Coloration by Microphase-separated Structures of Block Copolymer

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Abstract: When we prepared a film of a block copolymer with a number-average molecular weight (M_n) of 6.7×10^5 by solvent-casting, the solution had color and the hue that varied as the casting proceeded, and finally colored solvent-cast films were obtained. It was found that the wavelength at the maximum in the reflectivity spectrum related to the domain size of the microphase-separated structures in the solvent-cast films determined by ultra small-angle X-ray scattering (USAXS) measurement and using Bragg's law.

Introduction

When the domain size of microphase-separated structures of block copolymers is close to the wavelength of visible light, a cast film of those block copolymers will show a color caused by the Bragg-diffraction of visible wavelengths of light. In the case of microphase-separated structures of block copolymers, Bragg's law can be described by

$$2d\sin\theta = m(\lambda_0/n) \qquad \text{equation (1)}$$

where d, λ_0, and n are, respectively, domain size of microphase-separated structure, wavelength of light, and refractive index of the cast film. n is an

integer and is the order of the Bragg's reflection. If the cast film of the block copolymer showed some colors, d of the block copolymer in the cast film should be a few hundred nm, because the wavelength of visible light is 380 nm $<\lambda_0<$ 770 nm.

Recently we observed such colors as blue and green in the solvent-cast films of neat diblock copolymer (polystyrene-*block*-polyisoprene (PS-*b*-PI)) and of the mixture of the block copolymer with homopolystyrene (HPS) or dioctyl terephthalate (DOP). In this study, we will discuss the mechanism of the coloration observed in these solvent-cast films.

Experimental methods

Two kinds of the PS-*b*-PI and HPS were prepared by living anionic polymerization in cyclohexane with *sec*-butyllithium as an initiator. The number-average molecular weight, M_n's, of the PS-*b*-PI were 6.7×10^5 and 3.9×10^5, and their weight fractions of PS block were 0.24 and 0.39, respectively. The M_n of HPS was 9.3×10^4.

The PS-*b*-PI was mixed with HPS or DOP in various concentrations, and the solvent-cast films were prepared by solvent-casting from toluene solution.

The color of these solvent-cast films was determined by optical observation under white light. The reflectivity spectrum of the solvent-cast films was measured to determine the maximum reflective wavelength. The microdomain structure and the domain size were measured by USAXS.

Result and Discussion

The solvent-cast film, which consists of PS-*b*-PI and HPS with the weight fraction of HPS of 50 wt%, had a blue color, and the maximum reflective wavelength of this film was 509 nm (Fig 1). The microdomain structure

determined by USAXS was lamella structure with domain size being 165 nm.

From equation (1), the value of λ_0 at m=1 was estimated by using the domain size obtained by USAXS as d and the refractive index of polystyrene (1.59) as n. The obtained value was compared with the maximum reflective wavelength. In the blue colored solvent-cast film, the value of λ_0 estimated from equation (1) was 525 nm which gave good agreement with the maximum reflective wavelength. In an other solvent-cast film, colored green, the maximum reflective wavelength was also well correlated with the domain size obtained by USAXS (Table I).

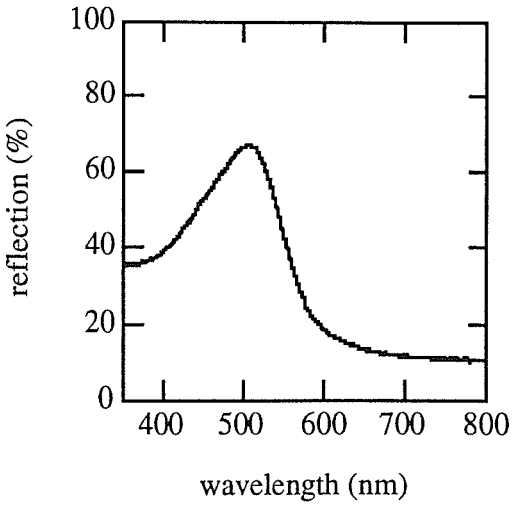

Figure 1. The reflectivity spectrum plotted as a function of wavelength for the solvent-cast film colored with blue.

Table I. The comparison of the values of λ_0 and d between the measurements of the maximum reflective wavelength and USAXS.

color		maximum reflective wavelength (nm)	USAXS (nm)
blue	λ_0	509	525[a]
	d	160[a]	165
green	λ_0	534	586[a]
	d	168[a]	184

a) estimated from eq.(1)

Conclusion

The solvent-cast films of block copolymers showed some colors. The coloration observed in these films was attributed to the microphase-separated structures with suitable domain size. These results will indicate the possibility of the coloring in the cast films by the control of the domain spacing in the microphase-separated structures.