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ORIGINAL CONTRIBUTION

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The influence of nanoparticle fillers on the morphology of a spin-cast thin film polymer blend

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Abstract Polymer/nanoparticle composite films are receiving growing attention thanks to their potential for application in ultra-thin electronic and optical devices. Polymer blend demixing has been shown to be a suitable technique for the structuring of polymer thin films and the patterning of nanoparticles (NP) within them. In this work we show that the morphology of thin polymer films made by spin-casting a polymer blend solution containing NP fillers on a surface depends strongly on the concentration of NP fillers. More specifically, polystyrene/polymethylmethacrylate (PS/PMMA) films formed from a toluene solution, and which demix following a nucleation and growth mechanism, were studied. It was found that both the height and the surface density of PMMA domains increased as the concentration of CoPt:Cu NPs in the film was increased. We find that similar effects are induced in a NP-free PS/PMMA demixed film upon increasing the molecular weight of the PS molecules. This suggests that under certain conditions the NPs and the polymer molecules in the blend do not behave as separate species but form aggregates.

Keywords Nanostructures · Polymer blend demixing · Fillers · Nanoparticles · Microphase structure

Introduction

Polymer/nanoparticle composite films have been investigated and proposed for use in many different fields of technology such as solar cell devices [1], catalysis [2, 3], lithium battery devices [4], and magnetic storage devices [5, 6]. Techniques based on polymer layers instead of Si allow the manufacture of ultra-thin flexible devices, while the addition of nanoparticles (NPs) to a polymer medium allows the creation of charge transfer junctions with high interfacial area.

Polymer films possess exceptional self-organizing and self-assembling properties that allow the creation of order or complex structures on a large variety of substrates irrespective of their material and shape, with a remarkable reduction of manufacturing time, infrastructures and costs with respect to lithographic techniques such as photolithography. For example, a polymer film can be laterally structured using the demixing behaviour of a blend of immiscible polymers [7–10].

Recently, blends of immiscible polymers containing NPs have attracted the attention of several research groups. Numerical simulations of phase-separating binary fluids, such as polymer blends, have found that mobile NPs with a selective affinity for one of the phases will be concentrated into this phase during demixing [11–13]. These results are in general agreement with the few existing experimental studies [14, 15]. Both theoretical and experimental results agree on the fact that the presence of the NPs in one of the polymer phases slows the phase separation of the blend [14, 16, 17]. In particular, Chung et al. [18] made the first quantitative study of phase separation dynamics in a polymer blend containing mobile 22 nm silica NPs; they propose that the presence of the NPs in one of the phases of the polymer film slows domain growth due to an increase of the effective viscosity of the polymer.

In a previous paper, and in agreement with these publications, we demonstrated that the demixing behaviour of immiscible polymer blends can be used as a tool to organize nanosized objects on a surface [15]. This technique allowed the successful lateral organization of semiconductor NPs as well as biomolecules [19]. However, in our previous study we did not consider the influence that the presence of the NPs in the polymer solution has on the resulting morphology of a polymer thin film made by spin coating. In this communication we use atomic force microscopy (AFM) and transmission electron microscopy (TEM) to investigate the effect of the addition of $CoPt_3$:Cu NPs to a blend of polystyrene (PS) and polymethylmethacrylate (PMMA) on its microphase structure.

Numerical simulations of polymer/NP composites have shown that the introduction of hard spheres into a polymer blend has similar effects to the introduction of new polymer/hard-wall interfaces [20, 21]. Vacatello [22] performed simulations of polymer systems filled with particles of a size comparable to the polymer chains and found that even in the absence of specific interactions with the polymer, the filler particles behaved as highly functional physical cross-links, reducing the overall mobility of the polymer chains compared to the unfilled melt. Cole et al. [23] obtained similar results on the basis of simple geometrical considerations and numerical simulations: particles are linked together when the spacing between them is similar to the radius of gyration R_g of the individual polymer molecule.

These studies suggest that under certain conditions the polymer molecules and the NPs should not be regarded as individual entities within the blend, but instead as complex aggregates. In order to achieve a deeper understanding of the phenomena that determine the film morphology changes, we compared the effects on the film topography due to the presence of the NPs and of higher molecular weight polymers (but no NPs) in the same polymer phase.

