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Dicyclopentadiene Polymerization in Solutions under the Action of Various Catalytic Systems

Lyapkov, A.A.^{a*}, Gvozdkov, E.L.^a, Tarakanovskaya, A.N.^a, Tarnovskaya, O.D.^a,
Yakovleva, Y.S.^a

^a Tomsk Polytechnic University, Lenin Av., 30, Tomsk 634050, Russia

Abstract

The kinetics of dicyclopentadiene polymerization in toluene solution under the action of different catalytic systems through adiabatic thermometry was investigated. Unlike cationic metathesis polymerization has a sufficiently large induction period associated with low speed by implantation monomer on carbene bond of catalyst. It has been shown that the rate of metathesis polymerization of dicyclopentadiene in comparable circumstances is about three times lower than the rate of cationic polymerization of the same monomer.

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Keywords: Catalytic polymerization, dicyclopentadiene, titanium tetrachloride, triisobutylaluminum, original Hoveyda–Grubbs II type catalyst, adiabatic reactor, thermometric method, rates constants;

1. Introduction

Now researchers are highly interested in metathesis reactions under the action of ruthenium Grubbs catalysts¹. The most attractive approach is the one based on the ring opening metathesis polymerization (ROMP). It allows acquiring macromolecular compounds with specific structure and properties. Metathesis dicyclopentadiene polymerization has already been implemented on industrial scale². The polymer derived through ROMP is a solid

* Corresponding author. Tel.: +7-906-954-3336.
E-mail address: alexdes@tpu.ru

and nonflexible thermoset material that has a high degree of the IZOD impact resistance. However, polydicyclopentadiene acquired using this technology has a cross-linked two-dimensional structure and is inefficient for further processing that involves technology common for thermoplastic materials or thermoset polymers. At the same time, polydicyclopentadiene acquired by cationic polymerization has linear structure and can be processed using common technology.

As a rule, cationic polymerization of dicyclopentadiene on one of olefinic bonds proceeds with the catalytic system based on TiCl_4 and organoaluminum compounds³. This catalytic system is less hard if compared with AlCl_3 , SnCl_4 or TiCl_4 , and it allows handling diene hydrocarbons. Dicyclopentadiene polymerization with this catalytic system proceeds in homogeneous medium. This allows monitoring the factors of the process development precisely.

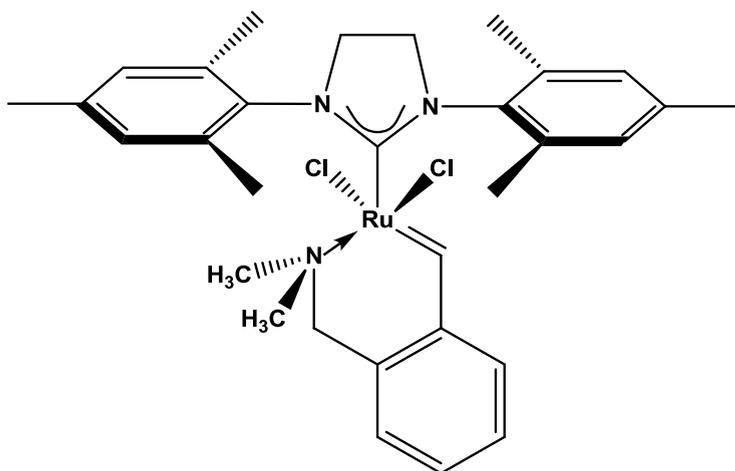
2. Experiment

Dicyclopentadiene produced by Hangzhou Uniwise International Co., Ltd. with 99% base material content was cleared from oxygen-containing impurities by boiling with sodium and distillation under reduced pressure.

The solvent was toluene dehydrated according to the known procedure⁷. The residual content of H_2O did not exceed 14 ppm.

Titanium tetrachloride with 99.9% base material content and the density of 1.727 g/cm^3 was used without additional clearing. Triisobutylaluminum (AliBu_3) was used as a solution in heptane in the concentration of 0.232 g/cm. Working solutions were prepared by diluting the main one with dry solvent until the needed concentration was achieved. All procedures with TiCl_4 and AliBu_3 were carried out in the Mbraun LabStar glove box with argon atmosphere (not less than 0.5 ppm of O_2 and H_2O).

