Butadiene Polymerization with Vanadium–Titanium–Aluminum Catalytic Systems

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ABSTRACT: Butadiene polymerization in the presence of mixed vanadium–titanium–aluminum catalytic systems containing various organoaluminum compounds (OACs) was investigated. The main factors influencing the activity and stereospecificity of the [$VOCl_3$–$TiCl_4$–OAC_1]–(heating)–OAC_2 catalysts [where OAC_1 and OAC_2 were Al(i-Bu)$_3$, Al(i-Bu)$_2$H, or Al(i-Bu)$_2$Cl] were considered. The kinetic parameters of the process were determined. The high activity and stereospecificity of the multicomponent systems proba-

bly accounted for the formation of polymerization active sites with both transition-metal derivatives in their structure. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 91: 211–217, 2004

Key words: Ziegler-Natta polymerization; polybutadiene; transition metal chemistry; stereospecific polymers; kinetics (polym.)

INTRODUCTION

During the polymerization of dienes and olefins, the activity of some Ziegler–Natta catalysts increases when the compound of the second transition metal is introduced into their structure.[1] Therefore, the introduction of some titanium chloride increases the yields and molecular masses of polymers during the synthesis of polydienes in the presence of trans-stereoregulating catalytic systems on the base of vanadium chloride in combination with an organoaluminum compound (OAC).[2]

The activity and stereospecificity of mixed vanadium–titanium systems depend on several factors: the nature of the vanadium and titanium compounds, the component ratio, the catalyst preparation conditions, the temperature regime, and the method of mixing. Therefore, the addition of $TiCl_4$ to the $VOCl_3$–Al(i-Bu)$_3$ system and OAC introduction in two stages in combination with a thermal treatment of the catalytic system during the first stage of its preparation lead to significant increases in the yields of 1,4-*trans*-polyisoprene and 1,4-*trans*-polypyperilene.[3,4] The introduction of OAC in two portions is conditioned by the various cocatalyst functions and by the reduction and alkylation of transition metals in optimal regimes. The

roles of $TiCl_4$ and the thermal treatment of the catalytic system in active-site (AS) formation are not clear. There is also no single interpretation of the presence of two maximums of activity of vanadium–titanium systems depending on the concentration of the first portion of OAC[3,4] added before the thermal treatment of the catalytic complex.

In this work, we tried to answer the following questions: would the same picture be obtained with the polymerization of a simpler monomer, butadiene on the [$VOCl_3$–$TiCl_4$–OAC_1]–(heating)–OAC_2 catalytic system [where OAC_1 and OAC_2 are Al(i-Bu)$_3$, Al(i-Bu)$_2$H, or Al(i-Bu)$_2$Cl]; how would the nature of titanium and OACs influence the working parameters of the catalyst, and would the optimal conditions of the catalyst preparation and component ratio change with the polymerization of butadiene.

To specialize the role of a nontransition metal in reduction and alkylation reactions in such multicomponent systems, we introduced the same and various OACs before and after the thermal treatment.

EXPERIMENTAL

Catalytic complexes were prepared as described in ref. 3. To a mixture of $VOCl_3$ and $TiCl_4$ with a concrete Ti/V ratio, the first portion of selected OAC (OAC_1) was added, and then the reaction mass was treated at 130°C for 60 min. After the mixture cooled down to room temperature, an additional portion of the cocatalyst (OAC_2) was added. The ready-made catalytic complex was added to a toluene solution of butadiene. The polymerization of butadiene was carried out in

toluene at $25 \pm 0.1°C$ under conditions excluding the penetration of air and moisture. The microstructure and molecular weight of polybutadiene (PB) were determined with IR spectroscopy and gel permeation chromatography.[5]

RESULTS AND DISCUSSION

Earlier, we determined the kinetic parameters of butadiene polymerization in the presence of the $VOCl_3$–$Al(i\text{-}Bu)_3$ catalytic system prepared at low temperatures ($<0°C$). This system displayed its maximum activity at $Al/V = 3.8$–4.0, and the apparent polymer chain propagation rate constant (k_p) at $25°C$ was 250 L mol/min. PB containing 90% 1,4-trans units and 10% 1,2-units was formed, and its number-average molecular weight (M_n) was 1.2×10^4.[6]