Experimental procedures

$CoPt_3$:Cu NPs with dimensions of (3.0 ± 0.3) nm were synthesized in a hexane/octane mixture as reported elsewhere [24]. Their organic capping shell consisted of oleic acid and oleyl-amine ligands. The NPs were dispersed in toluene by evaporation of the hexane/octane under vacuum and addition of toluene (Fluka, spectroscopy grade) to the NPs. The new dispersion was subjected to a 1 min sonication in ultrasound bath.

Silicon slides (<100>, Siltronix, Archamps, France) were cleaned in three steps: (a) 5 min sonication of the slides in a 50:50 solution of acetone/ethanol. Rinsing in MilliQ water. (b) 10 min in piranha solution (4:1 sulphuric acid/hydrogen peroxide) at 120 °C. Rinsing in MilliQ water. (c) 10 min in SC-1 solution (5:1:1 water/ammonia/hydrogen peroxide) at 70 °C. Rinsing in MilliQ water. The freshly cleaned silicon substrates were highly hydrophilic (advancing water contact angle below 5°).

PS and PMMA (Polymer Standard Service, Mainz, Germany) were diluted in toluene or in a dispersion of $CoPt_3$:Cu NPs in toluene and allowed to stand overnight. The solution concentrations varied from 1% (w/v) to 3% (w/v). Polymer blends were made by mixing the stock solutions of each polymer in the appropriate volume ratio (typically PS/PMMA:30/70). The molecular weights of the polymers used are shown in Table 1.

Polymer films were made by spin coating onto silicon from toluene solution at speeds between 7,000 rpm and 9,000 rpm for 60 s. In some cases, incubation of the film in cyclohexane for several minutes was used to remove the PS phase from the film.

Polymer films were characterized using TEM and AFM. TEM (CM 200, Philips, The Netherlands) was used to obtain images of the distribution of the NPs embedded in the films. Samples for TEM measurements were spin coated onto carbon coated TEM grids. In order to obtain small polymer domains suitable for TEM analysis, a low polymer concentration (typically 1% w/v) was used, together with a high-rotation speed (typically 9,000 rpm).

The film topography was characterized using AFM (Scanning Probe Microscope, Dimension 3100, Veeco Digital Instruments, NY, USA, equipped with a NanoScope IIIa controller, Veeco, NY, USA). Samples for AFM analysis were spin coated onto freshly cleaned Si substrates. Film thickness measurements were performed by scratching the polymer film and measuring the step height from the substrate.

Table 1 Parameters of the polymers used

Name	Abbreviation	M_w	M_w/M_n
Poly(styrene)	PS	101,000	1.03
		139,000	1.03
		226,000	1.06
		546,000	1.02
Poly(methylmethacrylate)	PMMA	106,000	1.05

Results and discussion

PS/PMMA films made by polymer blend demixing—without fillers—have been extensively studied using AFM [8, 25–27] to characterize the microphase structure. Figures 1a and b show topographic images of a typical PS/PMMA film (PS/PMMA blend 50/50, 3% (w/v) in toluene, M_w(PS) = 101,000, M_w(PMMA) = 106,000, spin coated at 7,000 rpm) made by spin coating on a clean (hydrophilic) SiO_2 surface. Figure 1a shows the film after spin coating, while Fig. 1b shows the effect of removing the PS microphase. Comparing the two images we see that the as-formed film consists of PMMA pillars in a sea of PS. The PMMA phase consists of a wetting layer that completely covers the highly hydrophilic SiO_2 surface and contains isolated pillars (see Fig. 1c for a schematic cross-section).

Similar PS/PMMA films containing different amounts of $CoPt_3$:Cu NPs were also analyzed using AFM. Figures 2a, b and c show AFM topography measurements of three different polymer films spin-coated from solutions containing 15 mg/ml of polymer molecules without NPs and with 0.2 mg/ml and 1.0 mg/ml of NPs respectively (corresponding to 1.3% and 6.3% of the total mass). Assuming a material density of 18 g/cm^3, the volumes occupied by the NPs in the polymer film were respectively 0%, 0.08% and 0.4%. These values are, however, lower limits to NP volume, due to the presence of the organic capping shell which is about 0.5 nm thick (as estimated from TEM measurements).

At the NP concentrations used in this study, the general film structure consisting of PMMA domains in a PS matrix, is not qualitatively altered by the addition of NPs. Quantitatively, however, a number of changes are observed. Firstly, increasing NP concentration results in an increase in the surface density and height of the PMMA domains. This effect was quantified using the film RMS roughness (the root mean square average of height deviations from the mean data plane). Roughness measurements were performed on different areas of the same film and on different films of the same composition. Figure 3a shows mean RMS roughness values as a function of NP content, where the errors are estimated from the maximal variation of measurements of the same film type. The film roughness increases approximately linearly with the NP concentration in the film.

