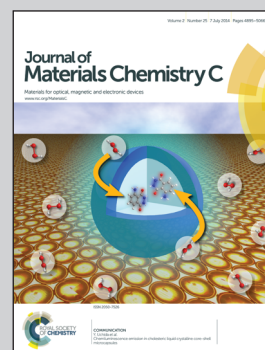


Showcasing research from DISIT, University of East Piemonte and Laboratorio MDM, IMM-CNR, Italy.

Title: Flash grafting of functional random copolymers for surface neutralization

Rapid Thermal Processing (RTP) technology was implemented to control grafting reactions of functional P(S-*r*-MMA) on the time scale of tens of second, leading to a neutralized silicon surface that is suitable for perpendicular orientation of symmetric and asymmetric PS-*b*-PMMA block copolymers.

As featured in:



See M. Perego, M. Laus *et al.*,  
*J. Mater. Chem. C*, 2014, 2, 4909.



[www.rsc.org/MaterialsC](http://www.rsc.org/MaterialsC)

Registered charity number: 207890

## Flash grafting of functional random copolymers for surface neutralization

Cite this: *J. Mater. Chem. C*, 2014, 2, 4909

F. Ferrarese Lupi,<sup>a</sup> T. J. Giammaria,<sup>a</sup> G. Seguini,<sup>a</sup> M. Ceresoli,<sup>a</sup> M. Perego,<sup>\*a</sup> D. Antonioli,<sup>b</sup> V. Gianotti,<sup>b</sup> K. Sparnacci<sup>b</sup> and M. Laus<sup>\*b</sup>

Tailoring surface energies is the key factor to control the orientation of nanoscopic structures in thin block copolymer (BCP) films. In the general frame of the “grafting to” approach, this paper reports on the use of Rapid Thermal Processing (RTP) technology to perform flash grafting reactions of a hydroxyl terminated poly(styrene-*r*-methylmethacrylate) random copolymer to the activated silicon wafer surface. The perpendicular orientation of the cylindrical morphology of an asymmetric PS-*b*-PMMA block copolymer is achieved when the thickness of the random copolymer layer is higher than 6.0 nm. The grafting time to achieve this thickness reduces from about 750 s, when the RTP grafting process is performed at 230 °C, to 15 s at 310 °C. For a symmetric PS-*b*-PMMA block copolymer, the perpendicularly oriented lamellar morphology is obtained when the random layer thickness is higher than 3.5 nm, that is after 60 s RTP grafting time at 250 °C. In addition, TGA-GC-MS analysis indicates that a chain structural reorganization, which occurs during the RTP treatment at high temperature, affords a more stable film structure without changing its surface characteristics. In conclusion, the RTP technology allows the “grafting to” approach to be successfully integrated into the next generation lithographic processes and affords the unprecedented opportunity to study the grafting of macromolecules on time scales and in temperature ranges that have never been explored before, shedding new light on the early stages and on the dynamics of these processes.

Received 18th February 2014  
Accepted 10th April 2014

DOI: 10.1039/c4tc00328d

www.rsc.org/MaterialsC

### Introduction

Tailoring surface energies represents a fundamental step to manipulate the orientation of nanoscopic structures in thin block copolymer (BCP) films.<sup>1–4</sup> When the BCP thin film is confined between substrate/polymer and air/polymer interfaces, the selective affinity of one block to either the substrate or the air-interface results in a parallel or perpendicular orientation of cylindrical or lamellar microdomains within the polymeric film.<sup>5–8</sup> For lithographic applications,<sup>9,10</sup> targeting the insertion of these self-assembled films in the fabrication processes of magnetic-storage media, quantum dots, and flash memory devices, the perpendicular BCP morphology is mandatory.

Several solutions have been envisioned and experimentally tested in order to achieve this important goal. The “grafting to” approach, consisting of the chemical linking of a functional preformed (co)polymer to the substrate, is a versatile and popular strategy to control the BCP morphology orientation. This approach was first introduced<sup>11</sup> for polystyrene-*b*-

polymethylmethacrylate (PS-*b*-PMMA) BCP thin films using a functional hydroxyl terminated poly(styrene-*r*-methylmethacrylate) (P(*S-r*-MMA)) random copolymer (RCP). By properly optimizing the RCP composition, optimal styrene mole fractions that balance the interfacial interactions at substrates were determined.<sup>6,12,13</sup> Binary and ternary random copolymers in which the functional groups are distributed along the chain, such as poly(styrene-*r*-4-vinylbenzylazide) (P(*S-r*-VBzAz))<sup>14</sup> and poly(styrene-*r*-2-vinylpyridine-*r*-hydroxyethylmethacrylate) (P(*S-r*-2VP-*r*-HEMA)),<sup>15</sup> were also investigated to orient normal to the film surface the microdomains of PS-*b*-PMMA and PS-*b*-P2VP thin films, respectively. Random copolymers of styrene and methylmethacrylate with a small amount of reactive benzocyclobutene were proposed as a viable and general approach to control the surface energies.<sup>16</sup> In this case, after film deposition, a thermally activated crosslinking reaction afforded a stable and robust random copolymer layer in contact but not chemically linked to the substrate. Quite recently, the “grafting to” approach has been extended to tethered homopolymers and block copolymers including, among others, hydroxyl terminated polystyrene<sup>17</sup> and PS-*b*-PMMA<sup>18</sup> as well as polystyrene-*b*-polyethylene oxide (PS-*b*-PEO)<sup>19</sup> having hydroxyl groups at the end of the PEO block. The surface chemistry involved in most of these systems consists of the thermally activated reaction of HO-Si substrates with the hydroxyl groups of the functional (co)polymers.

