Titanium compounds as catalysts of higher alpha-olefin-based super-high-molecular polymers synthesis

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Abstract. The synthesis of polymers of 10 million or more molecular weight is a difficult task even in a chemical lab. Higher α-olefin-based polymer agents of such kind have found a narrow but quite important niche, the reduction of drag in the turbulent flow of hydrocarbon fluids such as oil and oil-products. In its turn, searching for a catalytic system capable to produce molecules of such a high length and to synthesize polymers of a low molecular-mass distribution is part of a global task of obtaining a high-quality product. In this paper we had observed a number of industrial catalysts with respect to their suitability for higher poly-α-olefins synthesis. A number samples representing copolymers of 1-hexene with 1-decene obtained on a previous generation catalyst, a microsphere titanium chloride catalytic agent had been compared to samples synthesized using a titanium-magnesium catalyst both in solution and in a polymer medium.

1. Introduction

The first patents that described higher α-olefins polymerization in order to obtain hydrodynamic drag reduction agents for hydrocarbon fluids on Ziegler-Natta catalysts are dated late 1970 till early 1980. It is necessary to note that the catalytic systems which are active with respect to ethylene and propylene, can also be successfully used in higher α-olefins polymerization. One of the first catalysts applied was so called alumothermic titanium trichloride in presence of diethylaluminium chloride (DEAC) as a cocatalyst [1-3]. The activity of alumothermic catalyst was not higher than 2.5 kg of polymer per 1 kg of the catalyst, so its cost made an important piece of the actual cost of the dope. Next generation catalyst of Solvay-type was obtained by titanium tetrachloride reduction with an aluminorganic compound and characterized with much higher activity than previous types [3]. For the moment Solvay-type catalysts are rated as one of the most effective catalysts for obtaining of higher a-olefins super-high-molecular polymers [4]. The Russian-made version of Solvay-type, microsphere titanium trichloride with respect to higher α-olefins was patented in [5] and modified in [6].

It is considered as been proved that the monomer coordination with a transition metal compound is the necessary condition for the catalytic act implementation [7]. The metal organic intermediates being formed take part in the polymerization process, define its mechanism and affect significantly the structure of the polymer being synthesized. Nevertheless, the nature of the active centres and the methods for their action control are not still clear enough.

DEAC, trialkylaluminium, and dialkylaluminium oxide [8] can be used as titanium halogenide activators. The use of alkylalumoxanes in combination with titanium trichloride gives even more

effective catalytic system [9, 10]. Dichloroethane being added to alkylalumoxane as second cocatalyst is forming a synergistic pair with the latter so that titanium trichloride works more intensely [4].

Modern titanium-magnesium catalysts in lower olefins polymerization process show even more high activity than the microsphere titanium trichloride does [7, 11, 12]. Production and application method for titanium-magnesium catalyst in polymerization of higher α-olefins in solution has been patented [13, 16]. In case of propylene polymerization the process stereoselectivity is of significant importance: isotactic polypropylene possesses good working intrinsics. To increase the polymer stereoregularity some compounds having lone electron pairs, so-called electron-donor additives can be used [17]. In production of higher α-olefin-based roentgenoamorphous polymers of superhigh molecular weight the donor additives are obviously of minor effect, as far as the polymer's capability to lower hydrodynamic drag is caused not by the regularity but by the length of the carbon chain. Nevertheless, such donor additives as ketones and monoesters [18], phosphororganic compounds [19], amines, siloxanes [20], and also other classes of compounds [21] are patented.

It should be noted that the following trend appeared in the field under study: the use of titanium trichloride based catalysts for polymerization in the monomer medium and the application of titanium-magnesium catalyst for the poly-α-olefin synthesis in the solvent medium.

2.   Experimental Part

The synthesis was performed using microsphere $TiCl_3$, and titanium-magnesium catalyst as a polymerization promoter. Aluminorganic compounds, such as diethylaluminium chloride and triethyl aluminium were used as cocatalysts.

