Application of FTIR Microscopy in Combinatorial Experimentation on Polymer Blends

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Summary: A novel combinatorial, high-throughput experimentation (HTE) setup has been developed, which allows for rapid mapping of the phase behavior of blends of homopolymers and block copolymers. The principle is based on the preparation of composition (ϕ)-temperature (T) gradient films. Linear ϕ gradients were obtained over a large composition range, as shown by FTIR microscopy. The applicability of this combinatorial approach was demonstrated by studying the phase behavior of a poly(styrene-*co*-acrylonitrile) (SAN)/poly(methyl methacrylate-*co*-ethyl acrylate) (PMMA-EA) blend with varying EA content and a poly(styrene-*b*-butadiene-*b*-methyl methacrylate) (SBM) triblock copolymer.

Keywords: block copolymers; FTIR microscopy; high-throughput experimentation; phase behavior; polymer blends

Introduction

Pure polymers are rarely used in practical applications. Instead, polymeric materials generally consist of mixtures of several components, such as polymers, fillers, plasticizers and stabilizers. Blending two or more polymers is a convenient route to develop new polymeric materials, since synergy between the blend components can lead to materials with enhanced properties.[1,2] The material properties of polymer blends are the result of a complex interplay between the individual component properties and the blend morphology. Generally, polymer blends are classified into three categories depending on the thermodynamic miscibility, i.e. immiscible, partially miscible and fully miscible. Although most polymer blends are immiscible, a significant number of polymer systems is known to be partially miscible.[1–3] A key issue in partially miscible polymer blends is the control of the morphology, which is directly related to the thermally-induced demixing behavior of the blend.

It is known that small changes in the molecular structure of the blend components can have a significant influence on the miscibility of polymer blends.[3] Lee et al. showed that by varying just the end group of poly(dimethylsiloxane) (PDMS) from a methyl to an amide group, the upper critical solution temperature of poly(isoprene)/PDMS blends decreases by 165 °C.[4] Van Durme et al. showed that the miscibility of poly(vinyl methyl ether) (PVME) with water is highly influenced by the PVME end group. Compared to methoxy-terminated PVME, hydroxy-terminated PVME shifts the miscibility gap to higher temperatures, whereas bromine-terminated PVME is immiscible with water at room temperature.[5] These are only two of many examples that show the importance of the polymer chain architecture to control the miscibility of polymer blends.

The miscibility of polymer blends is typically studied by light scattering techniques to

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determine the cloud points.[2] However, cloud point measurements are generally time-consuming and fine-tuning of the miscibility gap of polymer blends by small variations in the chemical structure of the blend components is highly impracticable. Because of the expected time reduction, combinatorial methods for the evaluation of polymer blend phase behavior have recently received increasing attention.[6–12] A convenient approach to study the miscibility of polymer blends is based on the preparation of composition-temperature (ϕ-T) gradient films, where one single film provides extensive information on the phase diagram and the phase-separated morphology of the mixture.[6,8,11] The main limitations of the currently reported techniques lie in the achievable ϕ range, which is typically from ~15 to ~65 wt%, the reproducibility of the ϕ gradients, due to manual sampling and deposition methods, and the restriction to use polymers that dissolve at room temperature, which makes the preparation of ϕ gradients of most semi-crystalline polymers impossible.

This paper describes a method to rapidly screen the phase behavior of polymer blends, utilizing a high-throughput experimentation (HTE) setup for the preparation of ϕ-T gradient film libraries. The setup described in this work enables the preparation of ϕ-T gradients over the whole composition range and a temperature gradient between 25 and 300 °C. The experimental reproducibility is excellent, since the sampling and deposition processes are fully automated. The setup and the procedure for the preparation of ϕ-T gradient films are evaluated by using blends of poly(styrene-*co*-acrylonitrile) (SAN) and poly(methyl methacrylate) (PMMA). Subsequently, the method is used to study the phase behavior of SAN/P(MMA-EA) blends with different levels of ethyl acrylate (EA) comonomer and of a poly(styrene*b*-butadiene-*b*-methyl methacrylate) (SBM) triblock copolymer. Especially in blends with one of the homopolymers three regimes of phase separation can be distinguished: microphase separation, macrophase separation, and a combination of both. In the microphase separation regime, phase separation of the blocks of the triblock copolymer occurs upon mixing of one block with the homopolymer. In the macrophase separation regime, the homopolymer is separated from the triblock copolymer, which itself may be in the disordered state. The macro/microphase separation regime can be described by the coexistence of the microphase separated phase and the macrophase separated homopolymer.