As the height of the PMMA domains increases, their diameter is reduced, as shown in Fig. 3b where the mean diameter of the PMMA domains is plotted as a function of NP content. A further effect induced by the presence of the NPs is an increase of the film thickness. Figure 3c shows the mean film and the pillar thickness obtained for several films of the same composition.

The results shown in Fig. 2a, b and c and 3a, b and c are not trivial to interpret in terms of system dynamics. While the reduction of the pillar diameter with the increasing concentration of the NPs in the polymer blend suggests a slowing down of the demixing process in agreement with other studies [11–14, 16], the origin of the increase in film thickness and roughness is not clear. For a better understanding of the process, we tried to investigate the nature of the interaction between the polymer molecules and the NPs.

The distribution of NPs within similar PS/PMMA films was investigated using TEM. Because of the small field of view of TEM, it was necessary to use films with a smaller domain size; this implied the use of lower polymer concentrations and higher spin speeds for the film formation. Figure 4a and b are TEM images of $CoPt_3$:Cu NPs embedded in a PS/PMMA film (PS/PMMA blend 70/30, 1% (w/v) in toluene, [CoPt3:Cu NPs] = 0.7 mg/ml, M_w(PS) = 101,000, M_w(PMMA) = 106,000, spin coated on a TEM grid at 9,000 rpm). PS and PMMA can be distinguished by TEM, the PS phase appearing darker than the PMMA phase [28]. The NPs are clearly visible as dark spots. A slight defocusing of the images allowed the optimization of the contrast between the PS and the PMMA phases with neglible effect on the NP resolution.

From Fig. 4, it is clear that the NPs partition in the PS-rich phase of the polymer film. TEM analysis was performed on films made from polymer solutions containing different NP concentrations, from 0.1 mg/ml to 1.0 mg/ml. Eighty percentage of the 6,000 NPs counted were in the PS-rich phase, while about 15% were at or close to the interface between the PS and PMMA phases. These percentages were independent of the NP concentration in the original solution to within experimental error. In addition to the partitioning of the NPs in one of the polymer phases, we observed an enrichment of the NPs at the PS/PMMA interfaces, particularly for the larger PMMA domains. This can be clearly seen in Fig. 4b.

The NP distributions obtained from the TEM studies agrees well with theoretical simulations. The oleic acid and oleyl-amine ligands form an apolar organic shell around the NP, which we thus expect to be preferentially located in the less polar PS phase of the polymer film. A preferential partitioning of the NPs into one phase was found in the simulations of Ginzburg et al. [11] Tang and Ma [12] as well as Laradji and MacNevin [13]. In addition, we showed similar experimental results in a previous work [15], in agreement with Tanaka's original observations on spin-cast polymer blends [14]. Chung et al. observed similar effects [18]; however, in contrast to their work, the partitioning effect observed here takes place in non-equilibrium structures and does not require an annealing step.

The enrichment of NPs at interfaces between the PS and PMMA phases has also been found in numerical simulations [11, 12, 29, 30] that indicate that there may be an accumulation of the NPs at the phase interfaces of

