Synthesis of Polydimethylsiloxane-Containing Block Copolymers via Reversible Addition Fragmentation Chain Transfer (RAFT) Polymerization

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ABSTRACT: Low polydispersity polydimethylsiloxane (PDMS) was end functionalized with a reversible addition fragmentation chain transfer (RAFT) agent by the esterification of hydroxyl terminated PDMS with a carboxylic acid functional RAFT agent. These PDMS-RAFT agents were able to control the free radical polymerization of styrene and substituted styrene monomers to produce PDMS-containing block copolymers with low polydispersities and targeted molecular weights. A thin film of polydimethylsiloxane-*block*-polystyrene was prepared by spin coating and exhibited a microphase separated morphology from scanning force microscopy measurements. Controlled swelling of these films in solvent vapor produced morphologies with significant long-range order. This synthetic route will allow the straightforward production of PDMS-containing block copolymer libraries that will be useful for investigating their thin film morphological behavior, which has applications in the templating of nanostructured materials. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 115: 635–640, 2010

Key words: polysiloxanes; reversible addition fragmentation chain transfer (RAFT); block copolymers

INTRODUCTION

Block copolymers are ideal for fabricating nanostructured materials because of their thermodynamically driven self-assembly into periodic ordered structures, such as spheres, cylinder, and lamellae.[1] One application of these polymers is in thin films where the periodic pattern of the block copolymer can be used as a lithographic template.[2] Block copolymers containing poly(dimethylsiloxane) blocks are attractive for block copolymer lithography. First, they have large interaction parameters (χ) with other common organic polymers, such as polyisoprene (PI) and polystyrene (PS).[3] This allows low molecular weight polymers to assemble into structures with small domain sizes. At larger molecular weights, the large χ parameters lead to narrow interfacial widths, which is important for controlling the line edge roughness of the patterns.[4] In thin films, polydimethylsiloxane (PDMS) is converted to silica by treatment with oxygen plasma or ultraviolet/ozone.[5] The concurrent removal of the opposing block, such as PS, produces topographically patterned silica.[4,6–8] One area for development in these PDMS-containing polymers is broadening the range of available block copolymer chemistries. This will allow the characteristics of these materials to be tuned, such as the surface tension mismatch and solvent selectivity, which in turn will provide greater control over the thin film morphology.[9,10]

The standard method to prepare PDMS-containing block copolymers has been through sequential anionic polymerization where the non-PDMS block is polymerized first, followed by the PDMS block through the ring-opening polymerization of a cyclic siloxane.[11–14] This method is compatible with a limited range of blocks, such as PS and polydienes, although more complicated methods have been found to synthesize PDMS with other blocks, such as poly(vinylpyridine) and poly(methyl methacrylate).[15,16] More recently, controlled free radical polymerization techniques have been used to prepare PDMS-containing block copolymers by modifying an end-functional PDMS polymer to use as a macro-initiator in atom transfer radical polymerization (ATRP)[17–26] or nitroxide mediated polymerization (NMP)[27,28] or as a macro-chain transfer agent in reversible addition fragmentation chain transfer polymerization (RAFT).[29–32] These approaches expand the range of possible polymer chemistries available for PDMS-containing block copolymers. NMP and ATRP have been used to prepare PDMS-containing block copolymers with hydrophobic blocks, such as PS,[18,23,24,26–28] poly(alkyl methacrylates),[17,20,22,25] and poly(fluoroalkyl methacrylates) similar to those used in block copolymer lithography.[21]

However, RAFT polymerization has primarily been used to prepare amphiphilic block copolymers for biomedical applications, with blocks such as a copolymer of N,N-dimethylacrylamide and 2-N-butyl perfluorooctanefluoro-sulfonamido) ethyl acrylate,[31] poly (methacryloxyloxyethyl phosphorylcholine),[29] blocks of both poly(N,N-dimethyl acrylamide) and poly (2-hydroxyl ethyl acrylate),[30] and poly(N,N-dimethylacrylamide).[32]

This article describes the synthesis of a series of well-defined PDMS-containing AB diblock copolymers by the bulk RAFT polymerization of styrene, 4-methyl styrene and tert-butylstyrene using a PDMS macro-RAFT agent. The macro-RAFT agents were prepared by the esterification of a commercial hydroxyl terminated PDMS with a carboxylic acid functional trithiocarbonate RAFT agent. The thin film morphology of a polydimethylsiloxane-block-polystyrene copolymer was characterized by scanning force microscopy (SFM) to confirm that this synthetic method produces polymers that order into well-defined morphologies. This synthetic approach will be useful for the study of PDMS-containing block copolymer thin films because it will allow the synthesis of libraries of block copolymers where the parameters of the PDMS block remain constant. For example, this approach could be used to study the role of the surface tension mismatch on the thin film morphology.