When we used $[VOCl_3$–$TiCl_4$–$Al(i\text{-}Bu)_3]$–(heating)–$Al(i\text{-}Bu)_3$ (system I) for the transpolymerization of butadiene, the optimal component ratio and catalyst preparation conditions in relation to its activity proved to be the same as those for polyisoprene and polypyperilene synthesis.[3,4] The bimodal dependence of the PB yield on the first $Al(i\text{-}Bu)_3$/vanadium ratio (at $Al_1/V = 0.6$ and $Al_1/V = 1.6$) and at fixed ratios of Ti/V (0.5) and Al_2/V (4.0) was also observed [Fig. 1(a)]. The concentration of 1,4-trans units in the resulting polymer increased from 92 to 97% with a corresponding change in the content of 1,4-cis units from 5 to 0% when the Al_1/V ratio varied from 0.2 to 3.0. The concentration of 1,2-structures was constant (2–3%).

At the same time, the dependence of the polymer M_n value on the concentration of OAC_1 was also bimodal: the maximums of M_n were 4.2×10^{-5} at $Al_1/V = 0.6$ and 7.9×10^{-5} at $Al_1/V = 1.6$, and the minimum was 3.4×10^5 at $Al_1/V = 1.2$. For the $VOCl_3$–$Al(i\text{-}Bu)_3$ catalytic system, the content of 1,4-trans units in PB and its M_n decreased when the concentration of OAC in the polymerization medium increased.[6] We suppose that these differences in the polymer properties occurred for the following reasons: the polymerization AS structures were varied for $[VOCl_3$–$TiCl_4$–$Al(i\text{-}Bu)_3]$–(heating)–$Al(i\text{-}Bu)_3$ in comparison with $VOCl_3$–$Al(i\text{-}Bu)_3$; OAC in the double-component catalyst $VOCl_3$–$Al(i\text{-}Bu)_3$ simultaneously played the roles of reducer, alkylater, and chain-transfer agent; and in the vanadium–titanium catalyst, the first portion of OAC was mainly spent on the reduction of a mixture of transition-metal chlorides.

Further investigations of polymerization with the vanadium–titanium catalyst were carried out at two fixed ratios: $Al_1/V = 0.6$ (system IA) and $Al_1/V = 1.6$ (system IB; Table I).

The dependencies of the activities of catalytic complexes IA and IB on the second $Al(i\text{-}Bu)_3$/vanadium ratio were extremely monomodal [Fig. 1(b)]. The amount of OAC introduced during the first stage af-
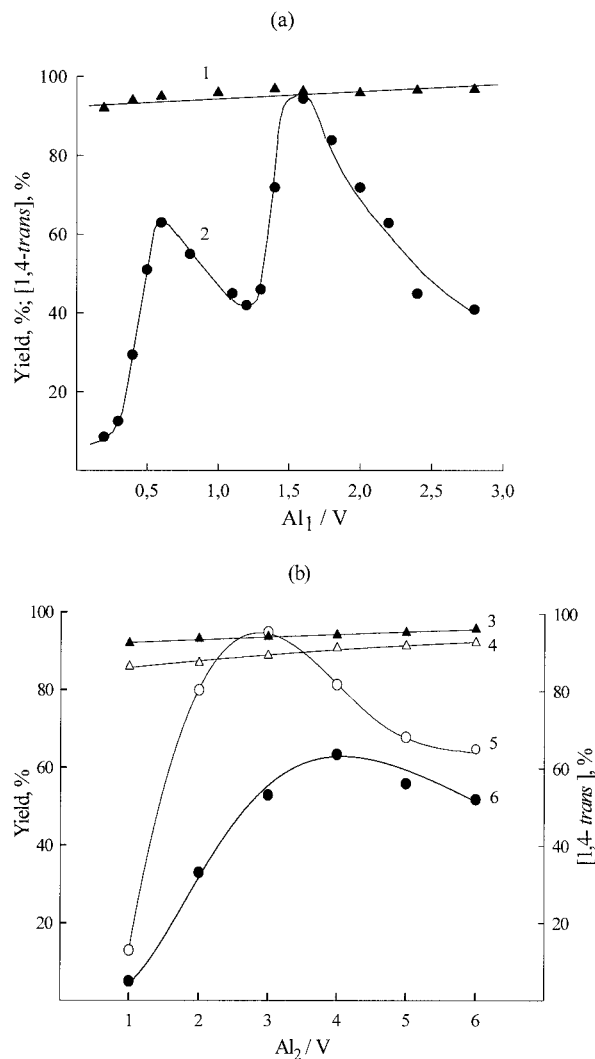

