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Responsive Block Copolymers: Transformations in the Solid State

**Russell, Thomas
MASSACHUSETTS UNIV AMHERST MA
70 BUTTERFIELD TERRACE
AMHERST, MA,
US**

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14. ABSTRACT
We have investigated the morphological evolution of the lamellar microdomains in the thin films of symmetric poly(solketal methacrylate-b-styrene) (PSM-b-PS) copolymers that can be converted into poly(glycerol monomethacrylate-b-styrene) (PGM-b-PS) copolymers through acid-catalyzed hydrolysis reaction. This simple chemical transformation was performed in the solid-state using an acid vapor, markedly increasing the segmental interaction parameter (χ) from 0.035 to 0.438 at 25 °C and a 118 Å³ reference volume. To control the orientation of the lamellar microdomains using this responsive block copolymer (BCP), a hydroxyl-containing random copolymer (P(SM-r-S)) was used to tune the interfacial energies at the substrate. As a result, a 9.4 nm full pitch lamellar microdomain morphology in the thin films was achieved after full conversion and thermal annealing. We have also developed the two-step chemical transformation of symmetric poly(styrene-b-solketal acrylate) (PS-b-PSA) copolymers as a new responsive BCP. The PSA block is converted into poly(glycerol acrylate) (PGA), which subsequently can be hydrolyzed to a poly(acrylic acid) (PAA) block, driving the stronger segmental interactions as the reaction proceeds. After conversion of PSA to PGA, the χ parameter for PS-b-PGA was found to be 0.558 at 25 °C, and then it increased further to 0.885 at 25 °C when the PGA block is fully transformed to PAA, which is ~15 times larger in magnitude than the χ value for PS and PSA (0.061 at 25 °C) calculated using a 118 Å³ reference volume. As a result of such a large increase in χ , the lamellar and cylindrical morphologies with the domain spacings of 7.4 nm and 6.9 nm were achieved after conversion to PS-b-PGA and PS-b-PAA, respectively.

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Responsive Block Copolymers: Transformations in the Solid State

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Thomas P. Russell, University of Massachusetts Amherst; 413-658-8380

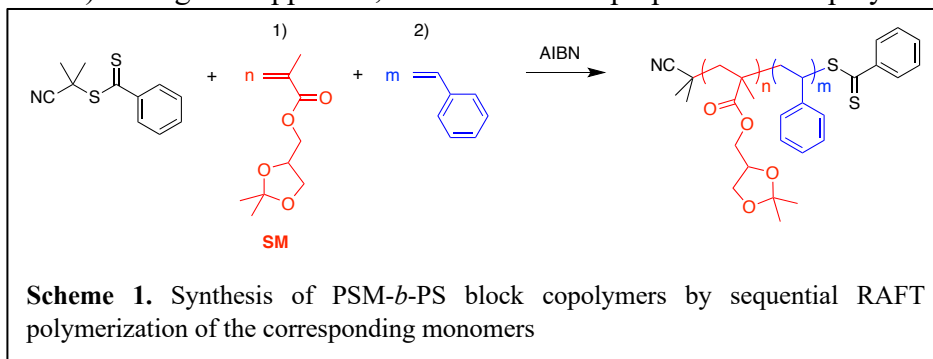
Javid Rzayev, University at Buffalo, SUNY; 716-645-4314

