Ionic Liquid for Directed Self-Assembly of PS-b-PMMA

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The most widely studied block copolymer (BCP) for directed self-assembly (DSA) is poly(styrene-block-methyl methacrylate) (PS-b-PMMA). However PS-b-PMMA has a limitation of patterning size in sub-10 nm because the Flory-Huggins interaction parameter (χ) of PS-b-PMMA is approximately 0.038 at room temperature. To obtain sub-10 nm patterning size, many high χ BCPs and systems have been studied. We investigate DSA of PS-b-PMMA with blended an ionic liquid (IL) via thermal annealing with free surface under nitrogen. L0 becomes larger than pure BCP by adding ILs in this system since χ parameter becomes higher. However there is a problem that long time (>30 min) and/or high temperature (>200 °C) annealing conditions causes L0 shrink than in mild annealing condition (200 °C /1 min). Here, we report IL design to prevent L0 shrink. The design of IL that we found in this study achieved less than 5 % L0 shrink at 215 °C for 30 min annealing.

Keywords: directed self-assembly, block copolymer, ionic liquid, high χ, L0 shrink

1. Introduction

Directed self-assembly (DSA) technology is a promising approach for new generation lithography. The most widely studied block copolymer (BCP) is poly(styrene-block-methyl methacrylate) (PS-b-PMMA) from some reasons such as relatively simple polymer synthesis, resolution around 12 nm features with reasonable thermal annealing process, and simple surface control for perpendicular orientation. In addition, many studies to fabricate precisely controlled patterns of PS-b-PMMA were reported [1,2]. To further enhance resolution, such as sub-10 nm features, increasing of Flory-Huggins interaction parameter (χ), which means repulsion between two blocks, are required. Many studies about ionic liquid (IL) additives into PS-b-PMMA have been reported to achieve increasing the χ parameter [3-5]. Blakey et al. reported that PS-b-PMMA with blended IL (PS-b-PMMA/IL blends) can increase repulsion between PS and PMMA domains. It means that the effective χ (χeff) of PS-b-PMMA/IL blends system can be increased. The domain size and morphology of the system are depended on amount of IL additive [6-8]. Recently, we confirmed that decreasing of L0 value (L0 shrink) was caused after long time and/or high temperature annealing in this system. The L0 shrink should mean decreasing of χeff because L0 value is proportional to χ and degree of polymerization N known as $L_0 \propto \chi^{1/6} N^{2/3}$ [9]. Therefore, ILs to prevent the L0 shrink should be required to maintain high χ system after long time and/or high temperature annealing.

In this paper, a mechanism of L0 shrink in PS-b-PMMA/IL blends system is examined from a viewpoint of volatilization of IL by
long time and/or high temperature annealing. Moreover we provide a design of ILs to prevent L₀ shrink.

### 2. Experimental

#### 2.1. Materials

PS-\textit{b}-PMMA with \( M_n = 45000 \), PDI = 1.02, PS weight ratio of 50\%, lamellae and \( L_0 = 25.6 \) nm was prepared for \( L_0 \) measurement. Poly(styrene-\textit{ran}-methyl methacrylate) based neutral layers were prepared with various PS weight ratio.

Homopolymer of methyl methacrylate (PMMA) with \( M_n = 96000 \) and PDI = 1.04 was used for film thickness loss examination and thermolysis examination.

All ILs used in this study (IL-A to IL-D) were commercial available. The ILs were used as received.

#### 2.2. \( L_0 \) measurement of fingerprint pattern

BCP solution (PS-\textit{b}-PMMA blended 1.3 mol\% IL) was prepared for 25 nm film thickness. The solution was coated on 300 mm silicon substrate with a neutral layer. Film thickness was measured by NanoSpec3000. After prebake at 100 °C for 1 min, BCP annealing was applied at each condition (200 °C for 1 min, 200 °C for 30 min, 215 °C for 30 min) under nitrogen. For selective removal of PMMA domain in phase-separated BCP material, wet development with organic solvent was carried out following UV irradiation. Top-view images were collected by CD-SEM of Hitachi CG5000. \( L_0 \) values were measured by Hitachi CD measurement software.

#### 2.3. \( L_0 \) shrink evaluation

\( L_0 \) shrink ratio was calculated by equation (1):

\[
\text{\( L_0 \) shrink ratio (\%) = (\( L_0^\beta / L_0^\alpha \)) \times 100}
\]

where \( L_0^\alpha \) is \( L_0 \) value after annealing at 200 °C for 1 min and \( L_0^\beta \) is \( L_0 \) value after annealing at 200 °C or 215 °C for 30 min.

#### 2.4. Film thickness loss examination

PMMA solution (PMMA blended 7.0 mol\% IL) was prepared for 30 nm film thickness. The solution was coated on 200 mm silicon substrate. After prebake at 90 °C for 1 min, annealing was applied at 230 °C for 15 min under atmosphere. Remaining film thickness ratio after annealing was calculated by equation (2):

\[
\text{Remaining film thickness ratio (\%) = (FT_{anneal}/FT_{bake}) \times 100}
\]

where \( FT_{bake} \) is the film thickness after prebake and \( FT_{anneal} \) is the film thickness after annealing.

#### 2.5. Thermolysis examination

Samples were prepared by blending 12 mol\% IL into PMMA. The temperature that thermal weight loss of the sample occurred was defined by \( T_w^{\text{PMMA/IL}} \). \( T_w^{\text{PMMA/IL}} \) was determined using a Hitachi-hightech TG/DTA6200R thermal analyzer at a heating rate of 10 °C min\(^{-1}\) under air.