EXPERIMENTAL

Materials

The 5 k and 10 k hydroxyl (carbinol) terminated PDMS (PDMS-OH) was purchased from Gelest and used as received. S-1-Dodecyl-S′-(α,α′-dimethyl-α″-acetic acid)trithiocarbonate (RAFT-COOH) was prepared using a previously reported method.[33] Styrene, 4-methyl styrene, and tert-butylstyrene were purchased from VWR, and the inhibitor was removed by passing through a column of basic alumina. Dicyclohexylcarbodiimide (DCC), 4-dimethylamino pyridine (DMAP), hexanes, methanol, chloroform, and anhydrous methylene chloride were purchased from VWR and used as received.

PDMS macro-RAFT chain transfer agent (PDMS-RAFT)

PDMS macro-RAFT agents were prepared by the DCC/DMAP catalyzed esterification of RAFT-COOH with PDMS-OH. A standard procedure was as follows: 10 g of 10 k PDMS-OH (1 mmol), 0.62 g of DCC (3 mmol), 0.18 g of DMAP (1.5 mmol), and 0.55 g of RAFT-COOH (1.5 mmol) were added to a three-neck round bottom flask. The flask was evac-uated under vacuum overnight to remove trace amounts of water. The flask was refilled with nitrogen, 50 mL of anhydrous methylene chloride was added and the contents were refluxed for 24 h. The reactor was cooled in the freezer and the contents were filtered through a Buchner funnel and passed through a silica gel column with methylene chloride. The methlyene chloride solution was concentrated on a rotary evaporator and was washed three times with methanol to remove the unreacted RAFT-COOH. The remaining viscous yellow oil was dried under vacuum overnight to yield a transparent, yellow oil. It was found that over time, a white precipitate formed in the PMDS-RAFT agent. This could be avoided by running the polymer through a second silica gel column with hexane and dried under vacuum at 100°C to produce a transparent, yellow oil.

Polymerization of block copolymers

The PDMS-RAFT agent, monomer, and stir-bar were added to a round-bottom flask and sealed with a rubber septum. In a typical polymerization, 0.1 g of PDMS-RAFT agent and 0.5 mL of monomer were used. The contents were degassed by sparging with dry nitrogen for 15 min. The polymerization was started by placing the flask in an aluminum reaction block thermostated at 120°C. Aliquots were removed from the flask under nitrogen pressure by a gas-tight syringe and precipitated into methanol at regular intervals to monitor the polymerization. The polymerization was terminated by quenching the flask in ice water and precipitating the polymer in methanol. The polymers were dried under vacuum at 100°C.

Characterization

Size exclusion chromatography measurements were performed using a Waters Breeze system with three Styragel columns using either tetrahydrofuran or toluene as the eluting solvent. Molecular weights were determined using PS standards. ^{1}H-NMR measurements were made using a Varian Mercury 300 NMR spectrometer. SFM measurements were made using a Digital Instruments Nanoscope IIIa scanning force microscope in tapping mode. For thin film samples, a PDMS-coated silicon wafer was first prepared by spin-coating a 10 mg/ml solution of 10 k PDMS-OH in toluene on a 4″ diameter silicon wafer using a Laurell Technologies WS-400B-6NPP/Lite spin-coater. This wafer was annealed at 180°C under vacuum overnight to form a PDMS brush layer and washed with toluene to remove the excess PDMS. PS-b-PDMS thin films were prepared by spin coating a 10 mg/ml solution of PS-b-PDMS onto 1 × 1 cm sections of this treated silicon wafer. Static contact
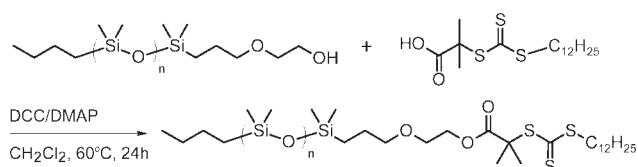
Scheme 1 Esterification of PDMS-OH with RAFT-COOH.

angle measurements were made with a Rame-Hart contact angle goniometer (model 100-00) with a Sony CCD camera under ambient conditions (1 atm, $24 \pm 2°C$). Optical microscope pictures were taken with a Leitz Laborlux 12 POL S microscope with a Qimaging Micropublisher 5.0 RTV camera.

