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# 1,4-*trans*-Polymerization of Dienes: 1. Synthesis of Polybutadiene in the Presence of Mixed Systems Based on $VOCl_3$ and Titanium Compounds

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**Abstract**—Polymerization of butadiene in toluene at 25°C in the presence of catalytic systems based on $VOCl_3$ and various titanium compounds in combination with $Al(i\text{-}C_4H_9)_3$ is studied. If the organoaluminum compound is added in portions to the $VOCl_3$–titanium component mixture and the primary suspension of the catalyst is heat-treated, two maxima are observed in the dependence of the activity of the catalytic system on the size of the first $Al(i\text{-}C_4H_9)_3$ portion. The kinetic parameters of the polymerization are determined. The difference in activity between the mixed catalytic systems is due to the difference in structure and reactivity between active sites containing atoms of both transition metals.

An efficient way of improving the activity, selectivity, and stability of operating parameters of hydrocarbon conversion catalysts is by using a mixture of derivatives of at least two metals [1, 2]. This approach is also appropriate for Ziegler-type metal complex catalysts used in the polymerization of unsaturated compounds [3, 4].

For example, catalytic systems containing compounds of two transition metals are employed in polydiene synthesis. The $TiCl_4$–$AlR_3$ system ($Al/Ti > 1$) catalyzes the formation of 1,4-*cis*-polyisoprene [5]. Introducing $CoCl_2$ [6] or $FeCl_3$ [7] into the above system affords an active 1,4-*trans*-governing catalyst for diene polymerization. Addition of Fe(III) chloride to the $Ti(OR)_4$–$AlR_3$ catalytic complex also results in polydienes containing 97% 1,4-*trans* units [8], whereas catalysts based on one of the above transition metal derivatives favor the formation of 1,2-polybutadiene (PB) or 3,4-polyisoprene [3].

Vanadium–titanium mixed catalysts for polymerization of dienes and alkenes are of prime interest. For example, a considerable increase in the yield of polyisoprene is observed on addition of $TiCl_4$ to the $VCl_4$–$AlR_3$ system [9]. With this vanadium–aluminum catalytic system, the rate of polymerization decreases abruptly at a conversion above 20–25%. Introducing titanium chloride into this system causes the process to proceed at a steady rate up to complete monomer consumption [10]. As this takes place, the molecular weight (MW) of isoprene rises substantially and a 1,4-*trans*-unit content of at least 96% persists. Furthermore, addition of $TiCl_4$ to the $VOCl_3$–triisobutyl aluminum (TIBA) system significantly increases the yield of 1,4-*trans*-polyisoprene and polypiperylene [11, 12]. It is essential that a mixture of transition metal chlorides should be heated with a cocatalyst to prepare a highly active and stereospecific catalyst based on $VOCl_3$. In this case, only part of the organoaluminum compound (OAC) is initially used and the rest is added to the complex at a low temperature [11, 12].

In this work, we consider factors in the activity and stereospecificity of the $VOCl_3$–titanium compound–TIBA system in butadiene polymerization.

## EXPERIMENTAL

Mixed catalysts were prepared by a procedure described in [11, 12]. A portion of OAC was added to a mixture of $VOCl_3$ and a Ti derivative ($TiCl_4$, $TiI_2Cl_2$, or $Ti(n\text{-}OC_4H_9)_4$) taken in certain proportions. The reaction mixture was heat-treated for 1 h at 130°C and then cooled down to room temperature. Next, the second portion of OAC was introduced into the reaction mixture. The catalytic complex was added to a butadiene solution in toluene. Polymerization was performed at $25 \pm 0.1$°C in the absence of any air or moisture. The microstructure and molecular weight of PB were determined using IR spectroscopy and gel permeation chromatography [13].