Experimental Part

Materials

SAN with 28 wt% acrylonitrile (AN) was obtained from the DOW Chemical Company ($M_n = 41$ kg/mol and a polydispersity of 2.2). P(MMA-EA$_x$) copolymers were provided by Arkema (France), where x indicates the wt% of ethyl acrylate (EA) comonomer. The samples contained 0.5, 5, 15 and 25 wt% of EA, with a M_n ranging from 40 to 55 kg/mol and a PDI ranging from 2.1 to 3.3. Two SBM triblock copolymers were supplied by Arkema, France, i.e. $S_{20}B_{25}M_{55}$ and $S_{60}B_{10}M_{30}$, where the subscripts represent the weight fraction of the respective blocks. Acetone and methyl ethyl ketone (MEK) were obtained from Sigma Aldrich and used as received.

Characterization Techniques

The composition of the library films was studied by Fourier transform infrared (FTIR) microscopy. Spectra were recorded with a BioRad UMA 500 microscope coupled to a BioRad FTS6000 spectrometer, equipped with a slide-on attenuated total reflection (ATR) crystal (germanium). For each spectrum 100 scans were taken at a resolution of 4 cm^{-1} over a spectral range of 600 to 5000 cm^{-1}. In order to quantitatively determine the composition of the library films, the ratio in peak intensity of the phenyl group of SAN at 698 cm^{-1} and the carbonyl band of P(MMA-EA$_{0.5}$) at 1740 cm^{-1} was compared to a calibration curve.

Light scattering was used to determine the cloud point curves of the SAN/P(MMA-EA$_{0.5}$) system. The set-up consisted of a 1 mW HeNe laser ($\lambda = 632.8$ nm) of which the light was directed through the sample positioned on a Linkam THMS600 hot-stage for temperature control. A light-sensitive diode was placed under a fixed angle of 20 ° with respect to the incident light. The output signal of the diode, which was coupled to a *xy*-recorder, registered the scattered light.

AFM investigations of the morphology of the block copolymer blends were performed by using a Smena P47H (NT-MDT Ltd, Moscow, Russia). The AFM was operated in semicontact mode in air using silicon cantilevers (NSG 11 NT-MDT), coated with a gold layer for a higher laser beam reflectivity. The resonance frequencies applied were 250–270 kHz. The neat copolymer was dissolved in MEK and cast on a glass substrate by evaporating the solvent at room temperature for 2 days. The samples were further dried at 130 °C under vacuum and N_2 for 24 h to ensure complete removal of the solvent.

Results and Discussion

High-throughput Experimentation (HTE) Setup

The preparation of the ϕ gradient films by using the HTE setup (Figure 1) involves several steps. First, each supply vessel is filled with a solution of the respective polymer dissolved in a common solvent. The two syringes can be filled with the solutions, since each syringe is connected to a supply vessel by means of a 6-way valve. After switching the position of the valve, the solutions are transferred from the filled syringes and are deposited from the deposition tip onto a glass slide of 70 × 70 mm, which is positioned on a movable stage. The speed of both syringes is individually controlled by an in-house developed computer program based on Labview to prepare a gradient in polymer composition during deposition. Simultaneously, the stage moves the glass slide under the deposition tip over a distance of 70 mm in the x-direction. The thin 70 mm long stripe prepared via the deposition procedure is spread out as a film over a distance of 70 mm by moving the

