

# Butadiene Polymerization in the Presence of $\text{VOCl}_3$ -Dialkylmagnesium Catalytic System

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**ABSTRACT:** The butadiene polymerization in toluene at 25°C on  $\text{VOCl}_3-(n\text{-C}_4\text{H}_9)\text{Mg}(\text{iso-C}_8\text{H}_{17})$  catalytic system was investigated. The kinetic parameters of polymerization and molecular characteristics of polybutadiene were determined. It was shown that substitution of traditional organoaluminum cocatalysts in *trans*-regulating vanadium systems

does not have an effect on its stereospecificity, but significantly influences on the active centers reaction ability. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 596–600, 2003

**Key words:** catalysts; microstructure; polybutadiene; Ziegler-Natta polymerization

## INTRODUCTION

It is known that vanadium catalytic systems of Ziegler type in combination with organoaluminum compounds (OAC) are *trans*-regulating under conjugated dienes polymerization.<sup>1,2</sup> It was interesting for us to clear up how the vanadium catalytic system's working parameters will change (first of all, activity and stereospecificity) if we use as a cocatalyst another organic derivative of nontransition metal–magnesium dialkyl. This question emerged while considering the results of work<sup>3</sup> in which the substitution of trialkylaluminum by magnesium dialkyl in a *cis*-regulating system on the base of neodymium chloride at butadiene polymerization leads to the formation of predominantly 1,4-*trans*-polybutadiene (PB). The use of the analogous method in the case of titanium catalytic systems also entails a significant increase of the 1,4-*trans*-units fraction in PB.<sup>4</sup>

In the present work, the fact that kinetic parameters of butadiene polymerization in the presence of  $\text{VOCl}_3$  in combination with  $\text{MgRR}'$  (where *R*-*n*-butyl, *R'*-2-ethylhexyl) is dependent on polymerization and catalyst preparation conditions are considered.

## EXPERIMENTAL

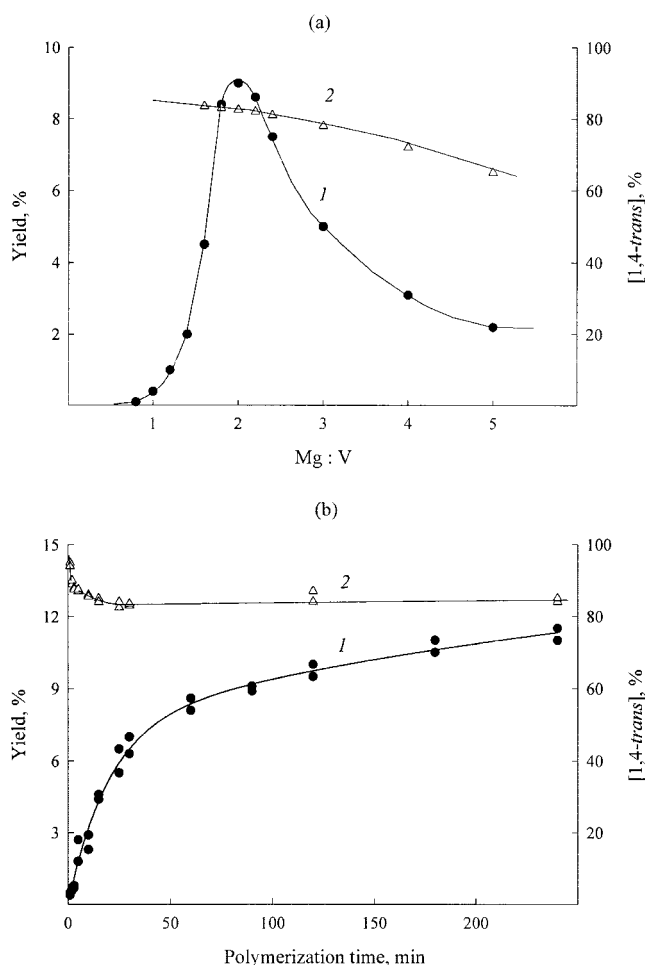
The polymerization of butadiene was carried out in toluene at 25°C under conditions excluding the penetration of air and moisture. The monomer and the solvent were purified using methods typical for