## RESULTS AND DISCUSSION

For the $VOCl_3$–$TiCl_4$–TIBA catalytic system (system I) used in the *trans* polymerization of butadiene, the optimum proportions of the components and catalyst preparation conditions (from the standpoint of catalytic activity) are identical to those for catalysts of isoprene and piperylene polymerization [11, 12]. Here, as in [11, 12], we observed a bimodal dependence of the PB yield on the ratio of the size of the first TIBA portion ($Al^1$) to $VOCl_3$ (maxima at $Al^1/V = 0.6$ and 1.6) at a fixed Ti/V and a fixed ratio of the second TIBA por-

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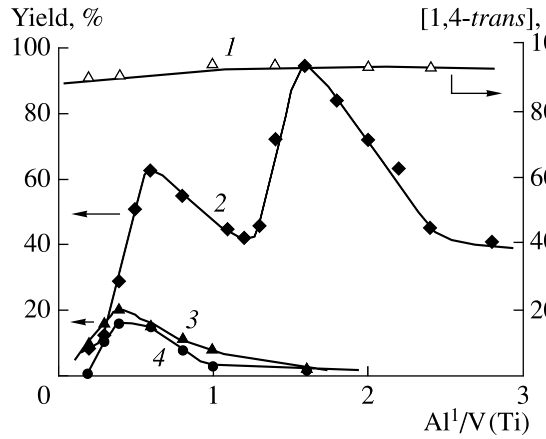


**Fig. 1.** (*1*) 1,4-*trans*-Unit content of PB and (*2–4*) PB yield as a function of Al/V and Al/Ti at the first stage of catalyst formation in systems (*1*, *2*) I, (*3*) II, and (*4*) III. Conditions: 25°C; toluene; $C_M = 1.0$; $C_V = 5 \times 10^{-3}$ mol/l (systems I, II); $C_{Ti} = 5 \times 10^{-3}$ mol/l (system III); Ti/V = 0.5 (system I); $Al^2$/V(Ti) = 4.0; heat treatment at 130°C for 1 h.

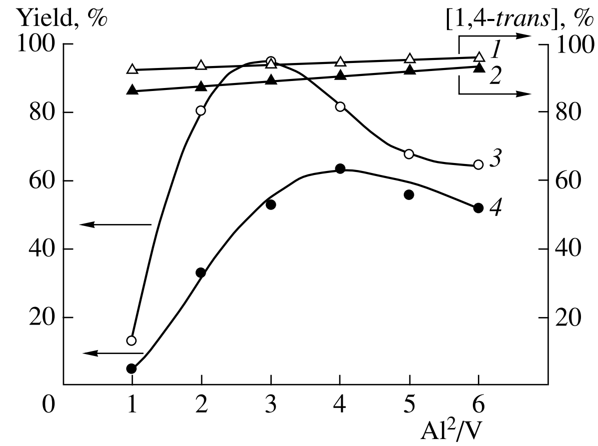


**Fig. 2.** (*1*, *2*) 1,4-*trans*-Unit content of PB and (*3*, *4*) PB yield as a function of Al/V at the second stage of catalyst formation in systems (*1*, *3*) IA and (*2*, *4*) IB. $Al^1$/V = 0.6 (system IA) and 1.6 (system IB); the other conditions are as in Fig. 1.

tion ($Al^2$) to $VOCl_3$ ($Al^2$/V) (Fig. 1). In the $Al^1$/V range examined (0.2–4.0), the 1,4-*trans*-unit content of PB grows slightly (from 92 to 97%), at the expense of a drop in the proportion of 1,4-*cis* structures (from 5 to 0%), as the OAC concentration in the first portion added increases. The proportion of 1,2-units is constant and equal to 2–3%. At the same time, the dependence of the number-average molecular weight of the polymer ($M_n$) on the concentration of the first OAC portion is also bimodal, with maxima at $Al^1/V = 0.6$ ($4.2 \times 10^5$) and 1.6 ($7.9 \times 10^5$) and a minimum at $Al^1$/V ($3.4 \times 10^5$), as in piperylene polymerization [12].

For the complexes $VOCl_3$–TIBA (system II) and $TiCl_4$–TIBA (system III), unimodal dependences of the catalyst activity on the $Al^1$/V (Ti) ratio are observed (Fig. 1). The PB yield in the presence of these catalysts is considerably lower than the PB yield achieved with the vanadium–titanium mixed complex under the same polymerization conditions.