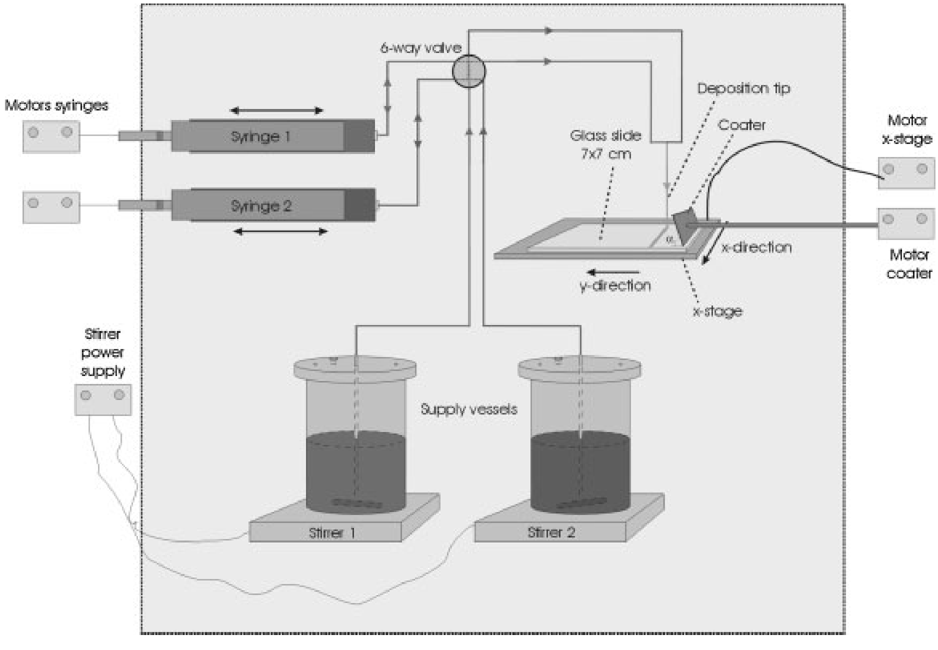

Figure 1.
Schematic representation of the HTE setup.

coater at a constant speed orthogonal to the ϕ gradient direction. The speed of the coater is typically in the order of 10 mm/s, to avoid extensive evaporation of the solvent before completion of the film formation. The distance and angle between the coater and the substrate are adjustable and are typically 200–600 μm and 75–85°, respectively. After evaporation of the solvent, a thin film with a gradient in polymer composition is obtained. Residual solvent is removed by annealing at elevated temperature under a N_2 flow for 1-2 hours. To increase the robustness of the setup, several additional features have been implemented. A delay in the composition gradient can be applied, which reduces the length of the gradient to less than 70 mm. This feature is convenient to exclude disturbances in the gradient close to the edges of the glass slide. The setup is designed to operate at temperatures up to 180 °C, which enables the use of semi-crystalline polymers that do not readily dissolve at room temperature, such as poly(ethylene) and poly(propylene). Furthermore, to enhance mixing of the two components, the dispension tip can be replaced by a static micromixer.

Calibration of HTE Setup

Many parameters affect the quality of the prepared ϕ gradient films, including software settings (e.g. speed of the syringes, x-stage and coater), hardware settings (e.g. coater distance and angle), as well as the properties of the polymer solutions (e.g. type of solvent, polymer concentration and solution viscosity). Optimization of those parameters was performed by preparing ϕ gradient films based on mixtures of SAN and P(MMA-$EA_{0.5}$). FTIR microscopy was used to determine the exact composition of the ϕ gradient. A calibration curve was constructed using SAN/P(MMA-$EA_{0.5}$) mixtures with pre-determined compositions.

