1,4-Regulated Thermoplastic Elastomers

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Abstract. A series of 3-methylenecyclopentene (MCP) based block polymers are prepared by sequential polymerization of MCP, isoprene (IP) and/or butadiene (BD) by using rare-earth metal cationic catalyst. The resulting block copolymers are constituted by 1,4-poly(MCP), cis-1,4-poly(IP) and cis-1,4-poly(BD), which afforded AB type, ABA-type and ABC type copolymers. The AFM micrographs of triblock copolymer showed a remarkable phase-separation morphology of the 1,4-poly(MCP) block and cis-1,4-poly(IP).

1. Introduction
Nowadays there is increasing interest to synthesize green polymers from renewable resources to replace and resemble existing polymeric materials derived from fossil resources, because of dwindling oil resources, greenhouse effect and the pursuit of sustainable development [1-3]. However, most of efforts have mainly focused on the conversion of carbohydrates, fats and oils, and lignin into bio-based polymers. Terpenes, as a large and diverse class of organic compounds produced by a variety of plants, are seldom taken into consideration, although they have been known for hundreds of years as a solvent for paints and varnishes and a starting material for pharmaceuticals and fragrances etc. Until recently, terpene-based polymers attract increasing interests from academic and some progress has been achieved. For instance, pinene, and limonene are used for the synthesis of high performance polymers with radical or cationic catalytic catalysts. The linear terpene β-myrcene, readily obtained from essential oils or from the pyrolysis of pinene, has been converted into regulated elastomers with high molecular weight by rare-earth metal or iron based catalyst systems [4-6]. β-farnesene has been transformed into trans/cis-1,4-polymers by the iminopyridine-supported iron catalysts. Recently, our group reported the coordination polymerization of bio-based 3-methylenecyclopentene (MCP) by using rare earth metal catalysts. Nearly all rare-earth metal catalysts show perfect 1,4-regio-selectivity in different activities [7].
In this contribution, we explored the block copolymerization of MCP with isoprene by using rare-earth metal catalysts. Using the sequential polymerization of MCP, isoprene, and MCP, a crystalline thermoplastic elastomer bearing high cis-1,4-polysoprene segment was synthesized. The thermal behaviours of block copolymers were investigated by differential scanning calorimetry and atomic force microscopy (AFM) observations revealed the obviously phase separation of hard and soft segments.

2. Experimental
All manipulations were performed under a dry and oxygen-free argon atmosphere using standard high-vacuum Schlenk techniques or in a glovebox. All solvents were purified via an SPS system. ¹H and
$^{13}$C NMR spectra were recorded on a Bruker AV400 (400 MHz for $^1$H; 100 MHz for $^{13}$C) spectrometer. The molecular weight (Mn) was measured by TOSOH HLC-8220 GPC at 40 °C using THF as eluent (the flow rate is 0.35 mL/min) against polystyrene standards. The glass transition temperature (Tg) and melting temperature of the polymer was measured through differential scanning calorimetry (DSC) analysis, which was carried out on a METTLER TOPEM DSC instrument under a nitrogen atmosphere. Any thermal history difference in the polymers was eliminated by first heating the specimen to above 130 °C, cooling at 10 °C/min to room temperature, and then recording the second DSC scan from -130 to 130 °C at 10 °C min$^{-1}$. MCP was synthesized by the ring-closure metathesis reaction of β-myrcene according to literature reported [8]. Complex 1-3 were prepared according to the literatures [9-10].

Typical procedure for MCP and isoprene copolymerization by the sequential addition of both monomers: A typical sequential copolymerization reaction is given as follows (Table 1, run 1): A solution of [Ph$_3$C][B(C$_6$F$_5$)$_4$] (9.2 mg, 10 mmol) in toluene (2 mL) was added to a solution of complex 1 (10.0 mg, 10 mmol) in toluene (2 mL) in a 25 mL flask under a nitrogen atmosphere. The mixture was stirred at room temperature for a few minutes, and isoprene (0.28 g, 4 mmol) was firstly added under vigorous stirring. After 10 min of polymerization, MCP (0.32 g, 4 mmol) was then added to the polymerization solution. The copolymerization continuously proceeded for an additional 60 min at 60 °C and then was terminated by the addition of a small amount of acidic methanol containing 2,6-di-tert-butyl-p-cresol (1 wt%) as an antioxidant reagent. The mixture was poured into methanol (60 mL) to precipitate the copolymer product. The copolymer was collected by filtration, and dried under vacuum at 40 °C to a constant weight.