Further investigation of butadiene polymerization with a vanadium–titanium catalyst was performed at fixed $Al^1$/V ratios of 0.6 and 1.6 (systems IA and IB, respectively). For these catalytic systems, the dependences of activity on the size of the second OAC portion ($Al^2$/V) are unimodal (Fig. 2). The positions and heights of the peaks depend on the amount of TIBA introduced into the system at the first stage of catalyst treatment. $M_n$ for polymers obtained with systems IA and IB passes through a maximum in the vicinity of $Al^2/V = 4.0$. Thus, at high TIBA concentrations, the OAC plays an important role as a chain transfer agent. At the same time, the 1,4-*trans*-unit content of PB grows to some extent with increasing TIBA concentration (Fig. 2). The 1,2-unit content is no greater 2–3% and is independent of $Al^2$/V. Unimodal dependences of the catalytic activity on $TiCl_4$ concentration (with a maximum at Ti/V = 0.5) are observed for systems IA and IB. The 1,4-*trans*-unit content of the polymer decreases (at the expense of an increase in the proportion of 1,4-*cis* units) as the amount of $TiCl_4$ in the catalytic complex increases (Fig. 3). The 1,2-unit content of PB is constant and equal to 2–3%. A similar situation was observed in isoprene polymerization in the presence of the same catalyst [11], with the only difference that 3,4-units were detected instead of 1,2-units.

Thus, it is believed that *trans*-governing active sites (AS's) in mixed catalysts contain atoms of both transition metals. According to the literature [12], the valence of these atoms in a catalytic system of similar composition is 3. At the same time, part of the titanium chloride appears to form AS's for *cis* polymerization of butadiene. $TiCl_4$ is known to yield β-$TiCl_3$ upon reac-

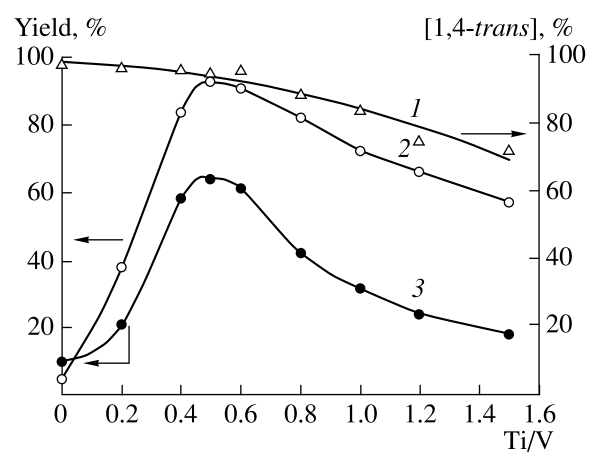


**Fig. 3.** (*1*) 1,4-*trans*-Unit content of PB and (*2*, *3*) PB yield as a function of the Ti/V molar ratio for systems (*1*, *2*) IB and (*3*) IA. The conditions are the same as in Fig. 1.

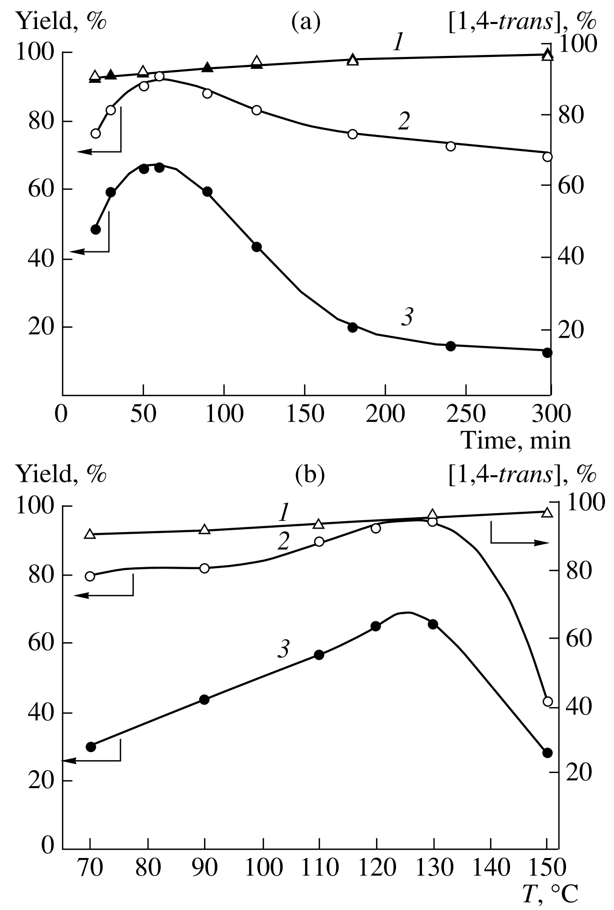


**Fig. 4.** (*1*) 1,4-*trans*-Unit content of PB and (*2*, *3*) PB yield as a function of heating (a) time and (b) temperature for systems (*1*, *3*) IA and (*1*, *2*) IB with a first portion of TIBA added. The conditions are the same as in Fig. 1.