RESULTS AND DISCUSSION

The PDMS-RAFT agents were synthesized by the DCC/DMAP catalyzed esterification of the carboxylic acid functional RAFT agent (RAFT-COOH) with the hydroxyl terminated PDMS (PDMS-OH) as shown in Scheme 1. SEC measurements indicated that both the starting PDMS-OH polymer and the PDMS-RAFT exhibited monomodal peaks as shown in Figure 1. Both PDMS-RAFT and PDMS-OH had polydispersities less than 1.1 when compared with PS standards. The quantitative conversion of the esterification reaction was confirmed by ^{1}H-NMR measurements as shown in Figure 2. This can be observed in the inset, which compares the spectra of PDMS-OH and PDMS-RAFT from 3 to 4.5 ppm. The peak at 3.75 ppm ($-CH_2-OH$) shifts to 4.25 ppm ($-CH_2-C(O)O-$) because of the formation of the ester. In addition, the peaks from the RAFT agent at 3.25 ppm ($-CH_2-S-$) has the same integrated intensity as the peak at 4.25 ppm ($-CH_2-C(O)O-$), indicating there is one RAFT agent per functional PDMS chain.

Figure 2 ^{1}H-NMR spectrum of PDMS-RAFT. The inset shows the spectra of PDMS-OH with peaks labeled a, b, and c and PDMS-RAFT with peaks labeled a′, b′, c′, and d′.

The controlled nature of the block copolymerization using the PDMS-RAFT agent is shown from the SEC traces of the polymerization of PDMS-*block*-polystyrene as a function of time in Figure 3. The molecular weight increases monotonically with time and the peaks remain narrow and monomodal. More detailed information about the polymerization kinetics was obtained by examining the molecular weight vs. conversion (Fig. 4) and conversion vs. time (Fig. 5). Figure 4 shows the M_n and PDI vs. conversion for the 5 and 10 k PDMS-RAFT agents with styrene, 4-methylstyrene and *tert*-butylstyrene monomers. The M_n and polydispersity were determined using PS standards from the SEC measurements while the conversion were obtained from the ^{1}H-NMR data by comparing the mol % of the styrenic block to the predicted mol % at 100% conversion. The molecular weights are not absolute
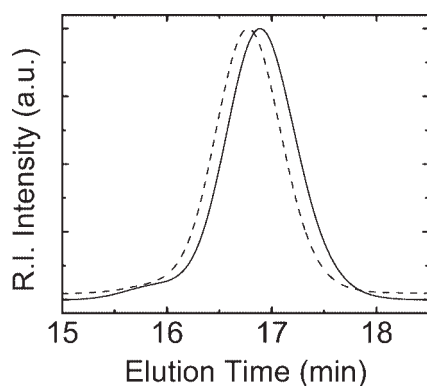
Figure 1 SEC traces of PDMS-OH (solid line) and PDMS-RAFT (dashed line). The peak intensity was normalized to one for clarity. PDMS-OH was eluted in toluene and PDMS-RAFT was eluted in THF.
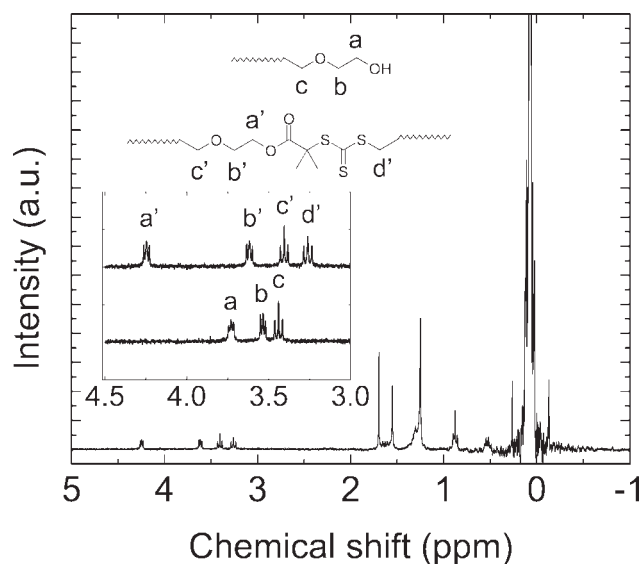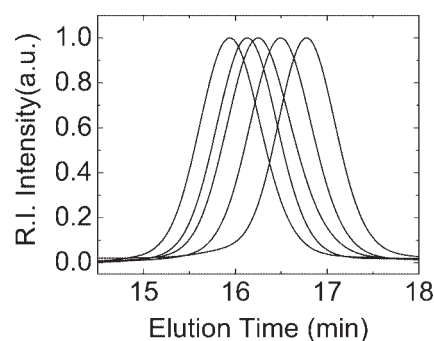
Figure 3 SEC traces of PDMS-*b*-PS as a function of time using the 10 k PDMS-RAFT agent. The peaks from right to left are at polymerization times of 0 h (10 k PDMS-RAFT), 1 h, 2h, 3 h, and 4 h. THF was used as the eluting solvent.
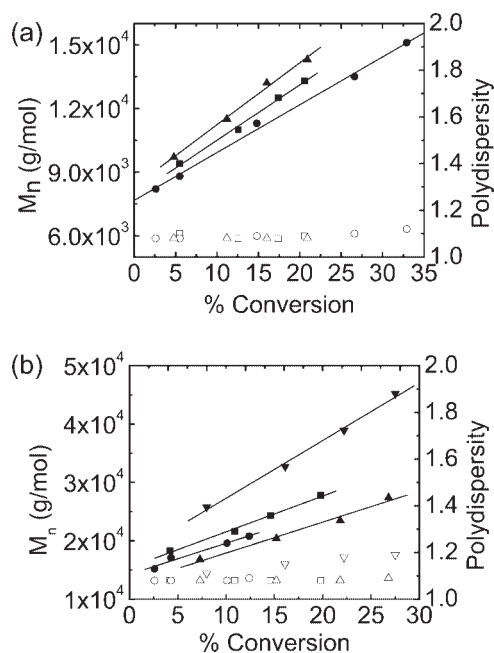
Figure 4 M_n and polydispersity vs. conversion for (a) 5 k PDMS-RAFT and (b) 10 k PDMS-RAFT, (■) styrene 0.5 ml : 0.1 g PDMS-RAFT (●) *tert*-butylstyrene 0.5 ml : 0.1 g PDMS-RAFT (▲) 4-methylstyrene 0.5 ml : 0.1 g PDMS-RAFT (▼) styrene 1 ml : 0.1 g PDMS-RAFT. The closed symbols refer to M_n, open symbols refer to polydispersity. The solid lines are linear fits to the data.

