



Polystyrene-poly(2-ethylhexylmethacrylate) block copolymers: Synthesis, bulk phase behavior, and thin film structure



Ha-Kyung Kwon¹, Vanessa E. Lopez², Raleigh L. Davis, So Youn Kim, Adam B. Burns, Richard A. Register*

Department of Chemical and Biological Engineering, and Princeton Institute for The Science and Technology of Materials, Princeton University, Princeton, NJ 08544, USA

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ABSTRACT

Anionic polymerization was employed to synthesize well-defined diblock copolymers of polystyrene and poly(2-ethylhexylmethacrylate), PS-PEHMA. Diblock morphologies in bulk and in substrate-supported thin films were characterized by small-angle X-ray scattering (SAXS) and atomic force microscopy (AFM), respectively. PS-PEHMA diblocks exhibited thermotropic order-disorder transitions; one diblock showed a thermoreversible transition between lamellae and a higher-temperature morphology assigned as perforated lamellae. Unlike PS-poly(alkylmethacrylate) diblocks where the alkyl group is *n*-butyl or *n*-pentyl, PS-PEHMA diblocks showed a typical decreasing Flory interaction parameter with increasing temperature. Thin films of PS-cylinder-forming PS-PEHMA diblocks showed a strong preference for the cylinders to lie in the plane of the film; films of incommensurate thickness readily formed terraces. Films of commensurate thickness were easily aligned over macroscopic areas through the application of mechanical shear.

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1. Introduction

Over the past few decades, block copolymers of polystyrene (PS) and a wide variety of poly(alkylmethacrylate)s (PaMAs) have been synthesized, and their morphology investigated in both bulk and thin films. When the alkyl substituent is of intermediate length, *n*-butyl or *n*-pentyl, the polymers show an unusual non-monotonic dependence of the Flory interaction parameter χ on temperature, leading to disorder-to-order (DOT) behavior upon heating [1,2] or closed-loop ordered phase behavior [3], though when the *n*-alkyl substituent is shorter or longer, the usual monotonic decrease of χ with increasing temperature (*T*) is observed [4,5]. Branching of the alkyl substituent can also qualitatively influence the temperature dependence of χ : in common with *n*-pentyl, PS-PaMA diblocks with neopentyl alkyl groups also show a maximum in $\chi(T)$ leading to closed-loop phase behavior, while analogous diblocks based on

isopentylmethacrylate show only the usual decrease of χ with increasing *T* [6].

PS-PaMA diblocks have also been studied extensively in thin films for applications in pattern transfer (“block copolymer nanolithography”), especially PS-PMMA [7–11], though PaMAs with longer alkyl side groups have also been employed. For example, shear-aligned thin films of cylinder-forming PS-PHMA diblocks, where PHMA is poly(*n*-hexylmethacrylate), have been extensively employed by our group as templates for the fabrication of in-plane nanowire arrays, useful as polarizers for deep-ultraviolet radiation [12–15]. One unusual aspect of cylinder-forming PS-PHMA diblocks is that the through-plane orientation of the microdomains depends strongly on the film thickness: a film thick enough to contain 1.5 layers of cylinders does not terrace into regions which are locally 1 and 2 layers thick, but instead, the cylinders orient perpendicular to the substrate, even on simple oxide-coated silicon wafers [16]. While this behavior is interesting, it is a drawback for applications where a strictly in-plane orientation of the cylinders is desired.

2-Ethylhexylmethacrylate (EHMA) is a well-established, commercially-produced monomer widely used in the synthesis of products ranging from coatings to inks to oil additives [17]. However, despite the monomer's ready availability, and numerous studies of EHMA-based polymers dating back to 1948 [18] (for more

* Corresponding author. Tel.: +1 609 258 4691; fax: +1 609 258 0211.

E-mail address: register@princeton.edu (R.A. Register).

¹ Present address: Department of Materials Science and Engineering, Northwestern University, Evanston, IL 60208 USA.

