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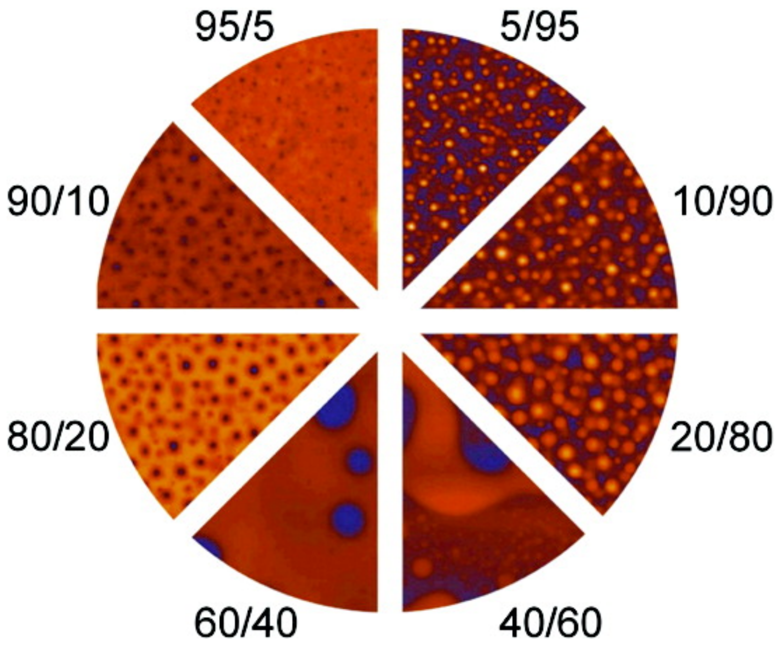

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Sector Spin Coating for Fast Preparation of Polymer Libraries

Berend-Jan de Gans, Sanne Wijnans, Daan Woutes, and Ulrich S. Schubert*

Laboratory of Macromolecular Chemistry and Nanoscience, Eindhoven University of Technology and
Dutch Polymer Institute, PO Box 513, 5600 MB Eindhoven, The Netherlands

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The feasibility of sector spin coating (or combinatorial spin-coating) is demonstrated (i.e., spin coating of various samples onto one single substrate using a metal template to divide the substrate into sectors). Film thickness increases in an angular direction against the sense of rotation. In the radial direction, the film thickness is constant within 2%. A library of 8 poly(methyl methacrylate)/polystyrene-blends with varying composition was spin coated and subsequently analyzed using automated atomic force microscopy: 24 measurements could be performed within 72 min. The contact angles of a library of 16 polyoxazoline diblock copolymers were measured using one substrate with 16 spin-coated sectors. Forty-eight measurements could be performed within 50 min. On the basis of the surface energies calculated using the Owens−Wendt−Rath−Kaeble method, the library can be divided into three groups of polymers: those containing a dispersive nonyloxazoline block, those containing a polar phenyloxazoline block, and those containing neither.

Introduction

Combinatorial materials research (CMR) is a cyclic process with four different steps. In the first step, materials are prepared in parallel, usually in solution. This is followed by the fast preparation of samples that are subsequently characterized. Results should be subjected to statistical analysis and after that, the process should start from the beginning, with the focus on that part of parameter space that offers the most promising results. The CMR approach holds the promise of an increased rate of discovery of new (polymeric) materials. However, to be implemented successfully all four steps must be addressed simultaneously. With the advent of robotic facilities for synthesis and formulation, the bottleneck in CMR has shifted to sample preparation and characterization, most notably if the property to be characterized requires a solid sample, like mechanical, thermal, electric, or surface properties.

Most of the CMR in the field of polymer science is on polymer films and coatings. A major challenge is the fast and reproducible preparation of a possibly large library of films onto a single support, in a format that is compatible with various characterization techniques. A number of different approaches can be discerned. The conceptually simplest is the dropcasting of different solutions to obtain a rectangular array of dots. However, a drying droplet deposits virtually all its solute as a ring that marks the perimeter of the sessile droplet, a phenomenon that is commonly referred to as the coffee-ring effect.[1] Ring formation can be prevented by drying samples in a “rotating-drum”-type centrifuge, which is rather laborious and time-consuming and requires dedicated equipment.[2,3] In addition, flexible, elastomeric substrates must be used because a rigid substrate would suffer from the effect of a nonhomogeneous gravity field.

