High Etch Resistant Ferrocene-Containing Block Copolymers with 5 nm Patterning Capability

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A series of fluorinated block copolymers (BCPs) with ferrocene-containing block were synthesized via reversible addition-fragmentation chain-transfer polymerization. Highly ordered lamellar or hexagonal homogeneous ferrocene containing domains were observed by TEM. The smallest domain spacing measured by SAXS was 9.8 nm. Benefiting from the intrinsic etch resistance from the metallic domains, a high etch resistant BCP with 5 nm patterning capability was obtained.

Keywords: Etch Resistance, Block copolymer, Directed self-assembly, Ferrocene polymer, Ferrocene domain, Sub-5 nm

1. Introduction

Driven by the Moore’s law, the semiconductor industry has focused on the scaling down of feature size for more than half century. Recently, 13.5 nm extreme ultraviolet lithography (EUVL) technology has been implemented into 5 nm node HVM. With current 0.33 NA limitation, EUVL cannot resolve features smaller than 13 nm line / space. Compared to EUVL, directed self-assembly (DSA) exhibits extremely fine resolution up to 5 nm L/S, which is viewed as potential patterning technology for sub-10 nm even sub-5 nm feature size [1-9].

Recently, metal-containing EUV resists have been developed to improve etch resistance of ultra-thin EUV resist film [10,11].

More recently, our group reported a series of BCPs with a fluorinated block quickly formed sub-5 nm domains after 1 min thermal annealing at moderate temperature [12,13]. It is our hypothesis that the fluorinated side chains played a key role for the ultra-fine resolution and the patterning speed. However, due to the ultra-thin film, etch resistance is a major concern for sub-5 nm DSA materials.

Similar to EUV resist, ferrocene-based block copolymers (BCPs) were studied due to their excellent plasma etching selectivity [14-16]. Recent work by Cherny et al. obtained poly(ferrocenylmethyl methacrylate)-b-poly(nonafluorohexyl methacrylate) block copolymer, which displayed 19 nm domain spacing in thin films [17]. However, previously reported ferrocene-containing BCPs did not achieve sub-8 nm domain size.

In order to obtain high etch resistant DSA materials with 5 nm resolution, we synthesized fluorinated BCPs with a ferrocene-containing block. By controlling the length of the ferrocene block, the resulted BCPs displayed homogeneous Fe-containing lamella domains with minimum 4.9 nm width. We thus successfully obtained a high etch resistant DSA material with 5 nm resolution.

2. Experimental

2.1. Synthesis and characterization

In this study, a series of ferrocene-containing BCPs with relatively narrow polydispersity (PDI) (< 1.13) were synthesized by RAFT polymerization. All the monomers, initiators and materials were purchased from Energy Chemical and J&K. All the solvents (THF, hexane, DCM, methanol) were obtained from Titan and used directly without purification unless noted otherwise. 1H,1H-perfluorobutyl methacrylate was purified by passing through a neutral alumina column to remove stabilizer, and the ferrocene monomers were synthesized according to the method reported before [17,18]. Azobisisobutyronitrile (AIBN) was used...
after recrystallization from ethanol. 1,1,1,3,3,3-Hexafluoro-2-propanol (HFIP) and cyclohexanone were dried and de-oxygenated following standard procedures. Other chemicals were used as received without other purification.

We synthesized two different ferrocene-containing BCPs as shown in Scheme 1. All the polymers were purified by dissolution twice and precipitation, and subsequently characterized by gel permeation chromatography (GPC) using THF as an eluent and nuclear magnetic resonance (NMR) analysis.

$^1$H-NMR spectra and $^{19}$F-NMR spectra were acquired on a 400 MHz AVANCE III instrument using CDCl$_3$ as solvent and TMS as an internal standard. GPC measurements were used to calculate the molecular weight ($M_n$) and PDI. Narrowly distributed polystyrene samples were used as calibration standards. Small-angle X-ray scattering (SAXS) patterns were collected on a Xenocs Xeuss 2.0 SAXS, equipped with monochromatized X-ray ($\lambda = 1.54$ Å).

The morphologies of bulk samples were investigated via Hitachi HT7800 electron high contrast transmission electron microscope (TEM) equipped with an AMT BioSprint16L-ActiveVu CCD camera, operated at an acceleration voltage of 100 kV.