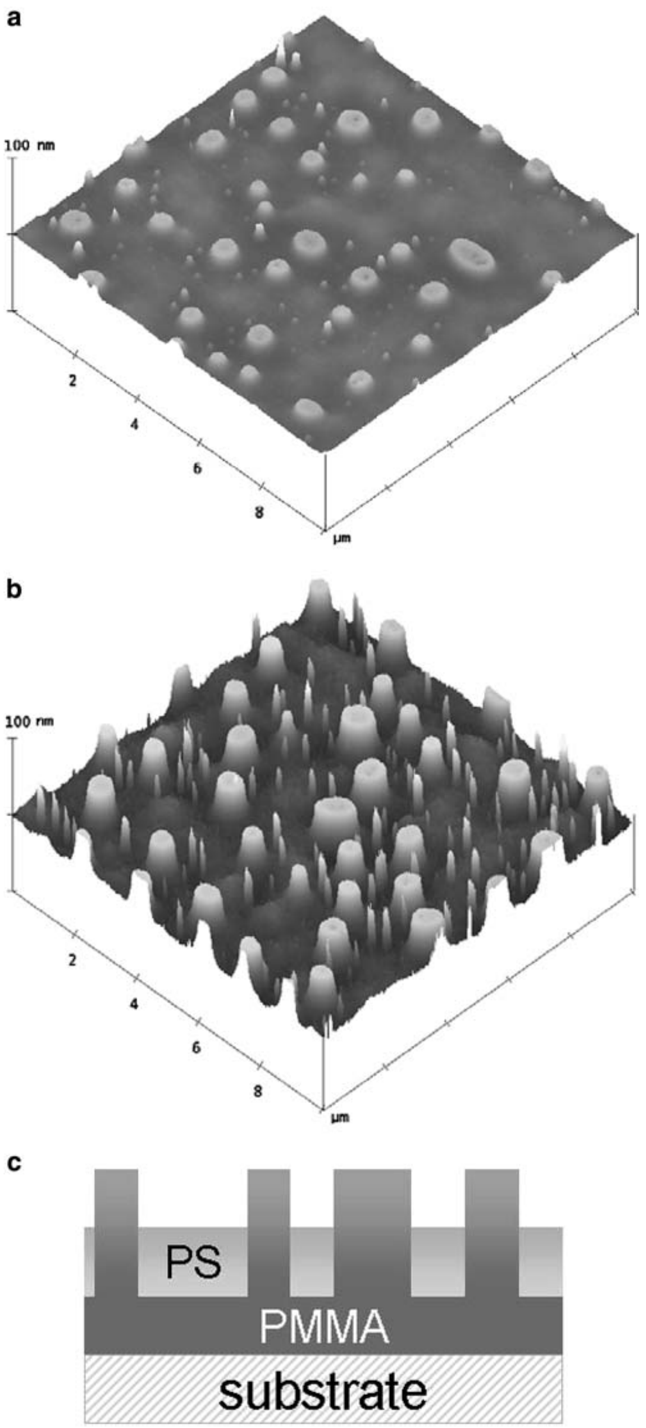

Fig. 1 Examples of typical films made by polymer blend demixing: AFM topography images (10 μm × 10 μm × 100 nm) of (**a**) a PS/PMMA blend 50/50, 3% toluene, M_w(PS) = 101,000, M_w(PMMA) = 106,000, spin-coated on an Si substrate at 7,000 rpm. **b** The same film after removal of the PS. **c** Schematic section of the film in (**a**)

both homopolymer blends and block copolymer films. This enrichment occurs when the presence of the NPs reduces the interfacial energy of the system, as is the case for particles with similar energies of interaction for both polymer phases. However, to our knowledge little experimental work has been performed on this effect.

We estimated from TEM measurements that 95% of the NPs are located either in the PS phase or at the interface between the PS and the PMMA domains. Assuming a homogeneous distribution of the NPs in the PS phase, we estimate that the average distance between the NPs embedded in the film in Fig. 4a is (10 nm; this value is comparable to the radius of gyration of the PS molecules R_g(PS) = 8.6 nm. R_g was estimated using the expression $R_g = \sqrt{(Nb^2/6)}$, where N is the degree of polymerization (N (1,000 for M_w(PS) (100,000) and b the statistical segment length of the PS monomer (b(PS) = 0.68 nm) [31]. Therefore, we believe that polymer bridging between NPs, as described by Vacatello and Coles, is relevant to the effects observed here.

To verify the hypothesis that the changes in film topography are caused by cross linking of the polymer chains by the NPs, we compared the effects of an increase in NP concentration inside the polymer film with the effects of an increase in the molecular weight of the PS. Polymer blend demixing of NP-free PS/PMMA blends in toluene was carried out using different PS molecular weights while keeping both the molecular weight of the PMMA and polymer ratio (by weight) constant. As before, the blends were spin cast on Si substrates. Figures 2d, e and f show AFM topography images of films having M_w(PMMA) = 106,000, while the M_w(PS) were respectively 139,000, 226,000, 546,000. A similar topographical analysis to that carried out on films containing NPs was also performed on the polymer films in Fig. 2d, e and f.

Figures 2d, e and f show that increasing the molecular weight of the PS clearly induces an increase in the surface density of PMMA pillars. This observation is in agreement with studies performed by other groups [32] that suggest that larger PS molecules hinder polymer diffusion of the PMMA molecules during film formation. Both the film roughness (Fig. 3d) and thickness (Fig. 3f) increased with increasing molecular weight of the PS. However, no significant change in the diameter of the PMMA domains was observed (Fig. 3e).