Spin coating is probably the standard method to produce polymer films. Unfortunately, it is impossible to produce rectangular arrays of films or dots by spin coating, as the spreading of the solution to be spin coated over the substrate cannot be controlled. Nevertheless, attempts are made to implement spin coating in the combinatorial workflow by switching a number of rotors in parallel.[4] Alternatively, several samples are still spin coated onto the same substrate, but they are ordered in a circular rather than rectangular fashion.[4] This approach has a number of advantages. The first and probably most important is the ease of automation, as the substrate need not be changed between two samples. Second, it is an efficient way to use substrates, especially if they are expensive or not available commercially as small rectangles (e.g., silicon wafers). If post-treatment is performed, conditions will be completely identical for all samples on the substrate. The method is particularly convenient in combination with high-throughput characterization equipment based on a Yθ-stage to move the sample. Disadvantages of the approach are its limitation to higher viscosities (typically 0.01−10 mPa s) and the lack of control over the shape and position of the film. A typical example is shown in Figure 1: because of inertia and side wind, the liquid front follows a curved trajectory and eventually breaks up into fingers under the action of surface tension.

In this article, we present a method to optimize the shape of the spin-coated films and to extend the range of applicability to low-viscosity solutions. We refer to our approach as “sector spin coating”, as the round glass substrate used is divided into sectors using a template, or combinatorial spin coating. The template is placed on top of the substrate during spin coating and confines the spreading liquid to a certain area. Various types of substrate can be used (i.e., glass, stainless steel, or plastic). We demonstrate the applicability of the method by spin coating libraries of up to

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* To whom correspondence should be addressed. Fax: 0031 40 247 4186. E-mail: u.s.schubert@tue.nl.

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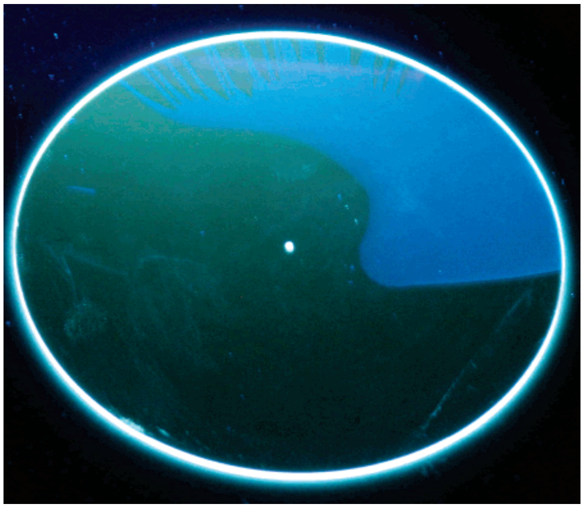

Figure 1. During spin coating, the liquid follows a curved track because of the combined action of inertia and side wind. The shape of the film is thus poorly defined.

16 samples onto one single substrate and subsequently characterizing them using automated atomic-force microscopy and automated contact-angle measurements.[5]

Experimental Section

Materials. N5000 grade polydisperse polystyrene (Shell Nederland, Den Haag, The Netherlands; $M_n = 80$ kD, $M_w = 282$ kD) was used. Poly(methyl methacrylate) was purchased from Sigma-Aldrich (Steinheim, Germany; $M_n = 130$ kD, $M_w = 240$ kD). Butyl acetate (Fluka Chemika, Buchs, Switzerland) and chloroform (Biosolve, Valkenswaard, The Netherlands) were used as solvents. 9-Hydroxymethyl anthracene (Fluka Chemika, Buchs, Switzerland) and 2-phenyl-fluorene, synthesized by Suzuki-coupling of phenylboronic acid to 2-bromo-fluorene, were used as fluorescent dyes. Solutions used for spin coating were prepared by gentle heating and shaking. NFR-016D4 negative photoresist was purchased from JSR (Tokyo, Japan).

A library of polyoxazolines was prepared by cationic ring-opening polymerization in a microwave, as described elsewhere.[6] 2-Methyl-2-oxazoline, 2-ethyl-2-oxazoline, 2-nonyl-2-oxazoline, and 2-phenyl-2-oxazoline were used as monomers. The library consists of all possible homo- and diblock copolymers of these 4 monomers, resulting in 16 polymers.

