

A New System for Catalytic Synthesis of Block Copolymers

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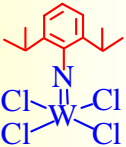
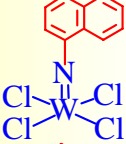
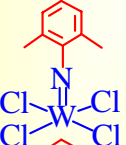
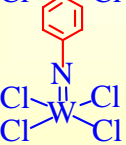
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Contents of the present study:

- 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 ΔH (deg, J/g)	T_m ΔH annealed	
 (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	<u>93/7</u>	<u>20/80</u>	272 51	258 33	

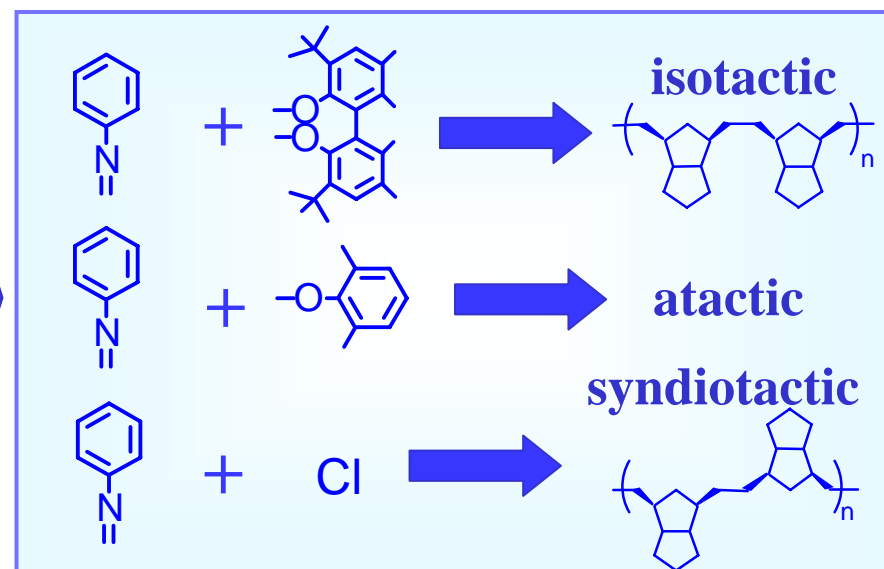
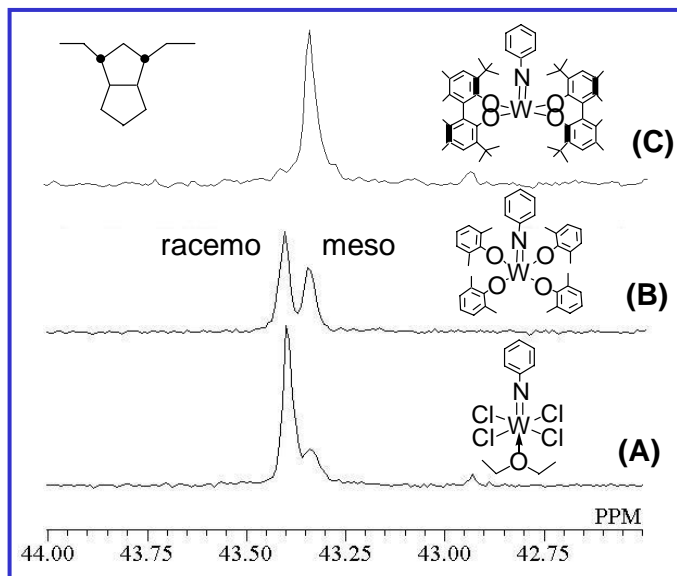
a) Polymerized in cyclohexane at 50 C for 3h; [DCPD]/[1-octene]/[W] = 1000/100/1; [W]:[Et₂AlOEt] = 1:3; [DCDP] = 20 wt%, hydrogenated in cyclohexane at 160 deg for 8-16 h, [DCPD unit]/[Ru] = 500/1, H₂ = 1.0 MPa.

W phenylimido (4) → syndioselective ROMP



endo-dicyclopentadiene (DCPD)

Stereoselective ROMPs by W imido phenolates



Summary of this section:

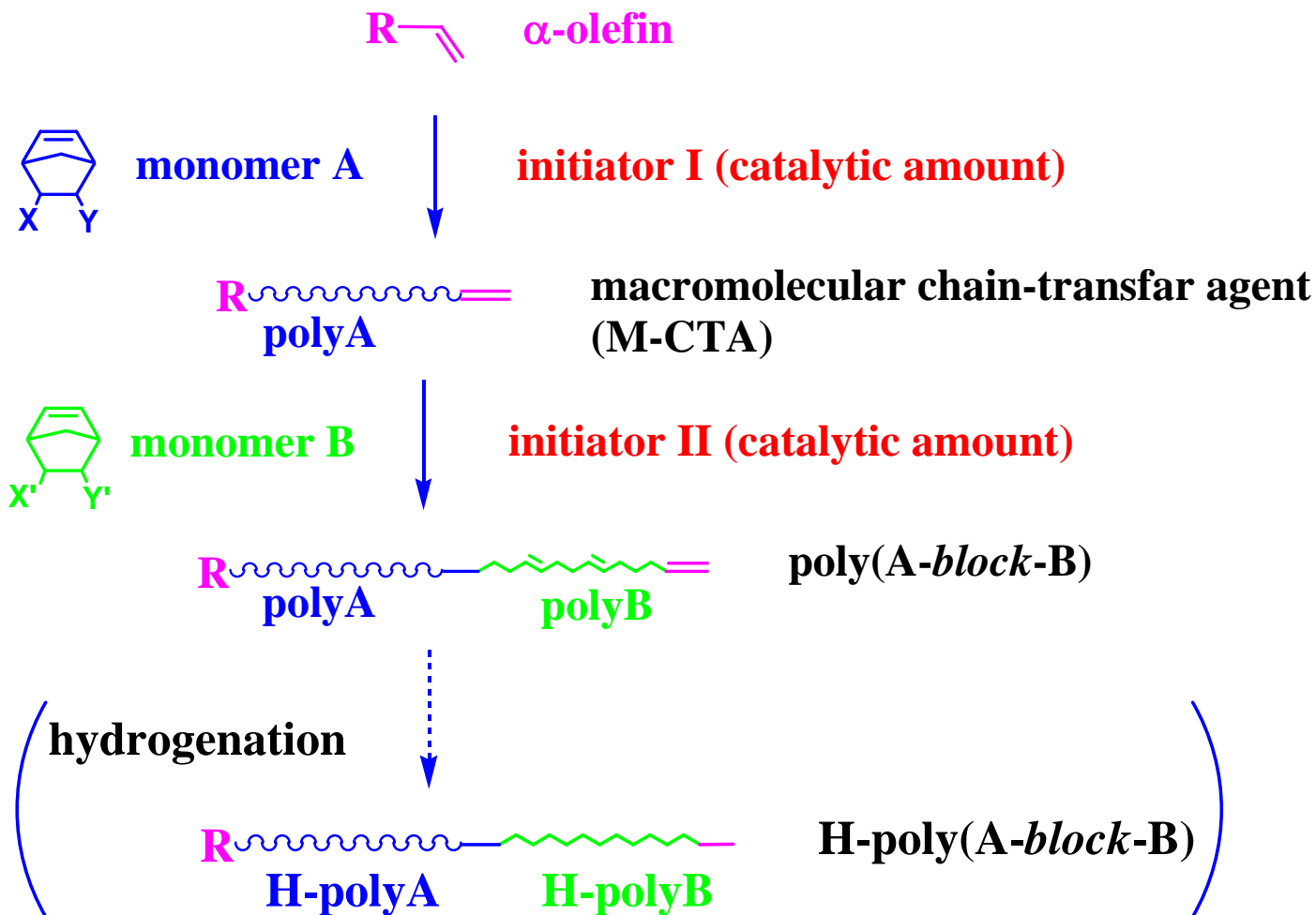
Tungsten phenylimido → **syndioselective**

Tungsten imido biphenolate → **isoselective**

Biphenolate canceled the stereoregulation of imido.

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

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.



 atactic

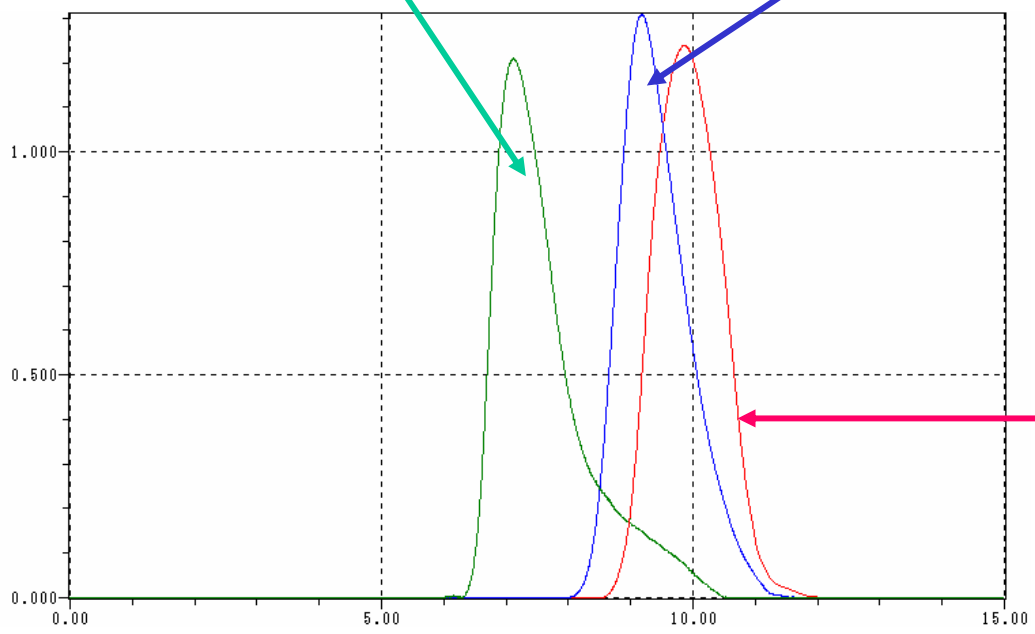
 
cis-syndio atactic

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


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

without a chain-transfer agent

with a macro-chain-transfer agent



macro-chain-transfer agent


cis-syndio chain-transfer
-polyDCPD end

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

Stereoblock copoly(DCPD) might be prepared catalytically.