Figure 1 Variations in (1,3,4) the 1,4-trans-unit content in the polymer and (2,5,6) the PB yield with the molar Al/V ratio in complex I at (a) the first stage and (b) the second stage of catalyst formation (conditions: toluene; temperature $= 25°C$; time $= 30$ min; vanadium concentration (C_V) $= 0.005$; monomer concentration (C_M) $= 1.0$ mol/L; Ti/V $= 0.5$; $Al_2/V = $ (a) 4.0 or (b) 0.6 or 1.6; thermal treatment $= 130°C$ for 1 h).

fected the positions and values of the maximums. The M_n values of the polymers were the highest at the optimal (in relation to the activity) ratio of Al_2 to V. Thus, when the concentration of the second portion of OAC was greater than necessary, OAC served as a transfer agent of the polymer chain. Nevertheless, the 1,4-trans-unit content in PB increased with a corresponding change in the content of 1,4-cis units when the Al_2/V ratio rose [Fig. 1(b)]. The concentration of 1,2-structures was 2–3%, being independent of Al_2/V. The 1,4-trans-unit content was lowered when the Al/V ratio rose in the $VOCl_3$–$Al(i\text{-}Bu)_3$ catalyst.[6] This fact may account for the different AS structures in the compared systems.

TABLE I
Optimum Ratios of the First and Second Part of OAC for
[VOCl$_3$–TiCl$_4$–OAC$_1$]–(Heating)–OAC$_2$ Complex Conditions as in Fig. 1.

OAC$_1$	OAC$_2$	Complex	Al$_1$/V	Al$_2$/V	PB yield (%)
Al(i-Bu)$_3$	Al(i-Bu)$_3$	IA	0.6	4.0	63.6
		IB	1.6	3.0	95.5
Al(i-Bu)$_2$H	Al(i-Bu)$_3$	IIA	0.6	3.0	60.4
		IIB	1.6	2.5	80.7
Al(i-Bu)$_3$	Al(i-Bu)$_2$H	IIIA	0.6	3.0	45.1
		IIIB	1.6	2.5	74.7
Al(i-Bu)$_2$H	Al(i-Bu)$_2$H	IVA	0.6	3.0	39.0
		IVB	2.4	2.5	71.6
Al(i-Bu)$_2$Cl	Al(i-Bu)$_3$	VA	1.6	5.0	68.9
		VB	2.4	4.0	95.6
Al(i-Bu)$_3$	Al(i-Bu)$_2$Cl	VIA	1.6	12	60.1
		VIB	2.2	12	91.6
Al(i-Bu)$_2$Cl	Al(i-Bu)$_2$Cl	VIIA	1.6	12	47.9
		VIIB	2.4	20	84.8

Conditions were the same as in Figure 1.

The rise of trans-stereospecificity of action in systems IA and IB may also have been conditioned by the presence of titanium chloride in the polymerization medium and by the thermal treatment of the catalytic complex. Indeed, the [VOCl$_3$–Al(i-Bu)$_3$]–(heating)–Al(i-Bu)$_3$ catalytic system, prepared under the conditions given in Figure 1 (including optimal ratios of Al$_1$/V), formed highly stereoregular *trans*-PB but displayed a very low activity (Fig. 2). There was synergism: the polymer yield increased several times when TiCl$_4$ was added to the vanadium catalyst. A monomodal dependence of the activity of systems IA and IB on the concentration of

TiCl$_4$ was observed (the maximum occurred at Ti/V = 0.5). The concentration of 1,4-cis units rose with a corresponding lowering of the 1,4-trans-structure content when the amount of TiCl$_4$ was increased (Fig. 2). The number of 1,2-units was constant: 2–3%. Consequently, we can suggest that transregulating AS in mixed catalysts may contain the atoms of both transition metals.

