

## Phase Separation of Block Copolymer Synthesized via Catalytic ROMP Reaction

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A new block copolymer of cycloolefin was synthesized by catalytic block copolymerization. Nanoscaled phase separation of the block copolymer was observed by TEM, demonstrating the formation of the block copolymer by this method. The coexistence of plural nanostructures might be caused by broader polydispersity of the block copolymer.

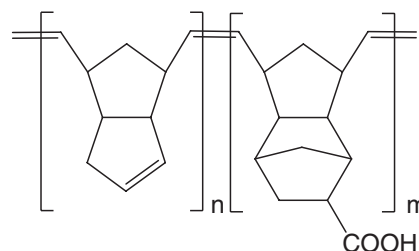
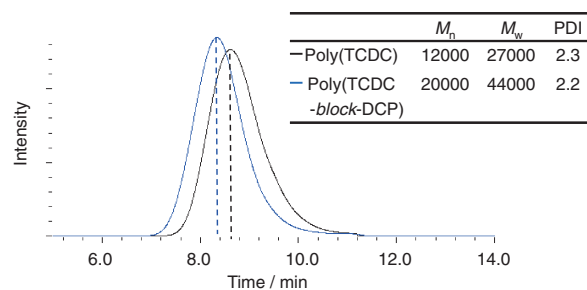
Ring-opening metathesis polymerization (ROMP) has been intensively studied in terms of both academic and industrial interest.<sup>1</sup> Living ROMP of cycloolefins can be carried out by choosing certain catalysts and multistage living ROMP of plural monomers enables block copolymerization easily.<sup>2</sup> Various block copolymers of cycloolefins have been investigated, since a lot of functional groups can be easily introduced into monomers and metal-carbene initiators are highly tolerant against several polar functional groups on the monomers.

However, one molecule of initiator is necessary to obtain one block copolymer chain by living polymerization. This indicates that a certain amount of metal complex is consumed for synthesis of a block copolymer. Production of block copolymers with reduced consumption of initiator is desirable for practical use.

To achieve this objective, two methods have been reported. (1) "Pulsed-addition" ROMP was studied by Matson et al.<sup>3</sup> where  $\alpha$ -olefin was employed as a chain-transfer agent (CTA), and 10 polymer chains with narrow polydispersity index (PDI) were produced by one Ru complex. (2) Catalytic synthesis of block copolymers via ROMP was investigated by our group.<sup>4</sup> A block copolymer of syndiotactic and atactic poly(*endo*-dicyclopentadiene), i.e., stereoblock poly(*endo*-dicyclopentadiene), was catalytically synthesized by utilizing reversible chain-transfer reaction of macro-CTA. Although obtained block copolymer had broader PDI, more than 800 block copolymer chains could be produced by one Ru carbene molecule. However, the synthesized stereoblock copolymer consisted of just one kind of monomer, which prevented us from further characterization of the formation of the block copolymer.

A block copolymer composed of incompatible polymer segments with narrow PDI is known to form nanometer-scale phase separation at an equilibrium state. In this report, a new block copolymer with polar and apolar segments has been prepared by the use of catalytic block copolymerization. 8-Carboxytetracyclo[4.4.0.1<sup>2,5</sup>.1<sup>7,10</sup>]dodeca-3-ene (TCDC) and *endo*-dicyclopentadiene (DCP) were used as monomers in order to satisfy this requirement of polymer design (Scheme 1). The self-assembling behavior of block copolymer with broad PDI is of high interest in this report.

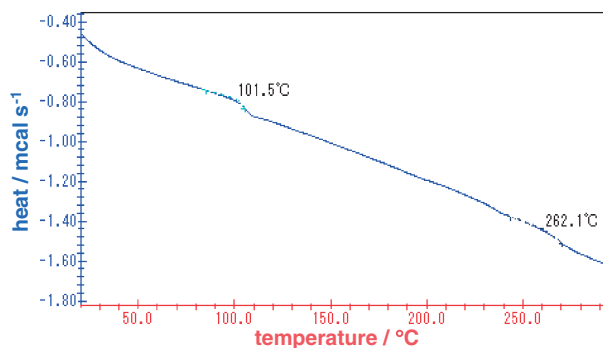
First, polymerization of TCDC was allowed to proceed with (H<sub>2</sub>IMes)(PCy<sub>3</sub>)Cl<sub>2</sub>Ru=C(H)Ph (Grubbs' 2nd generation catalyst) and 1-octene as a CTA, resulting in a tetrahydrofuran solution of poly(TCDC) with a terminal vinyl group after