Cationic polymerization of dicyclopentadiene was carried out in the toluene solution with the initial concentration of the catalytic system $\text{AliBu}_3 : \text{TiCl}_4$ (1 : 1) at $1.07 \cdot 10^{-3} \text{ mol/l}$. The catalyst in metathesis polymerization of dicyclopentadiene was ruthenium complex (1,3-bis-(2,4,6-trimethylphenyl)-2-imidazolidinylidene)-dichloro-(ortho-N,N-dimethyl-aminomethyl-phenylmethylene)-ruthenium with thermally controllable activity. It was developed by experts from 'United Research and Development Center', LLC. (Moscow) and further on modified in 'NIOST', LLC (Tomsk)⁶.



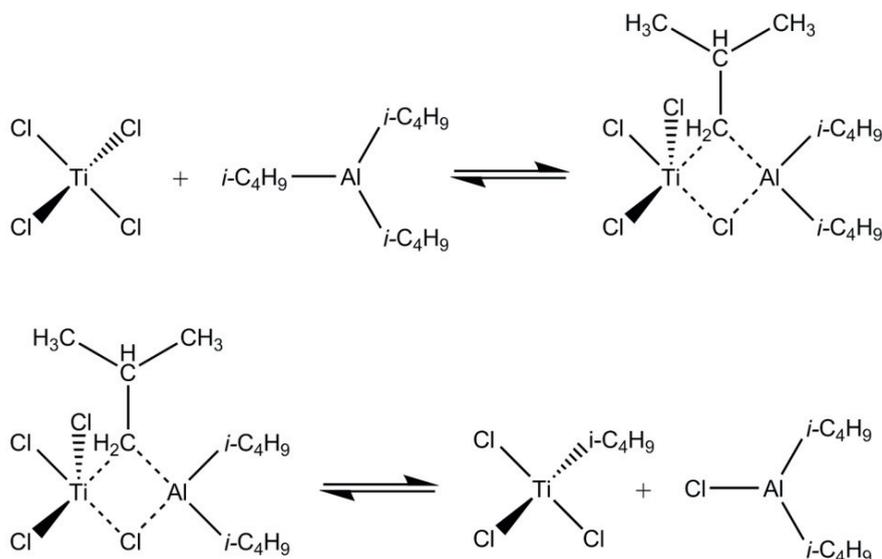
It is stable during storage, resistant to oxygen and air moisture. Therefore, it does not require inert atmosphere. The catalyst concentration was $1.07 \cdot 10^{-3} \text{ mol/l}$ (mole ratio of the monomer to the catalyst was 1400:1). The monomer concentration in all tests was 1.45 mol/l.

3. Results and Discussion

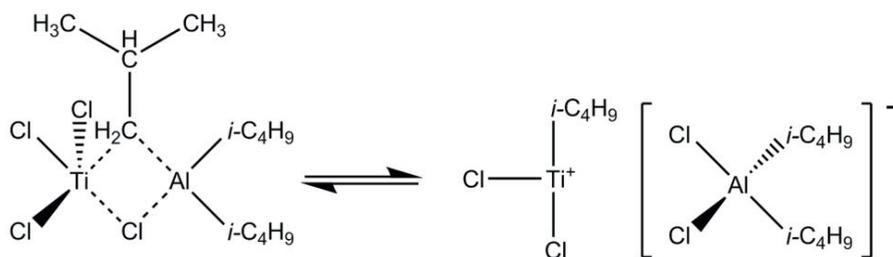
First, dicyclopentadiene polymerization was carried out with gradual adding of triisobutylaluminum in the solution of the monomer in toluene. Then, when the temperature setting in the adiabatic reactor was stable, we added titanium tetrachloride. During metathesis polymerization of dicyclopentadiene, we added the estimated amount of original Hoveyda–Grubbs II type catalyst dissolved in toluene into the monomer solution in toluene.