It is known that the interaction of TiCl$_4$ with trialkylaluminum leads to the formation of β-TiCl$_3$, on which *cis*-polydienes are formed. Thermal treatment at 170°C transforms it into α-TiCl$_3$, which synthesizes transpolymers.[7]
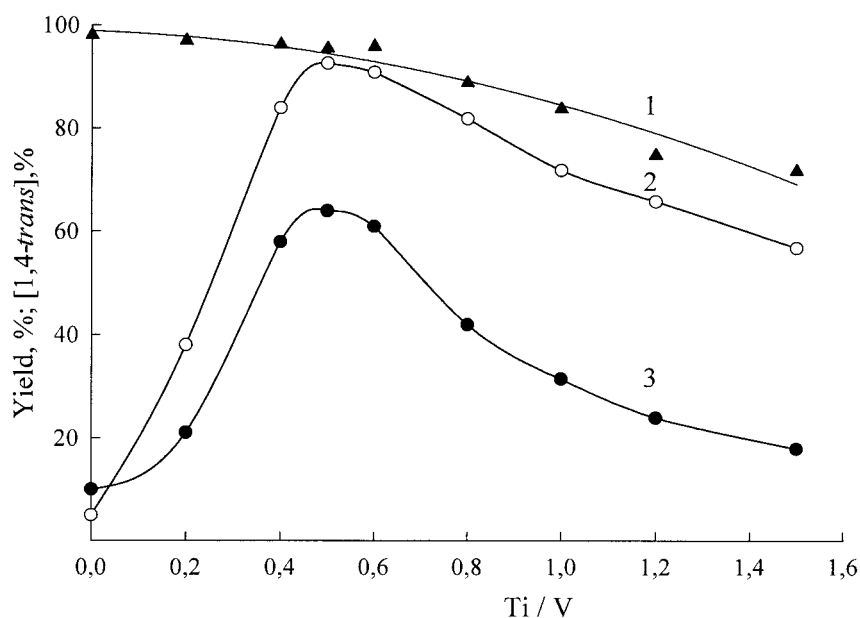