<sup>a</sup>Laboratorio MDM, IMM-CNR, Via C. Olivetti 2, 20864 Agrate Brianza, MB, Italy. E-mail: michele.perego@mdm.imm.cnr.it

<sup>b</sup>Dipartimento di Scienze e Innovazione Tecnologica (DISIT), Università del Piemonte Orientale “A. Avogadro”, INSTM, UdR Alessandria, Viale T. Michel 11, 15121 Alessandria, Italy. E-mail: michele.laus@mfn.unipmn.it

Compared to other techniques, the “grafting to” approach presents several advantages. As the random copolymer chemical composition can be precisely controlled, fine-tuning of the surface characteristics is provided and a straightforward integration into a lithographic process flow is possible. However, its industrial exploitation requires extremely fast grafting procedures. In quantitative terms, the time process limitations are dictated by the symbiotic integration of self-assembling materials into standard lithographic processes. According to the Semiconductor Industry Association's International Technology Roadmap for Semiconductors<sup>20</sup> (ITRS) 2007, to be competitive with the actual large-scale production lithographic techniques, the net time to form and fix the BCP pattern must lay around 4 minutes. Consequently, the time scale for the successful industrial exploitation of the “grafting to” approach in the production of neutral grafted layers should be within tens of seconds. In principle, alcohols could undergo a fast surface condensation reaction with silica, by performing alkoxylation at high temperatures.<sup>21,22</sup> However, reactions comprising polymers are generally slower than the analogous reactions involving the same functional groups in low molar mass reagents, because the former are, at least partially, diffusion controlled. In addition, the relatively low thermal stability of the employed functional (co)polymers prevents the grafting reaction to be performed at high temperatures. In spite of these advices, in a recent paper<sup>23</sup> a fast grafting reaction of a hydroxyl terminated P(S-*r*-MMA) copolymer was reported by heating the samples on a hotplate at 250 °C for a few minutes. The authors argued that the combination of high temperature and short time allowed the grafting reaction to occur with limited, if any, degradation of the random copolymer.

This paper focuses on the possibility to perform flash grafting reactions at very high temperature of hydroxyl terminated P(S-*r*-MMA) copolymers with the general structure reported in Chart 1, with styrene fractions of XS = 0.62 and XS = 0.58.

These random copolymers were demonstrated to be highly effective in inducing the perpendicular orientation of symmetric and asymmetric PS-*b*-PMMA. In the present paper, the thermal treatment is performed in a Rapid Thermal Processing (RTP) machine. This enabling technology was recently demonstrated<sup>24-26</sup> to be extremely efficient at affording perpendicular microdomain orientation in PS-*b*-PMMA thin films within a few seconds. We demonstrate the efficiency of RTP in performing the grafting reaction on the timescale of few

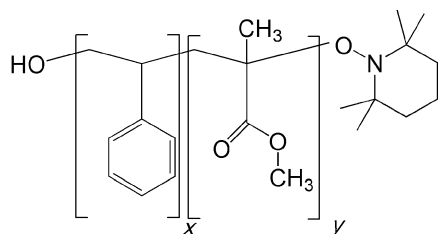


Chart 1 Schematic representation of the hydroxyl terminated poly(styrene-*r*-methylmethacrylate) (P(S-*r*-MMA)).

seconds, thus opening new possibilities in several fields of surfaces and interfaces in science and technology.<sup>27,28</sup>

## Experimental

### Materials

Three hydroxyl end-functionalized random copolymers P(S-*r*-MMA) with styrene fraction of XS = 0.62 ( $M_n = 13\,500\text{ g mol}^{-1}$  and PDI = 1.26 and  $M_n = 7000\text{ g mol}^{-1}$  and PDI = 1.48) and XS = 0.58 ( $M_n = 11\,400\text{ g mol}^{-1}$ , PDI = 1.64) and two block copolymers PS-*b*-PMMA with styrene fraction of XS = 0.70 (asymmetric copolymer,  $M_n = 67\,100\text{ g mol}^{-1}$  and PDI = 1.09, PMMA syndiotactic rich contents >78%) and XS = 0.50 (symmetric copolymer,  $M_n = 51\,000\text{ g mol}^{-1}$  and PDI = 1.06, PMMA syndiotactic rich contents >78%) were purchased from Polymer Source Inc. All the copolymers were used as obtained. BCPs and RCPs were marked B50, B70, R58, and R62, where B and R stand for block and random, respectively, and the number represents the percent styrene unit. In the case of R62, unless otherwise specified, the sample with  $M_n = 13\,500\text{ g mol}^{-1}$  was employed. P(S-*r*-MMA) TEMPO terminated (TR60) and hydroxyl end-functionalized P(S-*r*-MMA) Br terminated (BrR61) were synthesized as described in the following paragraphs. 2,2,6,6-Tetramethylpiperidinyloxy (TEMPO), 2,2'-azobis(2-methylpropionitrile) (AIBN), 2-hydroxyethyl(2-bromoisobutyrate) (HEBIB), tris(2-(dimethylamino)ethyl)amine (Me<sub>6</sub>TREN), copper(II) bromide (CuBr<sub>2</sub>), tin(II) 2-ethylhexanoate (Sn(EH)<sub>2</sub>) and solvents were purchased from Aldrich and used as received. Styrene and methylmethacrylate were purchased from Aldrich and purified by passing through an inhibitor removal column (Aldrich) before use.

### Synthesis procedures

**P(S-*r*-MMA) TEMPO terminated (TR60).** The random copolymer TR60 was obtained by nitroxide mediated polymerization (NMP) of styrene and methylmethacrylate employing a bimolecular initiating system AIBN/TEMPO.<sup>29</sup> A Schlenk tube was charged with 6.0 ml styrene (52.3 mmol), 2.5 ml methylmethacrylate (22.0 mmol), 50.0 mg AIBN (0.30 mmol) and 61.0 mg TEMPO (0.39 mmol). The mixture was degassed by three freeze-thaw cycles and then sealed under nitrogen. The polymerization was carried out at 90 °C for 19 hours. The reaction mixture was cooled to room temperature, and then diluted with THF (5 ml). The copolymer was precipitated into methanol, washed with methanol, and purified by precipitation from THF solution into methanol. The copolymer composition was evaluated by <sup>1</sup>H NMR and the styrene fraction resulted in XS = 0.60.  $M_n = 10\,500\text{ g mol}^{-1}$  and PDI = 1.40 were determined by SEC analysis.