Substrates. Custom-made D263 glass disks with a diameter of 120 mm and a thickness of 1.1 mm were used as a substrate. Alternatively, we used a stainless steel disk with the same diameter and a thickness of 0.3 mm. Both substrates had a hole drilled at their center so that the vacuum chuck of the spin coater holds both substrate and the template on top. Substrates were cleaned before use by ultrasonication for 10 min in acetone. Then, they were rubbed with a sodium dodecyl sulfate solution and ultrasonicated for 10 min. They were flushed extensively with demineralized water to remove soap. The disks were ultrasonicated in 2-propanol for 10 min to remove water and dried with a flow of air. The substrates were treated in a UV−ozone photoreactor (UVP PR-100, Upland, CA) for 20 min to remove any residual organic contamination.

Sample Preparation. Samples were spin coated with a RC8 spin coater (Suss Microtec, Garching, Germany) in series rather than in parallel. The template was placed on top of the substrate. A typical example of such a template is shown in Figure 2. It divides the substrate into 8 different sectors. The diameter of the template is equal to the diameter of the disks (i.e., 120 mm). Aluminum was used as the template material to save weight. The thickness of the rectangular bars is 5 mm. Alternatively, an aluminum template with 16 sectors and the same thickness was used.

Polymer layers with a thickness of several microns were spin coated from an NFR-016D4 negative photoresist. The photoresist was dried on a hotplate at 90 °C for 120 s and exposed to broadband UV light (Philips) for 5 min. The sample was finally baked at 90 °C for 5 min.

Morphological Characterization. To characterize the morphology of the samples, we used an automated atomic-force microscope (Solver LS, NT-MDT, Russia). The instrument is equipped with an Yθ-stage. The accessible workspace is circular and 15 cm in diameter. The maximum scan size is $100 \times 100 \times 10$ μm. Cantilevers with a spring constant of 5.5 N m^{-1} (NSG01, NT-MDT, Russia) were utilized. The scan rate was 2 lines per second with a lateral resolution of 2 nm. All measurements were performed in tapping mode.

Topography. Thickness and topography of the films was measured with a Zoomsurf interferomeric profilometer (Fogale, Nîmes, France).

Contact Angle Measurements. An OCA30 device from Dataphysics (Filderstadt, Germany) was used. The static contact angle is determined by axisymmetric drop shape analysis of the profile of a sessile droplet (ADSA-P) using an ellipse fit. The contact angle is determined from the derivative of the ellipse at the point of intersection with the baseline of the droplet. Details concerning automation of the method are described elsewhere.[5] Surface energies were calculated from the contact-angle data using the Owens−Wendt−Rath−Kaeble (OWRK) method, also referred to as geometric mean. The method assumes that the surface energy, γ_{12}, of two phases in close contact can be calculated from the surface energies of the individual phases, γ_1 and γ_2, as follows

$$\gamma_x = \gamma_x^d + \gamma_x^p$$

$$\gamma_{12} = \gamma_1 + \gamma_2 - 2\sqrt{\gamma_1^d\gamma_2^d} - 2\sqrt{\gamma_1^p\gamma_2^p} \qquad (1)$$

with γ_x^d and γ_x^p being the dispersive and the polar contributions to the surface energy, respectively. The validity of this assumption, and therefore the applicability of the method, is the subject of an ongoing debate.[7] Equation 1 is then combined with Young's equation

