

Enhancement of Thermal Stability of Structural Color by the Substituent Effect in Polyhedral Oligomeric Silsesquioxane in Block Copolymers

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ABSTRACT

We prepared high-molecular-weight block copolymers (BCPs) composed of polystyrene (PS) brush blocks and polyhedral oligomeric silsesquioxane (POSS)-tethered polynorbornenes with variable composition ratios. By changing the substituents at the vertex of POSS from isobutyl groups to cyclopentyl ones, we evaluated the substituent effect on structural color and thermal stability against annealing. The BCPs modified with isobutyl groups showed clear structural color, while color changes were observed after annealing. By replacing to cyclopentyl groups, structural color was also presented, and improvement of thermal resistance was observed by heating. From the series of thermal analyses, it was proposed that thermal enhancement of cyclopentyl-substituted POSS domains could be responsible for the improvement of thermal stability of structural color.

INTRODUCTION

Structural color, generated from ordered nanostructures consisting of periodic low and high refractive-index domain sequences, is advantageous for constructing a robust optical material because of extremely-high resistance against photo-degradation which is inevitable in organic pigments. Photonic crystals are regarded as a promising platform for obtaining structural color. BCPs occasionally have self-assembling properties, followed by the formation of 1D, 2D and 3D periodic structures [1–5]. Therefore, based on periodic structures observed in the films of BCPs, various types of photonic crystals have been fabricated [6,7]. Very high-molecular-weight polymers were synthesized, and it was shown that the films exhibit selective reflection of certain wavelength light in the visible region originating from regular structures on the order of several hundred nanometers [8–11]. However, structural colors were often perturbed after annealing due to intrinsic lower thermal stability of polymers than inorganics [8,12]. Therefore, construction of heat-resistant BCP photonic crystals is still challenging for developing robust materials.

When polymers and silicate are homogeneously mixed at the nanometer or molecular scale, thermally-stable materials, called as organic–inorganic hybrids, can be obtained [13]. Because of superior environmental resistance originating from inorganic components, hybrids are especially a suitable scaffold for constructing optical materials. However, intrinsic low miscibility of organic materials toward inorganic species is still a critical problem for obtaining desired functions from hybrid materials. To solve critical miscibility mismatches between polymers and inorganics and extend applicability to a wide variety of functional polymers, we have proposed the idea of POSS-based hybrids [14]. POSS has a silica cube and its physical properties can be tuned by various types of

chemical reactions at vertices [15–17]. Therefore, it is possible to realize good dispersion state in various matrices by selecting appropriate substituents with or without the connection through covalent bonds [18–31]. In particular, owing to rigidity of the silica cube, POSS-dispersed polymeric materials show higher thermal stability and mechanical durability than those of pristine polymers. For instance, we prepared elastic hybrids by introducing POSS into the chain ends of polyurethane [25]. Thermal stability can be enhanced by the POSS modification as we expected. Especially, owing to good affinity of the POSS units, conjugated polymers, such as polyfluorene, were able to be loaded into the hybrid [26]. As a result, mechanical sensors were obtained on the basis of luminescent-property changes when the hybrid films are deformed. Thus, POSS is a facile “element-block”, which is a minimum functional unit consisting of heteroatoms [32], for preparing hybrids according to preprogrammed designs.

By applying the idea of POSS-based hybrids, it has been demonstrated that thermal enhancements have been accomplished in various materials which have been hardly applied in organic–inorganic hybrids. As a typical example, by incorporating the POSS unit into ionic liquids and ionic liquid crystals, lower melting temperature and higher degradation one can be induced [33–35]. Consequently, the temperature range as a liquid crystal can be extended. As readily expected, simple addition of silicate in ionic liquids as well as ionic liquid crystals, thermal reinforcement is not detectable without increasing melting temperatures [36]. Furthermore, characteristic behaviors have been reported from the series of POSS ionic liquids [37,38]. From these results, we presumed that regulation of molecular distribution of the POSS unit should be a key strategy for improving thermal properties without losses of other functions. In this research, to evaluate the substituent

