Ziegler catalytic systems in cationic polymerization

1. Polymerization of isobutylene by the $AlBu^i_3$—$TiCl_4$—CCl_4 system

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The ternary catalytic system $AlBu^i_3$—$TiCl_4$—CCl_4 initiates the cationic polymerization of isobutylene in toluene at room temperature, whereas the binary combinations of these components do not induce isobutylene polymerization. At low CCl_4 concentrations, the polymerization rates decrease sharply with time, and the quantitative yield of the polymer is achieved at an excess of CCl_4 with respect to the titanium and aluminum components. The molecular weights of the polymers range within 1300—4000, and the index of polydispersity, as a rule, does not exceed 2.7. The influence of the conditions of component mixing (order of addition, duration of exposure prior to addition of the third component) on the yield and molecular weight of the polymerization product was found.

Key words: isobutylene, polyisobutylene, titanium tetrachloride, carbon tetrachloride, triisobutylaluminum, cationic polymerization.

Ziegler catalytic systems based on titanium halides and trialkylaluminum compounds are widely used in production of polyolefins and polydienes. Several works are devoted to the modification of these systems with various additives. The additives (or their complexes with components of the catalytic system) are assumed to be capable of deactivating and reactivating nonspecific centers of polymerization, transforming them into active stereospecific centers,[1—5] increasing the solubility of catalysts,[6] *etc.* Polymerization with Ziegler catalysts is usually considered an anionic coordination process.[7]

In many cases, the deviation of the real Al/Ti molar ratio from the optimum value results in a decrease in the catalytic activity and molecular weight, impairment of stereospecificity, gel formation (in the case of preparation of polydienes), *etc.*[8—10] The possibility of using these systems for cationic polymerization or oligomerization of monomers important in industry, for example, isobutylene (IB), has been poorly studied.[11—13]

In this work, we studied the modification of the $TiCl_4$—$AlBu^i_3$ Ziegler catalytic system resulting in the efficient production of cationic species capable of initiating IB polymerization.[14] Presently, the production of polyisobutylene (PIB) is mainly based on the use of $AlCl_3$. However, commercial aluminum chloride is contaminated with slime and poorly dissolves in hydrocarbon media. The polymerization process in its presence can hardly be controlled and is usually accompanied by the formation of undesirable oligomeric products (dimers, trimers of IB).[15] At the same time, $TiCl_4$ and $AlBu^i_3$ are commercially produced and used in the production of various large-tonnage polymers. They are of a sufficiently stable quality and highly soluble in hydrocarbons.

Experimental

Experiments on polymerization were carried out in a completely sealed glass setup using thoroughly purified and dried monomer and solvent (toluene) ("superdry" conditions); the residual moisture content was at most 10^{-5} mol L^{-1}.

Toluene was washed with H_2SO_4, water, a 10% solution of soda, and again with water, dried above $CaCl_2$, distilled, dried additionally with molecular sieves, deaerated, boiled with the potassium-sodium alloy, and condensed *in vacuo*.

Isobutylene was dried with granulated alkali, molecular sieves, CaH_2, and $AlBu^i_3$ or $AlBu^i_2Cl$. The solvent and monomer after drying were dosed into ampoules with thin glass membranes, in which they were kept in a vacuum. Solutions of the monomer were kept in the same manner.

Titanium tetrachloride was pre-boiled with copper chips and condensed *in vacuo*. CCl_4 was dried with molecular sieves and condensed *in vacuo*. Commercial toluene solutions of $AlBu^i_3$ were separated from slime on a glass filter. For experiments on polymerization, toluene solutions of components with known concentrations were prepared and dosed in thin-walled glass balls.

The kinetics of the process were studied dilatometrically. In several experiments, the yield of polymers was additionally monitored by the dry residue. The two methods gave close results. Polymers were precipitated with methanol and dried *in vacuo*.

The viscosity of toluene solutions of polymers was measured on the Ubellohde viscosimeter at 25 °C, and the data obtained were used for the calculation of the intrinsic viscosity $[\eta]$. The average and weighted-mean molecular weights $\bar{M}_n$ and $\bar{M}_w$ were determined by gel permeation chromatography (GPC) on a Waters 200 chromatograph with four columns packed with Stiragel (10^6, 10^5, 10^4, and 500 Å) and a differential refractometer, and toluene was used as the eluent (1 mL min^{-1}). Polystyrene standards were used for calibration. Corrections for "instrument broadening" were not made.