Figure 2 shows the FTIR spectra of the SAN/P(MMA-$EA_{0.5}$) blends with increasing SAN content. The spectra show a clear decrease in the absorption band at 1725 cm^{-1}, which is assigned to the carbonyl (C=O) stretching vibration of the methacrylate group in P(MMA-$EA_{0.5}$), and an increase in the absorption band at 698 cm^{-1}, which is assigned to the out-of-plane ring bending vibration of the phenyl group of SAN. The inset shows the peak positions of the carbonyl

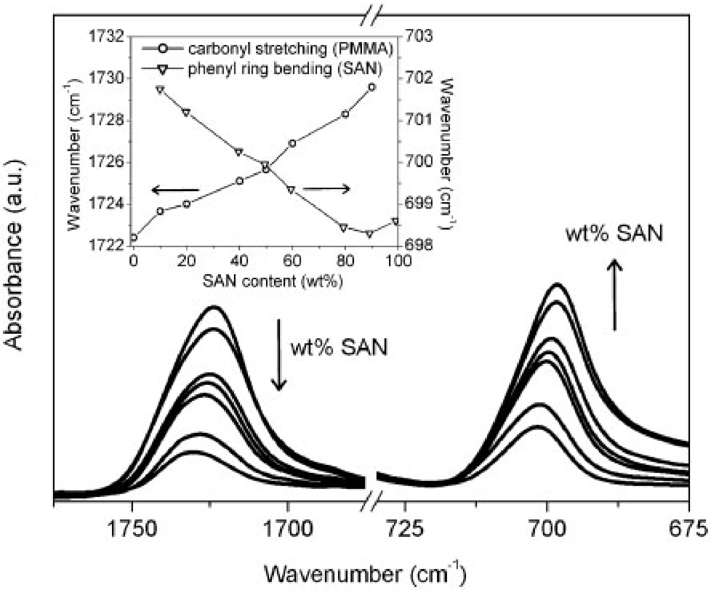

Figure 2.

FTIR spectra of SAN/P(MMA-$EA_{0.5}$) blends with increasing SAN content from 10, 20, 40, 50, 60, 80 to 90 wt%, indicated by the arrow.

stretching vibration of PMMA and the phenyl ring bending vibration of SAN, both as a function of the blend composition. Upon increasing the P(MMA-EA$_{0.5}$) content in the blend, the carbonyl peak shifts to lower wavenumbers, while the phenyl peak shifts to higher wavenumbers, indicating the existence of electron transfer interactions between the phenyl groups in SAN and the carbonyl groups in PMMA, which may be partially responsible for the miscibility of the blend.[13,14] This interaction is formed partially at the expense of the disruption of electron transfer complexes formed between the styrene and acrylonitrile comonomers within SAN, since the C≡N stretching vibration at 2238 cm^{-1} shifts to slightly higher wavenumbers.[15]

Based on the data presented in Figure 2, a calibration curve was constructed. The blend composition was plotted as a function of the intensity ratio of the representative SAN and P(MMA-EA$_{0.5}$) absorption bands (inset Figure 3). The experimental data can be reasonably well fitted by an allometric-type function.[16] Based on this calibration curve, the ϕ gradients of SAN/P(MMA-EA$_{0.5}$) as prepared with the HTE setup can now be determined. The HTE setup was used with the optimized settings to prepare ϕ gradient coatings, based on 8 wt% solutions of SAN and P(MMA-EA$_{0.5}$) in acetone. A maximum syringe speed of 0.85 mm/s, a table speed of 5.5 mm/s and a coater speed of 10 mm/s were used, in combination with a delay of 5 mm. By using these settings, the whole film preparation takes less than 20 seconds. Figure 3 shows that a fairly linear composition gradient is obtained in the x-direction. FTIR microscopy showed that the composition gradient is the same in the y-direction, which indicates that no diffusion or turbulent mixing occurs during the coating procedure. As determined by interferometry, the thickness of the coating typically varied from 1 to 1.8 μm in the direction orthogonal to the ϕ gradient.