$$\gamma_l \cos\theta = \gamma_s - \gamma_{sl} \qquad (2)$$

with θ as the contact angle. After some rearrangement, the

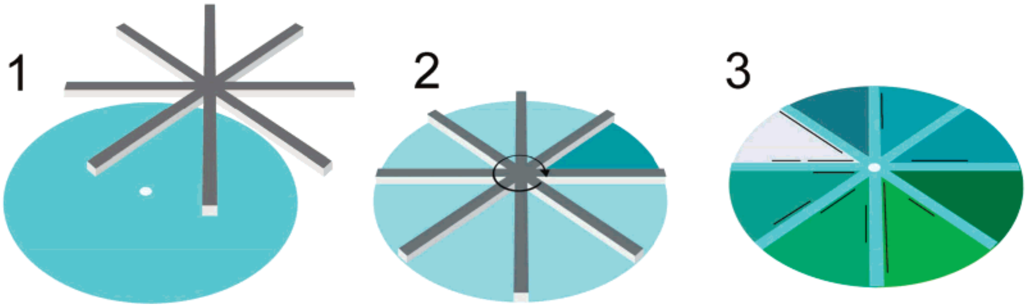

Figure 2. Principle of sector spin coating. (1) A star-shaped metal template is placed on top of a circular substrate that divides the substrate into 8 sectors. (2) The sectors are spin coated in series. (3) After the template is removed, one substrate with eight different polymer films is obtained.

Table 1. Surface Tension of Test Liquids and Their Polar and Dispersive Components

test liquid	γ_l (mN m^{-1})	γ_l^p (mN m^{-1})	γ_l^d (mN m^{-1})
ethylene glycol	47.70	16.80	30.90
diiodomethane	50.80	1.30	49.50

following equation is obtained

$$\frac{\gamma_l(1+\cos\theta)}{2\sqrt{\gamma_l^d}} = \sqrt{\gamma_s^p}\sqrt{\frac{\gamma_l^p}{\gamma_l^d}} + \sqrt{\gamma_s^d} \tag{3}$$

from which the components of the surface energy of the solid can be obtained by a linear least-squares fit, provided that two or more test liquids are used. Ethylene glycol and diiodomethane were used as polar and apolar test liquids, respectively. Surface-tension values and the dispersive and polar contribution are shown in Table 1.

Results

Film Quality. Two *n*-butyl acetate solutions containing 2 wt % polystyrene and 0.4 wt % of either 9-hydroxymethyl-anthracene or 2-phenyl-fluorene were spin coated onto a glass disk at 1200 rpm for 90 s. A template divided the substrate into 8 sectors. All sectors were spin coated in series, although in principle it is possible to spin coat them in parallel. The result is shown in Figure 3. This picture was taken under illumination with a UV-lamp at 254 nm. Because of the different emission spectra of the two fluorescent dyes, the 9-hydroxymethyl anthracene-containing polystyrene films are light gray, whereas the 2-phenyl-fluorene-containing films are dark. The different sectors are well separated and the homogeneous color indicates a homogeneous film thickness. The template left a clear stain. Close inspection reveals that this is caused in part by capillary flow underneath the template. However, this flow seems to be limited to the template. There is no sign of mutual contamination.

The topography and thickness of the films was investigated in more detail using an interferometric profilometer. Figure 4 shows a height map plus a 3D image of the innermost part of a sector. It can be seen that the edge of the sector is very well defined. The cross section shown in Figure 4 shows that ridges are formed near the edges. This is the result of a combination of wetting of the aluminum template and ring formation upon drying, according to the mechanism first described by Deegan.[1] The thickness of the spin-coated sectors and the reproducibility thereof was investigated by making a scratch with a scalpel near the innermost part of the sector and measuring the depth of the scratch using profilometry. The average of 5 sectors gives a thickness of 122 ± 5 nm (i.e., the thickness is reproducible within 4%).

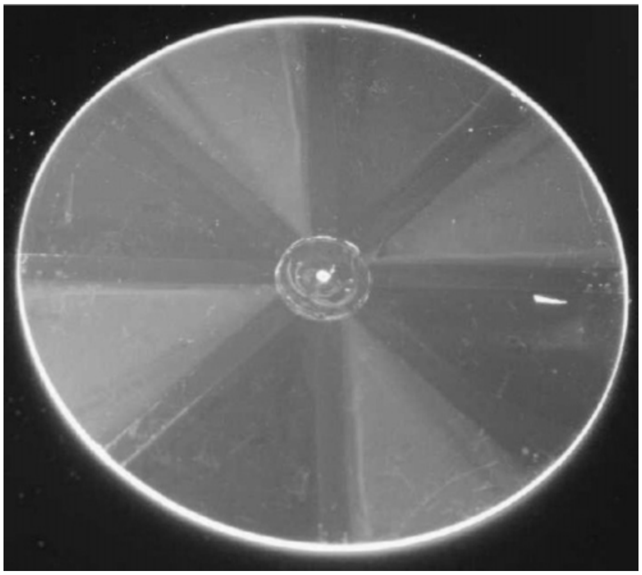

Figure 3. Photograph of a glass disk spin coated with solutions of polystyrene and dye in *n*-butyl acetate illuminated by a UV lamp at 254 nm. The strong fluorescence (light gray) is from 9-hydroxymethyl anthracene, and the weaker fluorescence is from 2-phenyl fluorine.

