

MACROMOLECULAR CHEMISTRY  
AND POLYMERIC MATERIALS

Polymerization of 1-Hexene on Catalytic System  
 $\text{TiCl}_4\text{-Al}(\text{C}_6\text{H}_{13})_3 \cdot \text{Mg}(\text{C}_6\text{H}_{13})_2$

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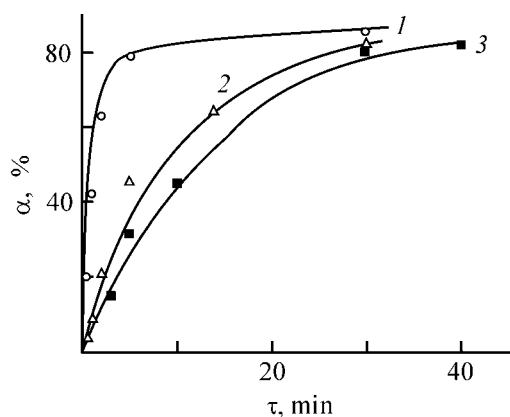
**Abstract**—Polymerization of 1-hexene on the catalytic system  $\text{TiCl}_4\text{-Al}(\text{C}_6\text{H}_{13})_3 \cdot \text{Mg}(\text{C}_6\text{H}_{13})_2$  was studied.

Copolymerization of ethylene and propylene with a small amount of higher  $\alpha$ -olefins yields polymeric materials with a wide range of consumer characteristics (density, melting point, crystallinity) [1–4]. Data on homopolymerization of higher  $\alpha$ -olefins allow better understanding of their behavior in copolymerization. At the same time, homopolymers based on higher  $\alpha$ -olefins with high molecular weight (MW) show promise as depressing agents, which improve the rheological characteristic of crude oil. Among the catalysts tested, the most efficient catalysts for production of these materials are supported titanium–magnesium catalytic systems [5, 6]. By contrast, metallocene catalysts, which have rather high activity, favor formation of polymers with low MW [2, 7–10].

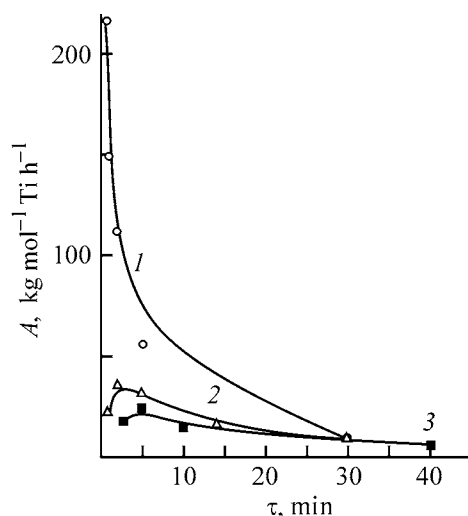
It has been shown previously [11] that the use of higher magnesium aluminum alkyls (MAA) as organo-

metallic components of Ziegler catalysts significantly increases the yield, MW, and isotacticity of polystyrene in comparison with the classic systems. The catalytic systems based on MAA are also effective in synthesis of ultra-high-molecular-weight polyethylene and its copolymers with higher  $\alpha$ -olefins [12]. In this context it was interest to study the polymerization of 1-hexene on the system  $\text{TiCl}_4\text{-Al}(\text{C}_6\text{H}_{13})_3 \cdot \text{Mg}(\text{C}_6\text{H}_{13})_2$ .

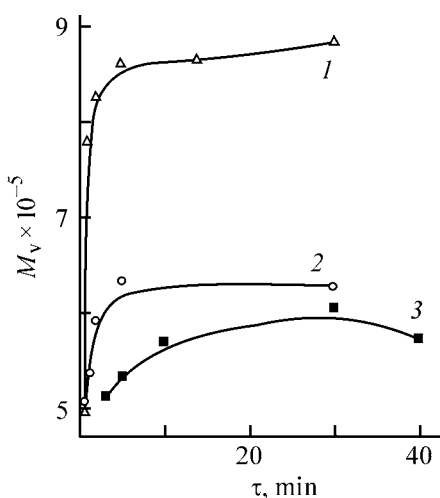
Data on the polymerization of 1-hexene on the catalytic system  $\text{TiCl}_4\text{-Al}(\text{C}_6\text{H}_{13})_3 \cdot \text{Mg}(\text{C}_6\text{H}_{13})_2$  at various temperatures are presented in Figs. 1 and 2. Figure 1 shows that the process decelerates on heating, whereas in polymerization of styrene the reaction rate on this system decreases with as the temperature is lowered [11, 13]. The maximum rate of hexene-1 polymerization is reached at 25°C. At this same temperature, the catalytic system exhibits the highest activity,