Comparing Figs. 2d, e and f with Fig. 2a, b and c we observe an increase of the surface density of the PMMA pillars upon increasing either the NP concentration or the molecular weight of the PS. Assuming a similar mechanism to be at the origin of the two phenomena, we suggest that increasing either the NP content or the PS molecular weight in the polymer blend hinders the diffusion of PMMA molecules during the demixing processes.

As for the polymer films containing NP fillers, the roughness (Fig. 3d) and thickness (Fig. 3f) of unfilled polymer films were found to increase upon increasing molecular weight of the PS. However, comparison of Fig. 3b with 3e shows that the diameters of the PMMA

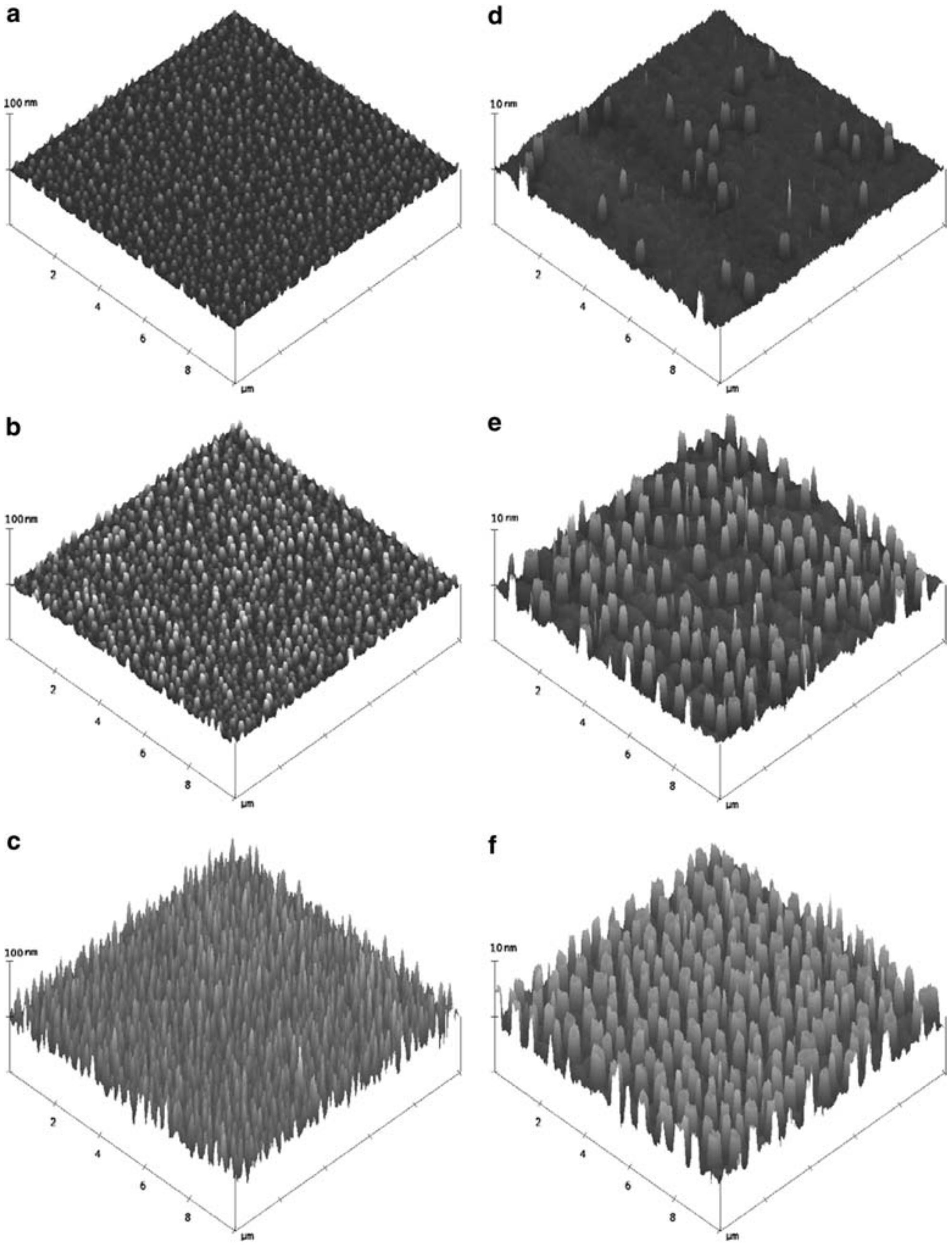

Fig. 2 Figures **a**, **b** and **c**: AFM topography images (10 µm × 10 µm × 100 nm) of polymer films containing $CoPt_3$:Cu NPs in concentration of **(a)** 0%, **(b)** 0.04% and **(c)** 0.2% by volume (PS/PMMA blend 80/20, 1.5% in toluene, M_w(PS) = 101,00, M_w(PMMA) = 106,00, spin-coated on an Si substrate at 8,000 rpm). Figures **d**, **e** and **f**: AFM topography images (10 µm × 10 µm × 10 nm) of polymer films spin-coated by PS/PMMA solutions PS molecular weight of **(a)** 139,000, **(b)** 226,000, **(c)** 546,000 (PS/PMMA blend 50/50, 1% in toluene, M_w(PMMA) = 106,000, spin-coated on an Si substrate at 7,000 rpm)

pillars in the polymer/NP films and in the films with increasing PS molecular weights do not follow the same trend.

Comparing Figs. 3a, b and c and 3d, e and f leads to the conclusion that increasing the density of filler NPs or increasing the PS molecular weight in a PS/PMMA blend induces similar (but not identical) effects on the morphology of a thin film made by polymer blend demixing. As these effects are similar to those reported in the work of Chung et al. [18] we assume that, in both cases, a change in the viscosity of the PS phase is at the root of the effects. This supports the hypothesis that the

