NATURE OF THE ACTIVE CENTRES OF THE CATALYTIC SYSTEM VOCl₃–TiCl₄–Al(*iso*-C₄H₉)₃ ON POLYMERIZATION OF PIPERILENE*

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The polymerization of piperilene has been studied on exposure to the catalytic system $VOCl_3$–$TiCl_4$–Al(*iso*-C_4H_9)₃ prepared with a fractionated supply of the organoaluminium component. It is known that the stereospecificity of the action and reactivity of the active centres and the molecular mass of the polymer obtained depend in a complex fashion on the relative concentration of the first portion of the organoaluminium compound. It was found that change in the content of V^{3+} and Ti^{3+} in the catalytic system correlates with the activity and stereospecificity of the action. It is assumed that in conditions of formation of the catalyst active centres form including, simultaneously, V and Ti atoms in trivalent forms.

IT IS KNOWN that the catalytic system $VOCl_3$–$TiCl_4$–Al(*iso*-C_4H_9)₃ activated by the fractionated supply of the organoaluminium compound and thermal exposure, is highly effective on *trans*-polymerization of piperilene: in its presence high molecular mass polymers form at good rates containing up to 98% 1,4-*trans* units [1, 2]. Change in the activity, the stereospecificity of the action of the catalyst and the molecular mass of the polymer depend in a complex fashion on the ratio of the components of the catalytic system [2, 3]. However, no data are available in the literature as to the reasons for such a dependence and the nature of the active centres (ACs) in such complex catalytic systems although catalysts based on two transition metals are finding ever growing use in polymerization and copolymerization both of olefins [4, 5] and dienes [6, 7]. The present work seeks to establish the nature of the AC on polymerization of piperilene on exposure to the catalytic system $VOCl_3$–$TiCl_4$–Al(*iso*-C_4H_9)₃ with study of the elemental composition, valency states of the metals in the catalytic system and the dependence of the stereospecificity of the action and the reactivity of the catalytic system on the ratio of the components.

The solvent (toluene), monomer (*trans*- and *cis*-piperilene), $VOCl_3$, $TiCl_4$ and triisobutyl aluminium Al(*iso*-C_4H_9)₃ were purified and dried by the techniques adopted in the study of ion-coordination polymerization.

Cis-piperilene was isolated from a mixture of isomers by binding *trans*-piperilene into a high boiling adduct with maleic anhydride by the technique of reference [8]. To isolate the *trans*-isomer, the *cis*-piperilene contained in the mixture was at first isomerized to the *trans*-form in the presence of iodine by the technique of reference [9].

The catalytic complex was prepared in ampoules filled with purified argon by mixing the toluene solutions of $VOCl_3$ and $TiCl_4$ (V:Ti = 2:2.5) with triisobutyl aluminium, Al(*iso*-C_4H_9)₃ being supplied in two portions. After addition of the first portion of Al(*iso*-C_4H_9)₃ the suspension obtained, called for the purpose of convenience of terminology—primary, was thermally treated at
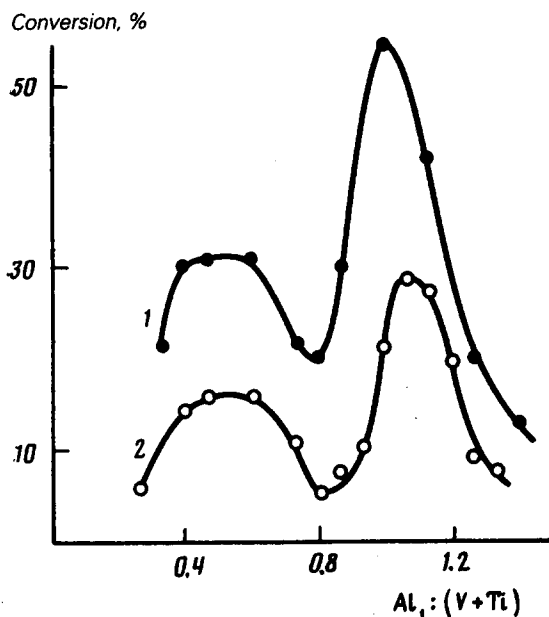