To demonstrate the applicability of the method to actual systems, a negative photoresist (NFR-016D4) was spin coated at 1000 rpm for 120 s, dried, irradiated, and baked to obtain a polymer layer with a thickness of several microns. To check its homogeneity, we measured the film thickness at a number of positions evenly distributed over the entire sector. Results are shown in Figure 5. The plane represents the average thickness, which is 6.4 ± 0.9 μm. The black bars denote the local deviation from the average value. Figure 5 shows a large systematic deviation in the angular direction. The thickness of the film increases with the angle against the sense of rotation of the substrate. This can be explained by assuming that during spin coating the photoresist flows under the influence of inertia. The template then dams it up, resulting in a local increase of the film thickness. The differences in the radial direction, however, are quite small, about 2%. We conclude that reasonably well-defined films with reproducible thickness can be spin coated. Sector spin

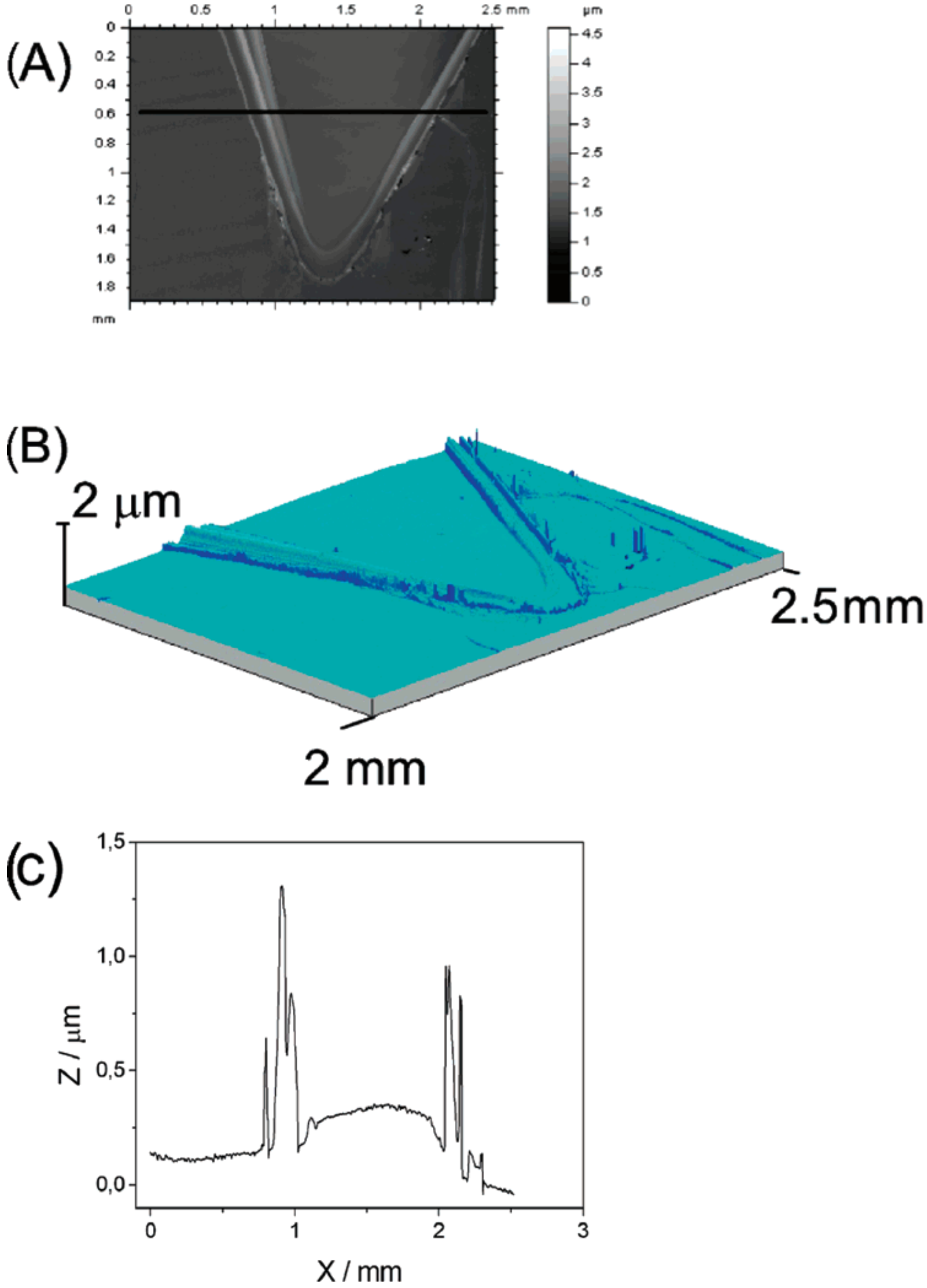

Figure 4. Angle of a spin coated sector as measured with profilometer: (A) height map, (B) 3D-image, and (C) profile. The black line on the map corresponds to the profile.

coating cannot be applied if large homogeneous surfaces (~1 cm^2) are required for characterization. However, the variation of film thickness with angle may even be used to generate thickness libraries via spin coating for the study of surface-pattern formation and dewetting phenomena.[8,9]

