A New Method for Catalytic Syntheses of Block Copolymers via ROMP: Development of Stereoblock Copoly(*endo*-dicyclopentadiene)

Shigetaka Hayano and Yasuo Tsunogae*
R&D Center, Zeon Corporation, 1-2-1 Yako, Kawasaki-ku, Kawasaki 210-9507

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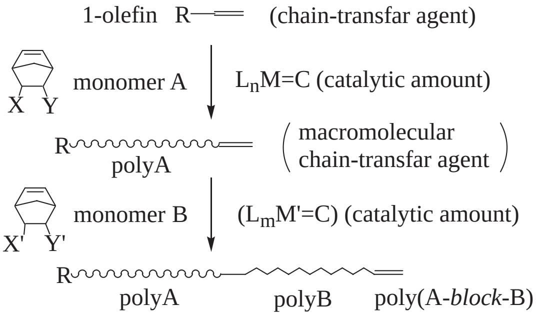
A new method for catalytic block copolymerization of cyclic olefins was developed for the first time. Cross metathesis was successfully utilized as a reversible chain-transfer reaction. Sequential addition of plural monomers to the polymeric terminal olefin provided a block copolymer of $M_w/M_n \approx 2.0$. This paper also focuses on the development of a new crystalline–amorphous block copolymer, hydrogenated stereoblock copoly(*endo*-dicyclopentadiene).

Block copolymers comprise two or more homopolymer segments linked by covalent bonds. One of the most convenient methods for preparing block copolymers is the multistage living polymerization of plural monomers. However, from the viewpoint of a practical application, the use of living polymerization seems a less efficient way, because one initiator molecule yields only one polymer chain. To date, many researchers have shown some excellent methods to overcome this defect.[1–3] To our best knowledge, precise control of chain-transfer might hold a key to accomplish “catalytic” block copolymerization.

The precise ring-opening metathesis polymerization (ROMP) of cycloolefins has also been intensively researched. The study of molybdenum alkylidenes and ruthenium carbenes has made a significant advancement upon metathesis chemistry, including living and/or stereoselective ROMPs and precise syntheses of tailor-made polymers.[4,5] Recently, we have developed iso- and syndio-selective ROMP catalysts useful for *endo*-dicyclopentadiene (DCP) and several norbornene monomers.[6] The tactic hydrogenated poly(DCP)s (H-poly(DCP)) are crystalline polymers, in contrast, the atactic counterpart is amorphous. Despite the great progress of metathesis chemistry, catalytic block copolymerization has not been studied yet.

Here, we wish to report a new ROMP system for a catalytic block copolymerization of exceptional versatility.[7] Scheme 1 describes a preliminary mechanism for the catalytic production of block copolymers based on the following hypothesis: in the early stage of the polymerization, a 1-olefin ($H_2C{=}CH\text{-}R$) is rapidly transformed into a polymeric terminal olefin ($H_2C{=}CH\text{-}P_n\text{-}R$) by cross metathesis, which might proceed via a α-addition selectively. In other words, the propagation reaction proceeds accompanying a reversible chain-transfer reaction (chain-swapping) in the presence of the 1-olefin and a suitable metathesis catalyst.



Scheme 1. Catalytic block copolymerization via ROMP.

The catalytic synthesis of stereoblock copoly(DCP), poly(*cis*,syndio-DCP-*block*-ata-DCP), was attempted by using a combination of $WNPhCl_4(Et_2O)\text{–}Et_2Al(OEt)$ (**1**) and $(H_2IMes)(PCy_3)Cl_2Ru{=}C(H)Ph$ (**2**; H_2IMes = 1,3-dimesityl-4,5-dihydroimidazolylidene). Figure 1 is the GPC elution curves of the stereoblock copoly(DCP). *cis*,Syndio-poly(DCP) having a terminal vinyl group was prepared with **1** and employed as a macromolecular chain-transfer agent (M-CTA).[8] To this M-CTA were added DCP and a catalytic amount of **2** for the second stage of the polymerization. It is quite interesting that the stereoblock copolymer was selectively afforded. That is, the molecular weight of the obtained polymer doubled retaining moderately narrow molecular weight distribution (MWD). No obvious peak attributable to remaining M-CTA and/or to a high molecular weight fraction was observed. The cis content of the obtained stereoblock copolymer was 75% and very close to the average of each segment. Indeed, M-CTA effectively controlled the molecular weight of the polymer: without using