Scheme 1. Chemical structure of poly(TCDC-*block*-DCP).Figure 1. GPC charts and molecular weights of poly(TCDC) and poly(TCDC-*block*-DCP).

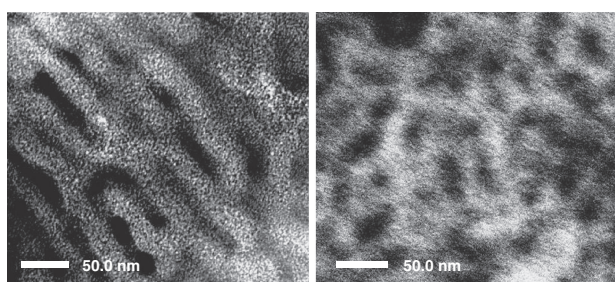
consumption of first monomer. A small amount of DCP was then added repeatedly to the solution, and the second stage of polymerization was completed. The detailed synthetic procedure is described in Notes.<sup>5</sup>

Figure 1 shows GPC charts and molecular weights of poly(TCDC) and poly(TCDC-*block*-DCP). The formation of the block copolymer is suggested by shift of the peak to higher molecular weight and retention of the PDI. This result is quite similar to our previously reported stereoblock copoly(*endo*-dicyclopentadiene). This indicates that many kinds of monomers with functional groups can be applied to this synthetic method. From <sup>1</sup>H NMR measurement, the composition ratio of the two segments was estimated to be TCDC:DCP = 45:55 (mol/mol).<sup>6</sup> Then, the double bonds in the obtained block copolymer were hydrogenated to form hydrogenated poly(TCDC-*block*-DCP) (H-poly(TCDC-*block*-DCP)) under the existence of hydrogen gas and Ru complex.<sup>7</sup> Less than 5% of unsaturated bonds remained in the polymer chain after the hydrogenation.

Differential scanning calorimetry was used to determine the thermal properties of H-poly(TCDC-*block*-DCP), and the results are shown in Figure 2. The observed glass-transition temperatures at 101.5 and 262.1 °C are quite similar to those of hydrogenated poly(DCP) and poly(TCDC), respectively. This implies that the large difference of the polarity of two block segments causes phase separation.



**Figure 2.** Second heating DSC chart of H-poly(TCDC-*block*-DCP) in the range of 20–300 °C under N<sub>2</sub> flow with a 10 °C min<sup>-1</sup> heating rate.



**Figure 3.** TEM images of the film of H-poly(TCDC-*block*-DCP). Sample preparation: After dying in CCl<sub>4</sub> solution of ruthenium oxide overnight, film was cut by microtome and the exposed section was observed.

In order to investigate the microstructure in the solid state, a film of H-poly(TCDC-*block*-DCP) was fabricated.<sup>8</sup> After dying with RuO<sub>4</sub>, the film was observed by transmission electron microscopy (TEM). The TEM images demonstrate that nanometer-scale phase-separation structures have been formed in the film, shown in Figure 3. The microdomain size was 20–30 nm and slightly larger than the average chain length of the present polymer. This phenomenon differs from block copolymers with narrow PDI and correlates well with published research from other groups about block copolymers with broad PDI.<sup>9</sup> The microdomain size is fixed by relatively longer chain segment in the block copolymer with broad PDI discussed by Noro et al.<sup>10</sup>

Furthermore, morphological regularity of the film was not so continuous as the small-angle X-ray scattering measurement of the film shows no peak. That is because different phase structures coexisted at an equilibrium state. Figure 3 shows lamellar-like phase and cylinder-like phase observed in the same film. This is quite different from the case of block copolymers with narrow PDI, where only lamellar structure should be obtained in this composition (45:55). It is assumed that this disorder is a result of the broad PDI of the polymer.<sup>11</sup>