effect on thermal stability of structural color, we prepared BCPs with two different types of substituents at the POSS moiety. Moreover, POSS has attracted attention as a building block for constructing nano-assembly and various unique functions have been discovered [39–44]. In the previous reports, POSS-containing BCPs were prepared [45], and particularly BCPs containing isobutyl-POSS show structural coloration [46–48]. We herein synthesized isobutyl-POSS-tethered high-molecular-weight BCPs and observed structural coloration from the films. However, by thermal annealing, undesired color changes were detected. Next, by replacing the substituents on the vertices of POSS to much more rigid substituents, such as a cyclopentyl group, color changes were successfully suppressed. From thermal analyses, it was clearly shown that cyclopentyl-tethered POSS domains should play a critical role in thermal reinforcement. This is the first example, to the best of our knowledge, to offer the enhancement of thermal stability of structural color in the hybrid materials by the substituent effect, which is the similar approach in the development of organic materials.

RESULTS AND DISCUSSION

Chemical structures of BCPs used in this study are shown in Figure 1. The POSS monomers for preparing BCPs were synthesized. From the incomplete cages, iBP(OH)₃[49] and CpP(OH)₃[50], the modified POSS derivatives with the single amine group, iBPNH₂ and CpNH₂, were prepared. The monomers (iPBNB and CpPNB) were obtained through the coupling reactions with *cis*-5-norbornene-*exo*-2,3-dicarboxylic anhydride. For constructing another block, the macromonomer PSNB was synthesized according to the previous literature ($M_n = 5.0 \times 10^3$ g/mol, PDI = 1.04) [8]. All monomers

can be kept in a glove box. Initially, with the synthesized POSS monomers, ring-opening polymerization was performed for preparing a macromonomer (Schemes S1–S3 and Tables S1 and S2). The molecular weights of the products were estimated as a relative value toward polystyrene standards with size-exclusion chromatography. It was shown that all products expectedly had high molecular weights (MW) and low polymerization distribution indices (PDI) [36]. Next, the BCPs involving POSS were synthesized (Scheme S4 and Tables S3 and S4). The series of products with variable molar fractions of the POSS unit (0.5, 0.55, 0.6, 0.65, 0.7 and 0.75) were prepared. From the analyses, it was shown that all polymers similarly have high MW and low PDI.

The polymer films were prepared through the solution method [18]. The tetrahydrofuran (THF) solution (about 2.5 mg / 50 μ L) of the polymer was dropped onto a quartz substrate. After drying in open air for 30 min, the samples were additionally dried under reduced pressure for 3 h. By increasing the POSS content, film-formability tends to be improved. Certain samples showed structural color and especially the series of (iBP)_x-*b*-(PS)_y with relatively high POSS contents exhibit obvious coloration (Figure 2). We surveyed morphology with scanning electron microscopy (SEM) with the (iBP)₁₅₀-*b*-(PS)₅₀ film, which show the most intense coloration of the samples (Figure S1). Significant periodic roughness[46] was hardly observed at the surface, implying that structural color should be generated from not structural pattern but distribution of each domain inside films.

To assess thermal properties, thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed with (iBP)₁₅₀-*b*-(PS)₅₀ and (CpP)₁₅₀-*b*-(PS)₅₀

having structural color (Table 1 and Figures S2 and S3). Almost same glass transition temperature (T_g) and decomposition temperature (T_d) were detected from both samples. According to the data on thermal properties of PS ($T_g = 73\text{ }^{\circ}\text{C}$, $T_d = \text{ca. } 380\text{ }^{\circ}\text{C}$), it is proposed that the PS brush domains are dominant on thermal properties. To assess the thermal properties of each component, the analyses were executed with homopolymers, p(iBP) and p(CpP). It was obviously observed that higher T_g and T_d were observed from p(CpP) than those from p(iBP), meaning that the cyclopentyl-POSS should intrinsically have larger stabilization effect. It is assumed that cyclopentyl groups can suppress molecular motions effectively because of the rigid cyclic structure, followed by improvement of thermal stability [51].