**Hydroxyl end-functionalized P(S-*r*-MMA) Br terminated (BrR61).** The hydroxyl terminated random copolymer BrR61 was obtained by ARGET ATRP of styrene and methylmethacrylate initiated by employing HEBIB and catalyzed by CuBr<sub>2</sub>/Me<sub>6</sub>TREN complexes in the presence of Sn(EH)<sub>2</sub> as the reducing agent.<sup>30</sup> 1.88 mg CuBr<sub>2</sub> (8.40 μmol) and 3.7 μl Me<sub>6</sub>TREN (8.40 μmol) were dissolved in 5.0 ml degassed anisole, and transferred *via*



degassed syringes to a dry Schlenk flask, purged by flushing with nitrogen. Then, 6.6 ml degassed styrene (57.7 mmol), 2.6 ml degassed methylmethacrylate (24.3 mmol) and 63.2  $\mu\text{l}$  HEBIB were added. The mixture was degassed by three freeze-thaw cycles and the flask was sealed under nitrogen. Then, a purged solution of  $\text{Sn}(\text{EH})_2$  (84.0  $\mu\text{mol}$ ) and  $\text{Me}_6\text{TREN}$  (84.0  $\mu\text{mol}$ ) in degassed anisole (1.0 ml) was added and polymerization was carried out at 90 °C for 22 hours. The final reaction mixture was cooled to room temperature, and then diluted with THF (5 ml). The copolymer was precipitated into methanol, washed with methanol, and purified by precipitation from THF solution into methanol. The copolymer composition was evaluated by  $^1\text{H}$  NMR and the styrene fraction resulted in  $X_S = 0.61$ .  $M_n = 14\,500\text{ g mol}^{-1}$  and  $\text{PDI} = 1.25$  were determined by SEC analysis.

**Sample preparation.** Oriented silicon (100) substrates with a 50 nm thick thermal silicon dioxide layer were employed. The oxidized substrates (about 1  $\text{cm}^2$  surface) were cleaned with piranha solution ( $\text{H}_2\text{SO}_4\text{-H}_2\text{O}_2$  with 3/1 vol ratio at 80 °C for 40 min) to eliminate any residual organic material and to increase the surface concentration of hydroxyl groups. The samples were then rinsed with  $\text{H}_2\text{O}$  and dried under  $\text{N}_2$  flow. After the cleaning process, a solution of P(S-*r*-MMA) (18.0 mg in 2.0 ml of toluene) was spin coated on the substrates for 30 s at 3000 rpm. The sample was then RTP thermally treated under different time and temperature conditions to promote the grafting reaction. The non-grafted P(S-*r*-MMA) fraction was removed by washing the samples with toluene in an ultrasonic bath.

A solution of PS-*b*-PMMA (18.0 mg in 2.0 ml of toluene for B50 and 16.0 mg in 2.0 ml of toluene for B70), prepared using an ultrasonic bath, was spun for 30 s between 3000 rpm and 4000 rpm, depending on the desired thickness. Films of controlled thickness (about 28 nm) of PS-*b*-PMMA were spun on the substrates, coated with the grafted P(S-*r*-MMA) layer. The resulting samples were then RTP thermally treated.

**RTP grafting and annealing procedure.** All the annealing processes described below were performed using a Jipelec Jet-First Series RTP tool in a  $\text{N}_2$  atmosphere. This tool is a standard semiconductor manufacturing equipment that employs radiative energy sources (normally halogen lamps) driving the desired temperature on the sample with extremely high heating (up to 50 °C  $\text{s}^{-1}$ ) and cooling (up to 20 °C  $\text{s}^{-1}$ ) rates. Due to a temporal delay between the temperature set in the nominal ramp and the temperature surveyed by the thermocouple, to reach the target temperature at the maximum speed, the nominal target temperature in the RTP software was set 10–20 °C higher than the desired target temperature. In this way, as the measured sample temperature approaches the nominal target temperature, the system progressively reduces the heating power achieving exactly the desired target temperature. This approach allows us to perfectly control the ramp-up of the temperature avoiding any over- or under-shooting phenomenon. The heating rate was set to 18 °C  $\text{s}^{-1}$ . The cooling ramp was controlled by properly adjusting the  $\text{N}_2$  flow rate in the chamber, in order to reproduce the same cooling profile irrespective of the target temperature. The grafting of both R62 and R58 was achieved by the RTP treatment with target

temperatures corresponding to 230, 250, 280 and 310 °C, whereas the annealing time ranged from 1 to 900 s. To develop the block copolymer morphology, the RTP thermal treatment was performed in all cases at 250 °C for 180 s, according to the procedure reported elsewhere.<sup>24</sup> The thicknesses of the BCP film were adjusted in order to ensure the best conditions in terms of commensurability with the characteristic periodicity of the nanodomains.

**Film characterization.** The thickness of the polymeric films was measured by means of a M-200U spectroscopic ellipsometer (J. A. Wollam Co. Inc.) using a Xenon laser lamp at 70° incident angle. Contact angle measurements were performed using an optical tensiometer Attention mod. Theta.

**Morphology characterization.** The morphology of the BCP films was characterized by Scanning Electron Microscopy (SEM) (Zeiss Supra 40 SEM). Opening of the cylindrical nano-template was completed by selective removal of the PMMA blocks in order to ensure good contrast in the SEM images. The degradation of the PMMA component *via* chain scission was achieved by exposing the samples to UV radiation (5  $\text{mW cm}^{-2}$ ,  $\lambda = 253.7\text{ nm}$ , 15 min) and washing in an acetic acid bath for 8 min. An oxygen plasma treatment was performed to cross-link the PS chains and remove the grafted R58 and R62 at the bottom of the pores.

**TGA-GC-MS characterization.** The thermal degradation of P(S-*r*-MMA) after deposition on the substrate, followed by the grafting process, was performed as previously described<sup>31</sup> in a Mettler TGA/SDTA 851<sup>e</sup> purged with a steady flow of helium at a scanning rate of 20 °C  $\text{min}^{-1}$  from room temperature to 800 °C. The polymeric films on the Si substrate were directly placed on the thermobalance plate. The TGA-GC-MS analyses were performed using a FINNIGAN TRACE GC ultra and TRACE DSQ. The GC separation was carried out using a Phenomenex DB5-5ms capillary column (30 m, 0.25 i.d., 0.25 thickness).

The evolved gas from TGA was transferred to the GC-MS system using an automatic interface (Automation) consisting of three components: a heated transfer-line (HTL1) from TGA to an automatic gas sampling system, an autoinjector (AI) equipped with a switch valve and a prefixed volume loop and a second heated transfer line (HTL2) from the AI to the GC-MS injector port. The automatic AI controls the repetitive pulsed transfer of known amounts of the evolved gas, with the desired frequency, in the injector of the GC-MS system. A LAN electronic controller and dedicated software were used to control all the parameters. The analyses were performed by setting HTL1 and HTL2 at 200 °C and AI at 150 °C. The capacity of the injection loop was 2.5 ml, the sampling frequency was 1.0 min and the sampled gas from the loop to the waste was switched after 10 s. The analysis of the gas evolved from the TGA was performed with the injector temperature at 250 °C in splitless mode and helium as carrier gas at a constant flow rate of 1.0  $\text{ml min}^{-1}$ . The transfer line and oven temperatures were set at 280 and 150 °C, respectively.

