# A New System for Catalytic Synthesis of Block Copolymers

**Shigetaka Hayano, Yasuo Tsunogae**

***Frontier Material Team, Zeon Corporation***

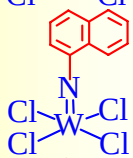
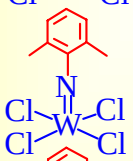
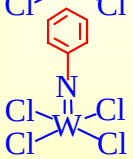
**Contents of the present study:**

1, New catalysts for the stereoselective ROMPs of cycloolefins.

2, A new ROMP system for catalytic syntheses of block copolymers.

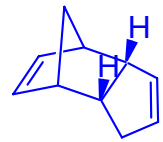
# 1, New catalysts for the stereoselective ROMPs of cycloolefins.

## Polymerization of DCPD by $WNRCl_4$–$Et_2Al(OEt)$ (1:3) and hydrogenation

| catalysts | | After polymerization | | | | After hydrogenation | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | yield | $M_n$ | $M_w/M_n$ | cis/trans | m/r | $T_m$ (deg, J/g) | $\Delta H$ | $T_m$ annealed | $\Delta H$ |
|  | **(1)** | 95 % | 16,000 | 3.1 | **72/28** | **47/53** | 177 | 13 | Tg 100 deg | |
|  | **(2)** | 98 % | 24,000 | 5.0 | **89/11** | **31/69** | 242 | 15 | Tg 101 deg | |
|  | **(3)** | 99 % | 27,000 | 6.0 | **86/14** | **29/71** | 239 | 37 | 234 | 4 |
|  | **(4)** | 99 % | 21,000 | 4.3 | **93/7** | **20/80** | 272 | 51 | 258 | 33 |

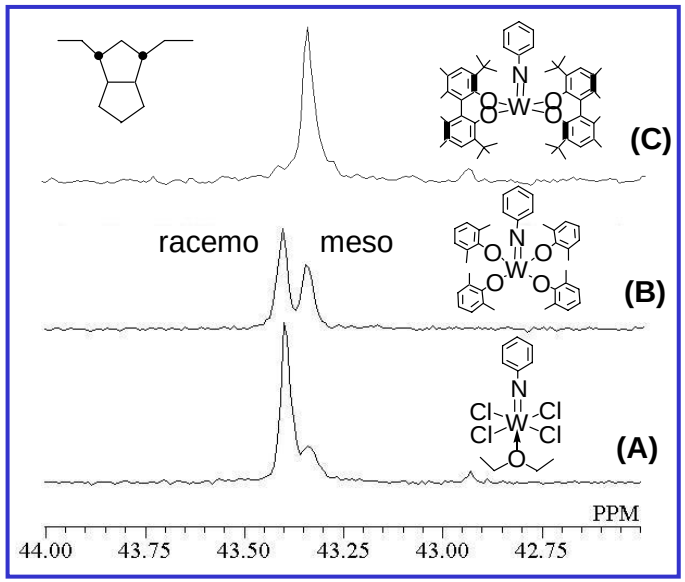
[a] Polymerized in cyclohexane at 50 C for 3h; [DCPD]/[1-octene]/[W] = 1000/100/1; [W]:[$Et_2AlOEt$] = 1:3; [DCDP] = 20 wt%, hydrogenated in cyclohexane at 160 deg for 8-16 h, [DCPD unit]/[Ru] = 500/1, $H_2$ = 1.0 MPa.

