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Comparison of the Turbulent Drag Reduction Effectiveness of Polymers from Higher Olefin Monomers (Hexene, Octene, Decene, Dodecene) in the Production of Hydrodynamic Drag Reducing Agents for Transportation of Hydrocarbon Liquids

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Abstract—Comparative studies (gel permeation chromatography and evaluation of turbulent drag reduction effectiveness on a turbulence rheometer) of ultra-high molecular weight polymers from a series of higher alpha-olefins (hexene, octene, decene, dodecene) used as hydrodynamic drag agents have been carried out. It was found that the activity of hexene in the polymerization on a titanium magnesium catalyst, if all other relevant factors remain unaltered, significantly exceeds the activity of octene, decene, and dodecene (the conversion of hexene in 24 h is almost 1.5 times higher than the conversion of other monomers over the same time), and the rates of polymerization of the latter differ slightly. The average molecular weights of all polymers differ only slightly: ~6 millions Da for polyhexene and ~5 millions Da for all the others. At the same time, the drag reduction effectiveness of the polymers showed a significant dependence on the nature of the initial monomers: the drag reduction effectiveness rapidly diminishes with an increase in the molecular weight of the corresponding alpha-olefin (3–4 times upon transition from polyhexene to polydodecene).

Keywords: hydrodynamic drag reducing agent, DRA, higher olefins, titanium magnesium catalyst, turbulence rheometer

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Drag reducing agents (DRA) based on ultra-high molecular weight polyolefins are widely used in pipeline transport for pumping oil and refined products, because due to the Toms effect [1] they can improve transportation of hydrocarbon liquids, as well as reduce energy consumption for pumping these liquids. This effect attracted the attention of researchers and caused a rapid growth in reports in the scientific and patent literature [2–6]. At the moment, the SciFinder search engine finds 2169 links for the keywords drag reducing polymer. Nevertheless, there is no single universally accepted theory explaining the drag reduction effectiveness of polymers (in [7] it can be found three groups of hypotheses), possibly due to a lack of experimental data, namely, studies of different polymers by the same methods. To prepare polyolefin drag reducing agents, terminal linear alkenes—hexene, octene, decene, and sometimes dodecene—are usually used. In this case, as a rule, polymers obtained from only one of the monomers or from a mixture of monomers are investigated. Therefore, according to the literature, it is very difficult to compare polyolefins made from various monomers with each other, since different polymerization conditions (different catalysts, different synthesis temperatures, etc.) and different methods of their study and quality criteria (intrinsic viscosity, molecular weighta characteristics, flow rate in the capillary of the turbulence rheometer, pressure reduction in the pipeline, etc.).

The purpose of this work is to fill this gap and compare higher olefins among themselves as raw materials for the production of drag reducing agents.

EXPERIMENTAL

Reagent preparation. Ethanol was boiled over magnesium metal until the reaction was completed and distilled under argon or nitrogen. Toluene was dried over sodium, degassed in vacuo, and saturated with argon. Heptane was purified efrom water and oxygen in the air similarly to toluene. Hexene-1 (Aldrich, 97%), octene-1 (Aldrich, 98%), decene-1 (Aldrich, 94%) and dodecene-1 (Aldrich, 95%) were dried with sodium in an argon atmosphere. Titanium tetrachloride (OTT-0 grade, State Standard TU 1715-455-05785388–2011) and triisobutylaluminum (Aldrich, 257206-500G) were used without purification.

A glass reactor (Ablize) of a 10 L nominal volume (total volume of 15 L) equipped with a mechanical stirrer with an electric drive, a distillation column, a descending cooler, a coolant jacket, a thermostat, and measuring tanks for loading liquid reagents were used for the synthesis of magnesium ethylate.

A glass reactor (Ablize) with a nominal volume of 30 L (total volume 40 L) equipped with a mechanical stirrer with an electric drive, a reflux condenser, a coolant jacket, a thermostat, and measuring tanks for loading liquid reagents were used for the synthesis of titanium magnesium catalyst (TMC).