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Abstract: We have investigated the morphological evolution of the lamellar microdomains in the thin films of symmetric poly(solketal methacrylate-*b*-styrene) (PSM-*b*-PS) copolymers that can be converted into poly(glycerol monomethacrylate-*b*-styrene) (PGM-*b*-PS) copolymers through acid-catalyzed hydrolysis reaction. This simple chemical transformation was performed in the solid-state using an acid vapor, markedly increasing the segmental interaction parameter (χ) from 0.035 to 0.438 at 25 °C and a 118 Å³ reference volume. To control the orientation of the lamellar microdomains using this responsive block copolymer (BCP), a hydroxyl-containing random copolymer (P(SM-*r*-S)) was used to tune the interfacial energies at the substrate. As a result, a 9.4 nm full pitch lamellar microdomain morphology in the thin films was achieved after full conversion and thermal annealing. We have also developed the two-step chemical transformation of symmetric poly(styrene-*b*-solketal acrylate) (PS-*b*-PSA) copolymers as a new responsive BCP. The PSA block is converted into poly(glycerol acrylate) (PGA), which subsequently can be hydrolyzed to a poly(acrylic acid) (PAA) block, driving the stronger segmental interactions as the reaction proceeds. After conversion of PSA to PGA, the χ parameter for PS-*b*-PGA was found to be 0.558 at 25 °C, and then it increased further to 0.885 at 25 °C when the PGA block is fully transformed to PAA, which is ~15 times larger in magnitude than the χ value for PS and PSA (0.061 at 25 °C) calculated using a 118 Å³ reference volume. As a result of such a large increase in χ , the lamellar and cylindrical morphologies with the domain spacings of 7.4 nm and 6.9 nm were achieved after conversion to PS-*b*-PGA and PS-*b*-PAA, respectively.

Accomplishments

Synthesis: We developed the synthesis of poly(solketal methacrylate)-*block*-polystyrene) block copolymers (PSM-*b*-PS) by reversible addition fragmentation chain transfer (RAFT) radical polymerization (Scheme 1). Using this approach, we were able to prepare block copolymers with a total molecular weight of < 2,000 kg/ml, which upon hydrolysis of the solketal pendant groups self-assembled into ordered lamella microstructures



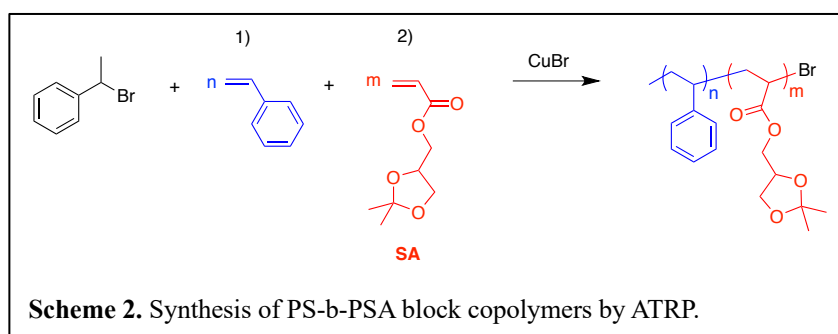
with domain spacings of less than 6 nm. Twelve compositionally symmetric samples were prepared for the evaluation of the segmental interaction parameter, χ , before and after hydrolysis. To access non-lamella morphologies, compositionally asymmetric PS-*b*-PSM

block copolymers were, specifically (PSM_{0.9k}-b-PS_{3.4k} and PSM_{1.4k}-b-PS_{7k}).

We also developed the synthesis of chiral analogs of PSM-*b*-PS block copolymers by using a (R)-solketal methacrylate ((R)-SM), which was synthesized in one step from commercially available reagents. Compositionally symmetric chiral block copolymer (P(R)SM_{1.3k}-b-PS_{1.3k}). Recent reports have indicated that chiral PSM exhibits different solid-state properties compared to its achiral analogs. Asymmetric solketal methacrylate monomers (with both R and S configurations) can provide a facile and inexpensive access to rare chiral block copolymers. These will be used to gain better understanding of the effect of chirality on χ and interfacial curvature during solid state self-assembly.

