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SHORT COMMUNICATION

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Organization of nanoscale objects via polymer demixing

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Abstract We present an extremely versatile method for the lateral organization of nano-scale objects (NOs) based on the phenomenon of polymer demixing. NOs are suspended in a solution of two immiscible polymers, which is used to form a thin polymer film by spin coating. During spin coating the two polymers separate to give a microphase structure, whose length scale depends on the experimental conditions. The NOs spontaneously partition into one or other of the polymer phases resulting in their lateral organization. In this work, the organization of CdSe nanoparticles and fluorescent organic dyes was studied by fluorescence microscopy. The NOs were organized in the polymer film in stochastic patterns or in ordered designs on substrates pre-patterned by soft-lithography techniques. Single-particle measurements, using confocal microscopy, showed that at low concentrations there was little aggregation of the particles.

Keywords Nanostructures · Particle organization · Polymer demixing · μ-contact printing · Nanoparticles

Introduction

Research into the structuring of surfaces on the nanometer scale has been very active in recent years, driven by the prospects of applications in the fields of biology, optics, and nanoelectronics. A number of different methods for the organization of nanoparticles (NPs) or other sub-micron and nano-scale objects on surfaces have been reported. These include the use of optical tweezers to individually position NPs [1], and the use of charge–charge interactions to build up either polyelectrolyte/NP layer structures [2] or lateral structures via contact printing of charged species [3]. In addition, nanoparticles have been synthesized in well-defined places to give an ordered structure: block copolymers are used to form an inverse micellar system in which gold (or other metal) ions are located in the polar phase. Reduction of the metal ions results in the formation of metallic nanoparticles within the micelles [4]. In a different approach, the diffusion properties of metal atoms on polymer surfaces can be exploited, e.g. a thin metal layer is evaporated onto the structured surface of a block copolymer substrate and the metal ions diffuse to form nanoparticles on one of the blocks, while leaving the other block bare [5]. In both of these last methods, highly ordered nanoparticle structures are obtained.

This article reports on the use of polymer demixing to organize NOs in a thin polymer film. This method is applied to nano-objects synthesized *before* formation of the polymer structure. This means that a very wide range of objects—metallic, semiconductor NPs or even organic molecules—can be used. We have chosen this approach because of its simplicity, versatility, low cost, and compatibility with clean room technologies.

Polymer demixing is a well-known effect [6, 7], which can be observed both in the bulk and in thin polymer films [8, 9, 10, 11]. In the latter case, a solution of immiscible polymers is deposited on a surface and undergoes solvent evaporation. The polymer concentration increases to a threshold value, above which demixing into two phases takes place. On continued evaporation of the solvent the polymer film solidifies, "freezing in" the non-equilibrium microphase structure. The choice of polymers, their molecular weights, concentrations and relative proportions, as well as the solvent, substrate and rate of solvent evaporation, all influence the characteristic shape and size of the microphase structure.

Recently, numerical simulations of phase-separating binary fluids, such as polymer blends, have found that small (nanometer-sized) mobile particles with a selective affinity for one of the phases will be concentrated into this phase during demixing [12, 13, 14] (Fig. 1). This partitioning of the particles into one of the two polymer phases is analogous to the partitioning of chemical species in immiscible two-phase solvent systems, often used by chemists as a purification method.

To date, little or no experimental work has been carried out on the distribution of nanoparticles in demixed polymer films. Tanaka et al. studied the effect of micron-sized glass beads on demixing in a polymer film a few microns thick [15]. However, with three orders of magnitude size difference between the particles used in our study and the particles used by Tanaka, the results of this paper are not directly relevant. A few authors have studied the distribution of nanoparticles in block copolymer films. These systems are quite similar to nanoparticles in demixed polymer films, but with two significant differences: the block copolymer/nanoparticle films are much more ordered systems and are much closer to thermodynamic equilibrium than demixed homopolymer films [16, 17, 18, 19, 20].

We investigated the use of polymer demixing to laterally organize fluorescent CdSe NPs [21, 22] in a demixed film of polystyrene (PS) and poly(methylmethacrylate) (PMMA). The size of the polymer microphase structure was tuned to allow easy observation of the different polymer phases. The lateral distribution of the nanoparticles within the film was characterized using optical microscopy and atomic force microscopy (AFM).