² Present address: Department of Physics and Astronomy, California State University, Northridge, CA 91330 USA.

recent examples, see Refs. [19,20]), it does not appear that well-defined block copolymers of PS-PEHMA have been synthesized previously. PEHMA would be expected to show certain advantages over PHMA in the thin-film application alluded to above: the higher carbon number and branched nature of the alkyl sidegroup should yield a lower solubility parameter and lower surface tension for PEHMA over PHMA [21]. The lower surface tension should better enforce an in-plane arrangement of the PS cylinders in a PEHMA (vs. PHMA) matrix [22,23], and the lower solubility parameter should yield a higher χ and thus smaller minimum feature size [24] for PS-PEHMA vs. PS-PHMA diblocks. Here, we present the synthesis of well-defined PS-PEHMA diblocks via anionic polymerization, and an overview of their phase behavior in bulk and their structure in thin films, with an emphasis on polymers forming cylinders of PS, attractive as templates for in-plane nanowire arrays.

2. Experimental

2.1. Synthesis

All polymers were synthesized via anionic polymerization in a nitrogen-atmosphere MBraun UNILab glove box (<0.1 ppm O₂ and H₂O), in a cold well cooled to approximately $-70\text{ }^{\circ}\text{C}$ throughout the polymerization using a dry ice/isopropanol bath. Tetrahydrofuran (THF) solvent (Fisher Scientific) was purified by vacuum transfer from the purple sodium–benzophenone complex; styrene monomer (Aldrich) was vacuum transferred from dibutyl magnesium. For the EHMA monomer, the key impurity to remove is the alcohol (2-ethylhexanol), which can be sequestered by titration with a trialkylaluminum [25]; however, trialkylaluminums can also initiate free-radical polymerization in the presence of oxygen [25], and the trialkylaluminum also sequesters the radical inhibitor normally added to EHMA for storage. Thus, oxygen was first removed from the EHMA by three freeze–pump–thaw cycles; the monomer was then titrated in the glove box with trioctylaluminum (TOA, 25 wt% in hexanes, Aldrich) until the bright green–yellow color of the trialkylaluminum:methacrylate complex [26] was observed, and finally vacuum-transferred using a short-path apparatus. Some radical polymerization of EHMA still occurred in the still pot, presumably due to polymerization photoinitiated by the TOA:EHMA complex under ambient illumination [26], but the vacuum-transferred EHMA could be stored in the glove box freezer at $-20\text{ }^{\circ}\text{C}$ for at least ten days without polymerization. 1,1-Diphenylethylene (DPE, Aldrich) was vacuum transferred from *sec*-butyllithium (sBuLi), which reacts to form the red diphenylhexyllithium adduct. Polymerizations were run at approximately 10 wt% final solids content, using a 1L stoppered Erlenmeyer flask as the reactor to provide a large surface for heat transfer through the bottom of the cold well; the reactor contents were mixed via continuous magnetic stirring through the cold well jacket. Prior to polymerization, the reactor was rinsed with a dilute solution of sBuLi in toluene, followed by rinsing with purified THF. Lithium chloride (LiCl, Aldrich, anhydrous, ampule opened in glove box), 10 eq based on the subsequent sBuLi initiator charge, was dissolved in THF in the reactor and allowed to thermally equilibrate in the cold well for 60 min. Approximately 40 μL of styrene was then added to the reactor and titrated with sBuLi (1.4 M in cyclohexane, Aldrich) until a persistent yellow color was observed, indicating that all reactive impurities had been eliminated. The calculated charge of sBuLi was then quickly added; the remaining charge of styrene monomer was then added dropwise to facilitate a uniform distribution of styrene throughout the reactor, whose contents were now dark orange, during the rapid styrene polymerization. Styrene polymerization was allowed to proceed for

