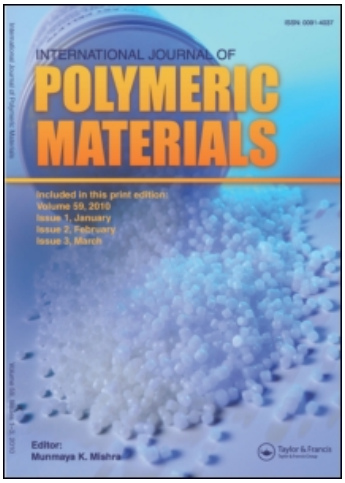

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Yu. B. Monakov[a]; I. R. Mullagaliev[a]
[a] Institute of Organic Chemistry, Ufa Scientific Center, Russian Academy of Science, Ufa, Russia

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On the Kinetic Parameters of Butadiene Polymerization on Titanium–Magnesium Catalytic Systems

Yu. B. MONAKOV* and I. R. MULLAGALIEV

Institute of Organic Chemistry, Ufa Scientific Center,
Russian Academy of Science, 71 prospekt Oktyabrya, Ufa 450054 Russia

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During the polymerization of butadiene on catalytic systems, containing TiI_2Cl_2 or $Ti(O\text{-}nC_4H_9)_4$ in combination with *n*-butyl-(2 ethyl)hexylmagnesium, the constants of chain propagation reaction were determined by the method of dose adding of inhibitor and by kinetic method. It was shown, that the addition of organomagnesium compound instead of organoaluminium cocatalyst changes the activity and stereospecificity of system. It shows the great influence of organic compound of nontransition metal not only on the formation, but also on the functioning of active centers of metallocomplex catalysts.

Keywords: Polymerization; Butadiene; Kinetic parameters; Titanium–magnesium catalytic systems

INTRODUCTION

It is known, that during the polymerization of conjugated dienes initiated by Ziegler–Natta metallocomplex catalysts polymers with different stereoregularity are formed in dependence on the nature of the transition metal. Catalytic systems of the very same metal are able to exhibit various stereospecificities by the change (regulation) of its valence state, ligand environment and so on [1]. The nature

*Corresponding author.

of the cocatalyst–organometallic compound of nontransition metal, its content in the reaction medium and the way of adding are of no small importance for activity, stability and other working parameters of the catalytic complex [2]. Alkyl derivatives of aluminium are the most widely used cocatalysts. At the same time, organic derivatives of other nontransition metals, especially magnesium derivatives are of great interest. Undoubtedly, this is associated with the appearance of high active supported catalysts for olefin polymerization [3]. There are some attempts to use them for polydienes creation [4]. So, the influence of a magnesium component of a catalytic complex on the activity and stereospecificity of the latter was noted, but there is no data about both reaction ability of active centers and their quality.

In addition, the aim of this work was to determine the kinetic parameters of butadiene polymerization on titanium–magnesium catalytic systems with various stereospecific action TiI_2Cl_2-MgRR' and Ti(O-nC$_4$H$_9$)$_4$-MgRR', where R = n-butyl, R' = 2-ethylhexyl, and the comparison of the determined parameters with those who are known for analogous titanium–aluminium catalytic systems TiI_2Cl_2-Al(i-C$_4$H$_9$)$_3$ (triisobutylaluminium–TIBA) and Ti(O-nC$_4$H$_9$)$_4$-TIBA [5, 6].

EXPERIMENTAL PART

Polymerization was carried out in toluene at 25°C in conditions adopted for ion-coordinated polymerization. The polymer was sedimented out and purified by alcohol, with Ionol, then dried in vacuum drier to constant weight. Catalytic systems were prepared *in situ*, by adding to butadiene solution at first MgRR', and then a titanium component.

Experiments showed that first order polymerization reaction on monomer and catalyst are observed for both titanium–magnesium catalytic systems, *i.e.*,

$$W_p = K_p \cdot C_m \cdot C_a, \tag{1}$$

where W_p – the rate of polymerization, C_m – the concentration of monomer.

Kinetic parameters of polymerization (reaction constant of polymer chain propagation K_p and number of active centers C_a) were determined by the method of dose adding of inhibitor according to [6] and derived from the polybutadiene molecular mass plotted *versus* time [7]. Cyclopentadiene (CPD) was used as inhibitor.

RESULTS AND DISCUSSION

In Figure 1 the typical dependence of the polymerization rate on concentration of added inhibitor is shown, extrapolation of W_p to 0 gives the value of C_a. The value of K_p was evaluated by correlation (1).

Independence of microstructure of the formed polybutadiene from the presence and concentration of added inhibitor indicates that the inhibitor only blocks the active center, but doesn't modify its nature.