In conclusion, a polar-apolar block copolymer H-poly(TCDC-*block*-DCP) was successfully synthesized by utilizing ROMP catalytic block copolymerization. Nanoscaled phase separation was observed in the film of the block copolymer. It was confirmed that the size of the microdomain structure was slightly larger than that of the polymer with narrow PDI. The macroscopic structural regularity was poor and plural phase

structures are observed, which might be the result of the broad PDI of the block copolymer. Further investigations about a relationship between the chemical structures of polymers and nanostructures in the solid state and about utilization of this synthetic method are currently under research.

## References and Notes

- 1 a) *Handbook of Metathesis*, ed. by R. H. Grubbs, Wiley-VCH, Weinheim, **2003**. b) K. J. Ivin, J. C. Mol, *Olefin Metathesis and Metathesis Polymerization*, Academic Press, San Diego, **1997**. c) G. C. Vougioukalakis, R. H. Grubbs, *Chem. Rev.* **2010**, *110*, 1746. d) R. R. Schrock, *Chem. Rev.* **2009**, *109*, 3211.
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- 3 J. B. Matson, S. C. Virgil, R. H. Grubbs, *J. Am. Chem. Soc.* **2009**, *131*, 3355.
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- 5 TCDC powder (50 g) and 1-octene (320 μL) was dissolved into tetrahydrofuran (THF) (500 mL). To this solution, (H<sub>2</sub>IMes)(PCy<sub>3</sub>)Cl<sub>2</sub>Ru=C(H)Ph (0.25 g) was added and heated up to 60 °C for 3 h with stirring. THF solution of DCP (50 g) was added separately in 5 portions at every 30 min. After the mixture was poured into methanol, poly(TCDC-*block*-DCP) was obtained as white powder (90 g).
- 6 By compared the area of vinyl proton to aliphatic proton of poly(TCDC-*block*-DCP), the composition ratio of the two segments was estimated (Figure S1 in Electronic Supporting Information (ESI) which is available electronically on the CSJ-Journal Web site, <http://www.csj.jp/journals/chem-lett/index.html>). Based on the polymerization nature of the (H<sub>2</sub>IMes)(PCy<sub>3</sub>)Cl<sub>2</sub>Ru=C(H)Ph, stereostructure of the obtained block copolymer was atactic. Ratio of the hydrogenated double bonds was estimated in the same manner with <sup>1</sup>H NMR chart of H-poly(TCDC-*block*-DCP) (Figure S2 in ESI).
- 7 THF solution (140 mL) of poly(TCDC-*block*-DCP) (10 g) was set into a 300-mL autoclave and a mixture of vinyl ethyl ether (0.5 mL) and (PCy<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>Ru=C(H)Ph (0.050 g) was added. Hydrogen gas was filled up to 1.0 MPa and reacted for 16 h at 160 °C. H-poly(TCDC-*block*-DCP) was obtained after reprecipitation from methanol (8 g).
- 8 The powder of H-poly(TCDC-*block*-DCP) was compressed under 8.0 MPa at 280 °C and kept under the identical condition for annealing. A transparent film of the block copolymer was obtained after 8 h of annealing.
- 9 a) A.-V. Ruzette, S. Tencé-Girault, L. Leibler, F. Chauvin, D. Bertin, O. Guerret, P. Gérard, *Macromolecules* **2006**, *39*, 5804. b) D. Bendejacq, V. Ponsinet, M. Joanicot, Y.-L. Loo, R. A. Register, *Macromolecules* **2002**, *35*, 6645.
- 10 A. Noro, D. Cho, A. Takano, Y. Matsushita, *Macromolecules* **2005**, *38*, 4371.
- 11 The present H-poly(TCDC-*block*-DCP) is a mixture of various block copolymers having different chain length of the two segments. This means some block copolymers are composed of long H-poly(TCDC) chain with short H-poly(DCP) chain, and some polymers might possess short H-poly(TCDC) chain with long H-poly(DCP) chain.