The MS signal was acquired in EI+ mode with an ionization energy of 70.0 eV and an ion source temperature of 250 °C. The acquisition was performed both in full-scan mode in the range 20–450  $m/z$  and in Single Ion Monitoring (SIM) acquisition mode. The identification of the evolved products was performed

by comparison of the retention times and spectra of commercial standards analyzed under the same experimental conditions.

**Copolymer characterization.** The copolymer composition was determined by  $^1\text{H-NMR}$  using a JEOL ECX-400 NMR spectrometer. SEC analysis was performed on a 590 Waters chromatograph equipped with a refractive index detector. Two Waters HSPgel columns (HR3 and HR4) connected in series were employed with THF as the mobile phase (flow rate  $0.6\text{ ml min}^{-1}$ ). The column set was calibrated against standard PS samples.

## Results and discussion

All the grafting reactions were performed using an RTP system. With respect to standard thermal treatment performed in a furnace/oven, in which the heat transfer is essentially governed by conduction or convection mechanisms, the radiative energy source (normally halogen lamps) of the RTP allows high heating rates to be obtained, coupled with a precise temperature control during the various stages of the thermal treatment (temperature fluctuations lower than  $\pm 1\text{ }^\circ\text{C}$ ). The heating ramp for all the experiments was fixed equal to  $18\text{ }^\circ\text{C s}^{-1}$ . This means that the maximum transient time, to heat the sample from  $180\text{ }^\circ\text{C}$  (temperature at which the grafting rate is very low) to  $300\text{ }^\circ\text{C}$ , is about 7 s. This low transient period allows the most part of the grafting process to be performed under isothermal conditions, unless very short isothermal periods are considered.

### Grafting process and morphology evolution

Fig. 1 shows the thickness of the grafted films of R62 as a function of time for the grafting temperatures of 230, 250, 280 and  $310\text{ }^\circ\text{C}$ . The evolution of the R62 film thickness as a function of time is very similar for all the grafting temperatures.

The thickness of the film increases very fast at the beginning and then levels off reaching the same plateau value at  $8.1 \pm 0.3\text{ nm}$ , which corresponds to the limiting saturation value

obtained by performing the thermal treatment in a conventional oven at  $170\text{ }^\circ\text{C}$  for 48 hours. In addition, the slopes of the thickness vs.  $\log t$  curves in the initial time region are very similar at different temperatures. This evidence suggests that the process generating the final random copolymer layer is the same irrespective of the annealing temperature. To further understand the chemistry of the RTP driven grafting process, a random copolymer sample TR60, with a styrene fraction  $X_S = 0.60$ ,  $M_n = 10\,500\text{ g mol}^{-1}$  and  $\text{PDI} = 1.40$ , was prepared by NMP employing the bimolecular initiating system AIBN/TEMPO<sup>29</sup> and a random copolymer sample BrR61, with a styrene fraction  $X_S = 0.61$ ,  $M_n = 14\,500\text{ g mol}^{-1}$  and  $\text{PDI} = 1.25$ , was prepared by ARGET ATRP employing HEBIB and catalyzed by  $\text{CuBr}_2/\text{Me}_6\text{TREN}$  complexes in the presence of  $\text{Sn}(\text{EH})_2$  as the reducing agent.<sup>30</sup> The monomeric compositions of TR60 and BrR61 are very similar to that of R62. However, in comparison with R62, TR60 and BrR61 present different end-terminations. In particular TR60 presents a TEMPO moiety at one end but not the hydroxyl terminal group whereas BrR61 exhibits the hydroxyl terminal group while the TEMPO moiety is substituted by a bromine atom. Both BrR61 and TR60 were subjected to the same RTP treatment of R62 at  $310\text{ }^\circ\text{C}$  for different time periods and the results are in Fig. 2, which reports also the data of R62 for comparison purposes.

The grafting process of sample BrR61 closely parallels the one of R62. The slight difference in the plateau values is due to the difference in the molar mass of the two copolymers. In contrast, no grafting is observed for TR60 irrespective of the annealing temperature. These data clearly indicate that the high temperature RTP driven grafting process involves only the surface condensation of the hydroxyl terminal groups of the random copolymers with silica and rule out the occurrence of thermally induced crosslinking reactions or the participation of the end group bearing the TEMPO moiety.

The film growth profile illustrated in Fig. 1 suggests the occurrence of two distinct regimes.<sup>32–35</sup> Initially, the process is diffusion or reaction limited, where the driving force is the

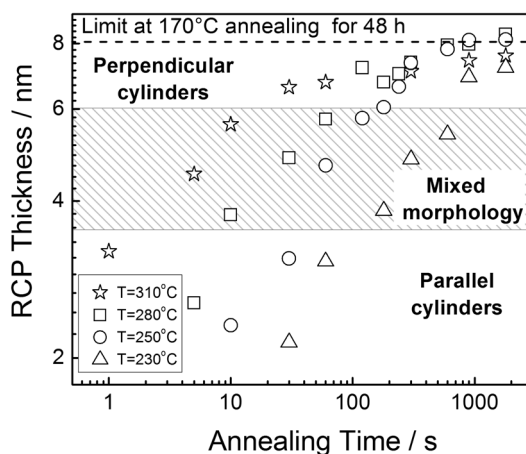


Fig. 1 Thickness of the RTP grafted films of R62 at 230, 250, 280 and  $310\text{ }^\circ\text{C}$  as a function of time. The three zones in which the orientation of the cylinders is changed (perpendicular cylinders, mixed morphology and parallel cylinders) are also indicated.