Casting polymerization of 1-octene was performed at 23°C. Into the 600 ml reactor made of polyethylene terephtalate (PETP) equipped with U-shaped three-necked cap, one inlet of which was supplied with a capillary for nitrogen-purging, 440 ml of monomer were loaded. The monomer was purged with dry nitrogen at ambient temperature during 30 minutes. Then, while keeping on purging, 15 ml (0.15 g) of aluminium chloride solution in petroleum solvent and 2 ml (0.08 g) of microsphere $TiCl_3$ preliminarily damped with a small amount of monomer were introduced using a dropping funnel. For a balanced distribution of catalyst in the monomer bulk, nitrogen was barbotated for 15 to 20 minutes until the thickening of the reaction mass, and then the stirring was terminated.

2.1.   Analytic procedures

We had determined medium viscosity molecular weights of the synthesized poly-1-octene samples.

2.1.1. Determination of intrinsic viscosity of poly-1-octene

Determination of intrinsic viscosity of 1-octene polymer solutions obtained under different conditions was performed using Ubbelohde viscosimeters, capillary diameter of 0.54 mm.

The viscosimeter was mounted in a thermostat and kept at 20ºC (determination temperature) for 10 to 15 minutes. Then the outflow duration was determined for pure tetrahydrofuran and for different concentration solutions. Then relative, corrected, and specific viscosity values were determined.
Intrinsic viscosity [η] (limiting viscosity number) is the limiting value of specific viscosity, when the solution concentration is approaching to zero. The intrinsic viscosity value was calculated using the linear regression equation.

2.1.2. Poly-1-octene average molecular weight determination

The medium viscosity molecular weight (M) was calculated using Mark-Kuhn-Houwink equation:

$$[\eta] = KM^{\alpha}$$

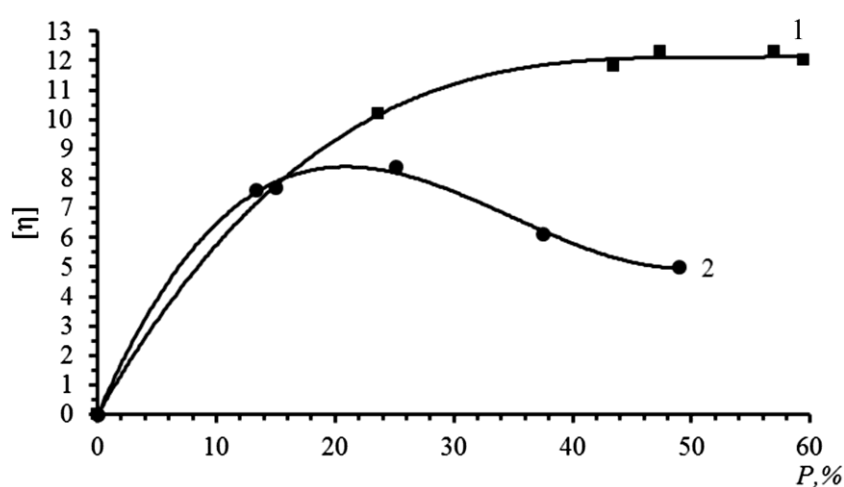where α is the constant for a given pair 'polymer-solvent' at a given temperature.
Constants K and α values for the system poly-1-octene – tetrahydrofuran are shown in Tab. 1.