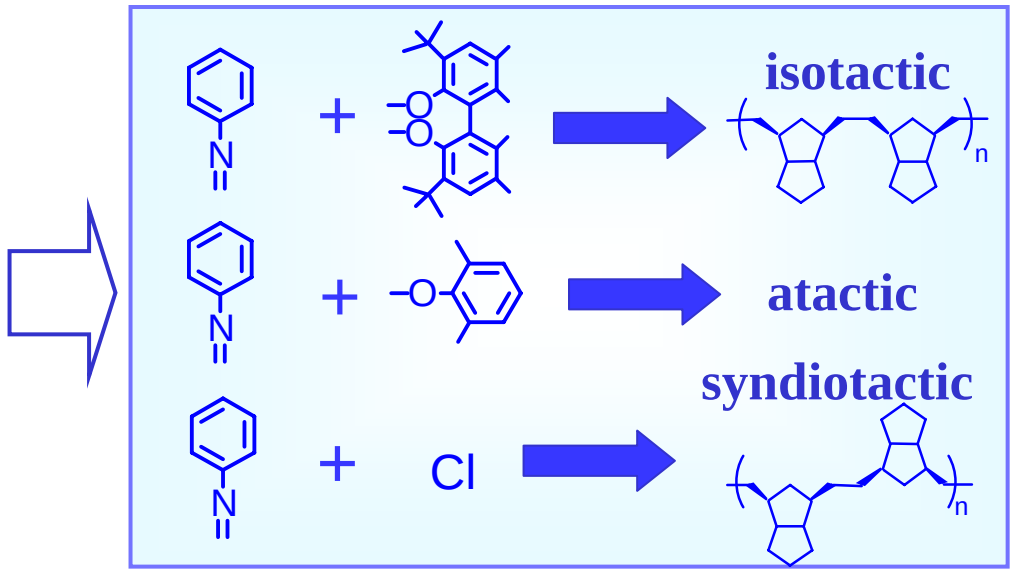
**W phenylimido (4)** ⟹ **syndioselective ROMP**




*endo*-dicyclopentadiene (DCPD)