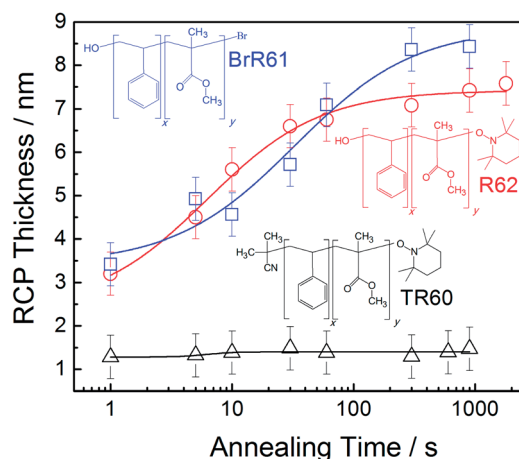


Fig. 2 Thickness of the RTP treated films of R62 (red circles), TR60 (black triangles) and BrR61 (blue squares) at  $310\text{ }^\circ\text{C}$  as a function of time.

diffusion of the polymers on the surface and the conformational rearrangements of the random coil to appropriately present the functional group to the silica surface. This diffusion/reaction process represents the rate-limiting step and corresponds to a surface grafting process characterized by a negligible interaction among individual polymer chains. Increasing the reaction time, the slope change indicates a transition from the diffusion or reaction limited adsorption regime to the penetration-limited regime. The penetration-limited regime results from the increased density of the grafted chains on the surface that creates an energy barrier for further grafting. This behavior is accompanied by the transition from random mushroom to brush arrangement of the grafted macromolecules and the grafting stops when the chains form stretched brushes.

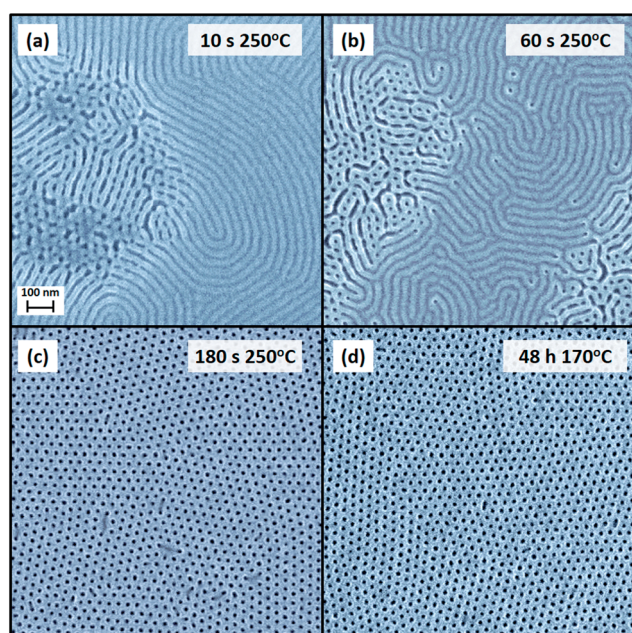


Fig. 3 Representative SEM images of the PS-*b*-PMMA B70 morphologies developed onto substrates functionalized with the random copolymer R62 subjected to RTP grafting at 250 °C under various annealing times (a–c). For comparison, the image of a sample in which grafting was promoted with the standard process in the furnace is also reported (d).

A close comparison of the data in Fig. 1 with the morphology information obtained by SEM images as depicted in Fig. 3 and 4 indicates that the propensity of the random copolymer layer to drive the orientation of the BCP microdomains depends essentially on its thickness. Fig. 3 collects selected SEM images after deposition and annealing of the B70 thin films on substrates functionalized with R62 subjected to RTP grafting at 250 °C for different times. In very thin grafted film layers (Fig. 3a, thickness < 3.6 nm), a parallel BCP morphology is observed, thus suggesting that the block copolymer is able to partly penetrate the grafted layer and interact with the surface.<sup>16</sup> For intermediate film thicknesses (Fig. 3b, 3.6 < thickness < 6 nm) mixed morphologies are obtained, whereas for thicknesses of the grafted layer higher than a critical value of 6 nm (Fig. 3c), the perpendicular orientation is obtained. These results are in good agreement with literature data.<sup>36,37</sup>

In Fig. 3d the SEM image of a sample in which grafting was promoted with the standard process in a furnace at 170 °C for 48 h is reported. The close comparison of this image with the one reported in Fig. 3c demonstrates that the RTP grafted layer annealed at 250 °C for 180 s has essentially the same surface characteristic achieved with standard furnace treatment and that RTP treatment provides an efficient tool to promote the grafting of the random copolymer and the concomitant neutralization of the substrate. This effect is further highlighted in Fig. 4, where the grafting process is accomplished at 310 °C. The morphology evolution perfectly reproduces the trend observed in Fig. 3, thus indicating that the process at 310 °C does not substantially modify the structural characteristics of the grafted macromolecules preserving the capability to form a neutral brush layer for the subsequent deposition and self-assembly of the block copolymers. The analysis of the SEM images indicates that the thickness thresholds, which allow changing from parallel to mixed, and from mixed to perpendicular morphology, are the same irrespective of the annealing temperature. In particular, the grafting time corresponding to the achievement of this critical thickness progressively reduces from about 900 s, when the RTP process is performed at 230 °C, to 180 s at 250 °C, 120 s at 280 °C and less than 30 s at 310 °C, in agreement with a transport-limited regime during the initial stage of the grafting process.

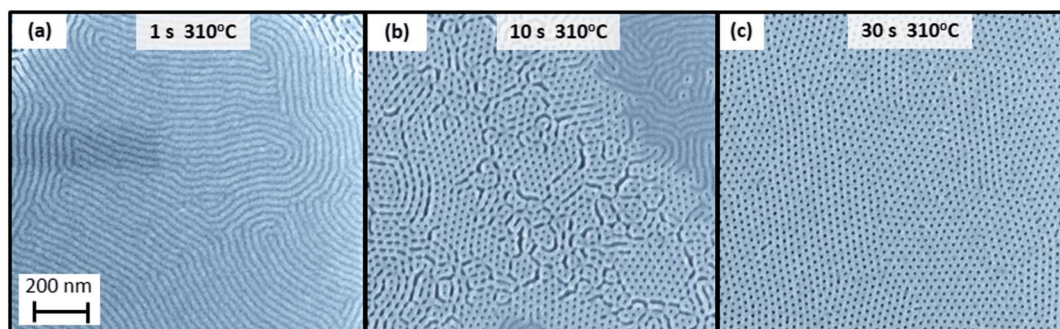


Fig. 4 SEM images of the PS-*b*-PMMA B70 morphologies obtained on the random copolymer R62 subjected to RTP grafting under various times at 310 °C.