Figure 2 Variations in (1) the 1,4-trans-unit content in the polymer and (2,3) the PB yield with the molar Ti/V ratio for catalytic systems (3) IA and (1,2) IB (conditions: Al$_1$/V = 0.6 for IA and 1.6 for IB; for the rest of the conditions, see Fig. 1).
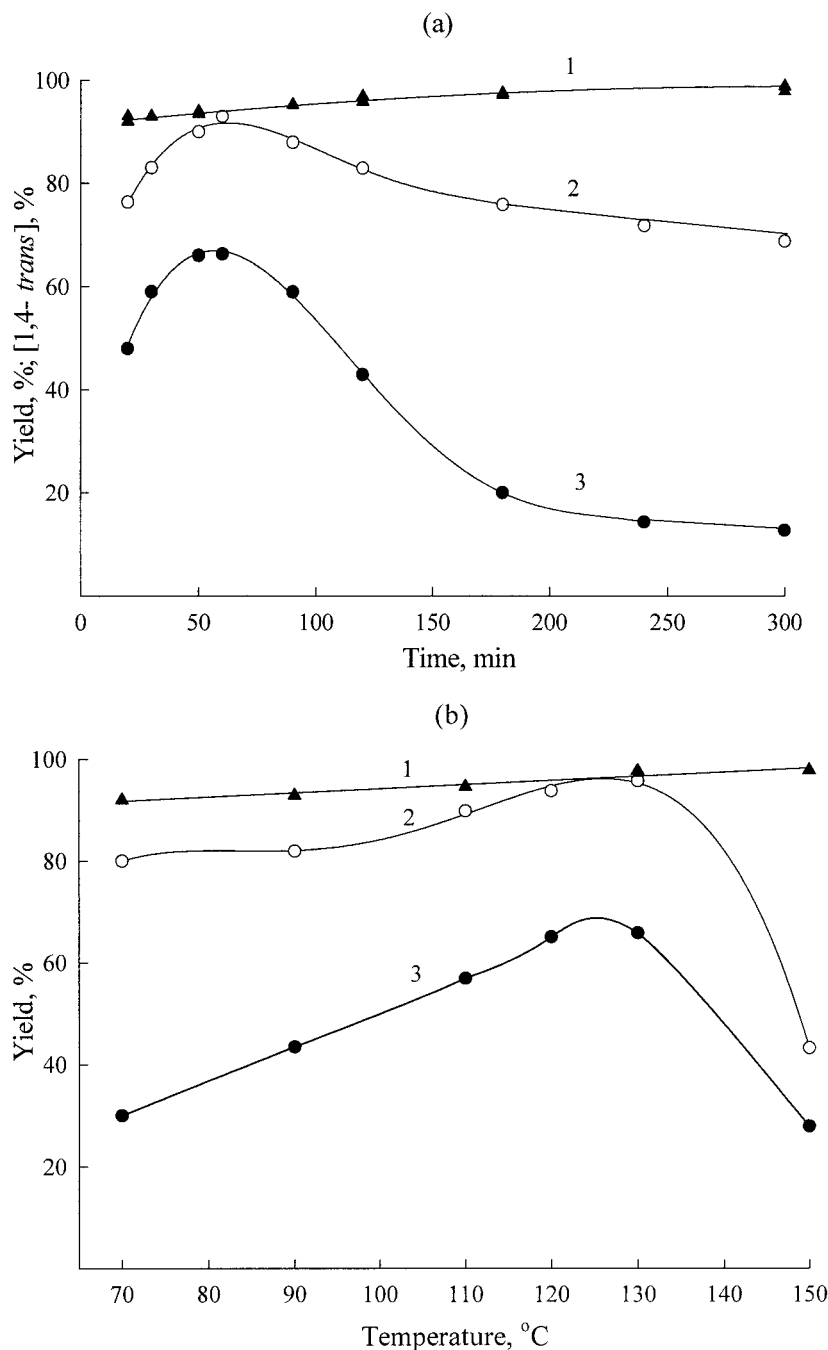
Figure 3 Variations in (1) the 1,4-trans-unit content in the polymer and (2,3) the PB yield with (a) the thermal treatment time and (b) the temperature for catalytic systems (1,3) IA and (1,2) IB with the first part of $Al(i\text{-Bu})_3$ (conditions: $Al_1/V = 0.6$ for IA and 1.6 for IB; for the rest of the conditions, see Fig. 1).

We showed that for systems IA and IB, the optimal conditions of the thermal treatment of $VOCl_3$ and $TiCl_4$ mixtures in the presence of the first portion of OAC were 60 min and 130°C. The catalyst activity was dependent on the time [Fig. 3(a)] and temperature [Fig. 3(b)] of exposition. These conditions were much sparer than required for the transformation of brown $TiCl_3$ into a violet allotrope modification. Therefore, it was not clear what type

of crystal structure of $TiCl_3$ was in the vanadium–titanium–aluminum complex. The rise of the 1,4-trans-unit content in PB (with a corresponding reduction in the 1,4-cis-structure concentration and a constant concentration of 1,2-units) when the time and temperature of the catalyst thermal treatment were increased testified to the formation of a violet modification of $TiCl_3$ during the exposition of the system [Fig. 3(a,b)].

TABLE II
Kinetic Parameters of Butadiene Polymerization on [VOCl$_3$–TiCl$_4$–OAC$_1$]–(Heating)–OAC$_2$ Catalytic Systems

Catalyst	k_p (L/mol min)	C_a (% from C)	1,4-trans units (%)	E_a (kD j/mole)
IA	1700 ± 300	0.57	93	30.1 ± 2.4
IB	5700 ± 800	0.46	96	41.8 ± 3.2
IIB	2800 ± 300	0.27	96	—
IIIB	2350 ± 400	0.14	96	—
IVA	350 ± 60	0.18	94	42.6 ± 3.4
IVB	650 ± 100	0.12	96	51.8 ± 4.1
VB	4300 ± 700	0.23	96	—
VIB	3600 ± 600	0.13	96	—
VIIA	1200 ± 200	0.12	97	32.6 ± 2.5
VIIB	3000 ± 500	0.11	98	45.1 ± 3.6

Conditions were the same as in Figure 1. C_v = 0.003 mol/L.