2.2. Preparation of bulk samples
For the preparation of bulk sample for SAXS measurement and TEM, solutions of the BCPs in THF was drop-cast on a silicon wafer and then dried in vacuum oven to remove the solvent. Then the samples were thermally annealed at corresponding temperature under a nitrogen atmosphere.

3. Results and discussion
3.1. Synthesis and characterization of BCPs
Two different ferrocene-containing methacrylate monomers were employed to synthesize BCPs. (Scheme 1).

The shift of GPC curves shows a good living nature of the RAFT polymerization of the two ferrocene monomers from fluorinated macro-initiator (PDI < 1.13, Fig. 1), which indicated the formation of the block copolymers. Resulted BCPs with different molecular weight ($M_n$) and various length of ferrocene-containing blocks were obtained by altering the monomer to initiator ratio.

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Fig. 2. $^1$H-NMR spectra of the block copolymers. Ferrocene peaks are observed in the spectra.

The $^1$H-NMR spectra further confirmed that ferrocene groups were incorporated into both BCPs, which showed the characteristic peaks around 4.0-5.0 ppm (Fig. 2).

3.2. TEM patterns and SAXS profiles

Morphologies and domain spacings of BCPs were further examined by TEM and SAXS. All the samples were thermally annealed at 160 °C for 12 h to complete phase separation. TEM pictures (Fig. 3) show clear bright and dark patterns. The dark part represents PMAEFC ferrocene-containing block, displaying a long-range ordered homogenous metal-containing domain in the BCPs. The domain size was consistent with the domain spacing obtained by SAXS (Fig. 4), the smallest domain spacing measured is 8.3 nm.

Fig. 3. TEM patterns of PHFBMA-b-PMAEFC. The bright and dark images correspond to PHFBMA (Fluro) and PMAEFC (Ferrocene) microdomains, respectively.

Similar to TEM, all the bulk samples were annealed at 160 °C for 12 h, followed by 2-D SAXS measurement at room temperature. The spectra were azimuthally integrated to obtain the 1-D scattering profiles (Fig. 4). The feature domain spacing $d$ was calculated by $d=2\pi/q^*$, in which $q^*$ is based on the location of the first order scattering peak.

The BCPs with ferrocene-containing block, PHFBMA-b-PMAEFC, all exhibited sharp first-order peaks, indicating a highly ordered structure (Fig. 4). Combined with TEM results, it can be concluded that lamella and hexagonal ferrocene domain exists in the BCPs, even though there is no 2$^{nd}$ or other scattering peaks were observed. The smallest domain spacing measured from $q^*$ was 9.8 nm similar to the TEM result.

Interestingly, a significant reduction of the peak intensity was observed, compared with our previous fluorine-containing BCPs [12,13], which might cause the disappearance of 2$^{nd}$ and other scattering peaks. It is very likely that the metalloocene domains reduced the X-ray scattering intensity.

Another BCP PHFBMA-b-PFMMA with conventional ferrocene block PFMMA displayed no SAXS scattering peak (Fig. 4), indicating no phase separation.

It is likely that the longer and more flexible spacer in PHFBMA-b-PMAEFC played an important role to achieved the fine phase separation.

Fig. 4. SAXS profiles of different ferrocene containing BCPs after 12 h thermal annealing at 160 °C. The domains spacing $d = 2\pi/q^*$, where $q^*$ is the position of the primary scattering peak. Data are shifted vertically for clarity.
4. Conclusion

In this study, we designed and synthesized a series of methacrylate BCPs composed of side chain ferrocene block and fluorinated ester block via RAFT polymerization. Confirmed by NMR and GPC characterization, ferrocene-containing BCPs with narrow polydispersity (PDI < 1.13) were successfully synthesized. PHFBMA-b-PMAEFC exhibits high chemistry incompatibility resulting in fine phase separation. The ferrocene methacrylate block with longer spacer formed homogeneous and highly ordered lamella or hexagonal domains after 12 h thermal annealing at 160 °C. So far, SAXS profiles and TEM patterns confirmed that the smallest domain spacing was ca. 9.8 nm (4.9 nm domain). Benefit from the homogeneous ferrocene-containing domains in the BCP thin film, intrinsic high etch resistance is expected. Hence, a high etch resistant ferrocene-containing 5 nm patterning material was obtained. Detailed investigation of etch resistance and DSA patterning capability is undergoing.

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