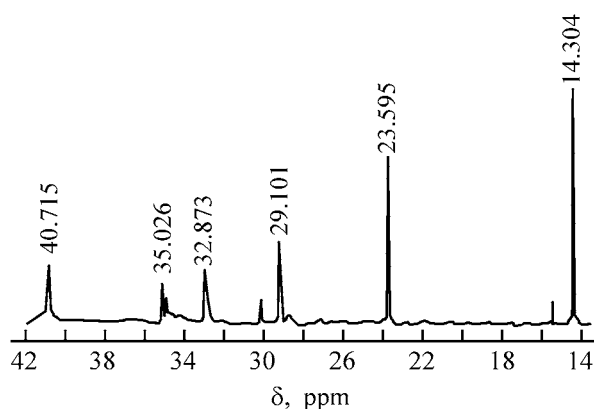
**Fig. 1.** Kinetic curves of polymerization of 1-hexene on the system  $\text{TiCl}_4\text{-AlMg}(\text{C}_6\text{H}_{13})_5$  at (1) 25, (2) 15, and (3) 45°C. Polymerization conditions:  $[\text{TiCl}_4] = 0.028 \text{ M}$ ,  $[\text{1-hexene}] = 2.24 \text{ M}$ ,  $[\text{TiCl}_4] : [\text{AlMgR}_5] = 1 : 1$ , solvent hexane; the same for Figs. 2 and 3. ( $\alpha$ ) Degree of conversion and ( $\tau$ ) time.



**Fig. 2.** Activity of the catalyst  $\text{TiCl}_4\text{-AlMg}(\text{C}_6\text{H}_{13})_5$ ,  $A$ , vs. the polymerization time  $\tau$  at (1) 25, (2) 15, and (3) 45°C.



**Fig. 3.** Molecular weight of poly-1-hexene,  $M_w$ , vs. the polymerization time  $\tau$  at (1) 15, (2) 25, and (3) 45°C.



**Fig. 4.**  $^{13}\text{C}$  NMR spectrum of poly-1-hexene prepared on the  $\text{TiCl}_4\text{-alMg}(\text{C}_6\text{H}_{13})_5$  system at 25°C. ( $\delta$ ) Chemical shift; the same for Fig. 5.

which abruptly decreases with time (Fig. 2). This abrupt decrease in the catalyst activity may be due to hindered diffusion of the monomer to the active centers, since within 10–15 s after the beginning of polymerization the reaction mixture becomes viscous. At other temperatures, the activity reaches a maximum within 2.5–5 min and then slightly decreases and tends to a constant value. The low activity of the catalyst is apparently caused at high temperatures by a high rate of deactivation of the active centers of polymerization, and at low temperatures, by slow activation of the catalyst. A similar temperature dependence of the catalyst activity was observed in polymerization of 1-hexene on post-metallocene catalyst (maximum activity of the catalyst was reached at 28°C) [14]. In polymerization of higher  $\alpha$ -olefins on supported titanium-magnesium catalyst in the range

25–60°C, the polymerization rate and the catalyst activity increase steadily with temperature [5, 6].

It should be noted that, in polymerization of 1-hexene, the catalytic system  $\text{TiCl}_4\text{-Al}(\text{C}_6\text{H}_{13})_3 \cdot \text{Mg}(\text{C}_6\text{H}_{13})_2$  is more active ( $30\text{--}100 \text{ kg mol}^{-1}\text{Ti h}^{-1}$ ) than the supported titanium-magnesium catalysts ( $15\text{--}35 \text{ kg mol}^{-1}\text{Ti h}^{-1}$ ) [5]. We showed that the maximum activity of the catalyst is reached at the  $\text{AlR}_3 : \text{MgR}_2$  ratio in MAA equal to 1 : 1, and a decrease or increase in the content of magnesium dialkyl results in a decreased activity of the catalytic system [15]. This is apparently due, on the one hand, to higher alkylating power of MAA, compared to the equivalent amount of  $\text{AlR}_3$ , which result from involvement of two radicals from  $\text{MgR}_2$  in this process, whereas in the case of  $\text{AlR}_3$  only one alkyl radical participates in the process [16]. On the other hand, at a high content of magnesium dialkyl in the organometallic component, the low activity can be caused by overreduction of  $\text{TiCl}_4$  with excess  $\text{MgR}_2$  [17]. It should be noted that the molecular-weight distribution (MWD) of the polymer synthesized is rather wide ( $M_w/M_n = 28\text{--}29$ ) and suggests the presence of several types of active centers, which can alter their activity in the course of polymerization [18]. This fact also confirms participation of both  $\text{AlR}_3$  and  $\text{MgR}_2$  in alkylation of  $\text{TiCl}_4$ .