Application of the HTE Setup to Blends of SAN/P(MMA-EA$_x$)

While traditional scattering experiments are very time-consuming, combinatorial experimentation is a much more effective tool to rapidly map the phase behavior of

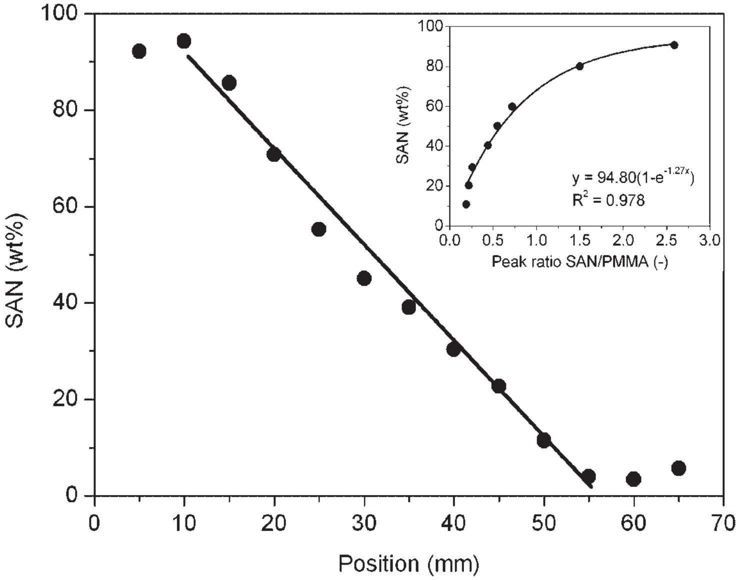

Figure 3.

ϕ–gradient of SAN/P(MMA-EA$_{0.5}$) prepared with the HTE setup. The inset shows the calibration curve based on discrete SAN/P(MMA-EA$_{0.5}$) blends.

polymer blends. Since the phase behavior of SAN/PMMA homopolymer blends was extensively studied in the past, it is a convenient system to validate the HTE setup.[17,18] The SAN/PMMA blend is miscible at room temperature and phase separates at elevated temperature, i.e. the system exhibits a lower critical solution temperature (LCST) behavior. Phase separation typically occurs far above the glass transition temperature (T_g) of the two components. This is convenient, since the phase-separated structure is frozen in after decreasing the temperature below T_g, which facilitates the off-line study of the phase-separated morphology as a function of temperature and composition. To demonstrate the applicability of the HTE setup, the phase behavior of SAN/P(MMA-EA_x) blends with a variation in EA content (x) is presented. Small amounts of EA are typically incorporated into PMMA to prevent unzipping of the polymer at elevated temperatures, but the influence of the EA content on the miscibility with SAN has not been documented.

70 × 70 mm coatings with a ϕ gradient in one direction were prepared. Subsequently, the films are annealed on a temperature (T) gradient heating stage, consisting of a metal block that is heated on one side and cooled on the other side. This yields a linear T gradient with a maximum temperature range from 25 to 300 °C. Upon placing the glass slide with the ϕ gradient film orthogonally onto the T gradient stage, a two-dimensional ϕ-T library is created. Typically, a T gradient over a range of 80 °C is applied under a N_2 flow to prevent oxidative degradation of the polymers. Subsequently, the phase-separated morphology is studied by optical microscopy. Figure 4 shows the phase diagram of SAN/P(MMA-EA_x) as obtained from the ϕ-T gradient films. Traditional cloud point measurements (CPMs) were performed on SAN/P(MMA-$EA_{0.5}$) blends to verify the phase behavior as determined from the ϕ-T gradient films. Figure 4 shows that the LCST behavior of the ϕ-T gradient library convincingly matches the CPMs and fully agree with data presented in literature for SAN/PMMA blends.[17,18] Incorporation of EA into PMMA leads to a significant shift of the binodal to lower temperatures. This result is consistent with the work of Paul et al., who visually determined the decreased