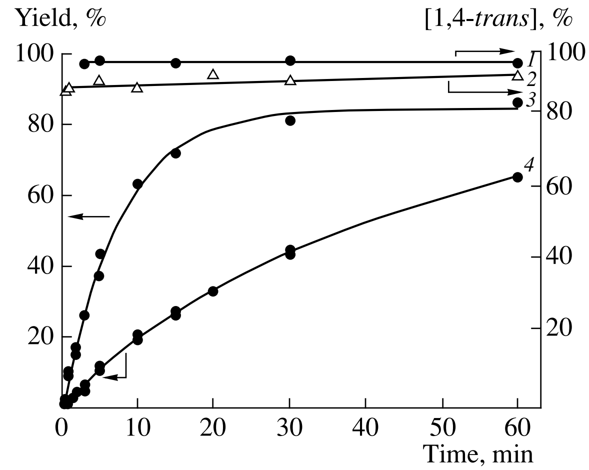


**Fig. 5.** (*1*, *2*) 1,4-*trans*-Unit content of PB and (*3*, *4*) PB yield as a function of polymerization time for systems (*1*, *3*) IA and (*2*, *4*) IB. $C_V = 3 \times 10^{-3}$ mol/l; the other conditions are as in Fig. 1.

tion with trialkylaluminum. This Ti(III) compound favors the formation of PB with a mixed microstructure (55–60% 1,4-*cis* units, 36–41% 1,4-*trans* units, and 4% 1,2-units) [3]. On being heated to 170°C, β-$TiCl_3$ turns into α-$TiCl_3$, which is the base of a *trans*-governing catalyst [14].

The observed variation of the catalytic activity of systems IA and IB with exposure time and temperature (Fig. 4) suggests that the optimum thermal treatment for the $VOCl_3$–$TiCl_4$–OAC mixture is heating for 60 min at 130°C. The peak positions for systems IA and IB are the same; that is, they are independent of $Al^1$/V. However, this ratio influences the maximum values of catalytic activity. The above conditions are substantially milder than required for the transition of $TiCl_3$ from the brown modification to the violet allotropic modification [14]. Thus, it is still unclear what is the crystal structure of $TiCl_3$ in the vanadium–titanium–aluminum complex. An indirect indication of the violet modification of Ti(III) chloride forming upon heat treatment of the catalyst is that the *trans*-unit content of PB increases with increasing exposure time or temperature (Fig. 4). As this takes place, the proportion of 1,2-*cis* structures remains constant and the proportion of 1,4-*cis* structures decreases.

The kinetics of butadiene polymerization was studied in the presence of systems IA and IB prepared under the optimum conditions considered above. Polybutadiene is formed without an induction period (Fig. 5). The reaction is first-order with respect to the monomer and catalyst ($VOCl_3$) at monomer concentrations ($C_M$) of 0.1–2.4 mol/l and catalyst concentrations ($C_V$) of 1–30 mmol/l. The rate equation for polymerization under these conditions takes the form $w = k_p C_M C_{AS}$, where $C_{AS}$ is the concentration of AS's.

The temperature dependence of the rate of butadiene polymerization obeys the Arrhenius law between 0 and 60°C. For systems IA and IB, the effective activation energy of the process is $30.1 \pm 2.4$ and $41.8 \pm 3.2$ kJ/mol, respectively. Clearly, $E_a$ depends considerably on catalyst composition, even though it is similar to the activation energies usually observed in diene polymerization on Ziegler–Natta catalysts [3]. The temperature of the process does not influence the microstructure of PB obtained in the presence of both complexes.

