<td>12</td>
<td>Sulphur</td>
<td>8.0</td>
</tr>
<tr>
<td>13</td>
<td>Zinc</td>
<td>9.0</td>
</tr>
</tbody>
</table>

After the final injection the solution was kept at 230°C for ten minutes and was then allowed to cool to around 60°C. The emulsion was centrifuged at 3000rpm for 1-2 min. The supernatant was decanted and the nanorods were redispersed in hexane. The emulsion was washed several times with methanol. A strongly fluorescing deep red solution was obtained. The nanorods were precipitated with acetone and centrifuged. The pellet was redispersed in Toluene.
**Patterning**

The patterning was carried out according to the procedure of Paquet and Kumacheva\textsuperscript{14}. The Quartz plate and glass plate was cleaned with a Harrick Plasma cleaner/Sterilizer PDC-3X6 before surface treatment. Volume fractions of 1%, 3.3%, 4.5% and 10% nanorods were used in the film. These concentrations were calculated assuming a 100% yield and the bulk density of CdSe for the nanorods. The masks that were used were transparent sheets with black lines printed on them. They were designed with vector graphics based software called Freehand max 11. They were printed by City Graphics at 3600dpi. Films where exposed 30cm above the sample with a Dr Hööle UVA print 40C UV-lamp

**Time experiments**

Different films with a mask with transparent lines of 100 µmeter and black lines (spacings) of 1200 µmeter were made by exposing for increasing durations, 8, 15, 20, 30, 40, 50 and 120min respectively. After exposure with the mask the entire film, including the monomer/nanorods solution under the dark lins, was exposed for another 15-20 minutes polymerising the whole film.

**Spatial variations**

Films were made by applying different masks during the exposure of 55min. The transparent lines in the masks were a 100 µmeter, the spacings varied for each mask. The spacings used were 300, 900, 1200 and 1500 µmeter.

**Increasing concentrations**

All films used where made width a 1% monomer solution. However, to study the effect of concentration we used 1% 3.3% and 10% concentrations of nanorods.

**Time intervals**

Finally, a film was made by exposing at time intervals to see if this would create more alignment. This film was repeatedly exposed and allowed to relax for the following times; 20min exposed, 10min relaxed, 20 exposed, 10 relaxed, 20 exposed, 20 relaxed and finally 10min. For this film a quantum rod solution of 4.5% was used.
**Imaging quantum rods**

All rods were imaged with a Hitachi HD-2000 STEM on pelco grids. The Quantum rod solution was diluted until the solution became almost transparent. Then a droplet of this solution was evaporated on a TEM grid that was used for imaging. Size distributions were determined by measuring the size of a hundred rods from a TEM image with image tool.

**Imaging quantum rod films**

The films where imaged by a Roper scientific photometric CCD under an Olympus EX51 microscope with 4x magnifying lens using three different modes, Transmission mode, polarising mode and polarised fluorescence mode. The latter two modes are described below in Figure 5. On the left the polarisation mode is shown. Here the film is studied while between two crossed polarisers therefore allowing only light that has been rotated, due to birefringence, to pass the second polariser. However, this method doesn’t give a quantitative description of alignment. The second is shown at the left. Here a rotatable polariser is located just after the filter cube and before the detector thereby allowing control of the polarisation direction of the UV-light that hits CCD. The filter cube passing excitation light of 535nm ±25 and passing fluorescent light of 610nm ±37.5 is represented by the diagonal line. This setup selectively acquires images that correspond to fluorescing dipoles having the same orientation as the orientation from the polariser. Since CdSe quantum rods have a transition dipole along their longitudinal axis this technique directly reveals the orientation of these rods in a film. Images were analysed, gaining and averaging intensity profiles, using photoshop cs3 in combination with Fovea pro plugins.
Safety

Although the properties of CdSe in bulk form has been well investigated not much is known about the safety of CdSe nanoparticles that are expected to behave differently. Derfus et al\textsuperscript{23} showed that CdSe nanorods are toxic mostly due to the release of Cd\textsuperscript{2+} ions by Cadmium oxidation on the cell surface resulting in cell death. CdSe ZnO-capped nanoparticles showed to be significantly less toxic however little is known about long term exposure. Safety precautions demanded wearing nitrile gloves, a lab coat, safety glasses at all time and caring out the experiments under the fume hood.