Ziegler-type polymerization. When the catalyst was prepared *in situ*, dialkylmagnesium was added to a butadiene solution, followed by the introduction of vanadium reagent (system I). An alternative technique consisted of mixing the components at a chosen temperature in the absence (system II) or with the addition (system III) of small amounts of conjugated dienes (butadiene, isoprene, or piperylene). After the catalyst components were stirred for a certain time, the catalyst was introduced into the reaction mixture. To estimate the number of active centers (ACs) in the vanadium–magnesium system, an attempt was made to apply the method of inletting dosed quantities of an inhibitor.<sup>5</sup> Weak electron donors, such as triphenylphosphine and cyclopentadiene, were used for this purpose. However, as in the case of butadiene polymerization with the vanadium–aluminum system, these compounds insignificantly affected the efficiency of the complex under study, even when taken in equimolar amounts with respect to vanadium. For this reason, the kinetic parameters of the polymerization ( $k_p$  and  $C_a$ ) were derived from the time dependence of the molecular parameters of polydiene as in ref. 6. The microstructure of PB was determined using a Specord M-80 spectrometer. The molecular characteristics of polymers were obtained with a Waters gel-chromatograph using toluene as an eluent.

## RESULTS AND DISCUSSION

The experimental study showed that the replacement of the aluminum alkyl by the organomagnesium compound in the synthesis of PB did not affect the high *trans*-stereospecificity of the  $\text{VOCl}_3$ -based complex. The extreme dependence of the activity on the cocata-

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**Figure 1** Variation in the (1) yield and microstructure (2) of PB with (a) the molar Mg : V ratio, and (b) the polymerization time. The  $\text{VOCl}_3$ -MgRR' catalyst was prepared *in situ*; toluene; polymerization temperature, 25°C;  $C_V = 5 \cdot 10^{-3}$  mol/L; (b) Mg : V = 2.0;  $C_M = 2.0$  mol/L; polymerization time (a) 1 h.

lyst-to-vanadium ratio was also retained, as follows from Figure 1(a). Observing distinctions investigating catalyst and complex containing an OAC, for example,  $\text{Al}(\text{i-Bu})_3$ , in butadiene polymerization under similar conditions are:<sup>7</sup> a lesser activity, the comparable content of *trans*-1,4 units.

On the other hand, the optimum efficiency of the MgRR'-based system under study is observed at a cocatalyst-to-vanadium ratio twice as small as that of the vanadium-aluminum catalysts. This result seems to be related to the greater alkylating and reducing capacity of MgRR' (the Grignard reagents) compared to aluminum alkyls. The concentration of *trans*-1,4 units in the resulting polymer is lowered from 84 to 67% with a corresponding change in the content of 1,2 units when the Mg : V ratio varies from 1.6 to 5.0 [Fig. 1(a)]. No *cis*-1,4 units were detected in PB. A similar behavior was observed when OACs were used as cocatalysts.<sup>7</sup>

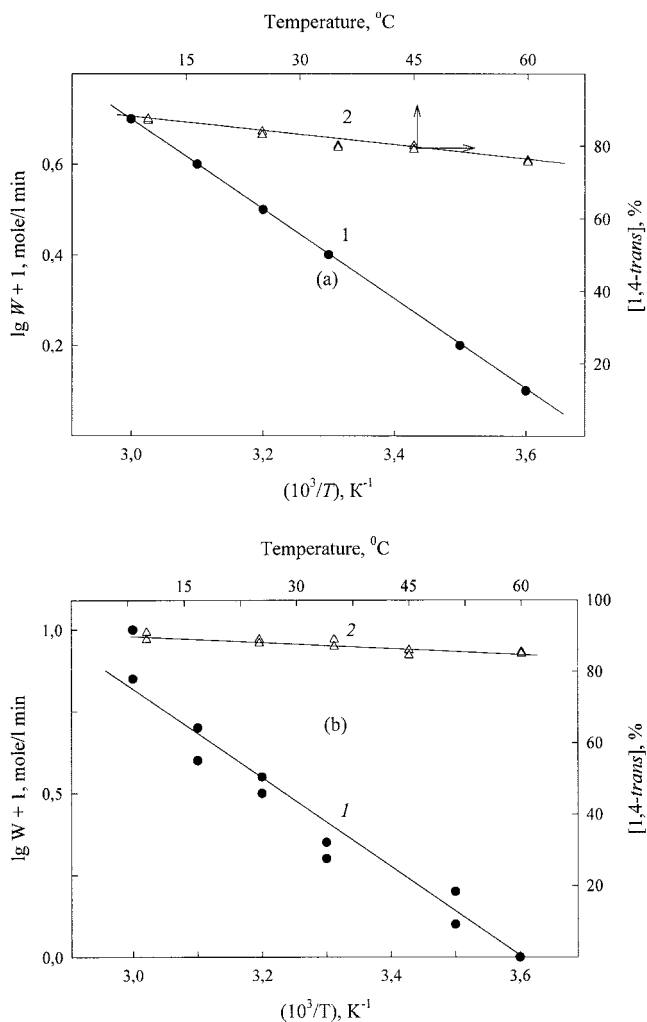
The obtained variation in the yield and microstructure of PB with the ratio of catalyst components may be caused by the several reasons. First, such a relationship is determined by a change in the  $V^{+3}$  content, as was shown for the polymerization of isoprene and isomers of piperylene in the presence of vanadium-aluminum complexes.<sup>8,9</sup> Second, a variation in the starting catalyst composition can alter the potential set of organomagnesium compounds forming, as we assume, bimetallic ACs in combination with transition-metal derivatives. These organomagnesium compounds are formed as a result of interaction between dialkylmagnesium and vanadium oxytrichloride similarly to the products of the reaction between trialkylaluminum and  $\text{VOCl}_3$ .<sup>10</sup>