A quite similar behavior is observed in the case of R58, as illustrated in Fig. 5 where the thickness of the grafted films of R58 is reported as a function of time for a grafting process performed at 250 °C. Initially, the thickness of the grafted copolymer increases steeply with the grafting time and then levels off corresponding to a saturation value of about 5.2 nm. This value is very close to the one typically obtained in the oven treatment at 170 °C for 48 hours (5.0 nm). In this system, a direct transition from parallel to perpendicular morphology is observed as demonstrated by the SEM images of Fig. 5b and c. The critical thickness, above which a well ordered perpendicular lamellar structure of B50 is observed, is about 3.5 nm. Interestingly, the saturation value of R58 is lower than the one of R62. This difference probably originates from the different molar mass distribution of the two samples. R58 presents a consistent tail of low molar mass species,<sup>27</sup> which are likely to react faster than the higher molar mass species in the diffusion controlled regime. Alternatively, the low molar mass species could be preferentially adsorbed to the substrate surface due to their higher affinity.<sup>38</sup> In this context it should be observed that the saturation value of a random copolymer sample with a styrene fraction of  $X_S = 0.62$  and  $M_n = 7000 \text{ g mol}^{-1}$  results 6.2 nm.

The same difference in the grafting behavior of the two random copolymers can be observed when plotting the layer thickness as a function of the annealing temperature keeping constant the annealing time (Fig. 6). Although the saturation values are independent of the annealing time, the temperature at which the saturation is reached is different for the two copolymers. In particular, for R58 the thickness saturation value is reached when the grafting is performed between 210 and 230 °C, whereas for R62 when the temperature reaches about 250 °C. This different behavior could be related to the different molar mass distribution of the two samples, as R58 (which features a consistent amount of low molar mass species) reaches the saturation at a lower temperature than R62. As a final point, it could be observed that the stability of the grafted

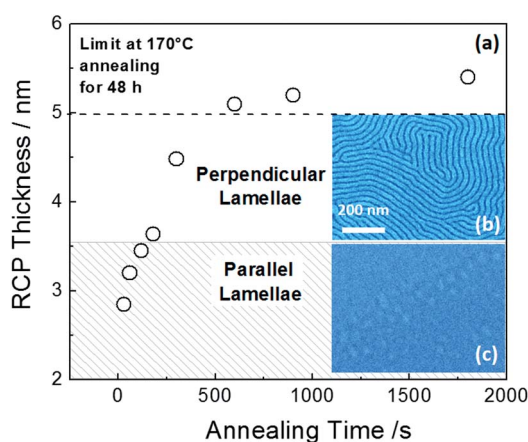


Fig. 5 Thickness of the RTP grafted films of R58 at 250 °C as a function of time. The two thickness widows corresponding to perpendicular and parallel orientations of the lamellae are also indicated. SEM images corresponding to parallel (b) and perpendicular (c) orientation of the lamella microdomains are reported.

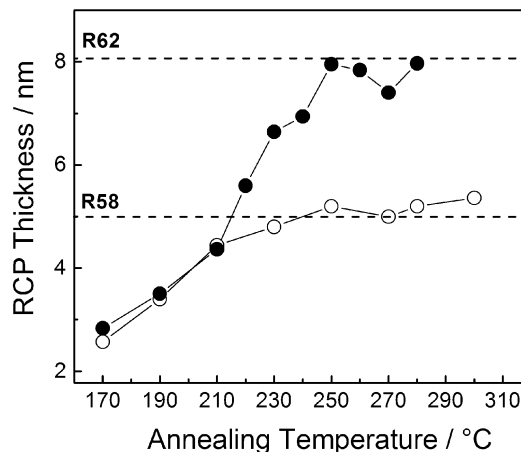


Fig. 6 Thickness trend for R62 (full symbol) and R58 (open symbol) as a function of the annealing temperature after 15 min annealing time. The dashed lines indicate the limiting thickness for grafting in an oven at 170 °C annealing for 48 h.

polymeric films against aging is similar in the case of the samples treated in RTP and in the standard furnace. Even if a specific study would be necessary to properly elucidate this point, we can point out that both of them were successfully employed to drive the orientation of the PS-*b*-PMMA block copolymer even one month after the surface modification process.

#### Random copolymer film TGA-GC-MS characterization

The effect of the RTP processing on the thermal stability of the grafted R62 and R58 was studied by TGA-GC-MS analysis from room temperature to 800 °C. Under these conditions, the degradation pathway of the P(S-*r*-MMA) random copolymers was demonstrated<sup>31</sup> to consist of depolymerization *via* an unzipping process and the main degradation products are the two monomers. Consequently, the monomer evolution under dynamic conditions is able to delineate the thermal degradation path.

In the present study, the styrene evolution only with temperature is reported because of the five times higher sensitivity of styrene than methylmethacrylate in the mass detector. Fig. 7 illustrates the TGA-GC-MS analysis performed on films of R62 subjected to various thermal treatments. The thermal degradation profile of the random copolymer after the RTP grafting treatment at 230 °C for 3 and 15 min is practically identical to the one of the thermally untreated thin film, thus clearly indicating that the structure of the random copolymers is not substantially affected by the above RTP process.

In contrast, for a sample in which the grafting process is performed under the conventional oven conditions (170 °C for 48 hours under high vacuum) the thermal degradation occurs at lower temperatures thus indicating the occurrence,<sup>27</sup> during the oven annealing procedure, of some molecular rearrangements or oxidation processes, leading to the formation of weaker bonds or reactive groups able to start the chain degradation.

In the right panel of Fig. 7, the degradation profiles of some RTP treated films are compared. The temperature and time have

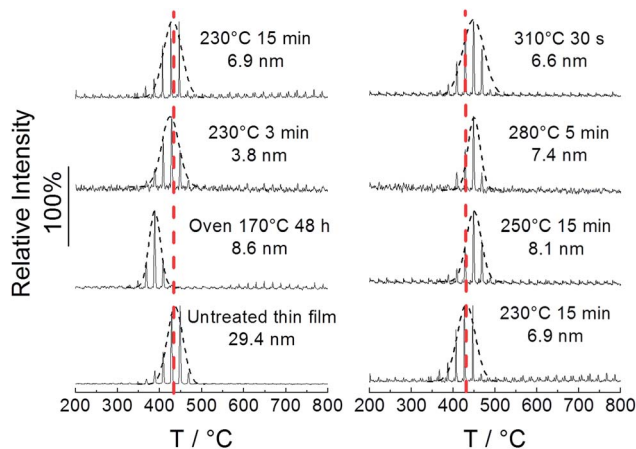


Fig. 7 TGA-GC-MS analysis of styrene performed on R62 films, featuring different thicknesses and subjected to distinct thermal treatments. The dashed red line was added to guide the eyes.

been selected in order to check the stability of the brush layer when the thickness of the film is higher than the threshold value that guarantee the perpendicular orientation of the microdomains in the block copolymer film. The degradation profiles appear to slightly move toward the higher temperature side without changing their shape so much as the RTP temperature and time increase. This effect is particularly evident when comparing the degradation profile of the sample RTP treated at 250 °C for 15 min to the one of the sample RTP treated at 310 °C for 30 s. Although the thicknesses of the two samples are very similar, the degradation profile of the latter is translated by about 20 °C along the temperature scale. As the water contact angle of all the RTP treated films are identical ( $\sim 83 \pm 1^\circ$ ) within the experimental error and the orientation propensity does not change even after RTP grafting treatment at high temperature for relatively long time periods, these data suggest that the chain structural reorganization, which occurs during the RTP treatment, affords a more stable film structure without changing so much its surface characteristics.