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Results and Discussion

Our studies showed that under the superdry conditions, neither starting component ($TiCl_4$ and $AlBu^i_3$) nor their combination at a molar ratio Ti : Al < 1 result in a noticeable formation of the polymer even at a sufficiently prolonged contact with a solution of IB in toluene. For activation of the $TiCl_4$—$AlBu^i_3$ system, an additional modifying component, such as CCl_4, should be used (Table 1). The binary CCl_4—$AlBu^i_3$ and CCl_4—$TiCl_4$ systems at concentrations of the components of ~1 mmol L^{-1}, the ratio $AlBu^i_3 : TiCl_4 = 2—16$, and the temperature of 30 °C also do not initiate IB polymerization, at least in 2 days.

Some kinetic curves are presented in Fig. 1. The beginning of polymerization is preceded by an induction period, whose duration (t_{ind}) ranges from 3 to 20 min. After the relatively slow beginning of the polymerization process, its rates increase for 1—3 min and decrease rather sharply after the end of the active period with the duration t_{act} (the S-shaped character of the kinetic curves). In all these experiments, the conversion was noticeably lower than 100%. The molecular weight of the polymers depends weakly on the concentration and the ratio of components of the initiating system and only slightly decreases when the more active initiating systems are used. For example, the lowest-molecular product with $\bar{M}_n = 2550$ was obtained in entry *7* in 61% yield, and the polymer with $\bar{M}_n = 5340$ was obtained in entry *3* in ~30% yield. Probably, the polymerization regime becomes isothermic with an increase in the reaction rates and heat effect.

Comparison of entries *1*—*3* shows that an increase in the time of combined exposure of CCl_4 with $AlBu^i_3$ to a solution of the monomer from 1 min to 1 h decreases duration of the induction period by ~3 times. Probably, these two compounds react rather slowly, without formation of products capable of initiating the cationic polymerization. This reaction can also be responsible to some extent for the increase in the polymer yield when $TiCl_4$ is introduced instead of $AlBu^i_3$ as the second component (entries *1* and *7*). However, taking into account the relative slowness of the reaction of $AlBu^i_3$ with CCl_4, we can assume that the high yield of the polymer is due to different local concentrations of the reagents with different orders of mixing of the components.

At a constant concentration of $AlBu^i_3$, an increase in the content of $TiCl_4$ results in a noticeable shortening of the induction period (*cf.* entries *2*, *4*, and *5*). Similar shortening is observed when the concentration of $AlBu^i_3$ decreases along with an unchanged content of $TiCl_4$ (*cf.* entries *2* and *6*). In other words, when the $AlBu^i_3 : TiCl_4$ ratio decreases, a pronounced tendency for decreasing t_{ind} is observed.

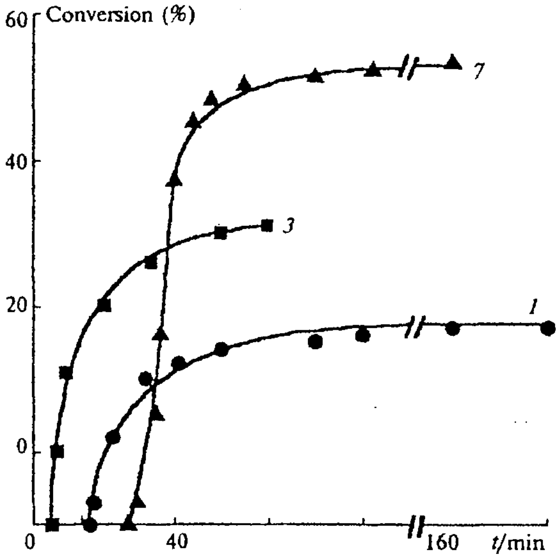

Fig. 1. Kinetic curves of IB polymerization in the $AlBu^i_3$—$TiCl_4$—CCl_4 system in toluene at 30 °C. The conditions and numeration of entries correspond to those in Table 1.

Table 1. Conditions and results of IB polymerization in the $TiCl_4$—$AlBu^i_3$—CCl_4 initiating system (toluene, 30 °C, [IB] = 10 wt.%)

Entry	$CCl_4 : AlBu^i_3 : TiCl_4$[a]	t_3[b]	t_{ind}[c]	t_{act}[d]	t_{pol}[e]	Yield (%)		[η]	$\bar{M}_w$	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$
		min				in 1 h	total	/dL g^{-1}	10^{-3}		
1	0.8 : 1.6 : 0.2	1	13	17	180	25	27	0.085	—	—	—
2	0.8 : 1.6 : 0.2	30	6	25	180	37	41	—	6.47	3.29	1.97
3	0.8 : 1.6 : 0.2	60	4	21	70	30	31	0.067	8.73	5.34	1.63
4	0.8 : 1.6 : 0.1	30	16	24	150	28	29	0.093	—	—	—
5	0.8 : 1.6 : 0.4	30	4	21	60	41	42	0.089	8.72	4.11	2.12
6	0.8 : 0.8 : 0.2	30	3	17	180	42	51	0.076	7.20	3.52	2.04
7[f]	0.8 : 1.6 : 0.2	1	20	20	150	61	62	0.082	6.84	2.55	2.68

[a] The ratio of concentrations/mmol L^{-1}. The order of introducing the components in entries corresponds to that indicated.
[b] Time interval between moments of introducing the second and third components.
[c] Duration of the induction period.
[d] Duration of the active polymerization period.
[e] Time interval from the moment of introducing the third component to the precipitation of the polymer.
[f] The components were introduced in the following order: CCl_4, $TiCl_4$, and $AlBu^i_3$.