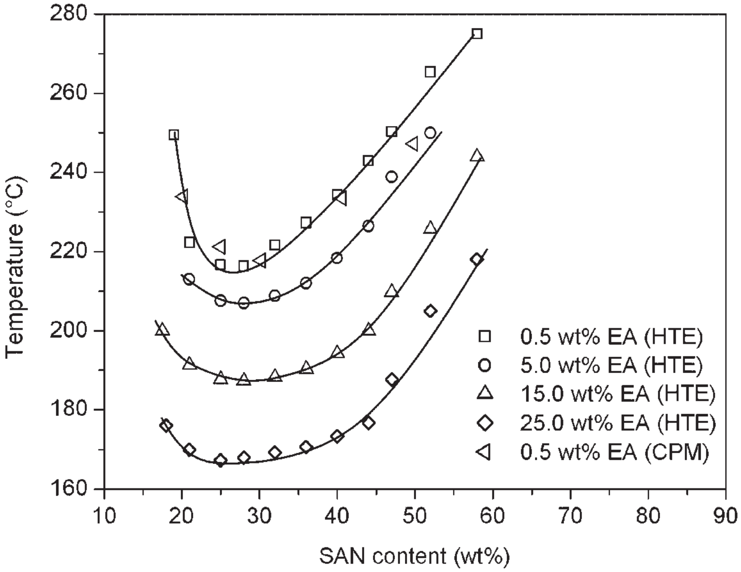

Figure 4.
Phase diagrams of SAN/P(MMA-EA_x) blends as determined from ϕ-T gradient films.

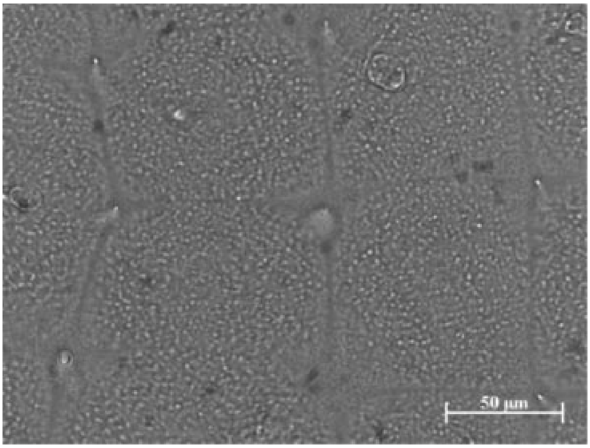

Figure 5.
OM image of a PMMA/$S_{20}B_{25}M_{55}$ blend prepared with the HTE setup.