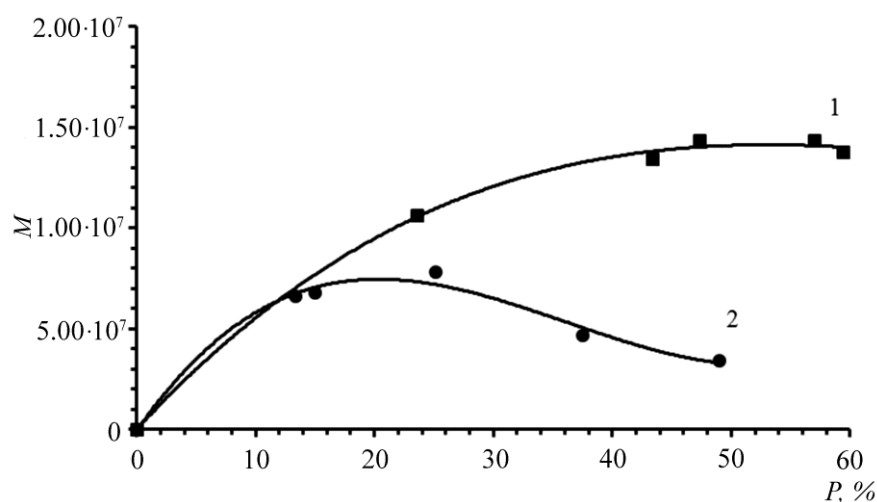**Table 1.** Viscosimetry Constants K and α Values for Polymer-Solvent Systems Studied [22]

Polymer	Solvent	Temperature, °C	K·10^5	α
Poly-1-octene	tetrahydrofuran	25.0	41.4	0.625

3. Results and discussion

The figure 1 shows dependences of intrinsic viscosity on the conversion depth for 1-octene using titanium trichloride (figure 1, curve 1) and titanium-magnesium catalyst (figure 1, curve 2). As it can be seen, the change of intrinsic viscosity value confirms that the polymer of a greater molecular weight was being formed on titanium trichloride when the monomer conversion is deeper.

Figure 1. Dependences of intrinsic viscosity value on the conversion depth for 1-octene using microsphere TiCl$_3$ (1) and titanium-magnesium catalyst (2)

The Figure 2 shows dependencies of medium viscosity molecular weight for poly-1-octene on the conversion depth of 1-octene in casting polymerization using titanium trichloride (figure 2, curve 1) and titanium-magnesium catalyst (figure 2, curve 2).

Figure 2. Dependencies of molecular weight value on octene polymerization depth using microsphere TiCl$_3$ (1) and titanium-magnesium catalyst (2)

The data presented show that the catalytic system 'titanium-magnesium catalyst – triethylaluminium' at conversion depth of 30 per cent when polymerization runs in the monomer medium produces the polymer of the molecular weight up to 7.5 million. Further polymerization on that catalytic system would not be expedient as far as low-molecular (ballast) polymer is formed; the latter deteriorates the final product capability to lower hydrodynamic drag in a turbulent flow of oil and oil products. During poly-1-octene synthesis runs on the catalytic system 'microsphere titanium trichloride – diethylaluminium chloride' the final product molecular weight grows up to 50 per cent conversion, after that it represents 'a plateau', the molecular weight being about 14.5 million.

Acknowledgments

References

[1]   Pat. 4289679 USA
[2]   Pat. 4358572 USA
[3]   Pat. 4415714 RU
[4]   Pat. 2232165 RU
[5]   Pat. 2075485 RU
[6]   Pat. 2238282 RU
[7]   Krencel B and Nehaeva L 1990 Russ. Chem. Rev. **12** 2034.
[8]   Pat. 4845178 USA
[9]   Pat. 2277103 RU
[10]   Pat. 6162773 USA
[11]   Sinn H, Kaminsky W, Vollmer H and Woldt R 1980 *Angew. Chem. Int. Ed. Engl.* **19** 390
[12]   Babushkin D, Semikolenova N, Zakharov V and Talsi E 2000 *Macromol. Chem. Phys.* **201** 558
[13]   Pat. 2171817 RU
[14]   Pat. 2221813 RU
[15]   Pat. 2152404 RU
[16]   Pat. 2230074 RU
[17]   Chirkov N 1976 *Polymerization on Complex Organometallic Catalyst* (Moscow: Chemistry)
[18]   Pat. 4493904 USA
[19]   Pat. 4433123 USA
[20]   Pat. 5028574 USA
[21]   Pat. 4945142 USA
[22]   Zhiqiang F, Linxian F and Shilin Y 1992 *Acta Polymerica Sinica.* **5** 577