

## Synthesis and microphase-separated structures of rod-coil triblock polymers

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### Introduction

The control of microphase-separated structures is one of the most important objects for polymer nanotechnology, and many studies were reported to develop the unique microphase-separated structures using special block copolymers such as branching block copolymers and crystalline-amorphous block copolymers. Especially, rod-coil type block copolymers have a potential to form unique microphase-separated structures. Poly(alkyl isocyanate)s (PIC) are constructed of amide main chains and behave as rigid rod polymers. The controlled polymerization of alkyl isocyanate monomers were reported by Novak [1] using organotitanium(IV) catalysts as an initiator for coordination polymerization.

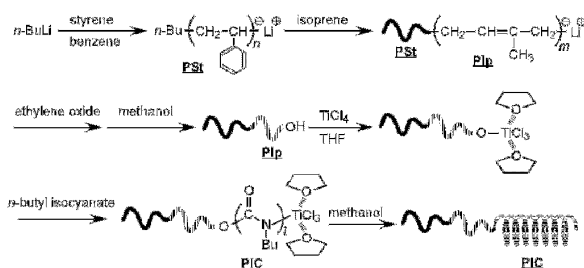
In this paper, using living anionic and coordination polymerization techniques, polystyrene (PSt)-*b*-polyisoprene (PIp)-*b*-PIC triblock polymers were synthesized and their microphase-separated structures were observed with TEM.

### Experimental

**Materials.** Styrene, isoprene, toluene, and THF were obtained from commercial suppliers and precisely purified for anionic polymerization. Ethylene oxide (EO; 3M Steri-EO Gas), *n*-butyl isocyanate (IC) and other solvents were used after distillation from calcium hydride. Titanium(IV) tetrachloride was used as received.

**Synthesis of triblock polymers.** Rod-coil triblock terpolymers were synthesized by a combination of anionic and coordination polymerization techniques shown in Scheme 1. First, hydroxy-terminated poly(styrene-*b*-isoprene) diblock precursors (PSt-PIp-OH) were synthesized by standard anionic polymerization procedure using EO as a terminator. The coordination polymerization of IC was completed from the macroinitiator prepared from PSt-PIp-OH and titanium(IV) tetrachloride in THF. The pure triblock terpolymers PSt-PIp-PIC were obtained after precipitation fractionation (THF/hexane = 1/1) to remove the unreacted macroinitiators.

Scheme 1. Synthesis of rod-coil block polymers



**Characterization.** The molecular weight and molecular weight distribution of triblock terpolymers and their precursors were determined using a gel permeation chromatography (GPC; Tohsok HLC-8120) equipped with three Styragel columns (G2000, GMH<sub>XL</sub> × 2) with THF as eluent at 40 °C and a flow rate of 1.0 mL/min. The GPC was calibrated with narrowly distributed polystyrene standards in the Mn range of 10<sup>3</sup> – 10<sup>6</sup> g/mol. The <sup>1</sup>H-NMR spectra were recorded on a JEOL GSX-500 NMR spectrometer using CDCl<sub>3</sub> as a solvent. The composition, total molecular weight and terminal functionality of the diblock precursors and triblock polymers were determined from the <sup>1</sup>H-NMR spectra.

**TEM Observation.** Transmission electron microscopic (TEM) observation was made on a JEOL JEM-200CX operated at 120 kV. The sample specimen was prepared by casting from 1 wt% chloroform solution on a carbon coated copper grid, and both polystyrene and polyisoprene domains were stained with RuO<sub>4</sub>.

### Results and discussion

**Synthesis of triblock polymers.** Hydroxy-terminated (PSt-PIp)s were prepared via anionic polymerization technique using EO as a terminator, and the introduction of hydroxyl groups were almost unity. The macroinitiators for the coordination polymerization of IC were synthesized with titanium(IV) tetrachloride and PSt-PIp-OH, and the molecular weight of PIC segments were controlled by feeding ratio of the macroinitiator to the IC monomer.

**Microphase-separated Structures.** The microphase-separated structures were observed with TEM (Figure 1). The zig-zag morphologies (Fig.1a,b) were observed for the high content of PIC ( $\phi_{PIC} > 0.6$ ) as reported by Thomas et. al. [2] Not only diblock copolymers, but also triblock polymers formed zig-zag morphologies. The hockey-puck structures (Fig.1c) were observed for only triblock polymers with  $\phi_{PIC} = 0.5$ . This hockey-puck structure has been predicted theoretically and not been reported experimentally. These unique morphologies were formed due to the crystallinity of PIC domains.

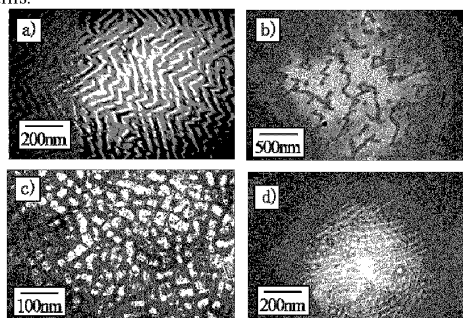


Figure 1. TEM micrographs of rod-coil block copolymers; a) PIP<sub>190</sub>-PIC<sub>450</sub>, b) PST<sub>140</sub>-PIp<sub>230</sub>-PIC<sub>1210</sub>, c) PST<sub>73</sub>-PIp<sub>39</sub>-PIC<sub>125</sub>, d) PST<sub>135</sub>-PIp<sub>33</sub>-PIC<sub>270</sub>

### Conclusions

The combination of living anionic and coordination polymerization techniques enabled to synthesize the polystyrene-*b*-polyisoprene-*b*-poly (butyl isocyanate) triblock polymers. Their microphase-separated structures observed with TEM were summarized in Figure 2. It shows the phase diagram for PSt-*b*-PIp-*b*-PIC rod-coil polymers, and it was found that  $\phi_{PIC}$  was the important factor to determine the microphase-separated structures.

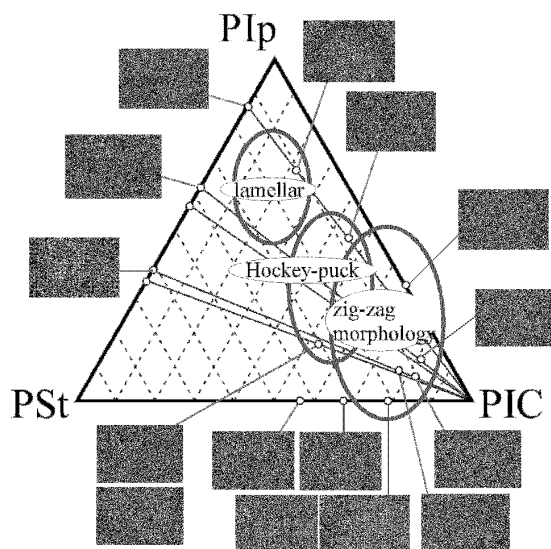


Figure 2. Phase diagram for the microphase-separated structures of the PSt-PIp-PIC observed with TEM

### References

- [1] Patten, T.E.; Novak, B.M., *J. Am. Chem. Soc.*, **1991**, *113*, 5056
- [2] Chen, J.T.; Thomas, E.L.; Ober, C.K.; Mao, G.P., *Science*, **1996**, *273*, 343