Furthermore, the use of other OACs influenced the conditions of the preparation of the vanadium–titanium catalyst and the yield and molecular characteristics of the resulting polymer. Al(i-Bu)$_2$H and Al(i-Bu)$_2$Cl were used instead of Al(i-Bu)$_3$ at both stages or at one of the stages of system preparation (Table I).

The substitution of trialkylaluminum by dialkylaluminum hydride or dialkylaluminum chloride in the [VOCl$_3$–Al(i-Bu)$_3$]–(heating)–Al(i-Bu)$_3$ catalytic system did not qualitatively change the dependence of the yield and molecular characteristics of the polymers on the aforementioned system component ratios. Catalysts with Al(i-Bu)$_2$H or Al(i-Bu)$_2$Cl also displayed a bimodal dependence of the activity on the first aluminum compound/vanadium ratio. The value of the Ti/V ratio (0.5) and the conditions of the thermal treatment (1 h at 130°C) that were optimal with respect to the activity were the same as for systems IA and IB with Al(i-Bu)$_3$. The replacement of trialkylaluminum by Al(i-Bu)$_2$H at any stage of the catalytic system preparation led to a catalyst activity decrease. The substitution of Al(i-Bu)$_3$ by Al(i-Bu)$_2$Cl displaced both maximums of the catalytic complex activity to the field of larger values of Al$_1$/V (Table I). The dependencies of the activities of the catalytic systems with Al(i-Bu)$_2$H and Al(i-Bu)$_2$Cl on the Al$_2$/V ratio were extremely monomodal, and the positions and values of the optimums were conditioned by the concentration and nature of the OAC introduced during the first and second stages of catalyst preparation (Table I).

The observed particularities of butadiene polymerization for systems with Al(i-Bu)$_2$Cl were probably due to its weaker alkylating and reducing ability with respect to the vanadium derivatives in comparison with Al(i-Bu)$_3$ and Al(i-Bu)$_2$H.

The kinetics of butadiene polymerization with catalytic systems I–VII under the optimal conditions of their preparation was investigated. In all cases, the kinetic curves did not show the induction periods. Apparent activation energy (E_a) values of butadiene polymerization with catalysts I, IV, and VII were cal-

culated from 0 to 60°C (Table II). The received values of E_a were close to those usually observed for diene polymerization with Ziegler–Natta catalysts.[8] The polymer microstructure did not depend on the polymerization temperature under the studied conditions (97–99% 1,4-trans units).

From the dependence of M_n on the polymerization time, k_p and the number of active sites (C_a) for systems I–VII were calculated with methods found in the literature.[9,10] The catalytic system activity change was conditioned by the various AS reaction abilities, and it was less at Al$_1$/V = 0.6 than at Al$_1$/V = 1.6 (Table II).

The values of k_p and C_a also depended on the nature of OAC used during the first and second stages of the catalytic complex preparation (Table II). k_p decreased as follows: Al(i-Bu)$_3$ > Al(i-Bu)$_2$Cl > Al(i-Bu)$_2$H (Table II). This coincided with the order of the VOCl$_3$–OAC complex activity.[6] It is obvious from Table II that k_p with the vanadium–titanium–aluminum systems was much higher (10–20 times) than k_p for butadiene polymerization with vanadium–aluminum catalysts.[6] Therefore, OAC took part not only in the formation of ASs but also in their functioning.

The high activity of the mixed vanadium–titanium complexes led us to conclude that ASs involving both transition metals were formed. We can propose that the fractional introduction of OAC to the VOCl$_3$–TiCl$_4$ mixture and the thermal treatment of the studied catalytic systems created favorable conditions for the formation of double chlorides of transition metals (VCl$_3$ and TiCl$_3$) because of the isomorphism of their crystal lattices.[9,11]

Perhaps the introduction of another atom of the transition metal into the closest environment of an AS led to the modification of its structure and consequently varied the electron density of V–C bond of the AS. Such changes probably promoted a monomer coordination reaction and polymer chain propagation, which were reflected in significant rises in k_p.