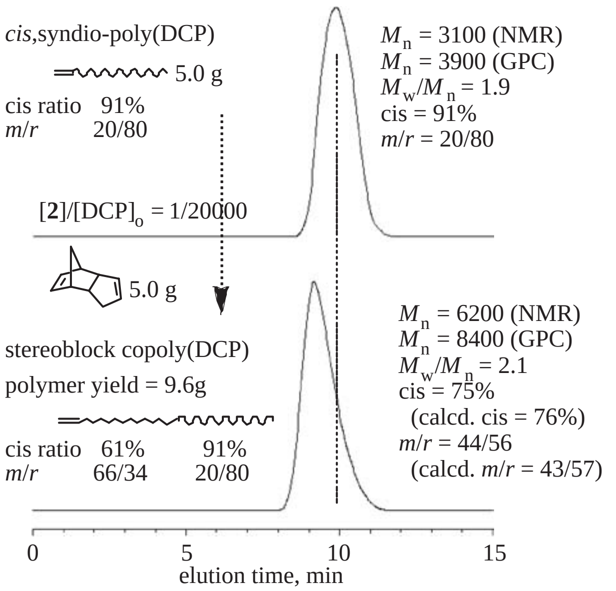


Figure 1. GPC profiles of the stereoblock copoly(DCP) obtained with **2** (polymerized in cyclohexane at 60 °C for 2 h, $[\text{M-CTA}]_o = [\text{DCP}]_o = 10\,\text{wt}\,\%$, $[\mathbf{2}]/[\text{DCP}]_o = 1/20000$ (mol/mol)).

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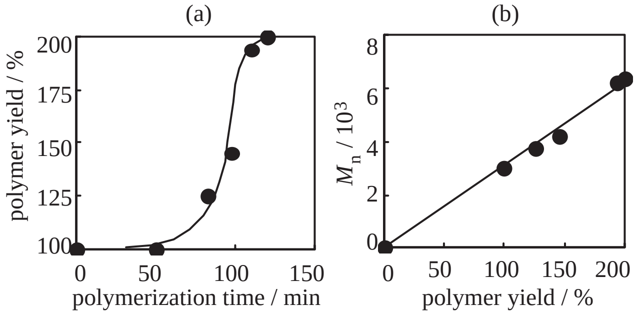

Figure 2. Time profile of the block copolymerization of DCP with **2** (polymerized in cyclohexane at 20 °C; $[\text{M-CTA}]_o = [\text{DCP}]_o = 10\,\text{wt}\,\%$, $[\mathbf{2}]/[\text{DCP}]_o = 1/20000$ (mol/mol)).

M-CTA, **2** polymerized DCP to produce ata-poly(DCP) of extremely high molecular weight.[9] The reversible chain-transfer seemed fast enough to produce block copolymer, but relatively slow: if chain swapping were more rapid than propagation, the M_w/M_n of the polymer chain would become smaller.

The time profile of the block copolymerization was investigated next. The polymerization had a long induction phase, indicating slow initial metathesis of **2** (Figure 2a). Polymer yield–M_n plot is shown in Figure 2b. The molecular weight of the polymer linearly increased with the incorporation of DCP, suggesting that the polymer chain number was identical to the number of M-CTA and constant during the present copolymerization. This result also supports the selective production of block copolymer.

It was confirmed that the internal olefins of the poly(DCP) were tolerant against catalyst **2** during the copolymerization. Both the *cis*,syndio-poly(DCP) and the ata-poly(DCP) were treated with various amount of **2** under similar reaction conditions.[10] It is noteworthy that the MWDs, cis contents and tacticities of the each polymer were not affected by **2**. This implies that no secondary metathesis proceeded for the polymer main chain.[11]