In a continuing effort to prepare block copolymers with larger χ , we focused on polystyrene-*block*-poly(solketal acrylate) copolymers (PS-*b*-PSA), which can allow a stepwise hydrolysis of the solketal block to produce glycerol and carboxylic acid units, increasing the incompatibility with the

polystyrene block. In the previous system, PSM-*b*-PS, PSM block had to be grown first due to a higher initiation efficiency of the PSM macro-chain transfer agent as compared to the PS



macro-chain transfer agent. This created practical difficulties in isolating oligomeric PSM blocks during purification by precipitation, resulting in low recovery yields. In the case of PS-*b*-PSA system, due to similar reactivities of the acrylate and styrene chain ends, the sequence of blocks could be reversed. To improve the yield and purification efficiencies, we installed the polystyrene block first. We also switched polymerization chemistry from RAFT to ATRP in order to avoid large sulfur containing end-groups that could affect the ordering of small molecular weight block copolymers. The overall scheme for the synthesis of PSA-*b*-PS block copolymers is shown in Scheme 2. Six PSA-*b*-PS block copolymers were prepared, and preliminary results indicate a higher χ for the PSA-*b*-PS system as compared to the PS-*b*-PSM system, which can potentially allow access to even lower domain spacings. Additionally, PSA can be further hydrolyzed to polyacrylic acid, which will provide an enhancement of the chi parameter.

In addition to developing new block copolymers that can allow access to ordered nanomaterials with even smaller *d*-spacings, we focused our research efforts on developing copolymer systems that can achieve orientational control of domains on the surface, a crucial technological challenge for high χ -low N block copolymers. Initially, we synthesized a random copolymer of SM and styrene in order to create neutral surface and eliminate preferential orientation of domains on the surface. This method proved to be effective for moderate molecular weight PSM-*b*-PS block copolymers, but not for the lowest ones.

Realizing Ultra-Small Domains by a Solid-State Transformation: PSM-*b*-PS diblock copolymers with volume fractions of PSM block (f_{PSM}) of ~ 0.5 and the total molecular weights ranging from 2,200 g/mol ($N = 16$) to 169,000 g/mol ($N = 1246$) were synthesized by a

sequential reversible addition–fragmentation chain-transfer (RAFT) polymerization of PSM and PS. The morphologies of PSM-*b*-PS and PGM-*b*-PS samples in the bulk were investigated using SAXS analysis measured at room temperature after thermal annealing. Before the hydrolysis of the copolymers, a well-ordered lamellar microdomain morphology was observed with higher order reflections and a $L_0 = 2\pi/q^*$ of 53.4 nm for the highest molecular weight copolymer. With decreasing the molecular weight, the number of scattering peaks and the intensity of the primary reflection decreased as expected. The smallest ordered microphase-separated structure of PSM-*b*-PS was obtained as an L_0 of 12.0 nm with the weak primary reflection from the 14,500 g/mol sample. Consequently, copolymers with molecular weights less than 14,500 g/mol showed a phase-mixed (or disordered) morphology.

For the solid state transformation in the bulk, trifluoroacetic acid (TFA) vapor was applied to PSM-*b*-PS copolymers, since it has a relatively high vapor pressure (97.5 mmHg at 20 °C) and low boiling point (72.4 °C) compared to other acids. For different period of time, a powder of PSM-*b*-PS was exposed to TFA vapor in a sealed jar, and then the evolution of lamellar nanostructure from a phase-mixed state was examined by SAXS. After just 1 min of exposure to TFA, the 8,400 g/mol sample showed a diffuse primary reflection, and this peak shifted to lower q region with an L_0 of 10.8 nm with the appearance of higher order reflections at $2q^*$ and $3q^*$ by increasing the exposure time. From these results, it demonstrated that a disordered or weakly ordered state can be transformed into a highly ordered microphase-separated nanostructure through a simple solid-state chemical conversion of hydrophobic PSM block to hydrophilic PGM block using TFA vapor. This translates into a marked increase in the segmental interaction between the two blocks of the copolymer, forcing the formation of ordered structures even from low molecular weight copolymers.

After full hydrolysis of a series of PSM-*b*-PS copolymers by exposure to TFA vapor, the largest increase of L_0 was observed from 53.4 to 81.7 nm at the highest molecular weight sample due to the increase in χ which makes the polymer chains stretch more. By the strong microphase separation, many higher order reflections also appeared after hydrolysis in comparison to before that. Moreover, acetone, which is a byproduct of the hydrolysis reaction, acted as a plasticizer of the copolymer enabling the persistence of the lamellar morphology by increasing the mobility of polymer chains. The smallest full pitch lamellar microdomain in this study was shown as 5.4 nm with a higher order reflection from the total molecular weight of 2,200 g/mol (Figure 1). These results indicate that it could be possible to use PSM-*b*-PS copolymers for high-resolution lithography with sub-3 nm features.