\textsuperscript{23} Derfus, A.M.; Chan, W. C.W.; Bhatia, S.N., *Nanoletters* 2004, 4, 11
Results and Discussion

CdSe Nanorods

The quantum rods in Figure 6 were synthesized according to the one-pot synthesis method. Their average length is 13.8 with a standard deviation of 15%.

To study the rods for the purpose of this study another method for making the rods was preferred. This injection method, yielding longer nanorods, is expected to be more suitable for orienting them in a film.

Figure 7 shows aliquots that were taken at given time intervals revealing how the quantum rods grow during synthesis. Their color shifts from yellow to red while they grow. The left TEM image show the rods after 10 min and the right show the rods after 2 hours.

Figure 7 C shows the fluorescence of the aliquots. The shift in color is qualitatively in agreement with their Plasmon frequency that should decrease with increasing size24.

Figure 7 Quantum Rods made with multiple injection a)daylight b)UVlight at 365nm

The rods’ fluorescence was quenched after a certain amount of time when dissolved in the monomer (ethylhexyl methacrylate). To overcome this quenching shells of respectively CdS and ZnS where deposited on the rods obtaining Core–shell nanorods. These nanorods didn’t quench in the monomer and show to have a much higher photoluminescence. The latter is in agreement with Taleb Mokari and Uri Banin25 who showed the increasing in photoluminescence quantum yield in CdSe /ZnS quantum rods.

In Figure 8 a lattice image from the core-shell nanorods is showed. The lattice seems to be regular, however in the image a core-shell structure cannot be discerned for the image is not clear enough. The TEM grids that were used were too thick for producing optimal lattice images. Ultrathin carbon holey grids were ordered to obtain better lattice images, unfortunately, they didn’t arrive on time. The

24 Nobile, C; Kudara, S; Fiora, A; Carbone et al, Physica Staus Solidi (a) 2007 204 438
25 Mokari, M; Banin, U Chem. Matter. 2003, 15, 3955
absorption and fluorescence spectrum of the rods before growing a shell and after growing a shell are shown in Figure 9. For the core-shell quantum rods the Plasmon frequency slightly blue-shifted and the fluorescence peak increased 43 times. The rods had a length of 23.8nm with standard deviation of 8.8% and a width of 3.4nm with a standard deviation of 22.9%.

**Figure 8** Lattice image CdSe core-shell nanorods obtained via multiple injections

**Figure 9** Absorption and fluorescence of core-shell CdSe nanorods and non core-shell CdSe nanorods. Peaks are at 585 605 611 and 622nm
**Patterning**

**Spatial distribution**

Figure 10 represents quantum rod films with different exposure times from left to right. The top images show the masks, the middle images are transmission microscope images and the graphs below are y-axis averaged intensity profiles from the fluorescence images plotted along the x-axis. The intensity profiles were taken from fluorescence measurements because the fluorescence intensity represents the local concentration of quantum rods (i.e. the quantum rod luminescence is linearly proportional to the absorbance). The images reveal how the rods diffuse from the exposed areas to the unexposed areas. The masks that were used for this experiment had transparent lines with a thickness of 100 µmeter separated by 1200 µmeter black lines (spacings). In the appendix “extra results: time experiments” some more films at different times of exposure are shown. Figure 10 only shows the most relevant films.

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Figure 10 Nanorod migration through monoethylhexylmethacrylate/polyethylhexylmethacrylate films at different times of exposure. The films were exposed to UV light with a mask between light source and the film. The exposed time is indicated at each image. Directly after, the films were exposed a second time for 20 min over the whole film without a mask. The masks are shown in the middle. They are shown in such a way that the transparent lines from the mask overlap with exposed areas of the film. The graphs below are the corresponding y-axis averaged fluorescence intensity plotted along the x-axis.