because they are compared to PS standards, but are still linear with conversion indicating a controlled polymerization.[34] The polydispersities are ≤1.1 when a ratio of monomer to PDMS-RAFT of 0.5 ml : 0.1 g was used. Higher molecular weight PS blocks were obtained using a ratio of styrene : PDMS-RAFT of 1.0 ml : 0.1 g, here the polydispersity was also found to increase up to 1.2 at high conversion indicating some loss of control of the polymerization at lower RAFT agent concentrations. The conversions in these polymerizations were limited to 30–35% because at times greater than 4 h, the polymerizations became too viscous to draw an aliquot for analysis and stirring would become sluggish.

Figure 5 shows the pseudo first order kinetic plots for the polymerizations. The monomer concentration [M] was determined using the NMR conversion data. The linearity of the data reflect the controlled nature of the polymerization where a constant concentration of radicals is expected.[34,35] There is a noticeable induction period for the polymerization for PDMS-*b*-poly(*tert*-butylstyrene) with both the 5 and 10 k PDMS-RAFT. This induction period has previously been observed in other RAFT polymerizations, and there is evidence that one factor influencing this induction period is the monomer chemistry.[36] Differences in the relative polymerization rates of the monomers are also observed. However, these could be due to a number of different factors, which are

not easily separable including the thermal initiation rate of the monomer, the propagation rate of the monomer, and the ratios of the monomer concentration, and the radical concentration to the RAFT agent concentration.[36–38]