Two activity maximums with respect to the Al$_1$/V ratio can be explained by elemental analysis data of
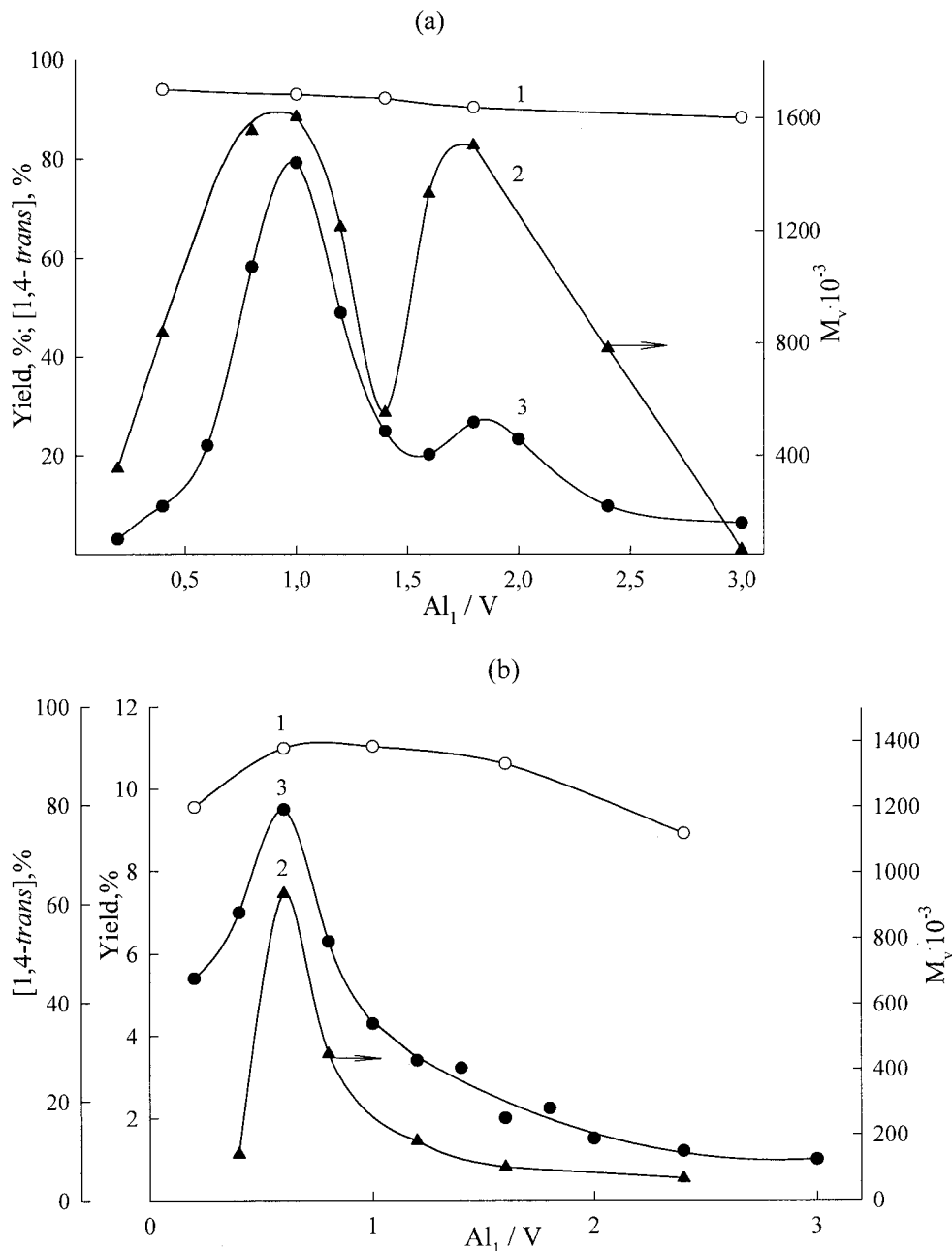
(a)