Further, the hydrogenation of the stereoblock copoly(DCP), which was yielded in Figure 1, was conducted in order to estimate its stereostructure. The C=C double bonds of the polymer chain were successfully saturated to obtain the corresponding hydrogenated product.[12] The m/r ratio was found to be 44/56 and almost identical to the expected value. The solubility of the hydrogenated poly(syndio-DCP-*block*-ata-DCP) was carefully investigated and found to be in between those of the crystalline syndio-H-poly(DCP) and of the amorphous ata-H-poly(DCP).[13] These results also support the selective formation of the stereoblock copolymer without any undesirable side reaction. DSC measurement characterized the crystalline nature of it. It displayed a glass transition ($T_g = 94\,°\text{C}$) and an endothermic peak at an elevated temperature ($T_m = 246\,°\text{C}$, $\Delta H = 17\,\text{J/g}$), which was comparable to those of the syndio-H-poly(DCP) ($T_m = 264\,°\text{C}$, $\Delta H = 39\,\text{J/g}$) and the ata-H-poly(DCP) ($T_g = 93\,°\text{C}$) of low MW (≈5000).

To conclude the present article, we have shown a new versatile method for the catalytic block copolymerization of cyclic olefins for the first time. This system was developed based on the introduction of the concept of reversible chain-transfer reaction into the ROMP chemistry. Not only DCP, but various kinds of norbornene derivatives could be potentially utilized with this system. The detailed nature of the present block copolymerization system will be reported in a future article.

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8 Polymerized in cyclohexane at 50 °C for 3 h; $[\text{DCP}]_o = 20\,\text{wt}\,\%$, isolated polymer yield was 90%. $[\text{DCP}]_o/[\text{1-octene}]_o/[\mathbf{1}] = 2000/600/1$ (mol/mol); $M_n = 3900$, $M_w/M_n = 1.9$ (by GPC); $M_n = 3100$ (by ^{1}H NMR), cis = 91%, $m/r = 20/80$. The degree of polymerization of the poly(DCP) could be estimated using the integration ratio of main chain peaks/chain transfer end peaks {i.e., the terminal n-C_6 [^{1}H NMR ($CDCl_3$) δ 0.88 (t, 3H, CH_3)] and the terminal vinyl group [^{1}H NMR ($CDCl_3$) δ 5.01 (dd, 2H, CH=CH_2)] on the opposite chain end}. Unfortunately, we have no information whether all the poly(DCP) chain possessed both chain-transfer end at this moment. At least, the results of block copolymerization suggested that almost all of the poly(DCP) possesses a terminal vinyl group.

9 Polymerized in cyclohexane at 60 °C for 2 h, $[\text{DCP}]_o = 20\,\text{wt}\,\%$, polymer yield was 95%. $[\text{DCP}]_o/[\mathbf{2}] = 20000/1$ (mol/mol); M_n 78000, $M_w/M_n = 7.1$, cis = 61%, $m/r = 66/34$.

10 Reacted in cyclohexane at 60 °C for 2 h; $[\text{poly(DCP)}] = 10\,\text{wt}\,\%$, $[\text{DCP unit}]/[\mathbf{2}] = 20000/1$–$2500/1$ (mol/mol).

11 In the course of the ROMP, intramolecular- and intermolecular-metathesis of the ring-opened polymer can potentially proceed. It is a side-reaction and known as a secondary metathesis. In order to attain the present catalytic block copolymerization, secondary metathesis must be completely avoided because it might yield various kinds of contamination, such as multi-block copolymers, some random copolymers via intermolecular-metathesis and oligomers produced via back-biting. When secondary metathesis occurs, the MWD and the microstructure of the polymer would also be influenced.

12 Hydrogenated by p-Tos-$NHNH_2$ in p-xylene at 120 °C for 6 h; $[\text{poly(DCP)}] = 5\,\text{wt}\,\%$, $[p\text{-Tos-NHNH}_2]/[\text{DCP unit}] = 4/1$.

13 Each of the H-poly(DCP)s was hardly soluble in *o*-dichlorobenzene at room temperature. The ata-H-poly(DCP) dissolved at 80 °C. As previously stated, the crystalline syndio-H-poly(DCP) was less soluble; it was slightly soluble at 150 °C and modestly soluble at 180 °C. It is worth to note that the stereoblock copoly(DCP) started to dissolve above 80 °C, and became completely soluble in *o*-dichlorobenzene at 140 °C.

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