The effectiveness of polymers as DRA was measured with the turbulence rheometer and heptane as a solvent. The effectiveness was determined by the formula $DR = 1 - (t_{sol}/t_0)^2$, where DR is the drag reduce effectiveness, t_{sol} is the expiration time of a fixed volume of polymer solution through the capillary, and t_0 is the expiration time of a pure solvent [5, 8]. The molecular weight characteristics of the polymers were studied on a PL GPC-220 gel permeation chromatograph, PL Olexis column (range of measured weights 10^3–10^7 Da), calibrated against polystyrene. The eluent is tetrahydrofuran, 1 mL min^{-1}, temperature 40°C.

Synthesis of magnesium ethylate. 531 g (21.85 mol) of magnesium metal, 5 g of freshly calcined ammonium chloride, and 1.5 L of ethyl alcohol were charged into the reactor through a loading hatch in a nitrogen flow. The reactor was heated to 60°C with stirring of the reaction mixture, and after the beginning of the violent stage of the process (intensive hydrogen evolution), 8 L of absolute ethanol was added from the measuring tank over 2 h, maintaining the temperature of the reaction mixture at ~70–75°C. After adding alcohol, the mixture was heated to ~75°C with stirring until the complete decomposition of magnesium metal (cessation of hydrogen evolution). Then the reactor was cooled, 5 L of toluene was introduced and the alcohol was distilled off to a boiling point of 109–110°C. The resulting suspension of magnesium ethylate (2.5 kg) in toluene was used in the synthesis of the catalyst.

Synthesis of titanium-magnesium catalyst. A suspension of the synthesized magnesium ethylate and 10 L absolute toluene were placed in a 30 L reactor. The reactor was heated to 60°C, and 7.5 L titanium tetrachloride was added, dosing from a measuring tank at such a rate that the temperature of the reaction mixture did not exceed 105°C (but not dropped below 90°C). After adding titanium tetrachloride, 588 mL of a donor (2-butyl-2-ethylpropanediol-1,3 dimethyl ether) was added to the reactor and the temperature of the reaction mixture was maintained at 112–114°C with stirring at a speed of 120 rpm for 4 h in argon atmosphere. Then the mixture was cooled, the solution was decanted over the precipitate, the precipitate was washed with 15 L absolute toluene at 50°C, 10 L absolute toluene, 5 L titanium tetrachloride were added and the reaction mixture was heated to 113–114°C with stirring at a speed of 80 rpm1 for 3 h. Then the mixture was cooled, the solution was decanted over the precipitate, the precipitate was washed first with 15 L absolute toluene, then five times with 10 L absolute heptane at 50°C and the reactor was filled with heptane to a total mixture volume of 25 L. 25 L of the catalyst with a 0.1 M titanium concentration was produced.

Polymerization procedure. In a three-necked 2 L flask equipped with a mechanical stirrer with an electric drive and a cooling mixture (ice with sodium chloride), 1 L of alkene was placed and cooled to –20°C. Then 5 mL (20 mmol) of triisobutylaluminium and 100 μL of 0.1 M titanium magnesium catalyst were added with vigorous stirring. The reaction mixture was taken with a syringe, dosed in 10 mL cans (three cans at a time), closed with a septum, and placed in a cooled mixture (water with ice). At certain intervals (Table 1), three cans

Table 1. The polymerization of hexene, octene, decene and dodecene in bulk

Run no.	Monomer	Duration of the polymerization, h	Yield, %	Drag reduction effectiveness, %		M_w, mln	M_w/M_n
				0.25 ppm	0.5 ppm		
1	Hexene	1	1.5	26.7	36.3	5.83	2.90
2	"	2	2.6	23.9	35.5	5.85	2.91
3	"	3	4.1	22.0	32.0	5.87	2.89
4	"	5	5.6	23.0	32.0	5.88	2.95
5	"	8	8.35	23.0	36.3	5.85	2.90
6	"	24	28.4	25.7	39.7	5.81	2.78
7	"	36	56.5	24.5	38.6	5.78	2.80
8	"	168	96.3	6.3	8.3	5.62*	2.84
9	Octene	1	2.75	13.4	18.2	4.83	2.84
10	"	3	3.75	12.4	23.0	4.88	2.70
11	"	5	4.90	12.5	23.3	5.14	2.88
12	"	8	7.00	12.4	23.1	5.40	2.95
13	"	24	18.15	16.3	23.7	5.47	2.65
14	"	72	31.5	13.4	23.0	5.44	2.89
15	"	192	70.0	15.5	24.5	5.71	3.07
16	"	336	91.0	9.3	17.3	5.64	2.88
17	Decene	1	2.05	8.3	14.3	5.47	3.02
18	"	3	3.73	8.3	15.3	5.62	2.74
19	"	5	5.50	8.7	14.3	5.62	2.70
20	"	8	7.50	9.3	18.2	5.46	2.65
21	"	24	20.82	7.9	14.3	5.30	2.79
22	"	96	66.0	8.3	13.4	5.33	2.65
23	"	336	93.0	8.3	11.4	5.47	3.02
24	Dodecene	1	2.05	5.2	10.4	5.35	3.02
25	"	3	3.73	7.3	14.3	5.22	2.74
26	"	5	5.50	6.3	12.4	5.25	2.70
27	"	8	7.50	5.2	13.4	5.17	2.57
28	"	24	20.82	7.3	11.4	5.37	2.65
29	"	336	90.2	6.3	10.4	5.12	2.51