When substitute OAC by dialkyl magnesium, the kinetic curves do not show induction periods [Fig. 1(b)], so the initiation insignificantly affects the rate of butadiene polymerization. On the other hand, the examination of the kinetic curve plotted in semilogarithmic coordinates indicates that the steady-state character of the process is maintained only at the initial stage of polymerization; that is, a partial loss of the active centers occurs. Some decrease in the content of *trans*-1,4 units takes place as the monomer conversion rises.

As with the vanadium-aluminum system, the polymerization is characterized by first orders in the monomer and the catalyst. This may be evidence that complex formation between the active center and the monomer is the rate-determining step of the propagation reaction. The PB microstructure is deteriorated as the concentration of both the catalyst (from 2 to 20 mmol/L) and the monomer (from 0.5 to 3 mol/L) increases: the content of *trans*-1,4 units decrease (from 90 to 70%) by 1,2-units number increase. Such an interrelation observed with varying the content of the catalyst complex does not have a plausible explanation thus far.

The effect of the monomer concentration on the polydiene microstructure can be associated with the *anti-syn* isomerization of  $\pi$ -allyl active centers of polymerization usually formed after the insertion of a diene molecule into the active center of the catalyst.<sup>11</sup> It is known, for example, that an increase in the *trans*-1,4 unit content at the expense of *cis*-1,4 units takes place at low butadiene concentrations in the case of titanium-containing *cis*-regulating systems. It is likely that similar isomerization processes are characteristic of the complex under study, because *anti*- $\pi$ -allyl active centers are precursors of both *cis*-1,4 and 1,2 units in polydienes.<sup>11</sup> Similar results were also reported for the vanadium-aluminum system, albeit in the lower concentration range.<sup>7</sup>

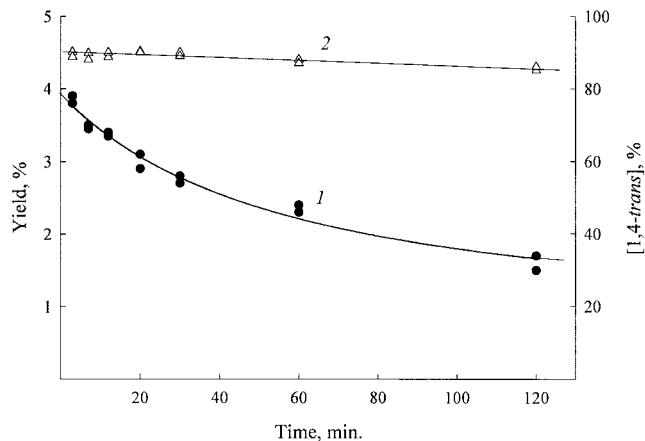
As the polymerization temperature changes from 0 to 60°C, the content of *trans*-1,4 units decreases from 83 to 78% and the rate of polymerization obeys the



**Figure 2** Plots of (1) polymerization rate and (2) PB microstructure as a function of the polymerization temperature. The conditions are the same as in Figure 1, (a) polymerization time 5 min; and (b) the  $\text{VOCl}_3$ -piperylene- $\text{MgRR}'$  catalyst,  $0^{\circ}\text{C}$ , 30 min, diene: V = 5, polymerization time 5 min.