The same effect is observed for R58, as illustrated in detail in Fig. 8 which collects several thermal degradation profiles of this random copolymer after the RTP grafting treatment for 15 min at different temperatures between 170 and 300 °C. When the RTP temperature is comprised between 170 and 230 °C, the thermal degradation profiles are practically identical to each other and to the one of the thermally untreated R58 thin film (not included in the figure). However, as the RTP temperature is raised above 250 °C, the degradation profiles appear regularly translated toward the higher temperature side without significant modification of their shape.

When the RTP grafting temperature is comprised between 250 and 300 °C, the high temperature shift of the degradation profiles of the films treated for 15 min is practically identical to the one observed after treatment for 1 min, as illustrated in Fig. 9.

Although further investigations are in progress to elucidate this behavior, a tentative explanation for the observed thermally induced stabilization of the random copolymers could be

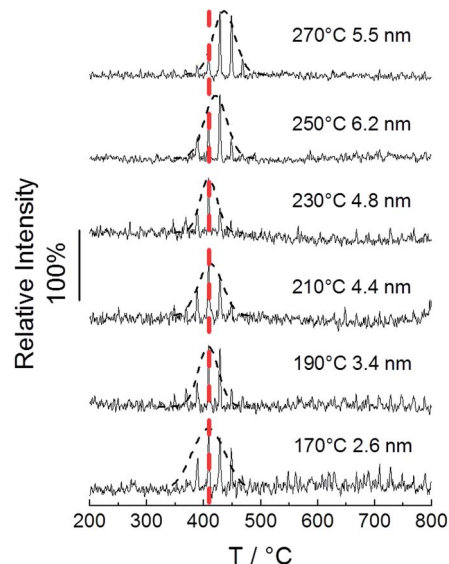


Fig. 8 TGA-GC-MS analysis of styrene for R58 after annealing the thin film in RTP for 15 min at temperatures comprised between 170 and 300 °C. The grafted film thickness is reported for each temperature. The dashed red line was added to guide the eyes.

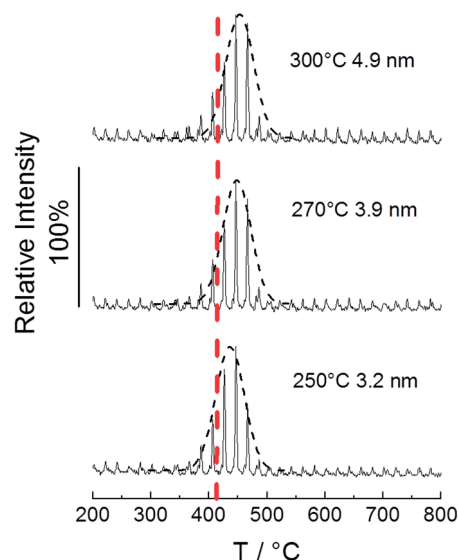


Fig. 9 TGA-GC-MS analysis of styrene for R58 after annealing the thin film in RTP for 1 min at temperatures comprised between 250 and 300 °C. The grafted film thickness is reported for each temperature. The dashed red line was added to guide the eyes.

proposed. When the random copolymers are heated to high temperatures, chain scission occurs at the bond between the polymer chain and the nitroxide group, followed by unzipping and at high temperatures, the concentration of the radicals derived from the terminal chain scission could become very high.

Consequently, because of their bimolecular nature, the incidence of radical recombination or disproportionation termination reactions, leading to the formation of more stable carbon-carbon bonds, increases so much as the RTP temperature increases. In this respect, the stabilization of the random



copolymers could be viewed as a thermally induced suppression of nitroxide end-groups. In this context, it is worth mentioning that a chemical post-synthesis modification of the nitroxide-terminated chain ends has been recently performed<sup>39</sup> using phenylhydrazine as a chain transfer agent. This modification yielded polymers with enhanced thermal stability in bulk.

## Conclusions

In conclusion, we demonstrated that the slowness of grafting in standard furnace treatment is related to the limited range of accessible temperatures in conventional furnace/oven systems. The long periods of time required to reach the target temperature and to cool down the sample after the thermal treatment impose severe restriction to the processing temperature due to the degradation of the polymeric film. The RTP technology overcomes these limitations. Significant time reduction has been achieved increasing the annealing temperature without detrimental degradation of the macromolecules. Moreover, the increased thermal stability of the grafted random copolymer after RTP annealing expands the range of temperatures for the subsequent block copolymer processing. In this frame, it is important to outline that RTP technology was recently demonstrated<sup>24</sup> to be extremely efficient at affording perpendicular microdomain orientation in PS-*b*-PMMA thin films within a few seconds, thus suggesting that RTP could represent the leading technology for the industrial exploitation of self-assembling materials. In addition, it could be anticipated that we are successfully extending this approach to other substrates, including tin oxide, hafnium oxide and silicon nitride among others. Finally, the RTP comes up with the unprecedented opportunity to study the grafting of macromolecules on time scales and in temperature ranges that have never been explored before, shedding new light on the early stages and on the dynamics of these processes.

## Acknowledgements

The research activity was financially supported by the NANO-BLOCK project (“NANO-device fabrication using block copolymer based technology”). Patent protection related to this work is pending.