[a] M_w of soluble fraction.

were opened, washed with 50 mL acetone and 50 mL of a 0.1% solution of ionol in methanol. Then the polymers were dried in vacuum at room temperature to constant weight, weighed, and the average yield was calculated.

RESULTS AND DISCUSSION

In the course of this work, polymers were synthesized and studied under the same conditions for

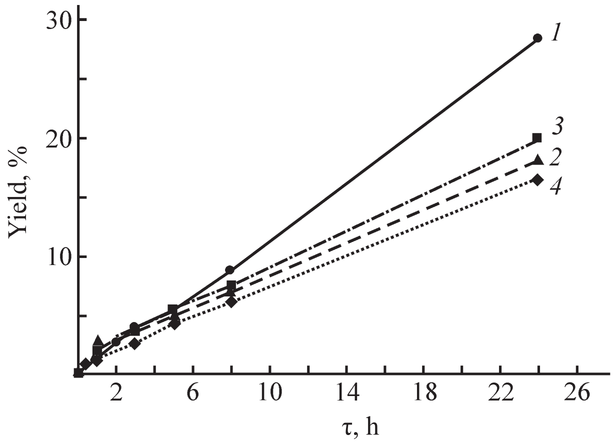

Fig. 1. Kinetic curves of coordination polymerization of higher alpha olefins. (*1*) Hexene, (*2*) octene, (*3*) decene, (*4*) dodecene.

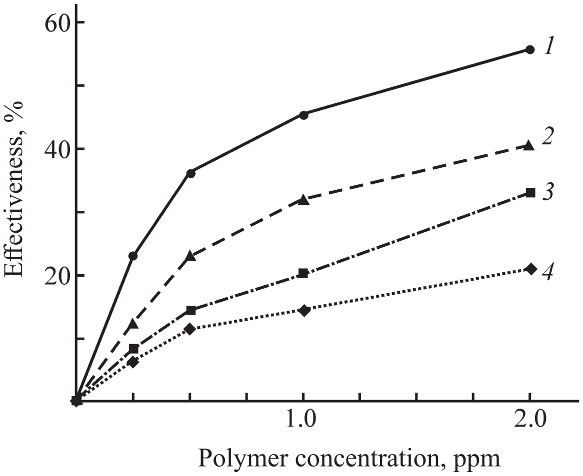

Fig. 2. Comparison of the drag reduction effectiveness of polymers of (*1*) hexene, (*2*) octene, (*3*) decene, and (*4*) dodecene (polymerization of 8 h).

the most accurate comparison among themselves of the main monomers used to prepare the drag reducing agent—hexene, octene, decene, and dodecene. The polymerization was carried out in bulk of monomer using a titanium magnesium catalyst. It should be noted that for the synthesis of ultra-high molecular weight polyolefins used in the preparation of DRA, titanium trichloride activated by organoaluminum cocatalyst is most often taken [9–12]. Nevertheless, according to the literature, the titanium magnesium catalyst is more promising. In a review [6], it is noted that in the general case, Titanium-magnesium Ziegler–Natta catalysts exhibit higher productivity compared to $TiCl_3$. The authors of [13] believe that the use of the titanium magnesium catalyst developed by them solves the problem of increasing the molecular weight of polyhexene prepared at an elevated polymerization temperature. It was shown in [8] that in order to achieve a 30% decrease in the hydrodynamic effect, it is necessary to use 3–4 times less polymer synthesized on TMC, in comparison with the polymer prepared on $TiCl_3$ under close conditions. The drag reduction effectiveness determined on the turbulence rheometer and the molecular weight characteristics derived on a gel permeation chromatograph were used as criteria for evaluating polymers.