Morphology of a Polymer Blend Library. A library of immiscible blends of polystyrene and poly(methyl methacrylate) was spin coated onto one common substrate to demonstrate the applicability of the method. The morphology depends on numerous factors, such as the mass ratio of polystyrene to poly(methyl methacrylate), but it also depends on the substrate, solubility differences, molecular weight, and film thickness.[10−13] Eight samples were prepared, containing 5.0, 10.0, 20, 40, 60, 80, 90, and 95.0% polystyrene by weight. Chloroform was used as the solvent. All solutions contained 2.0 wt % polymer. These were spin coated at 1000 rpm (acceleration 100 rpm s^{-1}) for 90 s. The milky, turbid appearance of the 40/60 and 60/40 blends indicates phase separation.

Subsequently, samples were characterized using automated atomic force microscopy. Per sample, three 10 × 10 μm scans were performed, 1.5 cm away from the substrate center. Thus, 24 scans were performed without human interference. The total measuring time required was 72 min. The three scans were always qualitatively identical. Typical results are shown in Figure 6. The mass ratio in weight percent of polystyrene to poly(methyl methacrylate) is given. At low concentrations, the polystyrene is present as small peaks in

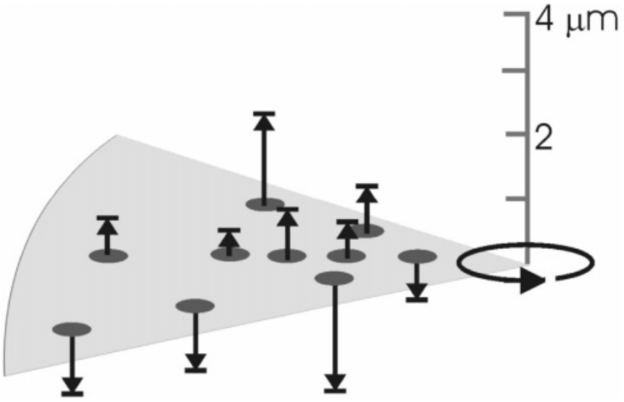

Figure 5. Film thickness of sector spin-coated photoresist film. The average thickness as represented by the plane was 6.4 ± 0.9 μm. The black bars denote the local deviation from the average value. The thickness of the film increases with angle against the sense of rotation of the substrate.