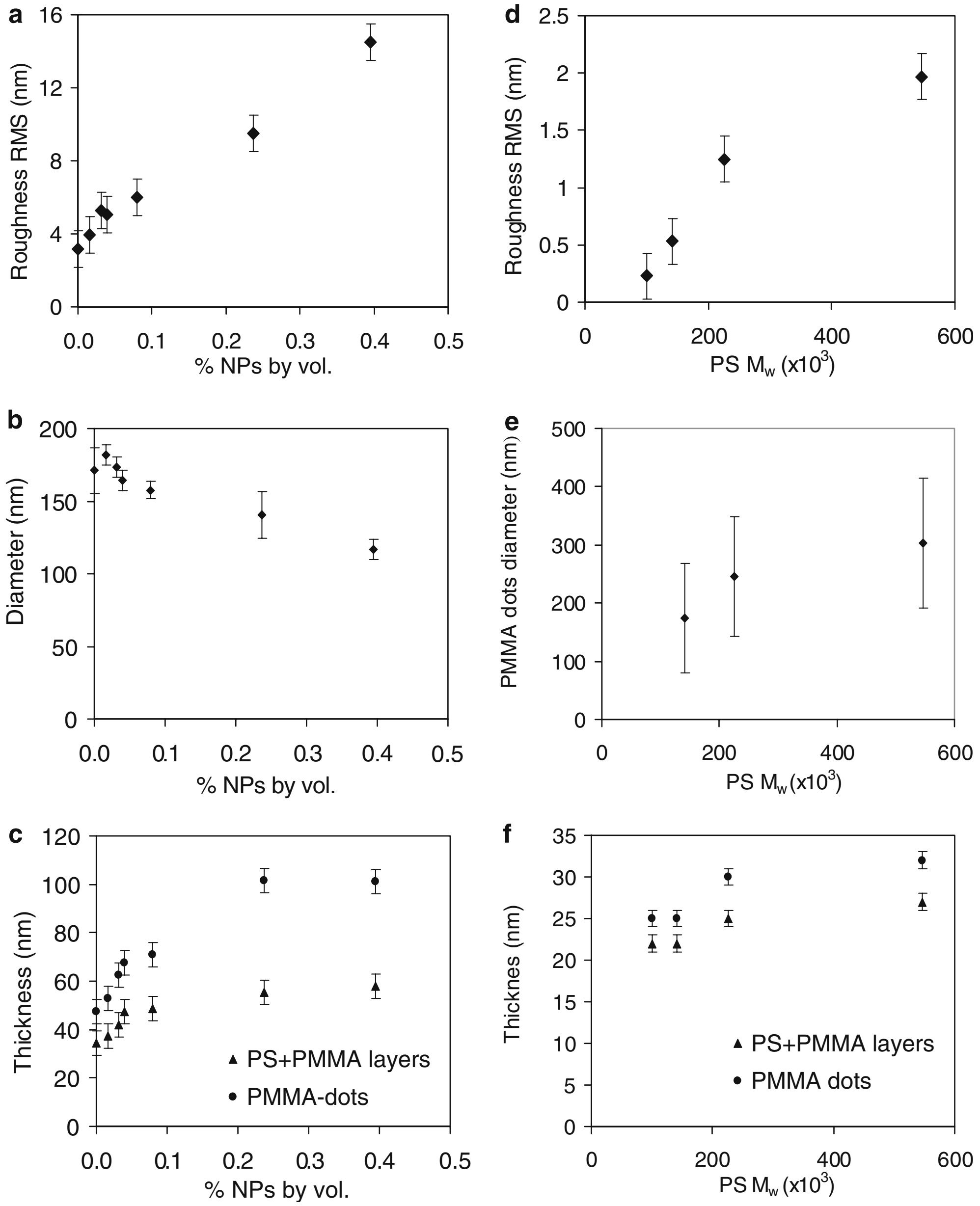

Fig. 3 Variation of (**a**) and (**d**) the roughness, (**b**) and (**e**) the PS/PMMA pillars average diameter and (**c**) and (**f**) the thickness of polymer films containing (**a**), (**b**) and (**c**) different concentrations of $CoPt_3$:Cu NPs (PS/PMMA 80/20, 1.5% from toluene, spin-coated at 8,000 rpm) and (**d**), (**e**) and (**f**) different PS molecular weight (PS/PMMA 50/50, 1% from toluene, M_w(PMMA) = 106,000, spin-coated at 7,000 rpm)

NPs act as physical links between the polymer molecules, forming large aggregates as indicated by the works of Vacatello [22] and Cole et al. [23].

Conclusions

In conclusion, we have shown that AFM and TEM are effective tools to investigate the influence of NP additives on polymer film microphase structure. We have used AFM to analyze the effect of $CoPt_3$:Cu NPs on the demixing behaviour of a PS/PMMA polymer blend. Increasing content of NPs in the polymer film induced an increase in the surface density of PMMA domains, as well as in the roughness and thickness of the polymer films. In contrast, the average diameter of the PMMA domains decreased with increasing NP content.