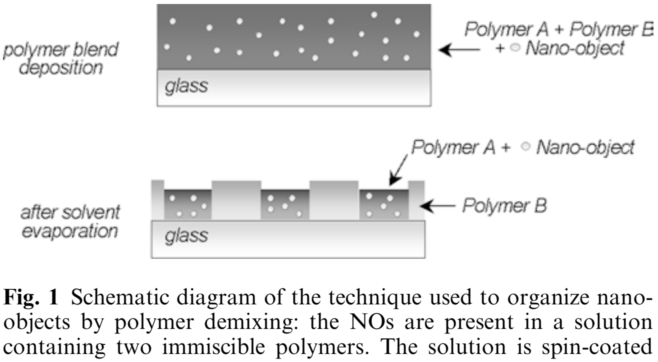

Fig. 1 Schematic diagram of the technique used to organize nano-objects by polymer demixing: the NOs are present in a solution containing two immiscible polymers. The solution is spin-coated onto a surface and demixing leads to the formation of microphases in the film. The nano-objects spontaneously partition into one of the two polymer phases

Experimental procedures

We produced semiconductor NPs with a CdSe core and a trioctylphosphine oxide outer shell, following the method developed by Murray et al. and modified by Qu et al. [23, 24]. Two different batches were used, with average NP diameters of 2.5 nm and 3.5 nm as estimated from their first absorption maximum positions [25]. Their emission peaks are centred at 520 nm and 565 nm, respectively. Bodipy 493/503 was purchased from Molecular Probes.

Stock solutions in toluene (Fluka) or tetrahydrofuran (THF, Fluka) were prepared using PS, $M_w \approx 100{,}000$, $M_w/M_n \approx 1.03$ (Polymer Standards Service), and PMMA, $M_w \approx 100{,}000$, $M_w/M_n \approx 2.12$ (Aldrich), at concentrations of 3% by weight. The final polymer blends were made by mixing the stock solutions of each polymer in the appropriate volume ratio (typically PS/PMMA: 30/70). The nanoparticles and Bodipy were first diluted in toluene, and then added to the final polymer solution.

Glass surfaces were cleaned by sonication for 30 min at 35°C in a 2% solution of Hellmanex in milliQ water, and washed in deionised water (three times 5 min with sonication). Gold surfaces were produced by thermal evaporation onto a cleaned glass substrate covered by a few nanometers of chromium. The gold films, approximately 40 nm thick, were sufficiently transparent to allow bright-field optical measurements. Immediately after preparation, the gold substrates were patterned by microcontact printing in order to create a surface energy variation, as described by Palacin et al. [26]: a PDMS stamp was inked with hexadecanethiol (Lancaster), 1 mM in ethanol (puriss. absolute, Fluka), for 1 min and put in contact with the gold surface for 10 s. The slide was then dipped in a solution of mercaptohexadecanoic acid (Aldrich), 0.5 mM in ethanol, for 30 s, and washed with ethanol. AFM friction measurements revealed the correct patterning of the substrate in areas of different surface energies.

Polymer films were made by spin coating at speeds between 500 and 9,000 rpm onto glass, silicon wafers or gold surfaces. In some cases, one polymer microphase was removed by treating the film with a selective solvent after the coating (acetic acid 50% in water to remove PMMA, and cyclohexane to remove PS).

Fluorescence images were taken with an Axiovert S100 microscope (Zeiss) equipped with a CCD camera system and a mercury vapour lamp as excitation light source.

Single NPs were imaged using a confocal optical microscope (WITec), equipped with a frequency doubled Nd:YAG laser ($\lambda = 532$ nm). AFM images of polymer films were acquired in tapping mode using a Dimension 3100 microscope (Digital Instruments).

Results and discussion

Thin polymer films containing PS, PMMA and CdSe NPs were prepared by spin coating as described above. Since CdSe NPs with diameters of a few nanometers fluoresce in the visible, their detection and localization within the polymer film were particularly easy using fluorescence microscopy. Fig. 2(i) and (ii) show typical fluorescence images, where the bright, fluorescent domains indicate the presence of NPs. In Fig. 2(i) the domains of NPs present a stochastic organization; altering the conditions of deposition of the film and the concentrations of the different components changes the size and shape of the bright domains but not their stochastic nature. In Fig. 2(ii) the film was prepared on a gold surface previously patterned using micro-contact printing of thiols to give hydrophilic and hydrophobic stripes. After fluorescence microscopy, the PS phase of the film was removed by selective solvent treatment and was characterized using AFM (Fig. 2iii). We observe that the dark dots of Fig. 2(ii) in region A correspond to the PMMA domains of Fig. 2(iii). From this and other similar observations we conclude that the NPs are located in the PS phase of the polymer film. Thus the NPs spontaneously partition in one polymer phase during the demixing process and self-organize within the polymer film. Analogous results have been obtained for other NOs such as metallic particles (results not shown) and organic molecules (see, e.g., the experiment with Bodipy below).