FIG. 1. Dependence of the activity of the catalytic system $VOCl_3$–$TiCl_4$–$Al(iso$-$C_4H_9)_3$ on the ratio $Al_1:(V+Ti)$ on polymerization of *trans* (1) and *cis* (2) piperilene. Here and in Fig. 2: 232 K, time of polymerization 15 min, $[C_5H_8] = 1$, $[VOCl_3] = 5 \times 10^{-3}$ mole/l, $Ti:V = 0.5$, $Al_2:V = 4.0$, temperature of thermal treatment 403 K, 1 h.

the temperature of the oil bath, 403 K. The second portion of $Al(iso$-$C_4H_9)_3$ was supplied after cooling the primary suspension to 263 K and its ratio to the initial $VOCl_3$ was constant and equal to four. The valency states of vanadium and titanium in the catalytic complex in their joint presence were determined after reference [10]. The microstructure of polypiperilene was calculated from the data of the IR and PMR spectra [11, 12]. The molecular parameters ($\bar{M}_w$, $\bar{M}_n$ and the MMD) of polypiperilene were evaluated by the GPC method with the KhZh-1304 instrument. The intrinsic viscosity was determined from measurements of the dilute solutions in toluene at 333 K in the suspended level viscometer of the Ubbelhode type. The values of the propagation rate constant k_p and the concentration of the AC c_{AC} were determined by a kinetic method [13].

The catalytic system $VOCl_3$–$TiCl_4$–$Al(iso$-$C_4H_9)_3$ is heterogeneous and consists of a sediment and soluble part, the latter separated from the sediment showing no activity.

The experiments showed that the stereospecificity of the action and activity of the catalytic system and the molecular mass of the polymer obtained depend in a complex fashion on the first portion of the organoaluminium compound to the $VOCl_3$ and $TiCl_4$ mixture $[Al_1:(V+Ti)]$. Thus the dependence of the activity of the catalytic system on the ratio $Al_1:(V+Ti)$ is described by a curve with two maxima, the activity of the catalytic complex in the region of the second maximum being higher than for the first (Fig. 1). The course of the dependence matches for both isomeric forms of piperilene although the *trans* monomer polymerizes at a higher rate.* a similar dependence (similar to change in the activity of the system) was also observed for the content of 1,4-*trans* units in the polymer and molecular mass (Fig. 2). Change in the content of V^{3+} and Ti^{3+} in the catalytic system also correlated with the activity and stereospecificity of action. In the region of the maximum

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* Since, as a whole, an identical course of the relationships was observed for both isomeric forms of piperilene, all the further data will be presented only for polymerization of *trans*-piperilene.
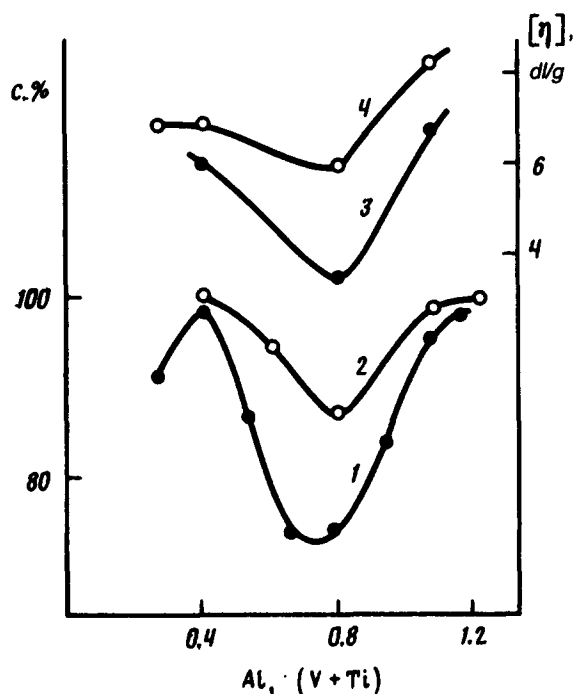
FIG. 2. Dependence of the microstructure (1, 2) and [η] (3, 4) on the ratio $Al_1 : (V + Ti)$ on polymerization of *trans-* (1, 3) and *cis-* (2, 4) piperilene. *c* is the content of 1,4-*trans* units.

manifestations of activity and stereospecificity the catalytic system had a maximum content of the trivalent forms of vanadium and titanium (Fig. 3).