Based on simulations performed by other groups, we hypothesized that the NPs act as cross-linking centres

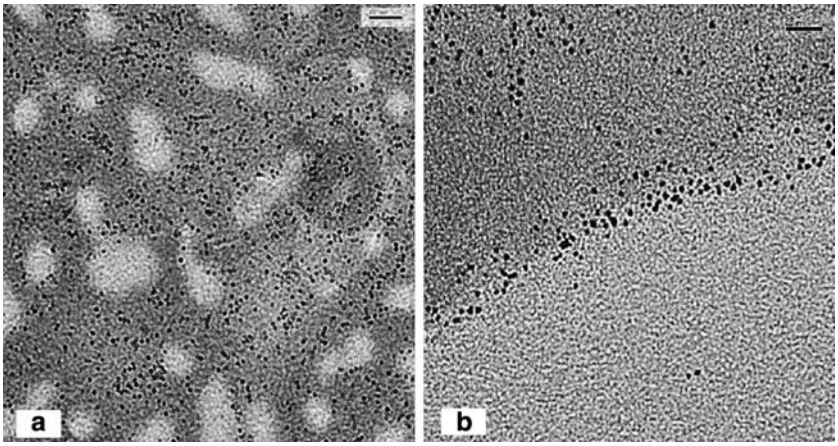

Fig. 4 TEM images of a PS/PMMA/CoPt3:Cu NPs blend spin coated on a TEM grid (PS/PMMA blend 70/30, 1% in toluene, [CoPt3:Cu NPs] = 0.7 mg/ml, M_w(PS) = 101,000, M_w(PMMA) = 106,000, spin-coated on an Si substrate at 9,000 rpm). The scale bar corresponds to (**a**) 50 nm and (**b**) 20 nm

between the polymer molecules. We produced a similar effect using a higher molecular weight PS as a model system for NP/polymer aggregates. Increasing the molecular weight of the PS reproduced, in part, the effects observed upon increasing the NP content in the polymer film. We speculate that the other observed effects of the NPs in the film may be caused by the NPs acting as a surfactant, reducing the interfacial energy between the two polymer phases [11, 12].

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