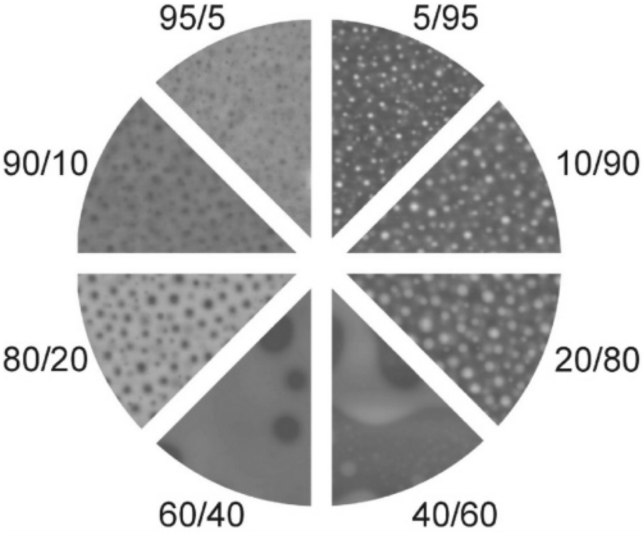

Figure 6. Library of polymer blends. The mass ratio of polystyrene to poly(methyl methacrylate) is given. The topography was measured with an automated AFM. The radius of the images corresponds to 10 μm. The color scale of the micrographs, in clockwise direction starting at 5/95, represents 24, 45, 70, 250, 250, 90, 50, and 15 nm, respectively.

a continuous phase of poly(methyl methacrylate). The height and diameter of the peaks increases with concentration. At 60 wt % polystyrene and higher, a phase inversion could be observed. Polystyrene now constitutes the continuous phase, whereas the poly(methyl methacrylate) is present as holes, not peaks. This is the result of the higher surface energy of the poly(methyl methacrylate) in comparison with that of polystyrene.[11]

Surface Properties of a Polyoxazoline Library. Again, to demonstrate the practical applicability of sector spin coating, a library of 16 oxazoline homo- and diblock copolymers was spin coated onto one common substrate at 1000 rpm (acceleration 100 rpm s^{-1}) for 90 s. The solutions used for spin coating contained 2.0 wt % polyoxazoline in chloroform. Samples were annealed at 80 °C for 24 h. Contact angles were determined according to the pattern shown in Figure 7. Each dot corresponds to one measurement with ethylene glycol and one with diiodomethane. Each sector was measured three times. In total, 96 measurements and 50 min were required for full characterization.

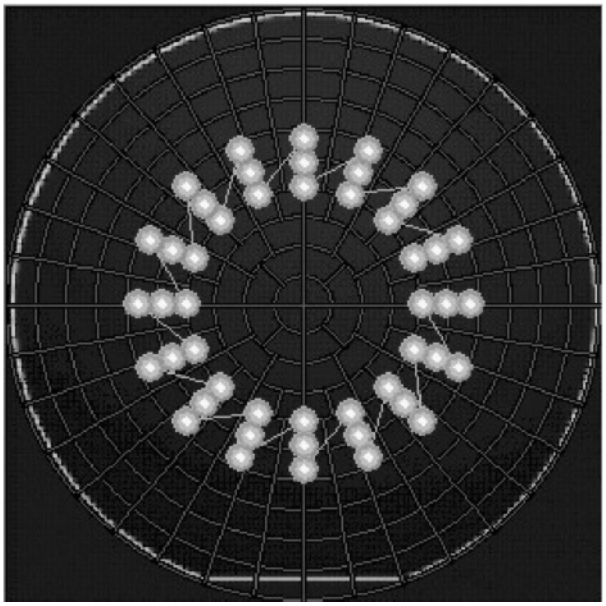

Figure 7. Coordinate map corresponding to a circular substrate with 16 spin-coated sectors, showing the points that are subsequently measured.

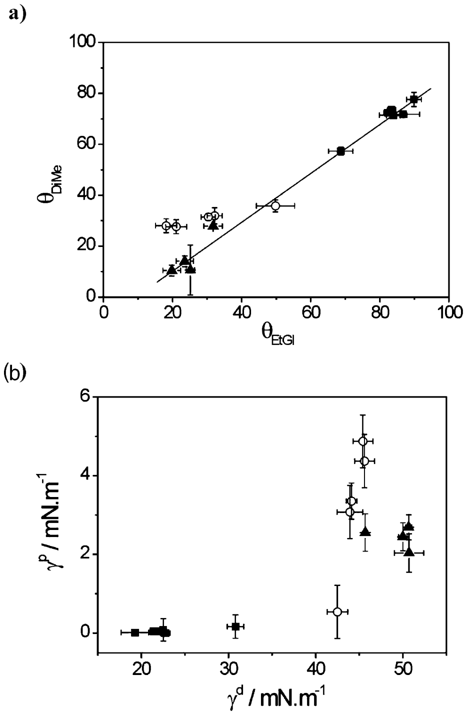

Figure 8. (a) Scatter plot of the contact angle of ethylene glycol versus the contact angle of diiodomethane: (■) polymers containing a nonyloxazoline block, (▲) polymers containing a phenyloxazoline block, and (●) polymers containing neither a nonyloxazoline nor a phenyloxazoline block. The straight line is drawn to guide the eye. (b) Scatter plot of the polar versus the dispersive component of the surface energy.