3. Results and Discussion

![Figure 1. Rare Earth Metal Dialkyl Complexes.](image)

All precursors 1, 2 and 3, in the presence of organoborate and aluminium alkyls, display high catalytic activity and cis-1,4 selectivity in isoprene and butadiene polymerization at room temperature. But in the MCP polymerization, the catalytic activity of precursor 1 is obviously lower than those of precursors 2 and 3 under same polymerization conditions. Interestingly, only precursor 1 can catalyse the block copolymerization of MCP with isoprene/butadiene with high 1,4-selectivity and moderate catalytic activity. Therefore, the copolymerization behaviour of precursor 1 was systematically explored and the polymerization data was summarized in Table 1.
Table 1. Block Copolymerization of MCP with IP and BDa

| Run  | Feed ratio [IP]/[MCP] | Temp. (°C) | Time (min) | MCP/IP | Yield (%) | 1,4-unit (%) | $M_n$ (10^4) | PDI | $T_g$ (°C) | $T_m$ (°C) |
|------|----------------------|------------|------------|--------|-----------|--------------|--------------|-----|------------|------------|
| 1    | 0/400/400*           | 25/60      | 10/60      | 50/50  | 100       | >99/>99      | 8.7          | 1.9 | -64.7/-1.1 | 66/111     |
| 2    | 0/400/400*           | 25         | 240/20     | 50/50  | 100       | >99/>99      | 8.1          | 1.8 | -64.8/-1.3 | 66/108     |
| 3    | 400/800/400          | 25/25/60   | 240/10/60  | 52/48  | 100       | >99/>99      | 13.2         | 2.3 | -64.6/-1.3 | 65/110     |
| 4    | 150/300/150          | 25/25/60   | 180/90/60  | 10/90  | 95        | >99/>99      | 25.1         | 1.4 | -64.8/-     | -113       |
| 5    | 400/800/400          | 25/25/60   | 240/90/60  | 45/55  | 94        | >99/>99      | 19.1         | 1.3 | -99.2/-     | -3.5/67/115|
| 6    | 600/400/400*         | 25/25/60   | 40/10/60   | 44/27/29| 99        | >99/>99      | 10.4         | 2.0 | -102.6/-    | -2.8/86/112|

[a] Polymerization conditions: cat. (10 umol), [Y]/[Ph(C6F5)4][Al/But] = 1:1:10, toluene (8 mL), unless otherwise noted.
[b] MCP/IP mole ratio in the copolymer. [c] Measured by $^1$H and $^{13}$C NMR spectrum in CDCl$_3$ at 25 °C. [d] Determined by GPC in THF at 40 °C against a polystyrene standard. [e] Determined by DSC. [f] Sequential addition of IP and then MCP. [g] Sequential addition of MCP and then IP. [h] Sequential addition of MCP, IP and then MCP. [i] Sequential addition of BD, IP and then MCP. [j] MCP/BD mole ratio in the copolymer. [k] Sequential addition of BD, IP and then MCP. [l] BD/IP/MCP mole ratio in the copolymer.

The sequential polymerization of MCP and isoprene (IP) afforded selectively the corresponding diblock copolymers with a perfect 1,4-PMCP and cis-1,4-PIP blocks (Table 1, run 1). Reversing the sequence of monomers addition, the molecular weights and molecular weight distributions of block copolymers were not nearly affected (Table 1, runs 1 and 2). According to the copolymerization data, we can see that completely converting all MCP monomer needs much more time or high reaction temperature (Table 1, runs 1 and 2). The 1,4-regularity of PIP and PMCP segments in copolymers is over 99% with moderate molecular weight distribution (PDI = 1.9-1.8) (Table 1, runs 1 and 2). A sequential polymerization of MCP, isoprene and MCP yielded an ABA-type triblock copolymer with two 1,4-PMCP blocks connected by one cis-1,4-polypipene block (Table 1, runs 3 and 4). Similarly, a ABA-type copolymer containing two blocks 1,4-PMCP and one middle block cis-1,4-polylbutadiene was also obtained by a sequential polymerization of MCP, butadiene and MCP under similar reaction conditions (Table 1, run 5). Interestingly, if butadiene, isoprene and MCP were sequentially added into the reaction vessel, then a ABC-type block copolymer having cis-1,4-polylbutadiene, cis-1,4-polypipene and 1,4-poly(MCP) blocks was generated (Table 1, run 6).
glassing transition temperature at -1.1–-1.3°C. The glass transition temperature of cis-1,4-PIP blocks were observed at -64.6 – -64.8°C and those of cis-1,4-polybutadiene blocks appeared at -99.2 and -102.6 °C. Interestingly, the melting points of 1,4-PMCP were not nearly influenced by their content, suggesting their strong crystallization ability and intense phase-separated tendency. To confirm the block distribution in the copolymers, one representative triblock copolymer sample was analysed by AFM. As shown in Figure 2, the AFM micrographs of the sample display a remarkable phase-separated morphology of the hard and soft domains containing of 1,4-PMCP and cis-1,4-PIP, respectively. This result further demonstrates the block architecture of these copolymers.

4. Conclusion
In summary, by use of a cationic yttrium alkyl catalyst, the block copolymerization of MCP, isoprene and butadiene has been achieved, which afforded a series of copolymers such as AB type MCP-IP diblock copolymer, ABA type MCP-IP-MCP triblock copolymer, ABA-type MCP-BD-MCP triblock copolymer and ABC-type MCP-BD-IP copolymer.

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