Synthesis of Ordered Fluorinated BCPs with One Block Composed of Random Copolymer

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A series of fluorinated block copolymers (BCPs), with one block composed of random vinyl copolymers were synthesized by reversible addition fragmentation chain-transfer (RAFT) polymerization. Despite of the hugely different properties of the two monomers in the random copolymer block, highly ordered lamellar structure with sub-10 nm resolution was observed by SAXS after 160 °C annealing for 24 h. Each micro-domain consisted of two uniformly distributed monomers, with a low T_g down to 24 °C.

Keywords: Random Copolymer, Fluorinated BCP, Low T_g , DSA

1. Introduction

As a potential candidate for sub-10 nm lithography technology, Directed Self-Assembly (DSA) with high resolution has attracted great attention from both academic and industrial fields. Block copolymers (BCPs) are the most common materials used for DSA [1-6]. Extreme Ultraviolet lithography technology (EUVL) [7] has entered high-volume-manufacture (HVM) era with 13 nm half-pitch resolution, while patterning technologies for sub-10 nm resolution is still under defined.

The most widely studied DSA material has been polystyrene-block-poly(methyl methacrylate) (PS-*b*-PMMA) [8-10], both of the two blocks show a high glass transition temperature (T_g), giving rise to plastic domains. Introducing rubbery block with low T_g into DSA material offers the possibility of thermal reflow to reduce the defect in the final pattern.

Our group recently reported several series of low-

T_g fluorinated BCPs capable of forming 4-8 nm microdomains, in which fluorinated block can drive BCPs to form lamellar line patterns [11-20]. In these cases, both of the two blocks are composed of one monomer. In this study, two monomers (one was methacrylate monomer, the other was a totally different vinyl monomer) of hugely different properties were randomly incorporated into one block, with the other block maintaining fluorinated methacrylate. After thermal annealing, ordered lamellar structure with sub-10 nm domain size was obtained, demonstrating that fluorinated block can also drive the two-component random copolymer block to form ordered structures. Each micro-domain consisted of two uniformly distributed monomers, with a low T_g down to 24 °C.

2. Experimental

2.1. Synthesis and characterization

Fig. 1. Synthesis route of PHFBMA-*b*-P(A-*r*-B) by RAFT polymerization

Table 1. Characterizations of P(HFBMA)₂₄-*b*-P(A-r-B)_n block copolymers

Sample	$M_{n,NMR}^a)$ (kg mol ⁻¹)	PDI ^{b)}	A/B ^{a)} in 2 nd block	DP _{A-B} ^{a)}	T _g ^{c)} (°C)	Morphology ^{d)}	<i>d</i> -spacing ^{e)} (nm)
S1	14.3	1.16	81/19	20	24&45	LAM	13.0
S2	9.8	1.13	74/26	8	46	LAM	12.9
S3	8.6	1.09	76/24	5	51	DIS	/

a) The molecular weight ($M_{n,NMR}$) and degrees of polymerization (DP) were determined by ¹H NMR. b) Polydispersity indexes (PDI) were determined by GPC in THF against PS standards. c) LAM represented lamellar morphology and DIS represented disordered structure. d) *d*-Spacing represented the domain spacing of block copolymer and was calculated by the equation as $d = 2\pi/q^*$, while q^* was the value of the first order peak in SAXS.

The PHFBMA-*b*-P(A-r-B) BCPs were synthesized via two-step RAFT polymerization. The macromolecular chain transfer agent PHFBMA was synthesized first, followed by adding monomer A and B to build the second block. All the other monomers and initiators were purchased from Energy Chemical or J&K and purified by neutral alumina column or recrystallization to remove inhibitors and impurities. All the solvents, including hexafluoroisopropanol (HFIP), tetrahydrofuran (THF), methanol and 2-acetoxy-1-methoxypropane (PGMEA) were purchased from Titan and used as received.

All the synthesized BCPs were purified by dissolution twice and precipitation.

Gel permeation chromatography (GPC) characterizations of the molecular weight (M_n) and molecular weight distribution (PDI = M_w/M_n) of the polymers were performed on a Shimadzu instrument equipped with a differential refractive index (RI) detector, and an ultraviolet (UV) detector. THF was used as the eluent at a flow rate of 1.0 mL min⁻¹.