To evaluate optical properties, reflection spectra with (iBP)_x-*b*-(PS)_y were measured (Figure 3a). Compared to (iBP)₁₀₀-*b*-(PS)₁₀₀, higher reflectance was observed from the films with higher POSS contents. In particular, (iBP)₁₄₀-*b*-(PS)₆₀ and (iBP)₁₅₀-*b*-(PS)₅₀ showed much higher reflectance and red-shifted optical bands in the spectra. It is proposed that the periodic structures could be clarified by increasing the POSS content because of enhancement of rigidity to the main chains by the POSS units [46–48]. Furthermore, it is likely that regular spaces could be enlarged by the elongation of rigid polymer chains involving POSS. As a consequence, enhanced light reflection with bathochromic shifts should be induced in the BCPs with relatively-higher POSS contents.

These films were annealed at 150 °C for 1h (Figure 3b). After the treatment, the films of (iBP)₁₀₀-*b*-(PS)₁₀₀ and (iBP)₁₁₀-*b*-(PS)₉₀ hardly showed significant peaks. Although (iBP)₁₂₀-*b*-(PS)₈₀ and (iBP)₁₃₀-*b*-(PS)₇₀ showed reflectance peaks, intensity was critically

lowered after annealing. From (iBP)₁₄₀-*b*-(PS)₆₀ and (iBP)₁₅₀-*b*-(PS)₅₀, structural color was observed, while red shift occurred, indicating that POSS should play a significant role in the preservation of nanostructures inside films [23]. It is likely that structural alteration could proceed although thermal motions are suppressed by POSS with some degree.

Next, we evaluated the substituent effect by replacing isobutyl groups in POSS to cyclopentyl ones. Because of rigidity, lower mobility of cyclopentyl groups could be proposed in the film. Therefore, we presumed that stability of structural color could be improved against heating. The reflectance spectra of (CpP)_{*x*}-*b*-(PS)_{*y*} are shown Figure 3c. Regarding the POSS content, higher reflection followed by clear structural color was observed from the films with higher POSS contents. Similarly to the (iBP)_{*x*}-*b*-(PS)_{*y*} films, it is likely that the periodic structures could be clarified by the POSS units. In the films of (iBP)_{*x*}-*b*-(PS)_{*y*}, peak positions were red-shifted by increasing the POSS content, whereas it was found that (CpP)_{*x*}-*b*-(PS)_{*y*} showed the reflection band with almost same positions regardless of the POSS content in the shorter-wavelength region than (iBP)_{*x*}-*b*-(PS)_{*y*}. In order to understand these results, X-ray diffraction (XRD) patterns with iBP, CpP, p(iBP) and p(CpP) were compared (Figure S4 and Table S5) [36]. It was found that the *d*-space values of iBP and p(iBP) were larger than those of CpP and p(CpP), respectively, indicating that isobutyl-POSS should occupy larger spaces in the films than cyclopentyl-POSS. We also investigated morphology by wide-angle X-ray scattering measurements with cast films. Accordingly, similar patterns were obtained from both in-plane and out-of-plane measurements, meaning that anisotropy toward the substrate might be not significant (Figure S5). From these results, it was proposed that the periodic

structure became smaller because $(\text{CpP})_x\text{-}b\text{-(PS)}_y$ had a smaller structure than $(\text{iBP})_x\text{-}b\text{-(PS)}_y$. Thus, the reflection spectra had a peak top in the shorter wavelength region.

In order to evaluate thermal stability of structural color, the films of $(\text{CpP})_x\text{-}b\text{-(PS)}_y$ were annealed under the same condition (150 °C for 1 h). These reflectance spectra are shown in Figure 3d. Surprisingly, it was clearly shown that $(\text{CpP})_{140}\text{-}b\text{-(PS)}_{60}$ and $(\text{CpP})_{150}\text{-}b\text{-(PS)}_{50}$ apparently presented structural color even after annealing. Correspondingly, their reflectance spectra kept after the treatment. As mentioned in the thermal properties of each brush domain, it was shown that the T_g s of p(iBP) and p(CpP) were 93 °C and about 180 °C, respectively, representing that cyclopentyl groups can greatly suppress molecular motions in the film. Therefore, $(\text{CpP})_x\text{-}b\text{-(PS)}_y$ with high POSS contents can preserve their reflectance properties during annealing. From the films with lower POSS contents, reflection peaks disappeared after annealing, similarly to the samples of $(\text{iBP})_x\text{-}b\text{-(PS)}_y$, suggesting that a certain degree of POSS could be essential for expressing the thermal reinforcement effect.