Table 2. Results of attempts to activate the $TiCl_4$—$AlBu^i_3$—CCl_4 initiating system (toluene, 30 °C, [IB] = 10 wt.%)[a]

Entry	$CCl_4 : AlBu^i_3 : TiCl_4$[b]	t_3[c]	t_4[d]	t_{pol}[e]	Yield of PIB	$\bar{M}_w$	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$
			min		(%)	10^{-3}		
1[f]	0.8 : 1.6 : 0.2	30	30	30	40			
				120	45	6.86	2.73	2.52
2[g]	0.8 : 1.6 : 0.2	40	40	40	37			
				160	37	—	—	—
3	0.2 : 0.8 : 0.2	30	—	90	24			
				2 days	29	11.0	5.28	2.08
4	0.8 : 0.8 : 0.2	30	—	60	76	9.46	3.92	2.41
5	1.6 : 0.8 : 0.2	30	—	40	83	6.89	3.71	1.86
6	2.5 : 0.8 : 0.2	30	—	15	100	5.96	3.08	1.93
7	5.0 : 1.6 : 0.2	30	—	5	100	11.4	2.20	5.18
8[h]	5.0 : 1.6 : 0.2	2 days	—	7	100	3.60	1.35	2.65

[a] In entries *1*—*6*, duration of the induction period (t_{ind}) is 3—6 min, and duration of active polymerization (t_{act}) is 10—25 min; in entries *7* and *8*, t_{ind} is ~2 min, and then the fast polymerization occurs to the complete conversion.

[b] The ratio of concentrations/mmol L^{-1}.

[c] The order of introducing the components in entries corresponds to that indicated. The time interval between moments of introducing the second and third components.

[d] Time interval between moments of introducing the third component and the last additive.

[e] Time interval from the moment of introducing the third component to the precipitation of the polymer.

[f] Then $TiCl_4$ (0.2 mmol L^{-1}) was added.

[g] Then $AlBu^i_3$ (1.6 mmol L^{-1}) was added.

[h] The components were introduced in the following order: $AlBu^i_3$, $TiCl_4$, and CCl_4; polymerization was not observed before the introduction of CCl_4.

The S-shaped character of the kinetic curves indicates that termination reactions occur in the system, and at the concentrations of components used, the loss of active centers in these reactions is not compensated. To reveal the possibility of increasing the activity of the system, three variants were studied: (a) the introduction of an additional amount of $TiCl_4$ after the kinetic curve reached a plateau; (b) similar procedure with $AlBu^i_3$; and (c) an increase in the amount of CCl_4. The results presented in Table 2 demonstrate that the first two variants gave no effect (entries *1* and *2*). By contrast, an increase in the initial concentration of CCl_4 results in a monotonic increase in the polymer yield, and an almost 100% yield was found for the mixture with a concentration of CCl_4 of 2.5 mmol L^{-1}. Under these conditions, t_{ind} is shortened to 2 min, and after the end of the induction period, polymerization occurs rapidly (for 3—5 min) to the complete conversion. It is noteworthy that the triple system obtained by the introduction of CCl_4 (in 2 days) to the product of the reaction of $AlBu^i_3$ with $TiCl_4$ (classical Ziegler—Natta catalyst) also possesses a very high activity (see Table 2, entry *8*). The formation of polymer was not observed in the presence of this binary system before the introduction of CCl_4, which disagrees with the published data,[11] which, however, have not been confirmed.[16]

Comparison of entries *6* (Table 1) and *4* (Table 2) carried out with deficient CCl_4, but formally under similar conditions, allows one to observe some difference in the yields of the polymers and their molecular weights. It is most likely that such hardly controlled factors as the rate of mixing or a change in the content of admixtures (for example, moisture) on going from one batch to another can play a certain role in this system.

Our results show that the formation of cationic active centers needs the presence of all three components in the system: $AlBu^i_3$, $TiCl_4$, and CCl_4. In addition, the formation of these centers is a sufficiently slow reaction, which is indicated by the induction period.

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