To compare the reactivity of monomers in coordination polymerization, kinetic experiments were carried out under the same conditions: polymerization in a monomer bulk (1 L) upon cooling to 0°C under the action of a titanium-magnesium catalyst. At the same time, a feature was established: A rise in the molecular weight of the monomer from hexene to octene leads to a noticeable decrease in the polymerization rate, however, a further rise in the mass of the monomer does not lead to a noticeable change in the rate of the process (Fig. 1). Perhaps this feature is associated with spatial factors—a growth in the chain length upon transition from hexene to octene significantly increases spatial obstacles in the interaction with the active site of the catalyst. We believe that a further rise in the chain length does not result in a decrease in activity due to the greater removal of additional carbon chain atoms from the active site.

The obtained polymers were investigated by two methods: gel permeation chromatography and measuring the effectiveness by the turbulence rheometer. The results of a study on the turbulence rheometer showed a rapid decrease in the drag reduction effectiveness during the transition from hexene to dodecene (Fig. 2). For example, at a polymer concentration of 0.5 ppm, the drag reduction effectiveness of polyhexene, polyoctene, polydecene, and polydecene is 36.3, 23.1, 18.2, and 13.4%, respectively (Table 1, runs nos. 5, 12, 20, 27).

Molecular weight (M_w) and drag reduction effectiveness are practically independent of the monomer conversion, which is quite common in coordination polymerization. The exception is observed only for hexene: a sharp decrease in the drag reduction effectiveness (about 4 times) with a conversion > 90% (Table 1, run no. 8).

The molecular weight of polyhexene does not change so dramatically. The decrease in the effectiveness can be explained by the fact that upon the synthesis of this polymer, the formation of insoluble fractions in the polymerization product is observed, as a result, the true polymer concentration is significantly lower than the calculated one. In the case of the remaining polymers, insoluble fractions are not formed in the entire conversion range. It can be assumed that, at high conversions, branched or crosslinked polymers for polyhexene are also formed in all polymerization products, which leads to the formation of insoluble fractions. In the case of the remaining polymers, longer substituents improve solubility. In addition, polyoctenes, polydecenes, and polydodecenes have significantly lower molecular weights, which also improves solubility.

Comparing the data on the activity of the monomers, molecular weights and the effectiveness of the polymers, we believe that in the case of hexene the chain growth rate is noticeably higher than in the case of the other monomers, but the chain termination rates are very close, which results in a significantly higher molecular weight and correspondingly higher drag reduction effectiveness of polyhexene. In the series polyoctene–polydecene–polydecene, the average molecular weights of the polymers differ slightly. Nevertheless, in this series there is a clear decrease in the drag reduction efficiency. It must be borne in mind that molecular weights determined by gel permeation chromatography are not absolute. These polyolefins can have different Mark–Kuhn–Houwink constants (which are not yet known for these polymers) and, correspondingly, different real molecular weights at the same weights determined by gel permeation chromatography.

CONCLUSIONS

Produced, if all other relevant factors remain unaltered, polyhexene has a significantly higher molecular weight and greater the drag reduction effectiveness than other polymers. However, a high conversion of hexene (>90%) leads to the formation of insoluble fractions of the polymer, which diminishes the drag reduction effectiveness. When using polymerization methods involving incomplete conversion (<<90%), it is preferable to utililze hexene, since this monomer provides the greatest drag reduction effectiveness. If methods involving practically quantitative conversion (>90%, block polymerization) are used, it is undesirable to utilize hexene, it is necessary to use olefins with a greater number of carbon atoms (octene, decene, dodecene), since the corresponding polymers do not form ballast (insoluble) fractions. These conclusions are true in the case of the synthesis of drag reducing agents for light oils and light refined products, since the heptane utilized in measuring the drag reduction effectiveness is closest to these liquids.

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CONFLICT OF INTERESTS

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