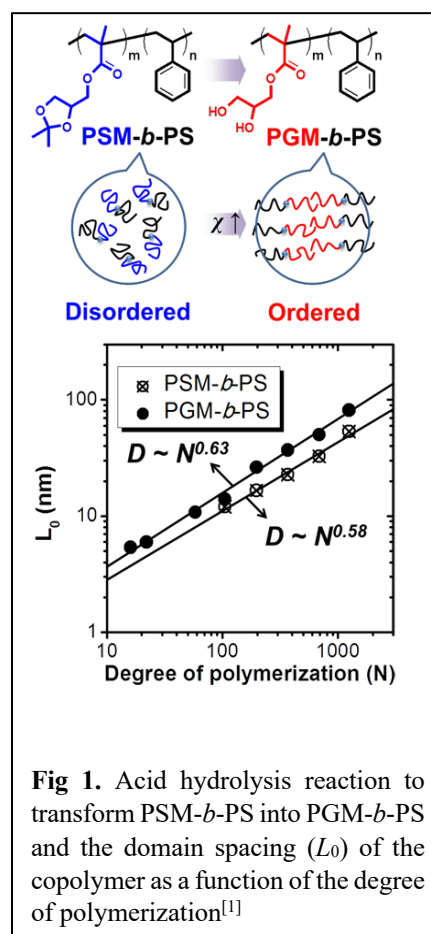
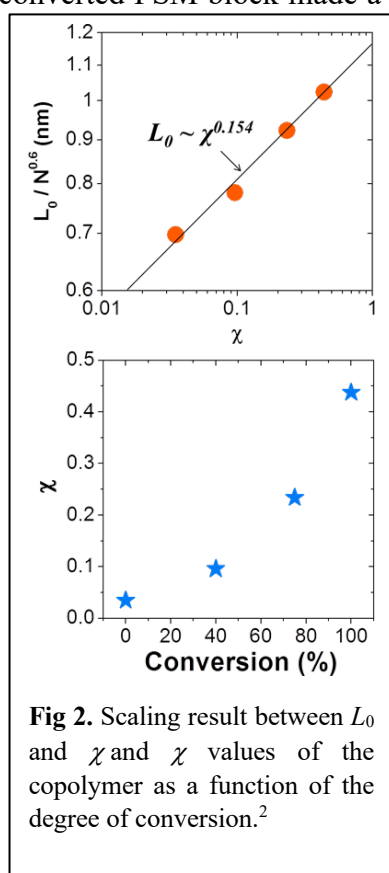


Fig 1. Acid hydrolysis reaction to transform PSM-*b*-PS into PGM-*b*-PS and the domain spacing (L_0) of the copolymer as a function of the degree of polymerization^[1]

Evaluation of the Interaction Parameter for PSM-*b*-PS Copolymers: The exact χ values for PSM-*b*-PS were determined as a function of the degree of hydrolysis of PSM into PGM using a mean-field correlation-hole analysis of the scattering in the phase-mixed state as shown Figure 2. Previously, we performed the solid-state chemical transformation of PSM block into PGM block using TFA vapor. However, it showed that PSM block in the copolymer did not convert randomly to PGM block because the acid vapor diffuses into the solid sample from the surface. As a result of this nonuniform conversion for the copolymer chains, broadening or splitting of the primary reflection was observed. To ensure that the conversion of PSM segments occurs randomly, acid hydrolysis was conducted in solution state instead of solid state. This solution route was also effective in adjusting the degree of conversion by the hydrolysis time. Therefore, PSM-*b*-PS copolymers dissolved in 1,4-dioxane were reacted with 1 N HCl for different periods of time and then ^1H NMR spectroscopy was used to quantify the transformation of PSM into PGM.

