

MODELING OF ROMP 5-NORBORNENE-2,3-DICARBOXIMIDE-N-METHYL ACETATE

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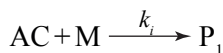
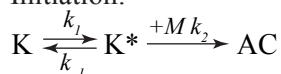
Due to the similarity of kinetic characteristics between ROMP and "living polymerizations" there was shown low decrease in reaction speed after several subsequent monomer additions. Moreover, each successful monomer addition increase obtained molecular weight of the polymer.

Obtained kinetic data of investigated system made it possible to propose a mathematical model of the polymerization reaction 2. Following comparison of experimental results and calculated theoretical data was used to check the kinetic reaction scheme as well as to identify the rate constants of elementary steps of the process.

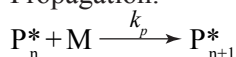
To simplify the calculations, there were made following assumptions, such as limitation between the polymerization rate and formation of active species, same activity of all propagating species and minimal influence of the solvent and the polymer.

The reaction mechanism proposed is the following:

Initiation:



Propagation:



In order to obtain the mean molecular weight and its distribution, it is important to calculate the molecular weight distribution moment for the growing polymer chains. With this aim the generating functions of the distribution moments must be introduced [1]:

$$G(s, \tau) = \sum_{n=1}^{\infty} s^n P_n^*(\tau) \text{ for the growing chains.}$$

By the use of the generating functions the moment of molecular weight distribution of j -th order are obtained [1]:

$$\varepsilon_j = \left(\frac{\partial^j G(s, \tau)}{\partial s^j} \right)_{s=1}$$

The physical significance of the leading moment is very helpful in forming the modeling equations.

The relevant equations of molecular weight and

polydispersity were:

$$\bar{M}_n = \frac{\varepsilon_1}{\varepsilon_0} W; \quad \bar{M}_w = \frac{\varepsilon_2}{\varepsilon_1} W; \quad \frac{\bar{M}_w}{\bar{M}_n} = \frac{\varepsilon_2 \varepsilon_0}{\varepsilon_1^2}.$$

A Gear method computer software [2] is used for an accelerated solution. At the same time, so-called rigid differential equations use Implicit Gear algorithms, based on the use of linear multistep methods that satisfy the requirements of rigid stability [3]. Nordsieck algorithm was used for the polynomial interpolation

The search for optimal values of the rate constants of the elementary stages of polymerization 2 was carried out by minimizing the functional $F(k)$ having the following form:

$$F(k) = \sum_{i=1}^n \sum_{j=1}^m \sum_{\tau} [y_{ij}(k, \tau) - x_{ij}(\tau)]^2,$$

where n is the number of experiments performed under different initial conditions; m is the number of experimentally measured components of the reaction (in our case, $m=2$, since the concentration 2 and weight average molecular mass was measured experimentally); x_{ij} are the experimental kinetic dependences; $y_{ij}(k, \tau)$ is calculated values of 2 concentrations and weight average molecular mass;

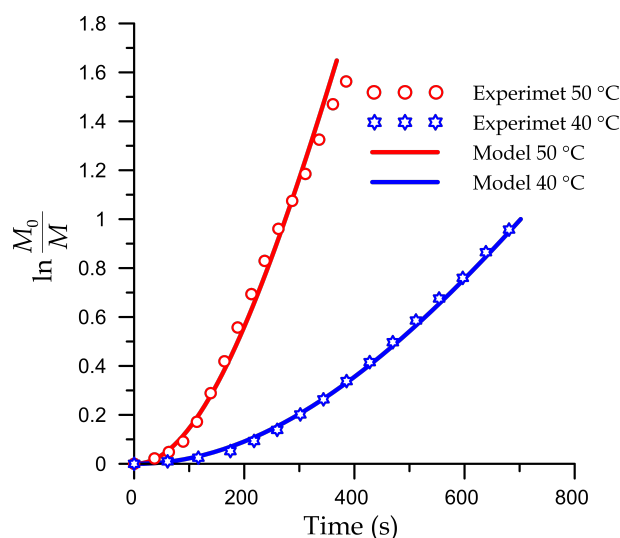


Fig. 1. Comparison of experimental and theoretical semilogarithmic conversion-time curves obtained at two various temperatures ($C_{k_0} = 5,3 \cdot 10^{-4} \text{ mol} \cdot \text{L}^{-1}$, $C_{M_0} = 0,354 \text{ mol} \cdot \text{L}^{-1}$)

τ is the reaction time.

Constraints allowed to replace variables, that were made on the rate constants, based on the available information [4]:

$$k = \frac{k_{upp} - k_{low}}{k_{upp} - k_0} + k_{low} \frac{k_0 - k_{low}}{k_0 - k_{low}} e^{-\xi} + 1$$

where k_{upp} and k_{low} are respectively the upper and lower limits of the variation of the corresponding rate constant; k_0 is its initial value; ξ is a new variable that varies from $-\infty$ to $+\infty$, which minimizes.

Following data determined by computer analysis: the theoretical curve of conversion-time, a the-

oretical curve linked with the concentration of the Ru-carbene complex and theoretical weight average molecular mass. Imposed values limitations of elementary polymerization events made it possible to describe the experimental data. The calculated values of the rate constants of initiation and chain

growth were as follows: $k_i = 5,4 \cdot 10^{15} \cdot e^{\frac{-92800}{RT}}$ and

$$k_p = 8,3 \cdot 10^{11} \cdot e^{\frac{-65200}{RT}} \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}.$$

In fig. 1 the experimental conversion-time curves relevant to the polymerization of 5-Norbornene-2,3-dicarboximide-N-methyl acetate in the presence of Hoveyda-Grubbs II catalytic system at two different temperature are directly compared with the computed ones.

References

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GASOLINE PRODUCTION USING THE ZEOFORMING PROCESS PRODUCTS AND STABLE GAS CONDENSATE AS FEEDSTOCK

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Stable gas condensate (SGC) is a blend of liquid hydrocarbons (C_{5+}), it was obtained as a by-product at fields, in the process of removing condensed hydrocarbon from natural gas. SGC is used as a feedstock in petrochemistry, as well as a blending component in the production of motor fuels.

The Zeoforming process allows the production of high-octane motor fuels by catalytic processing of low-octane gasoline fractions of various origins on zeolite catalysts [1].

The purpose of this work is to study the possibility of using zeoforming products (ZP) as blending components for the gasoline production. ZP were obtained under various process conditions and using SGC like a process feedstock.

In the course of the work, on the laboratory catalytic unit, the Zeoforming process was carried out, using a KN-30 zeolite catalyst. Test conditions are given in table 1.

Further, using the “Compounding” software [2], and based on various ZPs, recipes for blending gasoline AI-92 brand were developed (table 2). SGC, toluene and methyl tert-butyl ether (MTBE) were used as additional blending components. Characteristics of gasolines, obtained according to the developed recipes are presented in table 3. As can be seen from the table 3, all gasolines obtained according to the developed recipes meet the requirements of [3].

As can be seen from the data presented in Table 2, the most preferable is the recipe for blending