Up to 15 minutes no pattern can be discerned. At 20 min minutes an intermediate state is shown where rods are starting to migrate to the left and right from the exposed areas thereby creating two peaks left and right from the exposed lines. At 50 min minutes, by further migration from the exposed areas, the peaks between two exposed lines coincide in the middle. Migration still continues after this point as is shown that after two hour contrast still increasing.

It is surprising that there is not any patterning yet between 15 and 20 minutes. Photo-initiated radical polymerisation usually takes place fast. Although this reaction wasn’t carried out in an oxygen free environment and therefore inhibited by oxygen, the reaction should take place within a few seconds\textsuperscript{26,27}. This three orders of magnitude time difference remains unexplained.

\textsuperscript{26} Decker, C; Jenkins A,D, *Macromolecules* 1985 18 1241
After 20 min when exposed areas are sufficiently polymerised to induce a phase separation the quantum rods migrate towards the unexposed areas i.e. the monomer phase. After this, polymerisation continues in the unexposed areas. The quantum rods are enclosed by polymer fronts as they move from the exposed areas towards each other. There are two explanations taken in consideration concerning the polymerisation of the unexposed areas. First, the heat that is produced during polymerisation diffuses towards the unexposed areas and thereby continuing polymerisation by thermal initiation. Secondly, radicals, either polymer or activated initiator, that are produced at the exposed areas diffuse to the unexposed areas and subsequently continue the polymerisation there.

If assumed that polymerisation is continued by diffusing radicals, the patterning would be limited by the diffusion length of these radicals i.e. the spacing between the exposed lines can not be longer than the diffusion length without loss of resolution and contrast. In Figure 11 the contrast is plotted for each exposure time. The contrast was determined by simply dividing the maximum intensity over the minimum intensity indicated by the blue lines Figure 10. Note that from this figure a linear relation between contrast and exposure time can be inferred.

Figure 12 shows transmissive microscope images from films with different masks during exposure of 50min. The applied masks consisted of transparent lines with a width of 100 µmeter separated by black lines (spacings). Different spacings were used for each film, respectively from left to right 300, 900, 1200 and 1500 µmeter were used. The red dotted lines indicate where the film was exposed. The graphs in

Figure 12 Patterned films with variable masks. The exposed lines are 100µm in width as shown by the red dashed lines. The distance between the exposed lines is indicated above each image. The graphs below the films show the fluorescence intensities along the x-axis of the film.

Studer, K; Decker, C; Beck, E; Schwalm, R *Process in Organic Coatings* 2003 48 92
this figure show the corresponding average fluorescence intensities from each film. These graphs were obtained in the same way as the graphs in Figure 10.

All films reveal successful patterning that corresponds with the applied mask however the contrast of the films are significantly different for each film as can be seen in Figure 14. In Figure 14 the contrasts are plotted against the spacing. Contrast increases from a spacing of 300 to a maximum 1200 µmeter. The contrast drops at 1500 µmeter. This drop can be explained by diffusing free radicals that are not able to reach far enough to polymerise the whole film or, in case of thermal polymerisation, the film does not get warm enough to continue polymerisation. Note that the mask with a spacing of 1200 µmeter gives the best contrast that is the local highest concentrations. Quantum rods at the exposed areas and at unexposed areas contribute to the contrast. For large spacings, evidently, the quantum rods in the unexposed areas contribute more to the contrast than the rods at the exposed areas and for small spacings the quantum rods at the exposed areas contribute more to the contrast. This is shown by the energy diagrams in Figure 13. A fundamental difference between rods migrating from the exposed areas compared to migration at unexposed areas is the way the potential energy is changed by polymerisation. Since the rods have a higher affinity for the monomer phase the potential energy for the rods in the polymer phase is relatively high. So the polymer phase is indicated by the potential peaks in the energy diagram. For the quantum rods at the exposed areas the potential starts rising as the polymerisation increases. The black arrows on the right energy diagram in Figure 13 indicate in which direction the potential expands. For the rods to migrate towards to monomer phase the rods will have to diffuse out before the viscosity diverges i.e. the rods are trapped. Because illumination at the exposed areas is uniform the potential at these areas should be flat. Therefore the mechanism for migration at the exposed areas is expected to be self-diffusion. On the other hand, rods at the unexposed areas undergo a different type of migration. In this case, the potential represented by moving polymer fronts are closing in on each other scooping up the rods. This is indicated by the black arrows in the left energy diagrams. It is expected that the latter is more efficient and will result in higher contrasts.

