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*Trans*-1,4- stereospecific polymerization of isoprene with MgCl<sub>2</sub>-supported Ziegler-Natta catalyst I. Initial polymerization kinetic and polymerization mechanism

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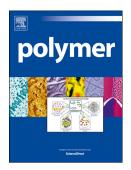
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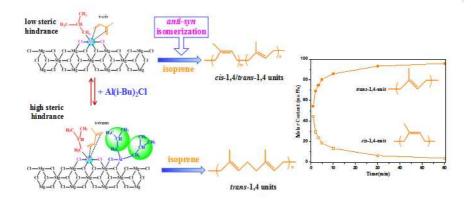
### ACCEPTED MANUSCRIPT

# Trans-1,4- Stereospecific Polymerization of Isoprene with MgCl<sub>2</sub>-Supported Ziegler-Natta Catalyst

## - Initial Polymerization Kinetic Behavior and Polymerization

#### Mechanism

Xiangyu Liu, Weitian Li, Qingtao Niu, Riguo Wang, Aihua He



Scheme 1. Proposed active center sites and polymerization mechanism of isoprene in  $TiCl_4/MgCl_2\,system.$ 

Trans-1,4 stereospecific polymerization mechanism of isoprene with heterogeneous TiCl<sub>4</sub>/MgCl<sub>2</sub>-Al(i-Bu)<sub>3</sub> Ziegler-Natta catalyst was investigated for the first time. The active centers with low steric hindrance gave the mixed cis-1,4/trans-1,4 units due to reversible anti-syn isomerization, the active centers with high steric hindrance formed by adsorption of Al(i-Bu)<sub>2</sub>Cl on Mg adjacent to the center Ti gave the high trans-1,4 units. The trans-1,4-polyisoprenes gradually increased with the increase in polymerization time accompanying with the gradually transformation of species with low steric hindrance to species with high steric species in the initial polymerization stage.

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