CONCLUSION

In this study, structural coloration was accomplished with two-types of POSS-modified BCPs with different substituents. By introducing cyclopentyl groups into POSS, thermal reinforcement toward annealing was confirmed in the films of POSS-tethered BCPs. Restrictedly speaking, our structural color materials is out of the classic definition of a hybrid material where inorganic components should be well dispersed in the matrix. On the other hand, by controlling domain formation, thermally-stable polymer hybrids with structural color can be obtained based on POSS according to preprogrammed designs.

Our findings can contribute to extending the applicability of polymer hybrids for the substances which have been never hybridized and creating advanced materials with multiple functions originating from both organic and inorganic components.

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CONFLICTS OF INTERESTS

There are no conflicts of interest to declare.

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FIGURES AND TABLE

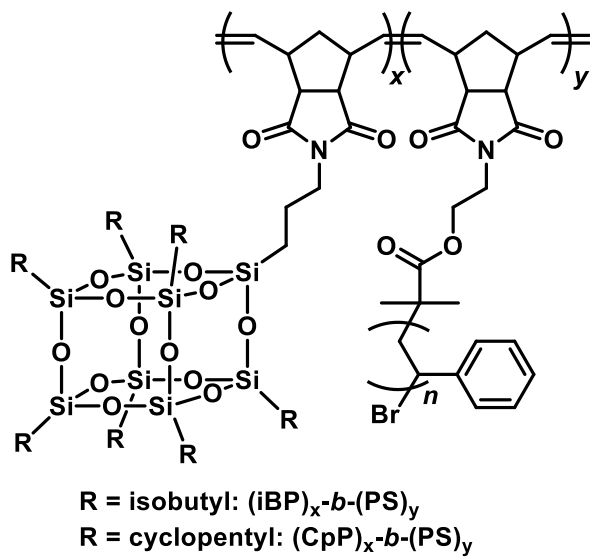


Figure 1. Chemical structures of BCPs with isobutyl- and cyclopentyl-substituted POSS.