Arrhenius dependence [Fig. 2(a)]. The apparent activation energy ( $E_a$ ) is low:  $18.8 \pm 2.1$  kJ/mol, but comparable to the analogous value for the butadiene polymerization catalyzed by a  $\text{VOCl}_3$ -TIBA complex ( $17.6 \pm 1.7$  kJ/mol); that is, the cocatalyst nature does not affect the value of  $E_a$ .

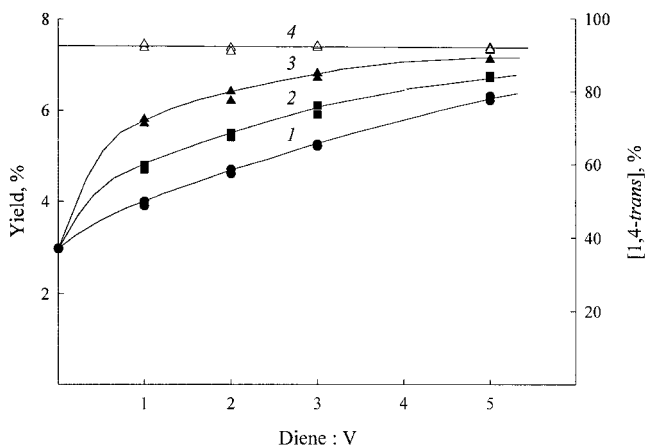
It has already been noted that the preparation method influences the activity and the stereospecificity of the Ziegler-Natta catalysts, including vanadium-containing systems. The replacement of the OAC by  $\text{MgRR}'$  does not significantly affect the previously obtained relationships. As was expected, the activity of vanadium-magnesium catalytic complex II prepared at  $0^{\circ}\text{C}$  in the absence of conjugated diene additives is lower than that of complex I that is formed *in situ* (Fig. 3). This is caused by a lesser stability of the C-V  $\pi$ -bonds compared to the  $\pi$ -allyl active centers of



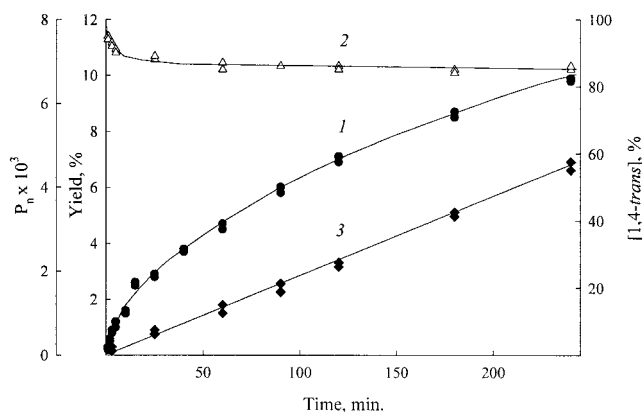
**Figure 3** Plots of (1) yield and (2) PB microstructure as a function of the time of  $\text{VOCl}_3$ - $\text{MgRR}'$  catalyst formation at  $0^{\circ}\text{C}$ . The conditions are the same as in Figure 1, Mg : V = 2.0.

polymerization.<sup>11</sup> The stereospecificity and efficiency of system II become poorer as the time of the system aging (prior to the onset of polymerization) increases. Probably, this results from the partial loss of active centers, which are stereospecific with respect to 1,4-*trans*-units but are less stable. In other words, several types of active centers are present in the system.

Data on the influence of small additives of conjugated dienes (butadiene, isoprene, piperylene) on the activity and stereospecificity of the vanadium-magnesium system, which were introduced into the system at the moment of its formation, proved to be somewhat unexpected. If for the  $\text{VOCl}_3$ -TIBA catalytic complex, the activity considerably increases even at equimolar quantities of dienes,<sup>7</sup> in the case of the vanadium-magnesium complex, this influence is slightly pronounced (Fig. 4). System III approaches, in



**Figure 4** Plots of (1-3) yield and (4) PB microstructure as a function of the molar diene : V ratio [(1) isoprene, (2) butadiene, (3) piperylene]. The  $\text{VOCl}_3$ -piperylene- $\text{MgRR}'$  catalyst ( $0^{\circ}\text{C}$ , 30 min). The conditions are the same as in Figure 1, Mg : V = 2.0.