The results of elemental analysis of the sediment isolated from the primary suspension after thermal treatment and washed with several portions of the purified solvent showed that for all the ratios of $Al_1 : (V + Ti)$ studied, all the initial vanadium passes into the sediment whereas the fraction of the titanium compounds in the sediment increases with rise in the ratio $Al_1 : (V + Ti)$ to reach
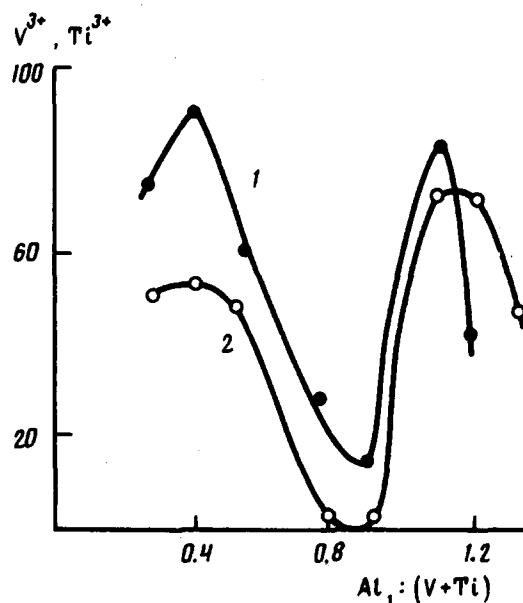

FIG. 3. Dependence of the content of V^{3+} (1) and Ti^{3+} (2) on the ratio $Al_1 : (V + Ti)$. $Ti : V = 0.5$. Exposure temperature of catalyst 403 K, 1 h. Content of V^{3+} and Ti^{3+} on the ordinate axis expressed in percentages.
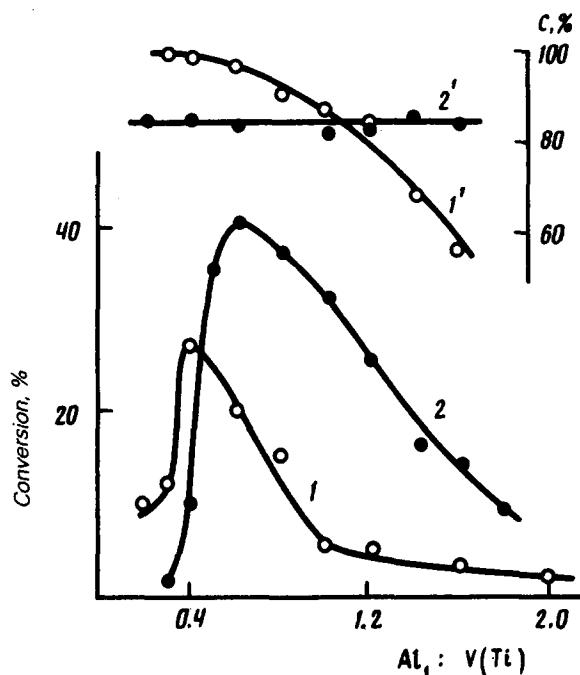
Fig. 4. Dependence of the activity and stereospecificity of the catalytic systems of $VOCl_3$-$Al(iso$-$C_4H_9)_3$ (1, 1')
and $TiCl_4$-$Al(iso$-$C_4H_9)_3$ (2, 2') on the ratio Al_1:V and Al_1:Ti, respectively. Conditions: time of
polymerization 4 h; remainder as in Fig. 1. c is the content of $trans$-(1, 4+1, 2) units.

100% only for Al_1:(V+Ti) = 1.07. The primary suspension and the sediment isolated from it possessed very low (roughly identical) activity and stereospecificity of action, for example, for Al_1:(V+Ti) = 1.07 in the primary suspension the polymer yield, in 30 h, was 90% and the content of the 1,4-$trans$ units, 87% while in the sediment of the primary suspension in 50 h of polymerization, 85% of the polymer formed containing 85% 1,4-$trans$ units. The polymers obtained under their influence were low molecular mass ($[\eta] < 0.1$ dl/g).

After addition of the second portion of $Al(iso$-$C_4H_9)_3$ to the sediment of the primary suspension, the activity and stereospecificity of the action of the system rose sharply to the corresponding values of the initial catalytic system prepared without intermediate isolation of the primary sediment. Thus, in 1-h polymerization the polymer yield reached 78% and the content of 1,4-$trans$ units was 90%.