During cationic polymerization of dicyclopentadiene, in the catalytic system $\text{Al}i\text{Bu}_3\text{-TiCl}_4$ the polymer chain growth reaction proceeds either on a norbornene or on a cyclopentene double bond.

The reaction is quite slow if compared with cationic polymerization of dicyclopentadiene in toluene under the action of TiCl_4 (4.00 ± 0.20 l/(mol·sec))⁸ or the catalytic system $\text{AlEt}_2\text{Cl} : \text{TiCl}_4$ (2.14 ± 0.04 l/(mol·sec))³. This can be due to that the system is less hard when exchange reaction proceeds between the components of the catalytic system:

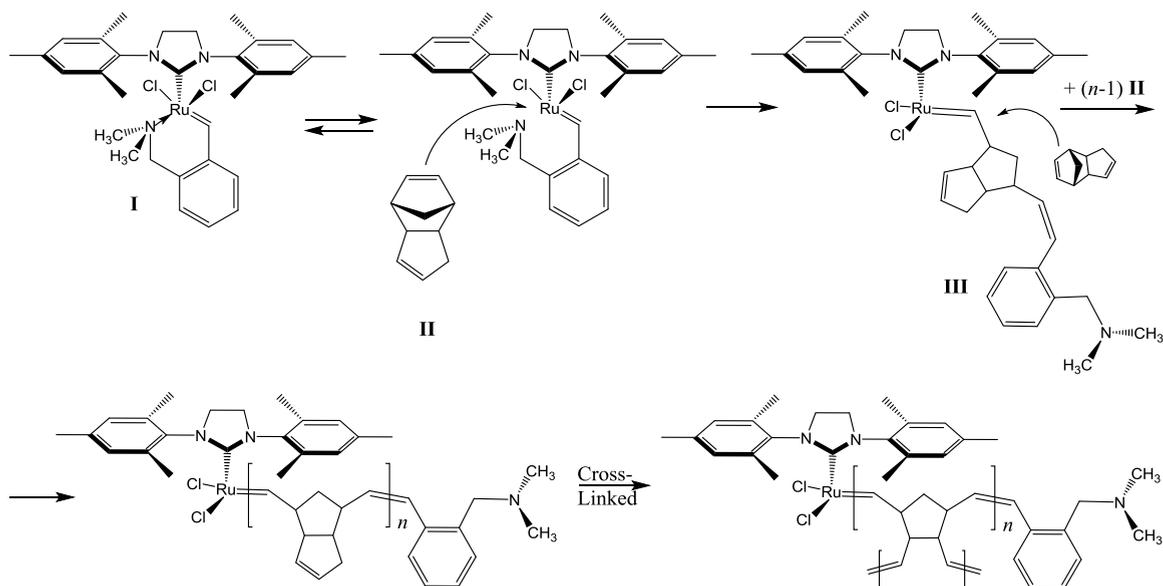


As a rule, aluminum is a part of complex counter ion that stabilizes the growing particle:



This does not contradict the known literature data⁹. An active particle formed comes against double bond of the monomer and this triggers polymerization.

During metathesis polymerization, norbornene cycle of the monomer (II) discloses. An unsaturated polymer of linear structure forms. The number of hydrogen atoms with unsaturated $\text{C}=\text{C}$ -bonds remains the same. The intrusion of a new monomer molecule into a polymer molecule through the carbene bond of the catalyst (I) between carbon and ruthenium causes the chain growth:



The rate-limiting stage that determines the total rate of metathesis polymerization is the stage of initial orientation and incorporation of the monomer through the carbene bond of the catalyst. Chelating ligand in the catalyst significantly slows down this process.

Having supposed that the stage of chain growth proceeds as the first-order reaction because of excessive amount of the monomer. For every test, we calculated the observed reaction constant of pseudo-first order by making a graph of the experimental curve in semilogarithmic coordinates.

In figure 1, there is a semilogarithmic anamorphosis of a thermometric curve of dicyclopentadiene polymerization with the catalytic system $\text{AliBu}_3\text{-TiCl}_4$.