**Figure 5** Plots of (1) yield, (2) microstructure and (3)  $P_n$  of PB as a function of the polymerization time. The  $\text{VOCl}_3$ -piperylene-MgRR' catalyst ( $0^\circ\text{C}$ , 30 min, diene : V = 5). The conditions are the same as in Figure 1, Mg : V = 2.0.

its activity, the catalyst formed *in situ* only when the diene content exceeds by tens of times the corresponding amount equimolar with respect to vanadium. Under the studied conditions, no change in stereospecificity was noticed upon variation of the nature of the diene added. Nevertheless, the effectiveness of dienes as additives increases in a series: isoprene < butadiene < piperylene, which coincides with a variation in the stability of  $\pi$ -allyl complexes of transition metals with these dienes.<sup>11</sup>

However, catalytic complex III behaves differently compared to complex I when the polymerization temperature varies. Although the activity of the system also obeys the Arrhenius dependence [Fig. 2(b)], the apparent activation energy of the butadiene polymerization carried out with this catalyst is greater by nearly 1.5 times, being equal to  $27.2 \pm 2.5$  kJ/mol. Most likely, this is explained by the fact that the activation energy of initiation is a complex value and, for the complex formed *in situ*,  $E_a$  is a constituent of this parameter. A similar situation was also observed with the vanadium-aluminum catalyst.<sup>7</sup> The *trans*-stereospecificity of system III decreases with the polymerization temperature, as in the case of complex I [cf. Figs. 2(a) and (b)].

The kinetic study of butadiene polymerization in the presence of system III (piperylene additives) revealed that the stereospecificity of the catalyst was also high (96–98% *trans*-1,4 units for the first minutes) at the early stage of the process. Further progress in the polymerization results in deterioration of the PB microstructure (Fig. 5). The kinetic curve becomes more extended along the time axis [cf. Figs. 1(b) and 3]. Further experiments were aimed at elucidating what parameter of the vanadium catalyst ( $k_p$  or  $C_a$ ) causes a reduction of its activity when  $\text{Al}(\text{i-Bu})_3$  are replaced by MgRR'. With both complex I and complex

III, in contrast to the vanadium-aluminum system, a slow linear growth of molecular mass occurs over a long period of time, up to 4 h (Fig. 5). The  $k_p$  value calculated from the time dependence of the molecular mass of PB slightly depends on the preparation method and amounts to  $\sim 15$  L/(mol min); that is, it is smaller by one order of magnitude than the corresponding value in the case of the vanadium-aluminum complex, 250 L/(mol min). The content of active centers at the starting moment of polymerization also is slightly lower (e.g., 5.3 mol % for system I compared to 6.4 mol % based on  $C_V$  for the  $\text{VOCl}_3$ - $\text{Al}(\text{i-Bu})_3$  system).<sup>7</sup>

The patterns of the PB microstructure dependence on the conditions of preparation of the vanadium-magnesium complex and polymerization in its presence are in many respects similar to those obtained for the polymerization of butadiene with  $\text{VOCl}_3$ -TIBA.<sup>7</sup> This allows the suggestion to be made the active centers have a similar structure. Due to a difference in the bond lengths of V-Mg and V-Al bridged complexes, they should behave in a different way in polymerization. On the other hand, organomagnesium compounds possess a more pronounced ability to form various associates compared to OACs.<sup>12</sup> One cannot exclude that the decrease in the activity of the vanadium-containing catalyst upon OAC being replaced by dialkylmagnesium is also related to the coordination of the organomagnesium compounds to the vacant sites of the active centers, providing hindrance to the monomer insertion. The reduced activity of the catalyst prepared in the presence of a diene, compared to the complex formed *in situ*, indicates, in particular, that the diene and the organomagnesium compounds are involved in competitive coordination to the V—C bond of the active center.

Thus, the substitution of OAC by dialkyl magnesium changes the efficiency of vanadium catalytic systems under butadiene polymerization ( $k_p$ ), but it does not influence the stereospecificity of their action (in contrast to *cis*-regulating titanium and lanthanide catalytic systems<sup>3,4</sup>). The influence of nontransition metal compound nature both on formation and functioning of active centers of Ziegler *trans*-regulating catalysts is obvious.

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