Figure 8a shows a scatter plot of the contact-angle of ethylene glycol versus the contact angle of diiodomethane. A straight line is drawn to guide the eye. The results were divided into 3 groups, depending on chemical composition. Polyoxazolines containing a nonyloxazoline block are characterized by high contact angles (70−90°) of both test liquids. Polyoxazolines containing a phenyl block have lower contact angles. The contact angle of diiodomethane is relatively large compared to that of the third group of polyoxazolines, which have neither a nonyl- nor a phenyloxazoline block. Poly(nonyloxazoline-*b*-phenyloxazoline) and poly(phenyloxazoline-*b*-nonyloxazoline) are both part of the first group; poly(phenyl oxazoline) is part of the third. Figure 8b shows a scatter plot of the polar component of the surface energy as calculated with the OWRK method versus the dispersive component. In the case of the polyoxazolines containing a nonyloxazoline block, the high contact angles result in low surface energies in the range of 20−30 mN m^{-1}. The surface energy is almost entirely dispersive, the polar component being almost zero. This indicates that the surface consists of closely packed methyl groups because of a preferential orientation of nonyl chains toward the surface.[14−16] The phenyloxazoline-containing polymers have a surface energy in the range of 36−41 mN m^{-1}. The higher contact angle of diiodomethane shows up as an increased polar surface-energy component. This is probably related to the polarizability of the phenyl side group and the dipole-induced dipole interaction with the polar test-liquid molecules. The absence of any polar contributions in case of poly(nonyloxazoline-*b*-phenyloxazoline) and poly(phenyloxazoline-*b*-nonyloxazoline), both part of the first group, again suggests the absence of phenyl and thus the presence of nonyl side groups at the surface. This result was also obtained by Cai et al., who studied the properties of films of polyundecyloxazoline and poly(phenyloxazoline-*b*-undecyloxazoline) using contact-angle measurements and electron-spectroscopic chemical analysis (ESCA).[17] The third cluster consists of polyoxazolines having neither a nonyloxazoline nor a phenyloxazoline block. These polymers have high surface energies, up to 50 mN m^{-1}, that are mainly dispersive.

Conclusions

We have demonstrated the feasibility of sector spin coating (i.e., spin coating of various samples onto a single substrate using a metal template to divide the substrate into sectors). The method yields well-defined films with reproducible thickness. Sector spin coating can, in principle, easily be automated using a pipetting robot, and it saves substrates. Experiments with viscous photoresist reveal an increase in the film thickness in the angular direction against the sense of rotation. This may be used to spin coat films with variable thickness. In the radial direction, the thickness is constant within 2%.

A library of 8 poly(methyl methacrylate)/polystyrene-blends with varying composition was spin coated and subsequently analyzed using automated atomic force microscopy; 24 measurements could be performed within 72 min. The morphology of the sectors indicates preferential enrichment with polystyrene at the surface.

A library of 16 polyoxazoline diblock copolymers was spin coated and subsequently analyzed using contact-angle measurements. Ninety-six measurements were performed within 50 min. The surface energy of the polyoxazolines was calculated using the Owens−Wendt−Rath−Kaeble method. When the polar versus dispersive components of the surface energy are plotted, three groups can be discerned: all polymers containing a nonyl-oxazoline block have a low surface energy (20−30 mN m^{-1}) with a negligible polar component, all polymers with a phenyl-oxazoline block have a high surface energy (36−41 mN m^{-1}) with an often large polar component (5−10 mN m^{-1}) because of the polarizability of the of the phenyl group, and the third cluster consists of polyoxazolines having neither a nonyloxazoline nor a phenyloxazoline block, and high, mainly dispersive, surface energies.

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