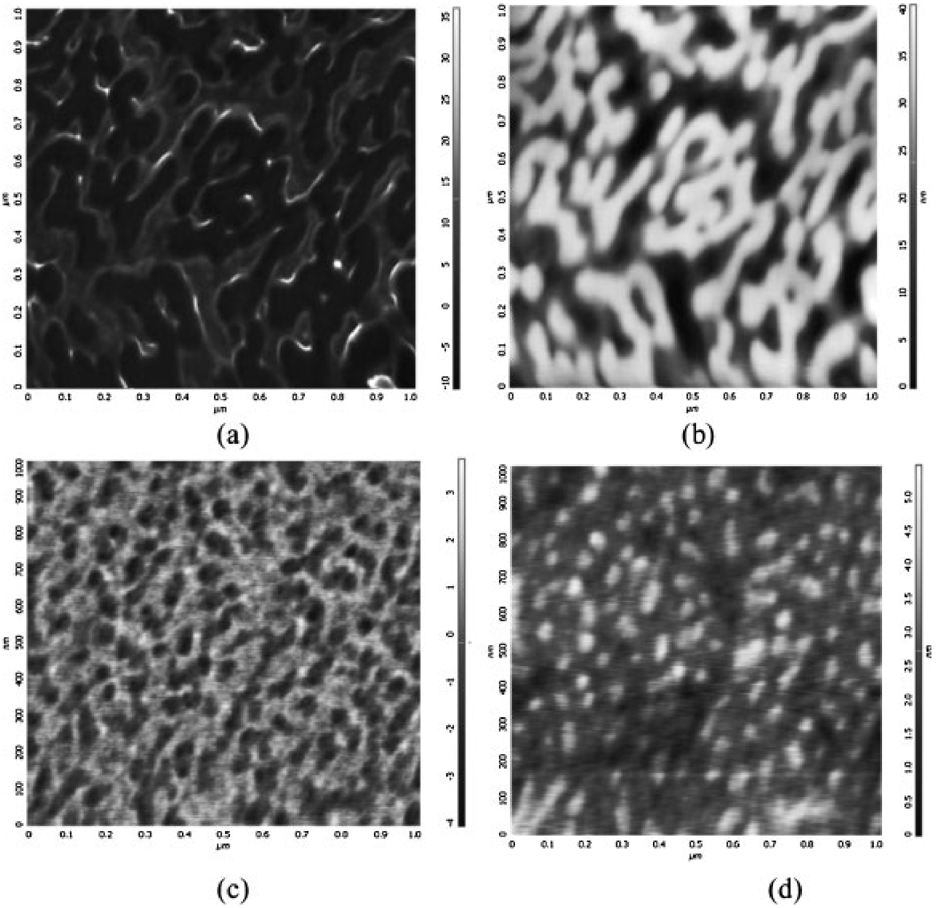

Figure 6.
AFM images of $S_{20}B_{25}M_{55}$: a) phase, b) height and $S_{60}B_{10}M_{30}$: c) phase, d) height.

miscibility of SAN/PMMA upon incorporation of EA from discrete polymer blends.[19]

Application of the HTE Setup to SBM Triblock Copolymer Systems

The HTE setup was also used to study the morphology of triblock copolymer blends. In Figure 5, the OM image of a PMMA/$S_{20}B_{25}M_{55}$ blend is shown. It is evident that the film is phase-separated. The spatial resolution of OM limits the observation to the level of macrophase separation. To get insight in the other phase separation regimes (micro- and micro-/macrophase separation), techniques with a higher spatial resolution are required, such as TEM or AFM, of which the latter has the advantage of being a surface technique. However, both techniques lack the possibility of chemical identification. The linearity of the ϕ-gradient over the 70 mm-film was checked by using FTIR microscopy using the ratio of the carbonyl (C=O) stretching vibration of the methacrylate group and the out-of-plane ring bending vibration of the phenyl group of PS for quantification.

The morphology, visualized by AFM, of the as-received $S_{20}B_{25}M_{55}$ copolymer (Figures 6a and b) shows an imperfect lamellar morphology, because of the presence of SB-diblock copolymer impurities.[20] For the $S_{60}B_{10}M_{30}$ system, PS forms the matrix and the PMMA cylinders are covered by little PB spheres (see Figure 6c and d). Future work will be focused on the influence of ϕ and T on the micro- and macrophase separation of homopolymer/triblock copolymer (PMMA/SBM) blends by applying the HTE setup.

Conclusions

A HTE setup has been developed to prepare ϕ gradient films of polymer blends. In combination with a T gradient heating stage, ϕ-T gradient films were prepared, yielding fast and detailed information on miscibility, demixing processes and final morphologies of polymer blends. The HTE setup has several advantages over the high-throughput techniques reported in literature so far: larger composition and temperature ranges, full automation of the preparation of the ϕ-T gradients and the possibility to extend the gradient preparation to elevated temperatures. FTIR microscopy has been used to show that linear ϕ gradients are obtained. FTIR microscopy is also the preferred technique to study the composition of the different phases after the temperature-induced phase separation, although time consuming. The recently developed macroATR accessory might be interesting to enable a much faster screening.[21] For the block copolymer systems, the spatial resolution of FTIR microscopy is far from sufficient, but the recent developments in combining AFM with either Raman spectroscopy[22] or with scanning near-field optical microscopy (SNOM)[23] are promising. Although this paper only discusses the phase behavior of polymer blends, the HTE setup is a promising tool to study other systems such as reactive polymer blends, block copolymer (dis)assembly processes and (nano)particle-controlled phase behavior of polymer blends.

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