Other authors have shown that the microphase structure of polymer films follows the structure prepatterned on the surface when their characteristic length scales are similar [27, 28]. Therefore, we repeated the same experiment as in Fig. 2(ii), tuning the rotation velocity of spin coating in order to get polymer domains of the same order of the patterned structures. These resulted in well-defined, non-stochastic patterns of NP domains such as, for example, aligned dots (Fig. 3i). The NPs were then organized into lines (Fig. 3ii) by fine-tuning the rotation speed during spin coating. We have organized nanoparticles in line and dot patterns with 20 μm and 2 μm periodicity. However, a huge variety of patterns is available, within certain constraints of structure size, radius of curvature and relative proportions of the different phases.

In order to quantify the partitioning of the NPs between the two phases, we counted the individual NPs and allocated them to a PS or PMMA phase, using confocal optical microscopy (excitation at 532 nm). This single particle detection and counting approach has the advantage over classical fluorescence microscopy that it does not rely upon the determination of the absolute level of fluorescence from the different regions of the film or on a quantitative subtraction of the background fluorescence from the polymers and the substrate. A polymer blend containing a low concentration of NPs was spin coated on a glass surface at a low rotation speed. These conditions resulted in domain sizes and spacings between the NPs much larger than the typical dimensions of a single NP image (~500 nm FWHM), so that the individual NPs within the film could be imaged and allocated to one of the two polymer phases. Figure 4 shows a typical fluorescence image of the film obtained.

The higher auto-fluorescence of PS in comparison to PMMA allowed us to directly observe the microphase structure of the film without additional labelling of the polymers; i.e. the round dark areas in Fig. 4 correspond

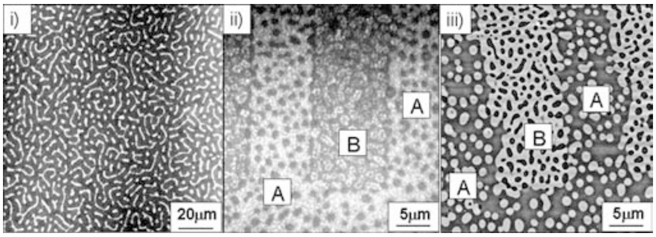

Fig. 2 i Fluorescence images of stochastic organization of the CdSe NPs in a thin polymer film (PS/PMMA 40/60, [NP]≈1 μM, spin coated from THF, 7,000 rpm). **ii** Fluorescence images of CdSe NPs in a thin polymer film spin coated onto a pre-patterned gold surface (A hydrophilic, B hydrophobic areas), (PS/PMMA 30/70, [NP]≈1 μM, spin coated from toluene, 6,000 rpm). **iii** AFM image of the same sample in Fig. 2ii after removal of PS phase. A comparison between the fluorescence and the topographical images reveals the location of NPs in the PS phase

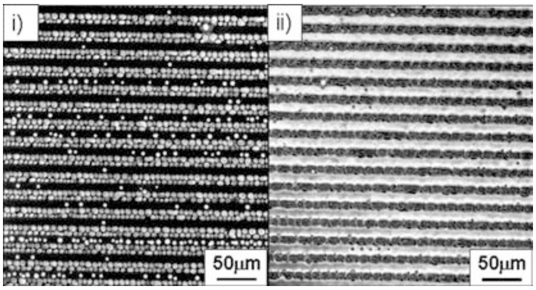

Fig. 3 i Guided NP organization on a gold surface with a pre-patterned variation of surface energies (PS/PMMA 30/70, [NP]≈1 μM, spin coated from toluene, 600 rpm). **ii** NP organization in stripes after fine-tuning the experimental parameters (PS/PMMA 30/70, [NP]≈1 μM, spin coated from toluene)

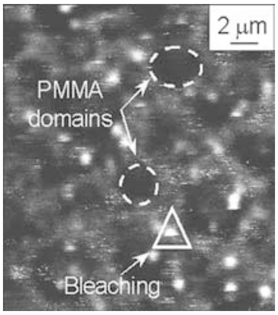

Fig. 4 Confocal fluorescence microscopy image showing single CdSe NPs embedded in a polymer film (PS/PMMA 50/50 [NP]≈0.06 μM spin coated from toluene at 500 rpm)

to PMMA domains, while the brighter regions are the surrounding PS matrix. Most of the bright spots with count rates above the usual PS background can be positively identified as single fluorescent NPs by means of characteristic properties such as blinking, bleaching and fluorescence polarization [29, 30]. This indicates that, under these conditions, the majority of the NPs in the film do not aggregate, but are present as isolated particles. Although these studies are not yet complete, a first estimation of the degree of the NPs partitioning indicates that around 90% of the NPs are located in the PS phase.