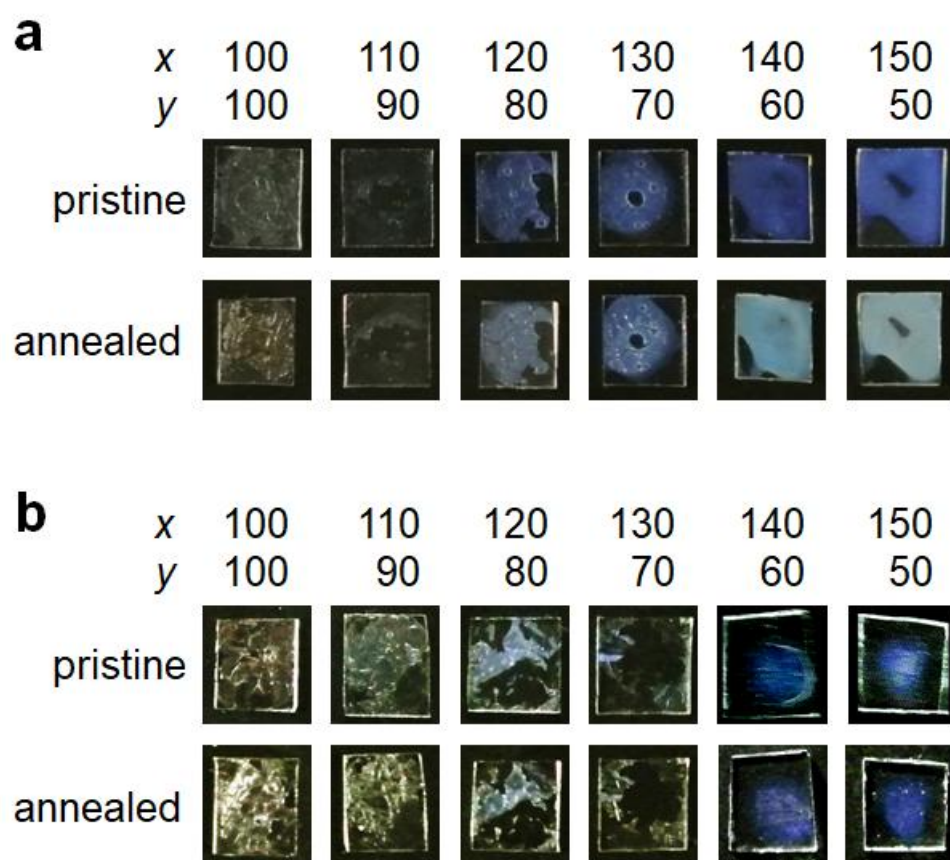


Figure 2. Pictures of the cast films of (a) $(iBP)_x-b-(PS)_y$ and (b) $(CpP)_x-b-(PS)_y$ before and after heating at 150 °C for 1 h.

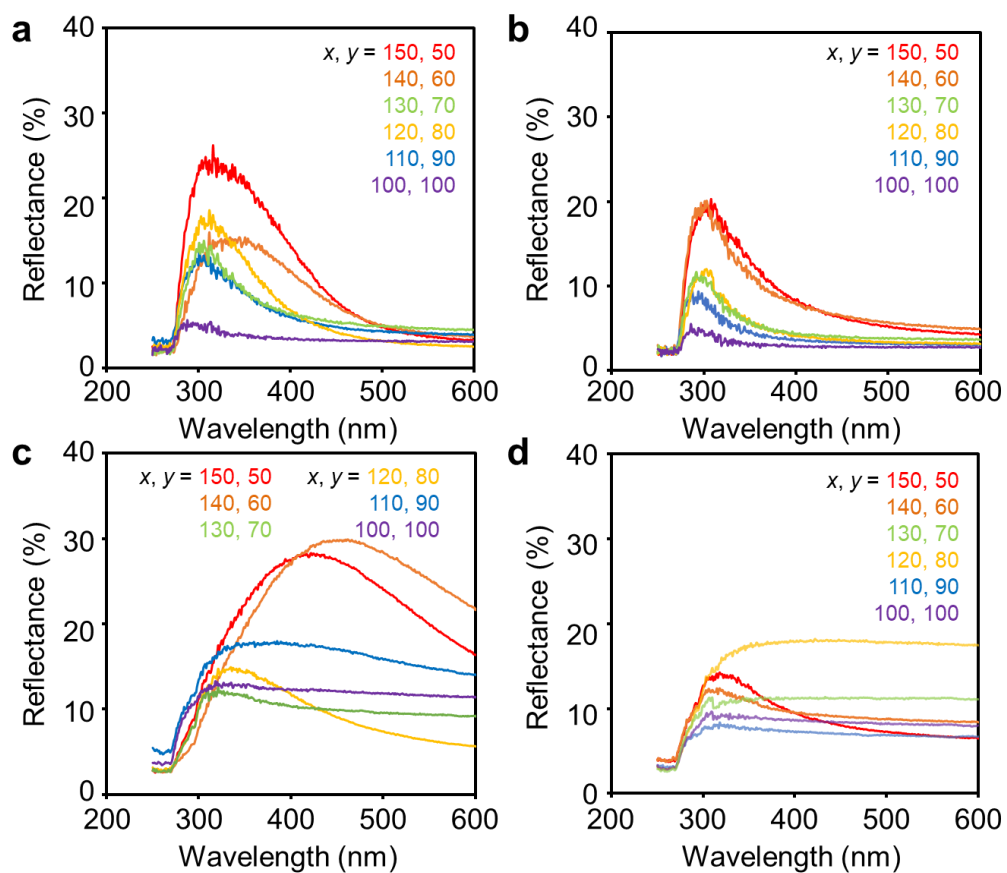


Figure 3. Reflection spectra of the films composed of (a,c) (iBP)_x-b-(PS)_y and (b,d) (CpP)_x-b-(PS)_y before (upper) and after (lower) heating at 150 °C for 1 h.

Table 1. Thermal properties of polymers

	T_g (°C) ^a	T_d (°C) ^b
(iBP) ₁₅₀ - <i>b</i> -(PS) ₅₀	105	410
(CpP) ₁₅₀ - <i>b</i> -(PS) ₅₀	105	406
p(iBP)	93	444
p(CpP)	182	453

^aDetermined from DSC curves.^bDetermined from TGA profiles.