To observe the changes in the self-assembly behavior, absolute intensity SAXS profiles for PSM-*b*-PS copolymers with different degree of hydrolysis were measured at room temperature after thermal annealing. A single microphase-separated lamellar structure was seen for all the SAXS profiles, indicating that the hydrolysis reaction occurred randomly. With increasing the degree of conversion, multiple higher order reflections appeared due to the strongly microphase-separated morphology between hydrophobic and hydrophilic blocks. From the full width at half-maximum (FWHM) result, it was evident that the randomly converted PSM block made a change in the symmetric lamellar morphology. In addition, the



remarkable shift in q^* to a lower region during the transformation indicated the increased stretching of the two blocks by the increase in nonfavorable interaction at the interface.

Using temperature-dependent SAXS profiles and correlation-hole scattering analysis^[3-5], χ for PSM and PS as a function of the degree of conversion was examined. For the pristine copolymer, the χ value was found to be given by $\chi = 0.020 + 4.7/T$ (~ 0.035 at 25 °C) at a 118 Å³ reference volume, which is larger than that of PS-*b*-PMMA (~ 0.031 at 25 °C)^[6], using the 26,800 g/mol sample. However, the phase-mixed state was not accessible even at 27% conversion due to $\chi N > 10.5$ even up to 270 °C by the increase in χ . Therefore, the lower molecular weight samples should be evaluated to obtain χ for the randomly or fully converted copolymers. Using the 10,500 g/mol sample, the χ values for 40% converted PSM and PS as a function of the inverse temperature were fit to $\chi = 0.051 + 13.33/T$ at the phase-mixed state (over 200 °C). ~ 0.096 at 25 °C was calculated from this equation, which is 2.7 times larger than that for PSM and PS. To obtain the χ values for 75% and 100% converted copolymers, SAXS analysis on the samples having 4,180 g/mol and 2,200 g/mol

was conducted. Owing to their lower N , the ODT behavior was observed with diffuse scattering

profile even at 75 and 100% conversion. With the reference volume of 118 \AA^3 , the χ values were plotted as a function of the inverse temperature and fit to $\chi = 0.159 + 22.5/T$ and $\chi = 0.314 + 36.9/T$ for 75% and 100% converted copolymers, respectively. From the equation for 100% hydrolysis, the χ value for PGM and PS was calculated to be ~ 0.44 at $25 \text{ }^\circ\text{C}$, which is much larger than those reported in recently^[7-9]. This noticeable increase in χ resulted in highly ordered lamellar microdomains evidenced by the multiple higher order reflections and enabled the access to lamellar structure with 5.4 nm full pitch domain from the smallest molecular weight sample.

Lamellar Microdomain Orientation of PSM-*b*-PS Thin Films: In general, BCP microdomains are oriented parallel to the substrate because one of blocks prefers to interact with the substrate when thermal annealing above the glass transition temperature is applied to BCP thin films. To orient the microdomains normal to the substrate, it is necessary to control the surface energy between a BCP and substrate by grafting hydroxyl-terminated random copolymers onto the substrate, called as a brush layer. This makes the surface of the substrate neutral and leads to a perpendicular orientation of the microdomains^[10].

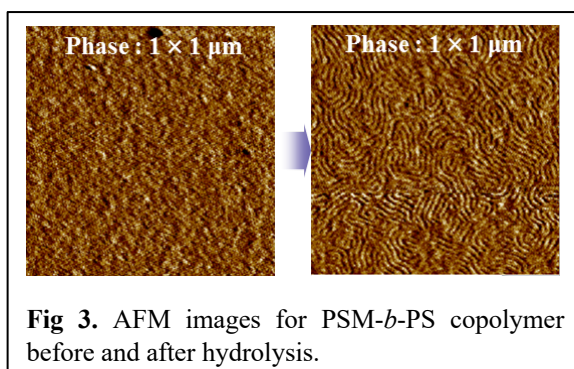


Fig 3. AFM images for PSM-*b*-PS copolymer before and after hydrolysis.