Figure 3 shows that the molecular weight of poly-1-hexene is significantly higher at lower synthesis temperature. The MW of the polymer increases with polymerization time [19]. This is apparently caused by stabilization of the Ti–C bond owing to formation of triple Ti–Al–Mg complexes, which hinders the deactivation of active centers and hampers the chain termination and transfer. It was found that the weight-average molecular weight of the synthesized polymer  $M_w$ , similarly to  $M_w$  of poly-1-hexene prepared on supported titanium-magnesium catalyst, is  $2 \times 10^5\text{--}6 \times 10^5$ , which is significantly higher than the molecular weight of the polymer synthesized on metallocene catalysts [7–10].

It has been shown previously that polymerization of styrene on the catalytic system  $\text{TiCl}_4\text{-Al}(\text{C}_6\text{H}_{13})_3 \cdot \text{Mg}(\text{C}_6\text{H}_{13})_2$  yields the polymer with a high degree of isotacticity [11]. Here, we studied the structure of the forming polymers by  $^{13}\text{C}$  NMR (Fig. 4). The  $^{13}\text{C}$  NMR spectrum of poly-1-hexene prepared at 25°C consists of six resonance lines. The chemical shifts of six carbon atoms well correlate with published data [8, 14]. As a rule, the degree of isotacticity of higher  $\alpha$ -olefins is evaluated as the ratio of the intensity of

the C-3 line at approximately 35.0 ppm (Fig. 5) to the total intensity of the signals at 34.0–35.0 ppm [8, 14]. The degree of isotacticity of the polymer, evaluated by this method, was 35%.

It should be noted in conclusion that the resulting polymers can be efficiently used as depressants for crude oils with a high solidification point.

## EXPERIMENTAL

Polymerization of 1-hexene was carried out in hexane at 15–65°C. The catalyst was prepared by reduction of  $\text{TiCl}_4$  with an  $\text{AlMg}(\text{C}_6\text{H}_{13})_5$  solution for 10 min at 20°C. The components were added in the following order:  $\text{TiCl}_4$ , metallorganic component and solution of monomer in hexane. The reaction was terminated by adding a mixture of ethanol and HCl. The polymer was separated from the reaction mixture, washed with ethanol, and dried in a vacuum at 60–75°C to constant weight. The compounds  $\text{Al}(\text{C}_6\text{H}_{13})_3$  and  $\text{Al}(\text{C}_6\text{H}_{13})_3 \cdot \text{Mg}(\text{C}_6\text{H}_{13})_2$  were prepared by the procedure described in [20]. All manipulations in synthesis of the catalysts and polymerization were performed under argon. 1-Hexene and hexane were dried and twice distilled from  $\text{CaH}_2$ . The viscosity-average molecular weight  $M_v$  of poly-1-hexene was evaluated by the equation  $[\eta] = 2.05 \times 10^{-4} M_v^{0.72}$  (cyclohexane, 25°C) [21]. The weight-average molecular weight and MWD of polymers were determined by gel-permeation chromatography on a Waters device equipped with three Styro-gel columns with the pore size of  $1 \times 10^3$ ,  $5 \times 10^4$ , and  $5 \times 10^5$  Å. THF was used as a solvent. The elution rate was  $1.2 \text{ ml min}^{-1}$ . The structure of the resulting polymers was studied by  $^{13}\text{C}$  NMR on a Bruker AC-400 spectrometer operating at 100.6 MHz. The spectra were recorded in  $\text{CD}_2\text{Cl}_2$  at 25°C.

## CONCLUSIONS

(1) The catalytic system  $\text{TiCl}_4\text{-Al}(\text{C}_6\text{H}_{13})_3 \cdot \text{Mg}(\text{C}_6\text{H}_{13})_2$  is more active in polymerization of 1-hexene than supported titanium-magnesium catalysts and favors synthesis of the polymer with a high molecular weight ( $M_w = 2 \times 10^5\text{--}6 \times 10^5$ ). The activity of the catalytic system and the molecular weight of the resulting polymers strongly depend on the polymerization temperature.

(2) The microstructure of the synthesized polymers was studied by  $^{13}\text{C}$  NMR. It was found that this system yields polymers with degree of isotacticity of approximately 35%.

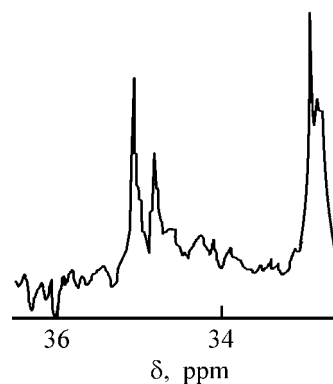


Fig. 5. C-3 region of the  $^{13}\text{C}$  NMR spectrum of poly-1-hexene prepared on the  $\text{TiCl}_4\text{-AlMg}(\text{C}_6\text{H}_{13})_5$  catalyst at 25°C.

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