Close study of Figs. 2 and 4 suggests that, in addition to the partitioning of the NPs in the PS phase, there may be an enrichment of the NPs at the interfaces between the PS and PMMA phases. This effect has been described in numerical simulations of both homopolymer blends and block copolymer films containing NPs [12, 13, 16, 19]; NPs accumulate at the interface between the different polymers when their presence reduces the interfacial energy of the system, as is the case for particles with similar energies of interaction for both polymer phases. Alternatively, the NPs may accumulate at the interface if their movement across the interface in the film is hindered. Unfortunately the resolution of confocal optical microscopy (some hundreds of nanometers) does not allow precise definition of the position of the phase interfaces in these images and requires a very low concentration of NPs in the film. These two limitations make it very difficult to come to a definite conclusion on this subject. A more detailed study of the distribution of the particles within the individual polymer phases of the film will require the use of AFM to identify the positions of the individual NPs more precisely.

This approach to organizing nano-objects via polymer demixing can also be used to simultaneously separate and organize two different species of objects. We used CdSe NPs and the fluorescent organic dye Bodipy 493/503, which were both added to the same polymer blend. The solution was spin coated onto a glass surface and imaged by fluorescence microscopy. Figure 5 shows two fluorescence images of the same film area taken at different times (the grey level and the contrast were adjusted for each image). At $t=0$ the dot-shaped domains have a higher fluorescence intensity than the surrounding matrix (Fig. 5i); after 10 min of constant irradiation, the emission from the domains is greatly reduced and the surrounding matrix now has the higher fluorescence intensity (Fig. 5ii). These findings can be explained by the different bleaching rates of the two species measured in control experiments (results not shown). At the concentrations used, the initial fluorescence signal of Bodipy is higher than that of the NPs, but rapidly photobleaches under constant irradiation of the sample. The same irradiation leaves the NPs fluorescence largely unchanged, and after 10 min their emission is more intense than that of the Bodipy. We conclude that the NPs and Bodipy spontaneously separate during the polymer demixing and that the NPs are located in the continuous matrix phase while the Bodipy is present in the dot-shaped domains.

Conclusions

To conclude, we have demonstrated the spontaneous lateral organization of nanoscale objects in thin polymer films. The underlying process depends on the properties of immiscible polymer blends and the different free energies of dispersion of the objects in the two polymers and has previously been described in numerical simulations. We have used this method to organize different NOs in PS/PMMA films. Single particle fluorescence studies indicate that good separation of the objects between the two phases (high partitioning coefficients) can be obtained. However, the resolution of this optical technique was not sufficient to characterise the distribution of the particles within the individual polymer phases. Because the distribution of the NOs in the polymer films was characterized by fluorescence microscopy, the length

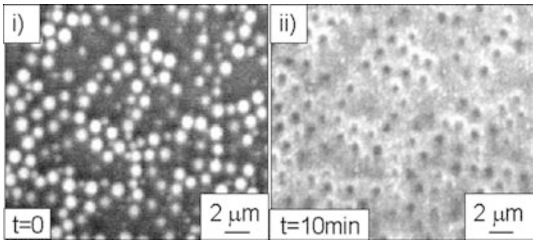

Fig. 5 Fluorescence images of a PS/PMMA film, containing CdSe NPs ([NP]≈5.0 μM) and Bodipy 493/503 ([Bodipy]≈25 μM). **i** Initially bright dot-shaped domains are observed in a dark continuous phase. **ii** After 10 min of irradiation, there is little fluorescence from the dot-shaped domains and the continuous phase is brighter

scale of the structures that we analysed was necessarily larger than 1 μm. At this scale of patterning we have found that the NOs can be easily self-organized in stochastic domain/matrix or spinodal patterns, while non-stochastic patterns are also possible if the surfaces are pre-patterned by micro-contact printing. However, polymer microphase structures in thin films can be made with length scales on or below 100 nm. It is therefore possible, in principle, to extend nanoparticle organization down well below the micron scale. Studies are currently underway on the organization of nanoparticles in lateral structures with 100 nm characteristic lengths. The flexibility of this method extends to the use of different polymers, solvents and surface chemistries—both aqueous and organic solvents can be used—making this technique an interesting tool wherever the organization of NOs in sub-micron patterns is required.

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