## Stereoselective ROMPs by W imido phenolates



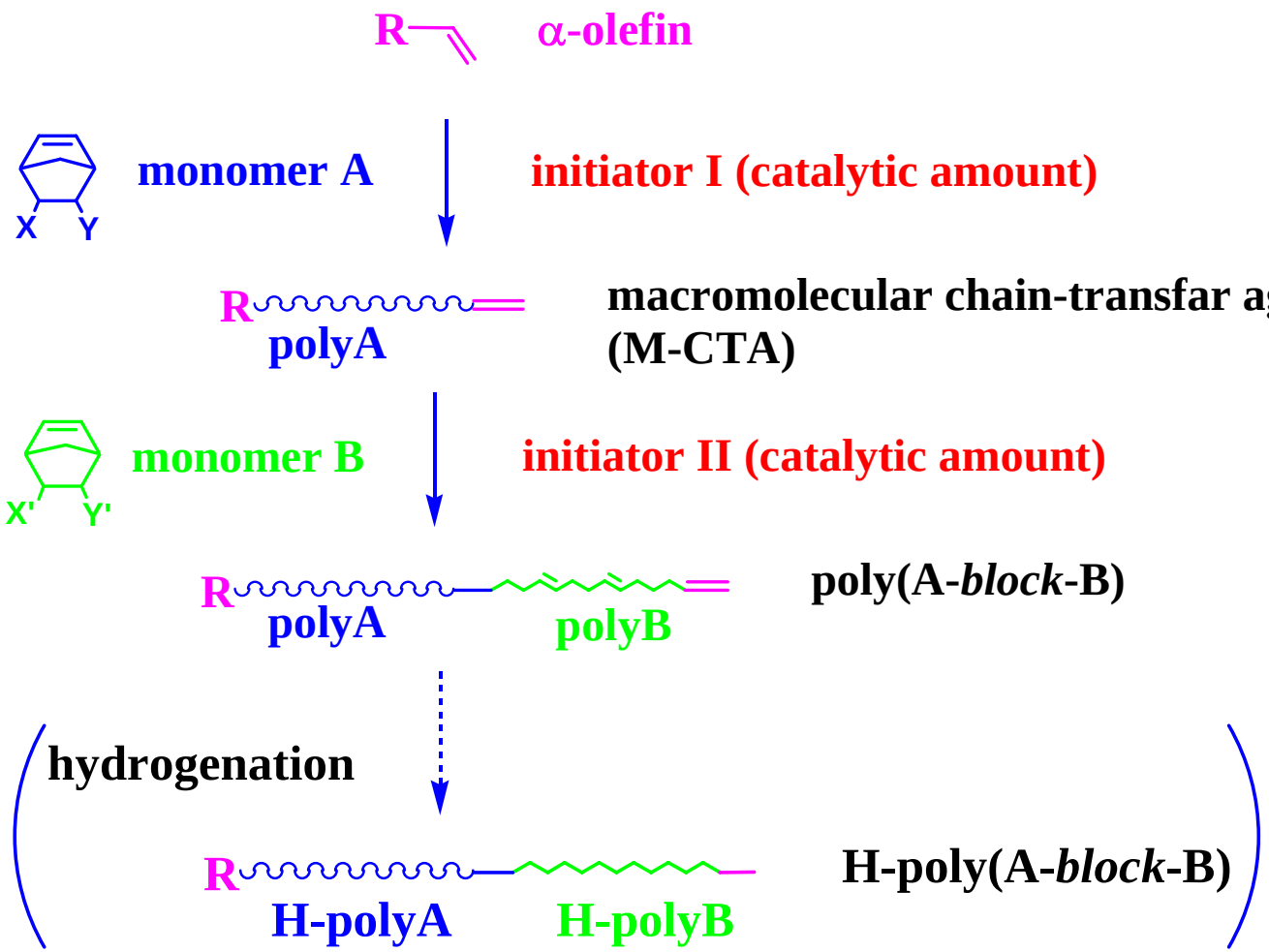

**Summary of this section:**

**Tungsten phenylimido ⇒ syndioselective**

**Tungsten imido biphenolate ⇒ isoselective**

**Biphenolate canceled the stereoregulation of imido.**

# A catalytic synthesis of block copolymers via ROMP.



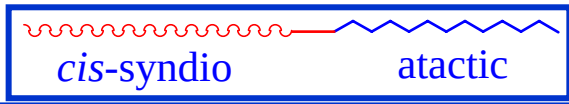
## 2, A new ROMP system for catalytic syntheses of block copolymers.

**Polymerization of DCPD by**  **Grubbs' catalyst 2nd Generation.**



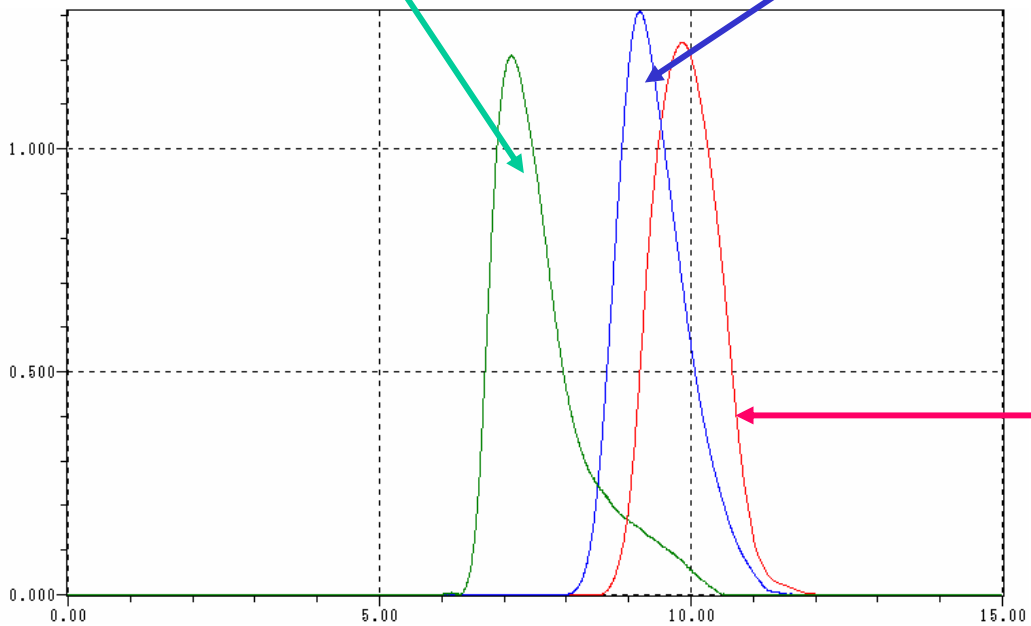

poly(DCPD), 5.0 g
GPC : Mn 78,000; Mw/Mn = 7.1

*without a chain-transfer agent*

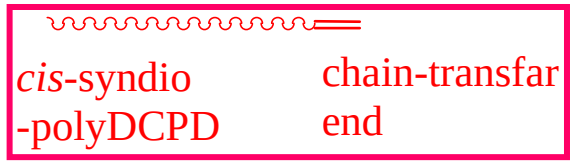



poly(*cis*-synDCPD-*block*-ataDCPD), 9.6 g (yield = 96%)
GPC : Mn 8,400 (calcd. Mn 7,800); Mw/Mn = 2.1

*with a macro-chain-transfer agent*




***macro-chain-transfer agent***




*cis*-syndio-poly(DCPD), 5.0 g
GPC : Mn 3,900; Mw/Mn = 1.9

**Stereoblock copoly(DCPD) might be prepared catalytically.**