The increasing contrast in Figure 14 up to 1200 µmeter can be explained by an increasing number of rods from the unexposed areas contributing.
Birefringence

All the films discussed before had a concentration of 1%. In Figure 15 films are shown with increasing concentration of 1, 3.3 and 10 the spacing between the illuminated areas is 1500 µmeter. The concentration is shown in volume percent. The 1% film shows to be clearly patterned whereas for the 3.3% the patterning is less clear and for the 10% almost no patterning can be discerned. Note that the 10% film has cracks. This film was too brittle to escape from the glass. It was noted during the dissolution of the rods in the monomers that with an increasing concentration the viscosity of the monomer-rod mixture also increased.

![1% v/v](image1)
![3.3% v/v](image2)
![10% v/v](image3)

Figure 15 Films with varying concentration

In Figure 16 the average dichroic ratio and the local concentrations are plotted against the distance along the x–axis. The red dotted lines show where on the x-axis the film is exposed. See appendix “dichroic ratio, concentration” to see how the dichroic ratio is determined for the CdSe rods. First, note that a peak shows up at the exposed areas for the 3.3% and the 10% film. This tells us that there is less or even no migration underneath the exposed areas. This could be explained by the increase in viscosity that was witnessed at these high rod concentrations. The increased viscosity decreases the time it takes for it to diverge. So above 3.3% the diffusion of rods takes place slower than the time to polymerise it. Furthermore, several things can be noted for the dichroic ratio results. First of all, measured dichroic ratios are low. Secondly, what would be expected is that the dichroic ratio is 0 at the exposed areas for the migration mechanism there should be self-diffusion resulting in preferred alignment of the rods. These results do show a dichroic minimum at the exposed areas. However, they aren’t zero and for the 1% film the exposed areas only have a local dichroic minimum.

![1%](image4)
![3.3%](image5)
![10%](image6)

Figure 16 Concentration and Dichroic ratio vs distance

The dichroic ratio and concentration of another film with a concentration of 4.5% and a spacing of 900 µm made with exposure intervals is show in Figure 17. For comparison, the data of a 1%-900 µmeter-spacing- film and the data of an evaporated droplet are also plotted in this figure. The intensity profile
for the evaporated droplet wasn’t averaged since this image wasn’t symmetric along the y-axis. This 4.5% film shows some similarities to the films from the previous figure. First, the peak at the exposed areas reveals there is no migration there. Secondly, dichroic ratios are close to zero at these areas. However, there is a striking difference with the other films shown the previous figure. The dichroic ratio has a minimum at the concentration maxima below zero indicating perpendicular alignment to the x-axis instead of parallel for a positive dichroic ratio. The evaporated droplet results are shown because this system is known for it’s highly aligned rods. It shows dichroic ratios of around 0.2.

Having said that, there are three reasons why these measurements of the dichroic ratios are not representing the order parameter well. Probably, the most important reason is that Lambert-Beer does no longer hold for absorbance higher than 1. Unfortunately, absorbance measurements haven’t been carried out so it is not possible to say whether the measurements are within the approximation of the Lambert-Beer law. Secondly, there weren’t any reference measurements carried to subtract a background (i.e. daylight, dark current, read out noise). From these one can conclude that these number merely gives a qualitative idea about the order in the film and that the measured dichroic ratio can not be considered as a measure for the order parameter.