#### 2.6. Simulation tool

LogP values of each anion of ILs were simulated by CAChe WorkSystem Pro Version 6.1.12.33.

### 3. Results and Discussion

#### 3.1. \( L_0 \) shrink of PS-\textit{b}-PMMA/IL blends system

\( L_0 \) values of PS-\textit{b}-PMMA/IL-A blends at each annealing condition are shown in Figure 1. The results indicated that \( L_0 \) value was decreased after long time and/or high temperature annealing. Therefore IL which prevents \( L_0 \) shrink is needed for applying long time and/or high temperature annealing.

#### 3.2. Investigation of \( L_0 \) shrink mechanism

It is well known that IL is a good solvent for the PMMA domain and a poor solvent for the PS domain in PS-\textit{b}-PMMA [5]. Hence IL blended into PS-\textit{b}-PMMA is distributed to PMMA domain. If IL volatilizes by long time and/or high temperature annealing, the decrease of remaining film thickness of PMMA/IL blends would be happened. To
confirm whether $L_0$ shrink happened by volatilization of IL from PMMA domain, the trend of remaining film thickness ratio was compared to the trend of $L_0$ shrink ratio. Figure 2 shows the trends of remaining film thickness ratio at 230 °C for 15 min and $L_0$ shrink ratio at 200 °C for 30 min applying different ILs. They were almost the same trend, hence $L_0$ shrink was attributed to the volatilization of IL from PMMA domain. The fact that remaining film thickness ratio becomes large is a positive for $L_0$ shrink, because IL remains a lot in PMMA domain. $L_0$ shrink mechanism is that IL in PMMA domain decreases by volatilization under long time and/or high temperature annealing condition. Therefore IL which prevents volatilization is needed for this system. One of approach to prevent volatilization of IL should be making strong interaction between IL and PMMA domain.

3.3. Thermal property of ILs in PMMA domain

![Fig. 2. Remaining film thickness ratio (left axis) and $L_0$ shrink ratio at 200 °C/30 min (right axis) plotted as a function of ILs.](image)

Figure 3 shows the trends of $T_w$ PMMA/IL and $L_0$ shrink ratio at 200 °C/30 min applying different ILs. They were almost the same trend. Hence IL with high $T_w$ PMMA/IL prevent $L_0$ shrink.

3.4. Design of IL desirable for PS-b-PMMA/IL blends system

To confirm what is needed for high $T_w$ PMMA/IL, $T_w$ PMMA/IL of various IL was compared. Figure 4 shows $T_w$ PMMA/IL of ILs which varies in only a cation. $T_w$ PMMA/IL of IL with Cation-A was higher than the others. From this result, the cation of IL was fixed by Cation-A to achieve the design of desirable IL.

![Fig. 4. The effect of IL cation on $T_w$ PMMA/IL.](image)

The polarity of IL is attributed to LogP of IL anion. High polarity of IL anion would show high affinity with PMMA domain. Therefore IL with high polarity anion prevents volatilization by interacting strongly to PMMA domain.

From result of Figure 4-5, the combination to achieve the design of desirable IL was Cation-A and Anion-D (IL-D). IL-D exhibited highest $T_w$ PMMA/IL in ILs evaluated in this study, hence IL-D would be expected to prevent $L_0$ shrink. To
confirm whether the design of IL desirable for PS-b-PMMA/IL blends system had an effect on $L_0$ shrink, $L_0$ shrink ratio of IL-D was compared to the others. Figure 6 shows $L_0$ shrink ratio at 215 °C for 30 min applying different ILs. $L_0$ shrink of IL-D was improved almost as same as No IL (PS-b-PMMA only). This result demonstrates that the design of desirable IL is effective for $L_0$ shrink. The characteristics of ILs used in this study are summarized in Table 1.

![Figure 6. $L_0$ shrink ratio plotted as a function of IL types for PS-b-PMMA/IL blends.](image)

Table 1. Characteristics of ILs.

<table>
<thead>
<tr>
<th>Ionic Liquid</th>
<th>Cation / Anion</th>
<th>LogP$^a$ of IL anion</th>
<th>$T_{2,500,000}$ (°C)</th>
<th>Remaining film thickness ratio (%)</th>
<th>$L_0$ shrink ratio (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>IL-A</td>
<td>A / A</td>
<td>3.24</td>
<td>331</td>
<td>86.1</td>
<td>89.1</td>
</tr>
<tr>
<td>IL-B</td>
<td>B / C</td>
<td>2.06</td>
<td>332</td>
<td>94.5</td>
<td>95.9</td>
</tr>
<tr>
<td>IL-C</td>
<td>C / A</td>
<td>3.24</td>
<td>322</td>
<td>84.5</td>
<td>&lt; 90</td>
</tr>
<tr>
<td>IL-D</td>
<td>A / D</td>
<td>1.12</td>
<td>344</td>
<td>96.0</td>
<td>96.7</td>
</tr>
</tbody>
</table>


4. Conclusion

In this study, we reported the mechanism of $L_0$ shrink which happened to PS-b-PMMA/IL blends system by long time and/or high temperature annealing. Moreover, the design of IL desirable for this system to prevent the $L_0$ shrink was obtained from this study. The designed IL can achieve less than 5 % $L_0$ shrink at 215 °C for 30 min annealing, which makes the approach to DSA application.

Acknowledgements

This work was supported by the Nealey’s group and imec.

References