The goal of these experiments was to produce well-defined PDMS-containing block copolymers for preparing thin film templates. Therefore, the thin film morphology was investigated for PDMS-*b*-PS 10-1.9 (1 h polymerization 10 kDa PDMS, 1.9 kDal PS) using SFM. Figure 6 shows the height and phase images for a thin film prepared by spin-coating from a 10 mg/mL solution in cyclohexane [Fig. 6(a,b)] and after annealing in saturated cyclohexane [Fig. 6(c,d)] and saturated chloroform [Fig. 6(e,f)] environments. In both the height and phase images, the light regions are assigned to PS domains, and the dark regions are assigned to PDMS domains. PDMS is softer than PS and should appear darker in the phase image. This assignment is also consistent with the low volume fraction of PS in the block copolymer, where dispersed domains of PS in a PDMS matrix are expected. In the as-spun film short, poorly ordered cylindrical domains of PS are formed. Annealing with cyclohexane improves the
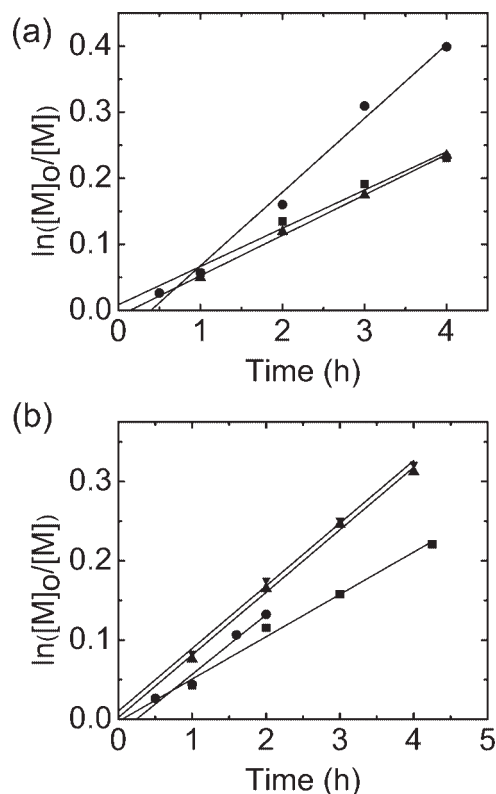

Figure 5 $\ln([M]_o/[M])$ vs. time (a) 5 k PDMS-RAFT, (b) 10 k PDMS-RAFT: (■) styrene 0.5 ml : 0.1 g PDMS-RAFT (●) *tert*-butylstyrene 0.5 ml : 0.1 g PDMS-RAFT (▲) 4-methylstyrene 0.5 ml : 0.1 g PDMS-RAFT (▼) styrene 1 ml : 0.1 g PDMS-RAFT. The solid lines are linear fits to the data.
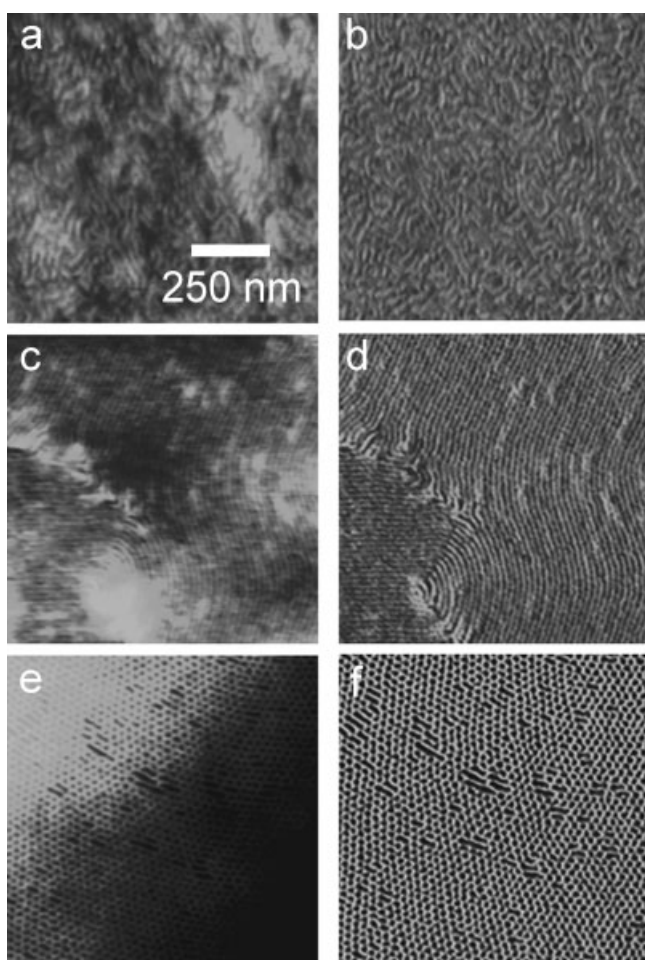
Figure 6 SFM height (a,c,e) and phase (b,d,f) images of PDMS-*b*-PS 10–1.9: (a,b) as-spun from cyclohexane, (c,d) annealed in saturated cyclohexane, (e,f) annealed in saturated chloroform. The range of the height and phase images are 25 nm and 20°, respectively.