The rate constants of polymer chain growth for catalysts IA and IB were derived from the dependences of $M_n$ of polybutadiene on polymerization time: $k_p = 1700 \pm 300$ and $5700 \pm 900$ l mol$^{-1}$ min$^{-1}$, respectively [15]. $C_{AS}$ for systems IA and IB is equal to $5.7 \times 10^{-3}$ $C_V$ and $4.6 \times 10^{-3}$ $C_V$, respectively. Consequently, the enhanced activity of the $VOCl_3$–$TiCl_4$–TIBA catalytic system near the second peak in the dependence of the PB yield on $Al^1$/V is mainly due to the rise in the reactivity of AS's. The AS concentration in both catalytic complexes is low compared to the initial concentration of vanadium, but these concentrations are comparable in the case of polymerization of piperylene isomers with catalytic systems of similar composition [12].

The high activity of mixed vanadium–titanium catalysts as compared to systems II and III suggests that the resulting AS's incorporate both transition metals. It is probable that, upon fractional addition of the OAC to the $VOCl_3$–$TiCl_4$ mixture followed by heat treatment of the catalyst, conditions favorable for the formation of binary chlorides are established in the catalytic system. Both transition metals are involved in chloride formation owing to the isomorphism of the crystal lattices of $VCl_3$ and $TiCl_3$ [14, 16]. The high probability of the formation of an isovalent isomorphous mixed chloride is also due to the $V^{3+}$ and $Ti^{3+}$ ions differing insignificantly in ionic radius and electronegativity [17]. The incorporation of a foreign transition-metal atom into the nearest environment of AS's appears both to modify the AS structure and to change the electron density of the transition metal–carbon bond and, accordingly, the reactivity of the AS's.

The presence of two maxima in the activity versus $Al^1/V$ dependence can be explained on the basis of elemental analysis data for catalyst deposits at various stages of the formation of the $VOCl_3$–$TiCl_4$–TIBA complex in the polymerization of piperylene isomers [12]. It was shown that the V/Ti/Al ratio in the heat-treated catalyst deposits decreases with increasing $Al^1/V$ ratio (1.00 : 0.27 : 0.33 and 1.00 : 0.50 : 0.22 for $Al^1/V$ = 0.6 and 1.2, respectively). Consequently, near the peaks, AS's may contain binary transition-metal chlorides with different (though fixed) amounts of $TiCl_3$. This is possible owing to the exclusion of part of the titanium chloride from the nearest environment of vanadium through the formation of V–Ti–Al ternary chlorides. These chlorides can form because the parameters of the crystal lattice of $AlCl_3$ differ only slightly from those of vanadium and titanium chlorides. In particular, solid solutions of the violet modifications of $TiCl_3$ and $AlCl_3$ are known [18]. Furthermore, ternary chlorides with different metal stoichiometries can yield, upon heating, different modifications of vanadium and titanium chlorides. It is believed that structurally different AS's are formed at low and high OAC concentrations in the first portion added.

In order to get a deeper insight into the nature of the two peaks of catalytic activity as a function of $Al^1/V$ and into the role of the ligand environment of titanium, we studied, in complex I, the effect of replacement of $TiCl_4$ by other Ti derivatives, namely, $TiI_2Cl_2$ (system IV) and $Ti(n\text{-}OC_4H_9)_4$ (system V). For the $TiI_2Cl_2$ complex, we also observed two peaks in the dependence of catalytic activity on $Al^1/V$ (Fig. 6a). The positions of these peaks almost coincide with those observed for catalyst I (Fig. 1). However, systems I and IV afford somewhat different relative yields of PB near both maxima (the first maximum is more pronounced in the case of catalyst IV). Moreover, with system IV, *trans* stereospecificity falls with increasing size of the first TIBA portion