## Notes and references

- I. W. Hamley, *Prog. Polym. Sci.*, 2009, **34**, 1161–1210.
- S. E. Mastroianni and T. H. Epps, *Langmuir*, 2013, **29**, 3864–3878.
- S. Sakurai, *Polymer*, 2008, **49**, 2781–2796.
- K. Koo, H. Ahn, S. W. Kim, D. Y. Ryu and T. P. Russell, *Soft Matter*, 2013, **9**, 9059–9071.
- E. Huang, S. Pruzinsky, T. P. Russell, J. Mays and C. J. Hawker, *Macromolecules*, 1999, **32**, 5299–5303.
- S. Ham, C. Shin, E. Kim, D. Y. Ryu, U. Jeong, T. P. Russell and C. J. Hawker, *Macromolecules*, 2008, **41**, 6431–6437.
- E. Kim, S. Choi, R. Guo, D. Y. Ryu, C. J. Hawker and T. P. Russell, *Polymer*, 2010, **51**, 6313–6318.
- C. M. Bates, T. Seshimo, M. J. Maher, W. J. Durand, J. D. Cushen, L. M. Dean, G. Blachut, C. J. Ellison and C. G. Willson, *Science*, 2012, **338**, 775–779.
- J. Bang, U. Jeong, D. Y. Ryu, T. P. Russell and C. J. Hawker, *Adv. Mater.*, 2009, **21**, 4769–4792.
- M. Li and C. K. Ober, *Mater. Today*, 2006, **9**, 30–39.
- P. Mansky, Y. Liu, E. Huang, T. P. Russell and C. Hawker, *Science*, 1997, **275**, 1458–1460.
- E. Han, K. O. Stuen, Y. H. La, P. F. Nealey and P. Gopalan, *Macromolecules*, 2008, **41**, 9090–9097.
- E. Han, K. O. Stuen, M. Leolukman, C. C. Liu, P. F. Nealey and P. Gopalan, *Macromolecules*, 2009, **42**, 4896–4901.
- C. M. Bates, J. R. Strahan, L. J. Santos, B. K. Mueller, B. O. Bamgbade, J. A. Lee, J. M. Katzenstein, C. J. Ellison and C. G. Willson, *Langmuir*, 2011, **27**, 2000–2006.
- S. Ji, C. C. Liu, J. G. Son, K. Gotrik, G. S. W. Craig, P. Gopalan, F. J. Himpfel, K. Char and P. F. Nealey, *Macromolecules*, 2008, **41**, 9098–9103.
- D. Y. Ryu, K. Shin, E. Drockenmuller, C. J. Hawker and T. P. Russell, *Science*, 2005, **308**, 236–239.
- A. M. Welander, G. S. W. Craig, Y. Tada, H. Yoshida and P. F. Nealey, *Macromolecules*, 2013, **46**, 3915–3921.
- E. Han, M. Leolukman, M. Kim and P. Gopalan, *ACS Nano*, 2010, **4**, 6527–6534.
- W. Gu, S. W. Hong and T. P. Russell, *ACS Nano*, 2012, **6**, 10250–10257.
- The International Technology Roadmap for Semiconductors (ITRS), “Emerging Research Materials” 2007.
- C. C. Ballard, E. C. Broge, R. K. Iler, D. S. St John and J. R. McWhorter, *J. Phys. Chem.*, 1961, **65**, 20–25.
- M. Dion, M. Rapp, N. Rorrer, D. H. Shin, S. M. Martin and W. A. Ducker, *Colloids Surf., A*, 2010, **362**, 65–70.
- C. C. Liu, C. J. Thode, P. A. Rincon Delgadillo, G. S. W. Craig, P. F. Nealey and R. Gronheid, *J. Vac. Sci. Technol., B: Nanotechnol. Microelectron.: Mater., Process., Meas., Phenom.*, 2011, **29**, 06F203.
- F. Ferrarese Lupi, T. J. Giammaria, M. Ceresoli, G. Seguini, K. Sparnacci, D. Antonioli, V. Gianotti, M. Laus and M. Perego, *Nanotechnology*, 2013, **24**, 315601.
- G. Seguini, T. J. Giammaria, F. Ferrarese Lupi, K. Sparnacci, D. Antonioli, V. Gianotti, F. Vita, I. F. Placentino, J. Hillhorst, C. Ferrero, O. Francescangeli, M. Laus and M. Perego, *Nanotechnology*, 2014, **25**, 045301.
- F. Ferrarese Lupi, T. J. Giammaria, G. Seguini, M. Laus, E. Enrico, N. De Leo, L. Boarino, C. K. Ober and M. Perego, *J. Mater. Chem. C*, 2014, **2**, 2175–2182.
- O. Azzaroni, *J. Polym. Sci., Part A: Polym. Chem.*, 2012, **50**, 3225–3258.
- B. Zhao and W. J. Brittain, *Prog. Polym. Sci.*, 2000, **25**, 677–710.
- C. J. Hawker, G. G. Barclay, A. Orellana, J. Dao and W. Devonport, *Macromolecules*, 1996, **29**, 5245–5254.
- W. Jakubowski, K. Min and K. Matyjaszewski, *Macromolecules*, 2006, **39**, 39–45.
- V. Gianotti, D. Antonioli, K. Sparnacci, M. Laus, T. Giammaria, F. Ferrarese Lupi, G. Seguini and M. Perego, *Macromolecules*, 2013, **46**, 8224–8234.

- 32 A. V. Berezkin, D. V. Guseva and Y. V. Kudryavtsev, *Macromolecules*, 2012, **45**, 8910–8920.
- 33 L. S. Penn, H. Huang, M. D. Sindkhedkar, S. E. Rankin, K. Chittenden, R. P. Quirk, R. T. Mathers and Y. Lee, *Macromolecules*, 2002, **35**, 7054–7066.
- 34 G. Liu, L. Yan, X. Chen and G. Zhang, *Polymer*, 2006, **47**, 3157–3163.
- 35 R. Hasegawa and M. Doi, *Macromolecules*, 1997, **30**, 5490–5493.
- 36 D. Y. Ryu, J. Wang, K. A. Lavery, E. Drockenmuller, S. K. Satija, C. J. Hawker and T. P. Russell, *Macromolecules*, 2007, **40**, 4296–4300.
- 37 E. Han and P. Gopalan, *Langmuir*, 2010, **26**, 1311–1315.
- 38 R. A. L. Jones, R. J. Lehnert, H. Schonherr and J. Vancso, *Polymer*, 1999, **40**, 525–530.
- 39 J. M. Widin, M. Kim, A. K. Schmitt, E. Han, P. Gopalan and M. K. Mahanthappa, *Macromolecules*, 2013, **46**, 4472–4480.