long-range order of the cylinders. Annealing the film with chloroform results in an ordered honeycomb pattern. Given the low surface free energy of PDMS (23 mJ/m^2) to PS (44 mJ/m^2), this morphology is likely due to a reconstruction of the surface to a hexagonally perforated lamellar phase.[39] This surface morphology is predicted to occur when the surface is strongly selective to the larger volume fraction block and has been observed previously in solvent annealed polystyrene-*block*-polybutadiene-*block*-polystyrene triblock copolymers.[9,40,41] Contact angle measurements with water on the as-spun, cyclohexane annealed and chloroform annealed films gave static contact angles of 101°, 107°, and 105°, respectively. These are consistent with PDMS-coated surfaces.[42] Figure 7 shows optical microscopy images of the annealed films. The interference colors indicate the terracing of the film thickness in cyclohexane and chloroform. This is known to occur when domains lying parallel to the film surface require quantization of the film thickness to relieve any

incommensurability with the domain spacing.[43] Given that well-defined morphologies are obtained in these PS-*b*-PDMS thin films, these polymers will be useful for studying the thin film morphological behavior of PDMS-containing block copolymers and for application in block copolymer lithography.

CONCLUSIONS

Hydroxyl end-functional PDMS polymers were modified by a one-pot esterification to produce macro-RAFT agents. These macro-RAFT agents were able to control the free radical polymerization of styrene and substituted styrene monomers to produce PDMS-containing diblock copolymers with low polydispersity and controlled molecular weights. A thin film of one PDMS-*b*-PS copolymer prepared by spin-coating showed a microphase separated structure that could be annealed to a significant degree of long-range order by solvent swelling. Therefore,
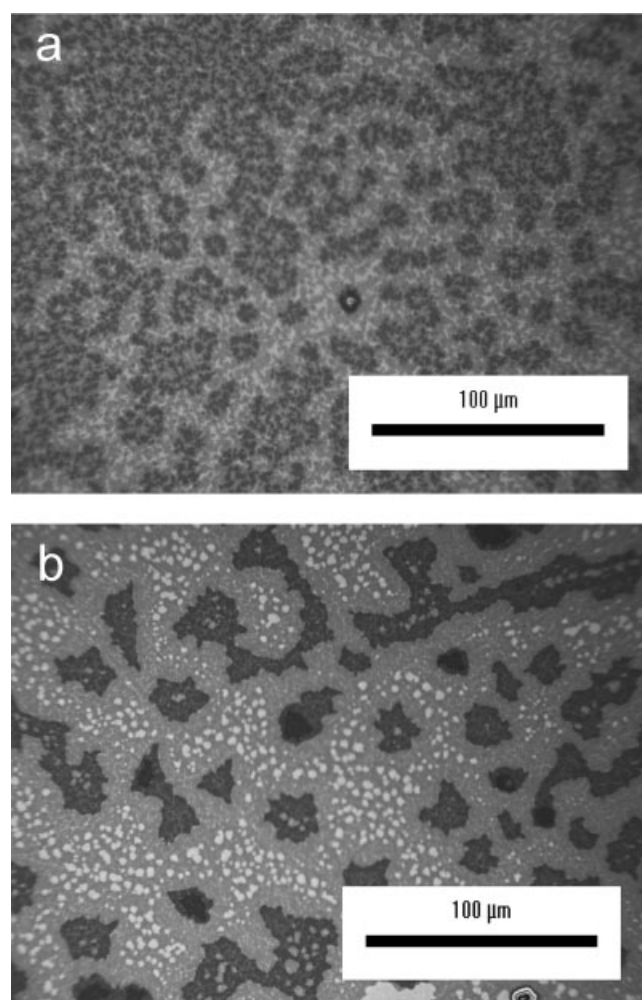

Figure 7 Optical microscopy images of PS-*b*-PDMS 10–1.9 solvent annealed films at 50× magnification: (a) annealed in saturated cyclohexane and (b) annealed in saturated chloroform.

these polymers will be effective for studying the thin-film morphological behavior of PDMS-containing block copolymers. This will be especially useful for understanding the relationships between the morphology, the polymer characteristics, such as volume fraction and molecular weight, and the film processing conditions and will be the subject of future reports.

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