The separately prepared catalytic systems $VOCl_3$-$Al(iso$-$C_4H_9)_3$ and $TiCl_4$-$Al(iso$-$C_4H_9)_3$ with a fractional supply of the organoaluminium compound and intermediate thermal treatment did not display such an oscillatory dependence as did the system $VOCl_3$-$TiCl_4$-$Al(iso$-$C_4H_9)_3$ and fell short of the latter in activity and stereospecificity of action (Fig. 4).

Determination of the k_p values in the critical regions of the behaviour of the system showed that change in activity is primarily related to change in the reactivity of the ACs governing polymerization. Thus, the k_p values at the points of maximum activity exceeded by ~ 1 order the corresponding value at the point of the minimum (Table 1).

It may, from the results, be assumed that the increased reactivity of the V–Ti system may be due to the incorporation of the atoms of one metal into the crystalline lattice of the other and to the formation of ACs simultaneously containing V and Ti atoms in trivalent forms. Probably, with fractional supply of $Al(iso$-$C_4H_9)_3$ to the mixture $VOCl_3 + TiCl_4$ and intermediate thermal treatment of the catalytic system, favourable conditions are created for the formation of double

TABLE 1. KINETIC PARAMETERS OF THE POLYMERIZATION OF PIPERILENE IN THE CATALYSTIC SYSTEM $VOCl_3$-$TiCl_4$-Al(iso-$C_4H_9)_3$ (323 K, $[C_5H_8]$ = 1, $[VOCl_3]$ = 5×10^{-3} mole/l, Ti : V = 0.4; Al_2 : V = 4.0; TEMPERATURE OF EXPOSURE OF CATALYST 403 K, 1 h)

$Al_1 : (V + Ti)$	Content of 1,4 $trans$-units, %	Polymerization rate, $w \times 10^2$, mole/l min	k_p, l/mole min	c_{AC}/c_V, %
0.4	97	2.6	900 ± 100	0.6
0.8	74	1.6	100 ± 20	2.5
1.07	95	3.7	1300 ± 130	0.5

chlorides of the transition metals by reason of the isomorphicity of the crystalline lattices of the individual chlorides VCl_3 and α-$TiCl_3$ [14, 15]. The first (small) portion of the organoaluminium compound is necessary to prevent the considerable simultaneous reduction of the vanadium and titanium compounds to forms with valency below three, since on addition immediately of the entire portion of Al(iso-$C_4H_9)_3$ reduction to the low valency forms (<3) probably occurs more rapidly than the formation of the total crystalline lattice of vanadium and titanium chlorides. The high
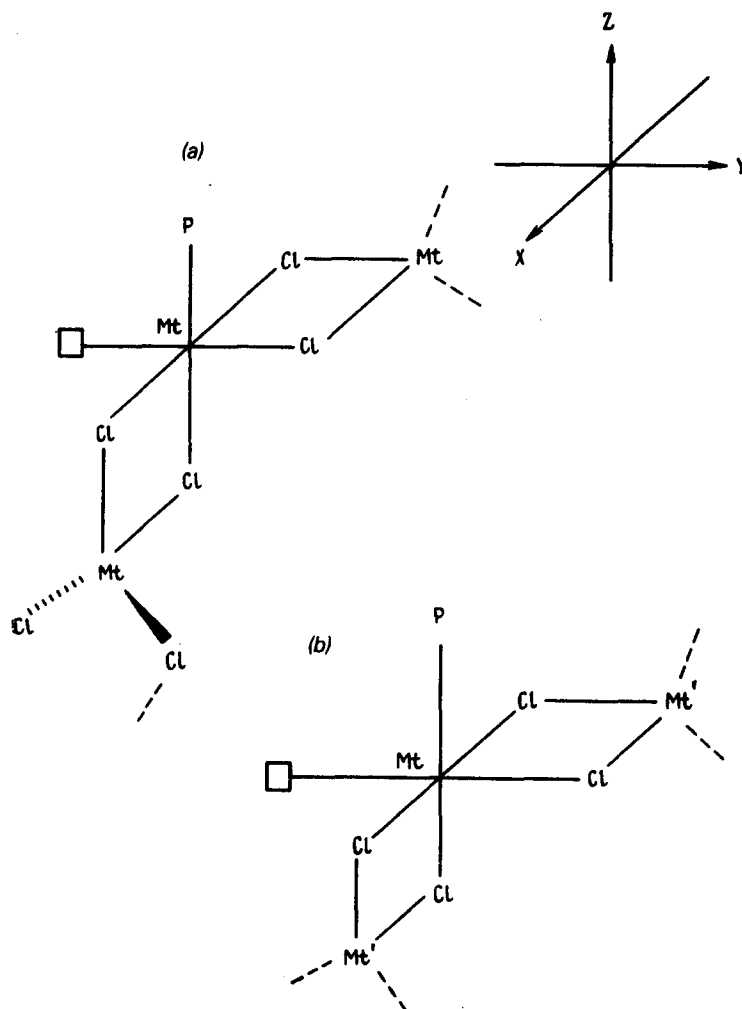