Out of kinetic data the value of K_p was found from the angle coefficient of dependence of $U(\tau)/P_n(\tau)$ on τ, where τ – time of

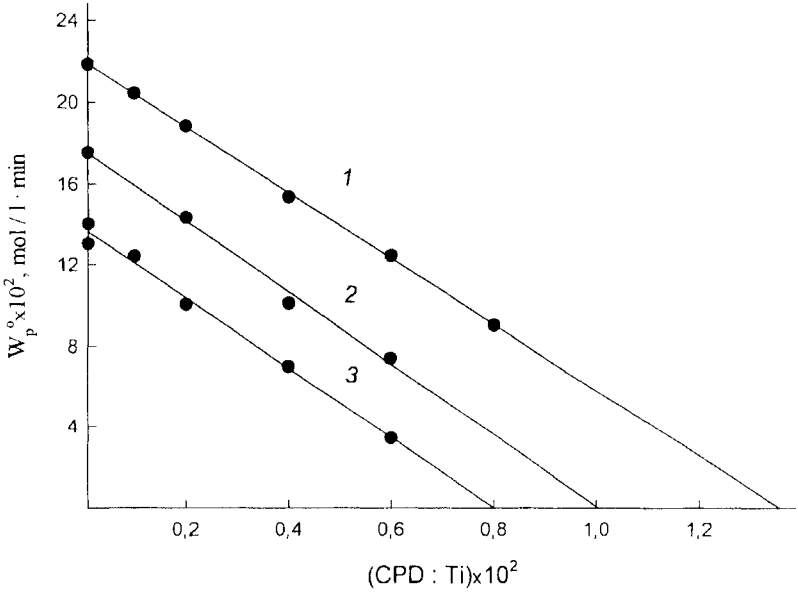

FIGURE 1 The W_p of butadiene polymerization on catalytic system TiI_2Cl_2-MgRR' *vs.* the quantity of adding of CPD. Mg : Ti = 1,0; $C_{Ti} = 5 \cdot 10^{-3}$, $C_m = 1{,}0$ mol/l.

polymerization, U – yield of polymer, P_n – number average degree of polymerization. In Figure 2, example of a plot of such dependence is shown. Similar values of K_p, determined by different methods, support their estimation.

The dependence of catalytic systems activity and content of units with different structure in polybutadiene on the correlation of components in catalytic systems is shown in Figures 3(a), (b). Extreme dependences of activity of the investigated titanium – magnesium catalysts and the content of units of different structure on the ratio of Mg : Ti in catalytic complex are observed.

Maximum of yield and content of 1,4-*cis*-units for TiI_2Cl_2-Mg*RR'* system is observed at the ratio of Mg : Ti = 1,0. By comparing this complex with catalytic system TiI_2Cl_2-TIBA, it is clear that the substitution of organoaluminium compound by magnesium derivative leads to the displacement of maximum of catalytic system activity to the range of lower ratio diioddichlorotitanium – organometallic compound. Because of this, activity and content of 1,4-*cis*-units in

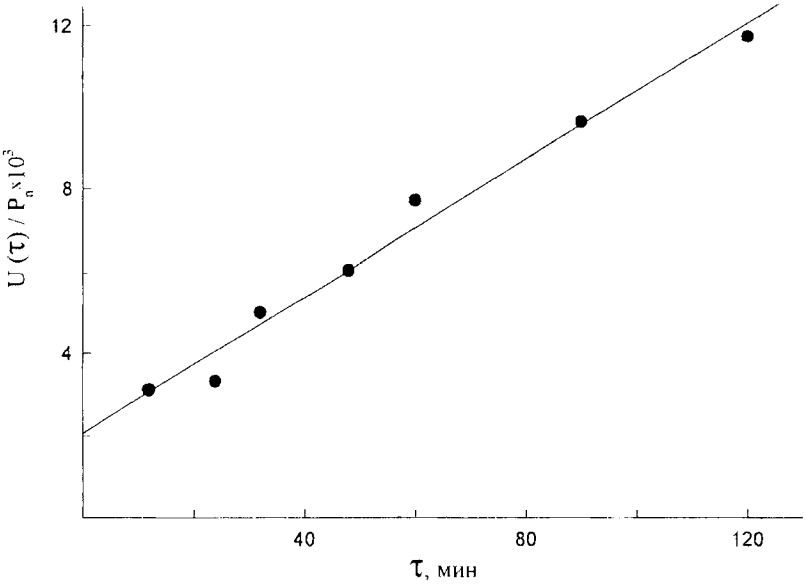

FIGURE 2 Plot of $U(\tau)/P_n(\tau)$ *vs.* the duration of butadiene polymerization on catalytic system Ti(O-C_4H_9)$_4$-Mg*RR'*. $C_{Ti} = 10^{-2}$, C_m = 2,0 mol/l, Mg : Ti = 4,0.