5 min after addition of the full styrene charge, whereupon 3 eq of DPE were added to the reactor, turning the reaction mixture dark red; a small aliquot was taken at this point for characterization of the PS first block. DPE reduces the nucleophilicity of the styryl anion [25,27,28], preventing unwanted side reactions during the crossover from PS to PEHMA, while LiCl prevents attack of the methacryloyl anion on the carbonyl group during EHMA polymerization [28]. The calculated EHMA charge was then added at once, turning the reaction mixture colorless; polymerization was allowed to proceed for 10 min, then terminated with excess degassed methanol. The polymer was recovered from the reaction mixture by precipitation into methanol, followed by vacuum drying at $160\text{ }^{\circ}\text{C}$. A PEHMA homopolymer was synthesized analogously, adding the DPE (3 eq based on intended initiator charge) to the THF and LiCl at the start of polymerization, and after thermal equilibration, titrating with sBuLi until the red color was observed; the calculated sBuLi charge was then added, and after approximately 1 min, the full EHMA monomer charge was added at once.

2.2. Molecular characterization

Diblock copolymer compositions (weight fraction polystyrene, W_{PS}) were determined via ¹H NMR spectroscopy in CDCl₃ on a 500 MHz Bruker AVANCE, using the areas of the PS aromatic protons (6.18–7.27 ppm) and the PEHMA sidegroup methylene protons (3.53–4.07 ppm). Polymer molecular weights were determined via gel permeation chromatography (GPC) in THF, using a Waters 515 HPLC Pump, two 30 cm Agilent PLgel Mixed-C columns operating at $35\text{ }^{\circ}\text{C}$, and Wyatt OptiLab T-rEX (differential refractive index, DRI) and miniDAWN TREOS (three-angle light scattering) detectors, both operating at 658 nm and $25\text{ }^{\circ}\text{C}$. The elution times measured via the DRI detector were calibrated with a series of narrow-distribution polystyrene standards. Measurements on the PEHMA homopolymer, using a separate Wyatt OptiLab rEX, yielded a specific refractive index increment $dn/dc = 0.0731\text{ ml/g}$ in THF at $25\text{ }^{\circ}\text{C}$. From comparison of this PEHMA homopolymer's true weight-average molecular weight from light scattering ($M_w = 144.4\text{ kg/mol}$) and its apparent "polystyrene-equivalent" molecular weight from the DRI data ($M_w = 100.6\text{ kg/mol}$), a hydrodynamic equivalence ratio [29] $r_h = 0.697$ for PEHMA (vs. PS) in THF was calculated.

The true molecular weights (M) of the diblocks can be determined from the GPC and NMR (W_{PS}) data in three different ways: 1) from M measured on the PS block aliquot, coupled with the NMR-derived W_{PS} ; 2) from the "polystyrene-equivalent" diblock M and the NMR-derived W_{PS} , using the Chang [29,30] combining rule and the measured $r_h = 0.697$; and 3) from the diblock light scattering data, using a weight-fraction-weighted [31] dn/dc (for PS in THF at $25\text{ }^{\circ}\text{C}$, analogous measurements yield $dn/dc = 0.1834\text{ ml/g}$ at 658 nm) and the NMR-derived W_{PS} . All computations were based on the number-average, M_n ; measured M_w values from light scattering were converted to M_n using the dispersity \mathcal{D} determined from the DRI data (polystyrene calibration). Below, we report M_n values determined using method #2, but we note that the values obtained with methods #1 and #3 were quite similar, with an average deviation of only 2.7%, a maximum deviation of only 6.5%, and no systematic bias (i.e., M_n values determined by one of the three methods were not systematically higher or lower than by the other two), further indicating the well-defined nature of these diblocks: narrow molecular weight distribution, and the absence of substantial contamination by homopolymer of either block. All diblocks are referred to as PS-PEHMA X-Y, where X and Y are the M_n values of the PS and PEHMA blocks, respectively, in kg/mol.

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