FIG. 5. Schematic representation of AC models: (a) with the atoms of one transition metal (Mt); (b) with the atoms of two transition metals (Mt and Mt'). The square denotes the vacant position for coordination; P is the polymer chain.

temperature of exposure of the primary suspension is also necessary to speed up the reaction of formation of the α-form* of $TiCl_3$. The stability of the total crystalline lattice of the sediment formed hampers the further reduction of the vanadium and titanium chlorides figuring in the lattice.

Let us see what the main effects possibly resulting from the formation of the joint crystalline lattice. Figure 5 shows, schematically, models of the possible structures of the active centres containing atoms of one and two transition metals. The incorporation of the "foreign" metal atom into the near surroundings of the AC must lead both to deformation of the structure of the AC (as a result of the incomplete matching of the parameters of the lattice of α-$TiCl_3$ and VCL_3) and to change in the electron density on the central atom of the AC. In all likelihood, at the points of the maximum, both these factors promote easier coordination of the monomer on the AC since in all cases in the two-stage propagation reaction

$$\text{(AC} + \text{M} \quad \underset{\text{Complexing}}{\rightleftharpoons} \quad \text{AC} \cdot \text{M} \quad \underset{\text{Insertion}}{\rightleftharpoons} \quad \text{AC} - \text{M)}$$

the limiting factor is the complexing stage (the first order of the polymerization reaction by the monomer is always observed). It may be assumed that at the point of minimum activity of the system as a result of a certain V^{3+} and Ti^{3+} ratio. In the sediment a less ordered total crystalline lattice forms from the vanadium and titanium chlorides with a large number of defects on which the ACs appear. This determines the rise in concentration (total number) of ACs but their reactivity sharply decreases probably because of change in the ligand surroundings of the central atom.

Thus, it has been established that change in the activity and stereospecificity of the catalytic system $VOCl_3$–$TiCl_4$–$Al(iso$-$C_4H_9)_3$ prepared by fractional supply of the organoaluminium compound and intermediate thermal treatment, with increase in the concentration of the first portion of the organoaluminium compound, is chiefly related to change in the eactivity k_p of the active centres. From the experimental data an assumption is advanced on the vanadium–titanium structure of the active centres governing the polymerization of piperilene.

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STUDY OF THE CONDITIONS OF THE FORMATION AND PROPERTIES OF EMULSIONS FORMED ON POLYMERIZATION OF SODIUM ACRYLATE IN AQUEOUS SOLUTION IN THE PRESENCE OF POLYETHYLENE OXIDE*

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Stable emulsions formed on polymerization of sodium acrylate in aqueous solution in the presence of PEO (emulsion of the water–water type) are described for the first time. The pH intervals, polymer concentrations and the sodium polyacrylate–PEO ratios at which the emulsion is stable for a sufficient length of time (>1 month) have been determined. The dispersion medium of such emulsions is the aqueous solution of PEO and the dispersed phase the aqueous solution of sodium polyacrylate. The emulsions studied are effective thickeners of different colloidal systems.

It is well known that on polymerization of acrylic (AA) and methacrylic (MAA) acids in acidic media in the presence of PEO, stoichiometric complexes form stabilized by hydrogen bonds [1, 2]. The cooperative interactions of the growing macroradical of the polycarboxylic acid with the PEO chain turn out to be possible only for a certain critical length of the macroradical. This interaction significantly influences the kinetics of radical polymerization of unsaturated carboxylic acids.

Quite a different picture is observed on polymerization of the salts of unsaturated carboxylic acids