The constant rate of dicyclopentadiene polymerization in toluene solution under the action of the catalytic system $\text{AliBu}_3\text{-TiCl}_4$ is discovered from figure 1. This constant rate is $0.57 \text{ l}/(\text{mol}\cdot\text{sec})$.

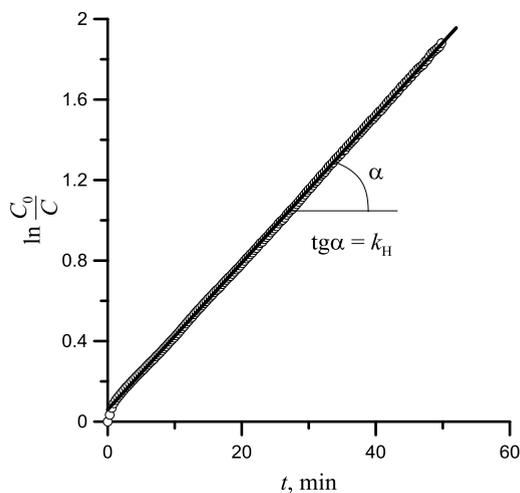


Fig. 1. Semilogarithmic kinetic curve of dicyclopentadiene polymerization (1.45 mol/l) in toluene solution under the action of the catalytic system $\text{AliBu}_3\text{-TiCl}_4$ ($1.07 \cdot 10^{-3} \text{ mol/l}$)

In figure 2, there is a semilogarithmic anamorphosis of a thermometric curve of dicyclopentadiene polymerization in toluene under the action of the original Hoveyda–Grubbs II type catalyst.

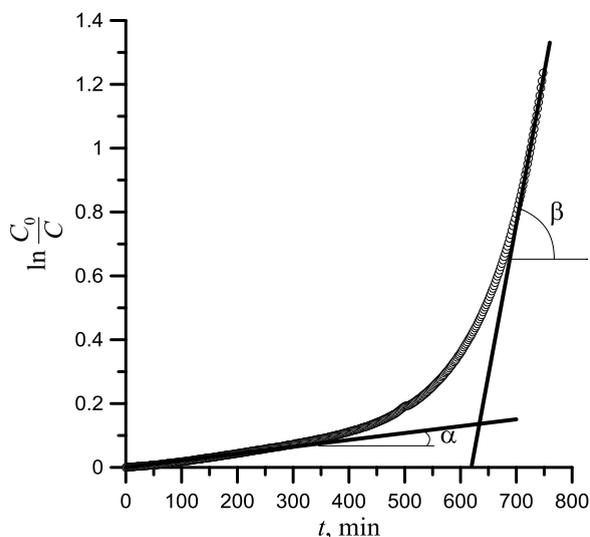


Fig. 2. Semilogarithmic kinetic curve of dicyclopentadiene polymerization (1.45 mol/l) in toluene solution under the action of the original Hoveyda–Grubbs II type catalyst ($1.07 \cdot 10^{-3}$ mol/l)

It can be seen from the curve that polymerization has a quite large induction period because of a low rate of incorporation of the monomer through the carbene bond of the catalyst. However, as the system temperature increases, incorporation of every succeeding molecule of monomer through the carbene bond of the catalyst accelerates.

There can be clearly determined two parts with different slopes in the curve (fig. 2). The part with the slope on the α angle refers to the rate of initiation. The part with the slope on the β angle refers to the chain growth rate.

Determined constants of initiation and chain growth rates were $k_i = 0.0035$ l/(mol·sec) and $k_p = 0.16$ l/(mol·sec).

4. Conclusion

It has been shown that in comparable circumstances the rate of metathesis polymerization of dicyclopentadiene in toluene solution under the action of the original Hoveyda–Grubbs II type catalyst is about three times lower than the rate of cationic polymerization of the same monomer under the action of the catalytic system $\text{Al}(\text{Bu})_3\text{-TiCl}_4$. This is because the optimum range of temperatures for the used catalyst of metathesis polymerization is above 60 °C.

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