The hydroxyl terminated PSM-*r*-PS copolymer with $f_{\text{PSM}} = 0.5$ was anchored to the substrate to neutralize the surface. When PSM-*b*-PS is transformed into PGM-*b*-PS, the brush layer is also simultaneously changed to PGM-*r*-PS by exposure of acid vapor. Considering this effect, the fraction of the random copolymer between two components is important to balance the interfacial interaction and orient the lamellar microdomains perpendicular to the substrate. From atomic force microscopy (AFM) measurement, we confirmed that the microphase-separated lamellar microdomains were observed on the surface of film after TFA vapor treatment using the $26,800 \text{ g/mol}$ sample (Figure 3). To obtain the well-ordered BCP microdomains normal to the surface using the lower molecular weight samples, the effect of the film thickness, the composition of brush layer, and the degree of conversion on the surface morphologies will be researched further.

1. Morphological Evolution of PSM-*b*-PS Copolymers in Thin Films:

In this work, we have examined the morphological evolution of lamellar-forming PSM-*b*-PS copolymers in the thin films as a function of exposure time to trifluoroacetic acid (TFA) vapor.^{1,2,11,12} Through solid-state hydrolysis of the hydrophobic SM segments to hydrophilic GM segments, a large difference in the interfacial energies between PS and PGM on the silicon substrate was generated;

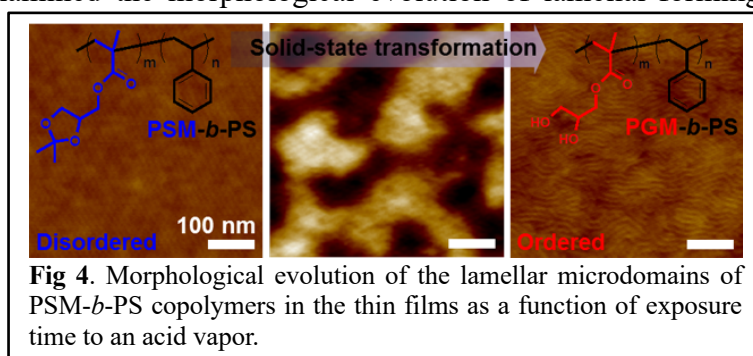


Fig 4. Morphological evolution of the lamellar microdomains of PSM-*b*-PS copolymers in the thin films as a function of exposure time to an acid vapor.

however, it was mitigated by using a hydroxyl-containing P(SM-*r*-S) copolymer with 31 mol % SM, which can be concurrently transformed into P(GM-*r*-S) with the BCP, to mediate interfacial interactions. AFM and GISAXS measurements showed that the disordered PSM-*b*-PS was converted into well-ordered PGM-*b*-PS in the thin film with lamellar microdomains oriented normal to the substrate surface arising from the strong microphase separation due to a significant increase in χ . The minimum period of vertically-oriented lamellar microdomains on a random copolymer brush layer was 9.4 nm, achieving sub-10 nm full pitch lamellae oriented normal to the substrate via thermal annealing without any additional layer is notable since these features are smaller than those reported for most of the thermally annealed BCPs. In addition, this responsive BCP showed sufficient etching contrast with RIE which can be useful for advanced nano-patterning. The further advancement of the current method to achieve a perpendicular orientation of the lamellar microdomains using PSM-*b*-PS with even lower molecular weights (2,200–4,000 g/mol) can enable a route to sub-6 nm full pitch lamellar patterns for the next-generation lithographic technology.

Two-Step Chemical Transformation of PS-*b*-PSA Copolymers for Increasing χ : We have demonstrated the self-assembly of PS-*b*-PSA copolymers, synthesized by sequential ATRP as

a new responsive high χ BCP, into lamellar or cylindrical nanostructures with sub-8 nm domain spacings through a two-step acid-catalyzed hydrolysis.¹² In contrast to PSM-*b*-PS copolymers, when PS-*b*-PSA is exposed to a dilute strong acid, the PSA block is converted to PGA block, and then further hydrolysis yields PAA, since the acrylic ester of PGA is more susceptible to hydrolysis than the methacrylic ester found in PGM.