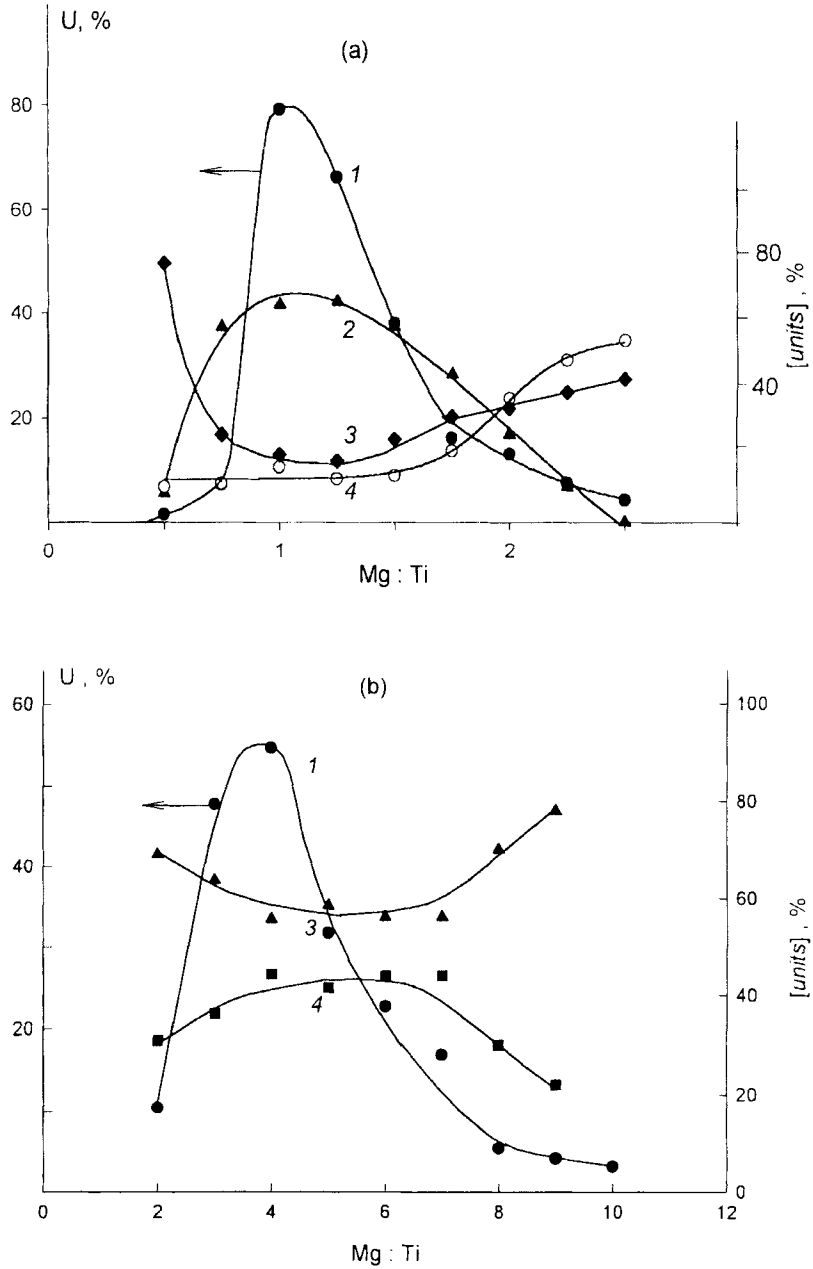

FIGURE 3 Plots of (1) yield and (2–4) microstructure of polybutadiene on catalytic system TiI_2Cl_2-Mg*RR'*(a) and Ti(O-C_4H_9)$_4$-Mg*RR'*(b) *vs.* the correlation Mg/Ti. (2) – 1,4-*cis*-, (3) – 1,2-, (4) – 1,4-*trans*-units, $C_{Ti} - 3 \cdot 10^{-3}$(a), $2 \cdot 10^{-2}$(b), $C_m = 1{,}0$ mol/l, 1 h (a), 3 h (b).

polybutadiene is also reduced. These results are similar to the data on maximum of activity and microstructure of polybutadiene, that were obtained in the presence of titanium–magnesium complexes on the base of $TiCl_4$, for which it was showed, that 98 and 96% of titanium are in the trivalent state at the ratio of Mg-R:Ti = 2,2 [8] and 2,5 [9], respectively. One can suppose, that in our case the active centers contain Ti(III) compounds.

Activity of Ti(O-nC$_4$H$_9$)$_4$-MgRR' system is maximum at a ratio of Mg:Ti = 4. At this components ratio of catalyst, the formed polybutadiene is characterized by a maximum content of 1,4-*trans* and minimum of 1,2-units, having no 1,4-*cis*-structures at all.

The calculated values of K_p for titanium–magnesium catalytic systems in the field of their maximum activity are smaller than the analogous values for titanium–aluminium catalysts. Thus, in the case of TiI_2Cl_2 K_p reduces from $(7{,}8 \pm 0{,}4) \cdot 10^3$ to $(3{,}3 \pm 0{,}2) \cdot 10^3$, and for Ti(O-$nC_4H_9$)$_4$ from 40 ± 2 to 3 ± 1 mol/l·min, respectively, under substitution of TIBA by MgRR'. Probably, the higher 1,4-*trans*-units content for titanium–magnesium complexes as compared with titanium–aluminium may be explained by this.

CONCLUSIONS

Thus, the difference in stereospecific activity of the compared systems with different cocatalysts is caused by different reactivity of the active centers. It is an indication of the great influence of organic compound of nontransition metal not only on the formation, but also on the function of active centers.

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