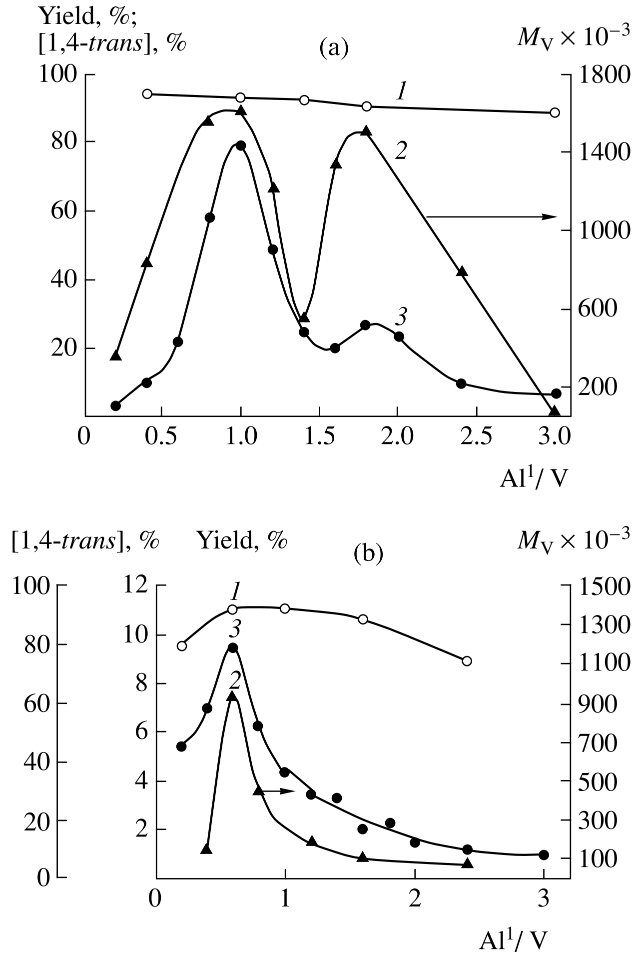


**Fig. 6.** (*1*) 1,4-*trans*-Unit content of PB, (*2*) $M_V$, and (*3*) PB yield as a function of the relative size of the first TIBA portion for systems (a) IV and (b) V. The conditions are the same as in Fig. 1.

and the molecular weight of the polymer depends more strongly on the $Al^1/V$ ratio (Fig. 6a). Nevertheless, we assume that AS's in systems I and IV are identical and incorporate vanadium and titanium chlorides.

When a titanium derivative containing no chloride ion [$Ti(n\text{-}OBu)_4$] is contained the vanadium–titanium catalyst, a unimodal dependence of catalytic activity on the first portion of TIBA is observed, an optimum being found at $Al^1/V$ = 0.6 (Fig. 6b). The 1,4-*trans*-unit content and the MW of the polymer as a function of the $Al^1/V$ value also pass through an extremum. The viscosity-average molecular weight observed for the optimum ratio of catalyst components is relatively low, 9.4 × $10^4$. It is believed that the presence of titanium and vanadium chlorides is essential for the dependence of catalytic activity on the relative amount of the OAC to be bimodal. This view is supported by the results of butadiene polymerization catalyzed by the $VO(acac)_2$–$TiCl_4$–TIBA complex (system VI). For this low-activity catalyst, the dependence of the PB yield on the size of the first OAC portion has a single peak at $Al^1/V$ = 0.8

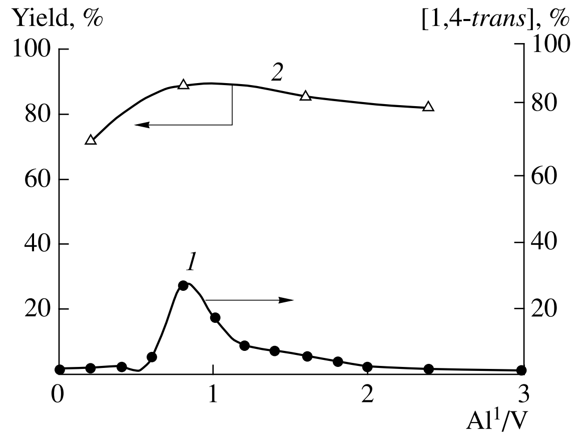


**Fig. 7.** (*1*) 1,4-*trans*-Unit content of PB and (*2*) PB yield as a function of $Al^1/V$ for system VI. $Al^2/V = 4.0$; the other conditions are as in Fig. 1.

(Fig. 7). The resulting polymer contains no more than 90% *trans* structures.

Thus, we assume that the existence of two maxima of the activity of the $VOCl_3$–$TiCl_4$–TIBA systems is due to the formation of at least two types of AS's, which contain binary isomorphous chlorides composed of various proportions of different modifications of $VCl_3$ and $TiCl_3$.

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