![Dichroic ratio versus distance](image)

**Figure 17 Dichroic ratio versus distance**

In Figure 18, polarised fluorescence microscope images and polarising microscope images are shown for the samples that were discussed in Figure 17. This is done to get a better insight of the meaning this data. The left image represents the evaporated droplet, the middle image represents the 4.5% film, and the right image represents the 1% film. The images with the arrow are the polarised fluorescence images where the arrow shows the orientation of the polarised light. The images below are polarising microscope images. The evaporated droplet at the top image shows slightly curved lines against a dark background whereas at the middle image it shows dark curved lines at a light background. These differences in intensity for different polarisation angles reveal that the rods must be significantly aligned. In the 4.5 % image the difference between the intensity of the polymerized and monomer region are clear however there can be seen that the two white lines in the bottom image are brighter than in the top image and the four grey band left and right from these bright lines are more bright for the top image than for the bottom. For the 1% image it hard to see any difference between the two polarisation angles. All the images show birefringence as can be seen in the bottom images.
Figure 18 Fluorescence Polarisation and Birefringence. The top and middle images are made in fluorescence mode with a rotatable polariser. The polariser in the top images is rotated 90° compared to the polariser in the middle images. The images below are made in polarisation mode. The dashed lines in the films show where the films are irradiated with UV-light. The top two images on the far left show to have a curved line that is white at top image but black at the one below. This indicates that along this line the rods are highly oriented in the line’s directions.
Conclusion

CdSe/ZnS core-shell quantum rods where successfully synthesised with an aspect ratio of 7 and an average length of 23.8nm. Subsequently, the rods were successfully patterned by using polymerisation-induced phase separation in combination with UV light and a quasi-1D mask. Migration in the film started after 15min of exposure and continued up to 2 hours. Exposure of two hours using spacings in the mask of 1200µmeter produced the highest contrast of 4.6 in fluorescence mode. The migration of nanorods at the exposed areas stopped above a concentration of 3.3%. The fluorescence measurements indicate that there is alignment but they are not conclusive.

In future experiments it would be important to quantify the alignment in the film to see if a phase transition took place or not. A problem here is that on one hand the Lambert-Beer law brakes down at high absorbance and on the other hand high concentrations are needed to induce the phase transition. This means that to be able to measure the order parameter using the dichroic ratio high concentration are needed and on the other hand and small film thicknesses are required to make sure the absorbance stays within The Lambert-Beer limits.
**Appendices**

**Dichroic ratio and Concentration**

The dichroic ratio was determined by formula 2 were $I$ is the fluorescence intensity $A$ the absorbance and $d$ the dichroic ratio. The dichroic ratio which is a value between -1 and 1 gives an idea of the alignment either perpendicular or parallel to the polariser. The dichroic ratio is usually expressed in the absorbance as shown in formula (2). However, as the fluorescence intensity scales with the absorption shown in formula (1) the dichroic ratio can also be expressed in terms of fluorescence intensity (left hand side) formula (2). The determined dichroic ratio, in turn, equals when the order parameter if assumed that that rods emit 100% polarised fluorescing light. This assumption appears to be plausible as shown by Hu et al who measured 0 fluorescence for CdSe rods perpendicular to the polarised light source and a 100% fluorescence for CdSe rods parallel towards the polarised light source after correcting for the depolarising effect of the applied lens.

\[
I \propto A \quad (1)
\]

\[
d = \frac{A_\perp - A_\parallel}{A_\perp + A_\parallel} = \frac{I_\parallel - I_\perp}{I_\parallel + I_\perp} \quad (2)
\]

Because of formula (1) and lambert-beer the fluorescence also scales with the concentration. By determining the average intensity in the film, which corresponds to the average concentration, and by assuming there is zero fluorescence intensity when there are no rods the concentrations were calculated.
Extra results: time experiments

This image shows some more transmissive microscope images at given times of exposure.