Simultaneously, the strength of segmental interactions increases as the PSA block is transformed to PGA and then to PAA, indicating that one block of this new responsive BCP becomes increasingly hydrophilic as the reaction proceeds. Therefore, SAXS analysis showed that the phase-mixed PS-*b*-PSA was converted into well-ordered PS-*b*-PGA and PS-*b*-PAA with multiple higher order reflections even at the very low molecular weight samples. Using the correlation-hole scattering analysis⁵⁻⁷ for the BCPs in the phase-mixed state, the χ values for PS-*b*-PGA and PS-*b*-PAA were found to be given by $\chi = 0.4886 + 20.89/T$ and $\chi = 0.8122 + 21.55/T$, with 0.558 and 0.885 at 25 °C and a 118 Å³ reference volume, which are ~9 and ~15 times greater than the pristine copolymer (0.061 at 25 °C), respectively. With the significant increase in χ after transformation, the cylindrical microdomain morphology having an L_0 of 6.9 nm was achieved from the low molecular weight of PS-*b*-PAA (~1,600 g/mol) which is the smallest domain pitch in this study. Consequently, it would be possible to use PS-*b*-PSA copolymers for the fabrication of ultrahigh-density arrays with a single nanometer feature size through a simple chemical transformation.

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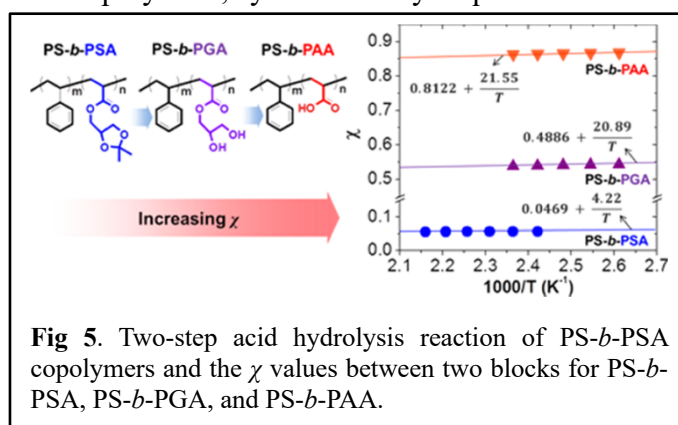


Fig 5. Two-step acid hydrolysis reaction of PS-*b*-PSA copolymers and the χ values between two blocks for PS-*b*-PSA, PS-*b*-PGA, and PS-*b*-PAA.

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6. Yu, D. M.; Smith, D. M.; Kim, H.; Mapas, J. K. D.; Rzyayev, J.; Russell, T. P. Morphological Evolution of Poly(solketal methacrylate)-*block*-polystyrene Copolymers in Thin Films. *Macromolecules* **2019**, *52*, 3592-3600. DOI: 10.1021/acs.macromol.9b00488.
7. Yu, D. M.; Smith, D. M.; Kim, H.; Rzyayev, J.; Russell, T. P. Two-Step Chemical Transformation of Polystyrene-*block*-poly(solketal acrylate) Copolymers for Increasing χ . *Macromolecules* **2019**, Accepted.

Invited Presentations

Yu, D. M.; Mappas, J. K. D.; Rzyayev, J.; Russell, T. P. Realizing 5.4 nm Full Pitch Lamellar Microdomains by a Solid-State Transformation. ACS March Meeting 2018, March 18-22, New Orleans, LA.

Graduate Students Supported (all Full Time)

Jaewon Choi, Hyeyoung Kim, Duk Man Yu, Mingqiu Hu

Patents

Russell, T. P.; Yu, D. M.; Rzayev, J.; Mapas, J. D. K. Method of Forming a Microphase Separated Block Copolymer and Microphase Separated Block Copolymer. Patent Application No. 16/179,078. (Filed with USPTO Nov. 2, 2018)