(b)

Figure 4 Variations in (1) the 1,4-trans-unit content in the polymer, (2) M_V, and (3) the PB yield with the molar Al_1/V ratio in catalytic systems (a) VIII and (b) IX (for the conditions, see Fig. 1).

the catalytic residue during the different stages of $[VOCl_3–TiCl_4–Al(i\text{-}Bu)_3]–(\text{heating})–Al(i\text{-}Bu)_3$ catalytic complex formation during the polymerization of pyperilene isomers.[5] The amount of titanium in relation to vanadium in the residue of the catalytic system changed when Al_1/V varied. Consequently, ASs of polymerization at the two mentioned maximums $(Al_1/V = 0.6$ and $Al_1/V = 1.6)$ contained double chlorides of transition metals with different (but fixed) amounts of $TiCl_3$. We also suggest that because the parameters of the $AlCl_3$ crystal lattice were close to those of vanadium and titanium chlorides, triple chlo-

rides of V, Ti, and Al may have been formed.[12] Furthermore, these triple chlorides containing various amounts of metals (V/Ti/Al) may have involved vanadium and titanium chlorides in the different modifications (α, δ, or γ) that could be formed during the thermal treatment. The dependence of k_p on the nature of OAC introduced during the first stage of the catalytic complex preparation indicated the active participation of aluminum derivatives in AS formation (Table II).

We can suggest that titanium additives led to a change in the electron density on the vanadium atom

by retracting some electrons to the chloride of the second transition metal, titanium. We propose that when the first portion of OAC was small (Al/V = 0.6), the ASs of one structure were formed, and when the first part of OAC was large (Al/V = 1.6), the ASs of another structure were formed.

To confirm the correlation between the bimodal activity of the studied catalysts (in relation to the Al_1/V ratio) and the double vanadium and titanium chloride formation, we investigated the addition of other titanium derivatives, TiI_2Cl_2 (system VIII) and $Ti(O—Bu)_4$ (system IX), instead of $TiCl_4$, to complex I.

It was found [Fig. 3(a)] that there were two maximums of activity of the $[VOCl_3–TiI_2Cl_2–Al(i-Bu)_3]$–(heating)–$Al(i-Bu)_3$ catalytic complex in relation to the Al_1/V ratio and that their positions practically coincided with those for catalyst I [see Fig. 1(a)]. The PB yields in both maximum fields were different (in this case, the first maximum was higher), and the trans-stereospecificity of system VIII decreased when the first portion of $Al(i-Bu)_3$ increased. The dependence of the polymer viscosity-average molecular weight (M_V) on the Al_1/V ratio was more noticeable [Fig. 4(a)]. Therefore, we can propose that ASs for systems I and VIII were identical and contained vanadium and titanium chlorides.

With the use in the vanadium–titanium catalyst of a titanium derivative without chlorine [$Ti(O—Bu)_4$], a monomodal dependence of activity on the first portion of $Al(i-Bu)_3$ was observed, and the optimum was at Al_1/V = 0.6 [Fig. 3(b)]. The dependence of the 1,4-trans-unit content and molecular weight of the polymer on Al_1/V was also extreme. The molecular weight of the polymer with the optimal catalyst ratio was not large: $M_V = 9.4 \times 10^{-5}$. To obtain a bimodal dependence of the catalyst activity on Al_1/V, perhaps the presence of titanium chloride was necessary. The re-sults of the butadiene polymerization in the presence of the complex $[VO(AcAc)_2–TiCl_4–Al(i-Bu)_3]$–(heating)–$Al(i-Bu)_3$ also indicated that the catalyst was less active, and there was one maximum of the PB yield in relation to the first part of OAC (Al_1/V = 0.8). The polymer did not contain more than 96% of trans units.

Thus, the existence of two maximums of activity of the catalyst system $[VOCl_3–TiCl_4–OAC_1]$–(heating)–OAC_2 was determined by the different AS types in the system, which contained the double isomorphic chlorides VCl_3 and $TiCl_3$ in various ratios and in different crystal modifications.

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