Differential scanning calorimetry (DSC) of polymers was performed on a TA Instruments Q2000 equipped with a RCS 90 electric freezing machine under nitrogen flow at a heating or cooling rate of 10 °C min⁻¹. TGA was performed on a PE Pyris 1 and measurements were taken under a nitrogen flow with a heating rate of 10 °C min⁻¹.

The small-angle X-ray scattering (SAXS) diffraction patterns of powder polymer samples were collected on a Xenocs Xeuss 2.0 scattering system with a Pilatus 3R 200 K-A detector, which is equipped with Cu K α radiation wavelength of 1.54 Å.

2.2. BCP bulk sample preparation

For SAXS characterizations, the bulk samples were prepared as follows: 1 mL 10 wt % BCP solution in THF was drop-casted on a clean Si wafer. After the evaporation of THF, the samples were annealed at 160 °C under a nitrogen atmosphere for

24 h on a hot plate.

3. Results and discussion

3.1. Synthesis of PHFBMA-*b*-P(A-r-B)

The PHFBMA-*b*-P(A-r-B) BCPs were synthesized via two-step RAFT polymerization, and the corresponding synthetic route were presented in Fig. 1. The degree of polymerization (DP) of the macromolecular chain transfer agent PHFBMA was kept as 24. The GPC curves in Fig. 2 completely shifted to higher molecular weight, with PDI keeping relatively low (1.16), despite that the second block was composed of two monomers, indicating a uniform chain-to-chain monomer distribution.

Fig. 2. Overlaid GPC curves of PHFBMA (black) and PHFBMA-*b*-P(A-r-B) block copolymers (red) of block copolymer S1.

M_n , DP and composition of the random copolymer block (A/B) of PHFBMA-*b*-P(A-r-B) were measured by ¹H NMR and summarized in Table 1. All the PHFBMA-*b*-P(A-r-B) BCPs have various M_n , ranged from 8.6 kg mol⁻¹ to 14.3 kg mol⁻¹ with low PDI (<1.16), and the composition of the two monomers in the random block could be tuned

from 81/19 to 76/24.

3.2. Phase separation in the bulk

If the random copolymer is uniform enough to act as one-component block, microphase separation is expected in such BCPs. Actually, the resulting BCPs could sub-10 nm lamellar morphology after annealing at 160 °C for 24 h, as seen with SAXS in Fig. 3. Interestingly, BCP S1 and S2 exhibited similar d-spacings (13.0 nm vs 12.9 nm), although the DP of A-r-B block in BCP S1 was distinctly higher than that in BCP S2, which was attributed to the different incorporation amount of bulky monomer B in the random copolymer block. Further decrease of the DP of A-r-B block further to 5 resulted in disordered BCP.

Fig. 3. SAXS profiles of PHFBMA-*b*-P(A-r-B) block copolymers S1-S3.

3.3. Thermal analysis of PHFBMA-*b*-P(A-r-B)

The formation of random copolymer block was also demonstrated by the thermal analysis. As was shown in the DSC curves presented in Fig. 4, the T_g of PHFBMA homopolymer was 53 °C. With the DP of A-r-B increasing from 5 to 20, two T_g s were observed in the PHFBMA-*b*-P(A-r-B), the higher T_g corresponded to PHFBMA block and the lower T_g was assigned to P(A-r-B) block. This was because that the incorporation of low T_g monomer B (T_g of the homopolymer of B was below 0 °C while T_g of polymethacrylate was around 105 °C) would

dramatically decrease the T_g of the whole random copolymer block.

The thermal stability of PHFBMA-*b*-P(A-r-B) was also investigated by TGA, with a decomposition temperature (T_d) of 245 °C, ensuring their stability under 160 °C thermal annealing.

Fig. 4. DSC curves of block copolymers S1-S3 and PHFBMA homopolymer.

4. Conclusion

A series of fluorinated block copolymers with one block composed of random copolymer was synthesized by two-step RAFT polymerization. The resulted BCPs could form ordered lamellar structure with sub-10 nm domain size driven by fluorinated block after thermal annealing, confirming the uniformity of the random copolymer block. Each micro-domain consisted of two uniformly distributed monomers. Such a random copolymer block exhibited a low T_g , which could be tuned by the incorporated two components, indicating the possibility of achieving fine-tuning T_g as well as improved roughness for DSA patterning material.

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