Preparation and reactivity of metal-containing monomers
40.* Polymerization transformations of monomers based on vanadyl alkoxy derivatives

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Homo- and copolymerization of vanadium-containing monomers (VCM) have been studied. Radical homopolymerization of VCM is accompanied by some side reactions, such as monomer disproportionation, copolymerization with ligand *in situ*, cyclopolymerization, $V^{5+} \rightarrow V^{4+}$ reduction, *etc*. These reactions complicate the interpretation of the results obtained. The character of radical copolymerization of VCM with styrene or acrylonitrile is preferably radical complex. Catalytic properties of vanadium-containing homo- and copolymers (in combination with organoaluminum compounds as cocatalysts) in Ziegler—Natta ethylene polymerization have been studied. It has been shown that the products inherit the properties of immobilized polymer catalysts.

Key words: metal-containing monomers; vanadium-containing polymers; copolymerization; ethylene polymerization; immobilized catalysts.

Polymerization transformations of vanadium-containing monomers (VCM) are interesting, at least, in two respects. First, immobilized vanadium-containing catalysts can be obtained at one stage by this method. Second, one may expect that homo- and copolymerization of VCM prevents or retards reduction processes, which are typical of compounds of high-valent vanadium, as is commonly known.

Previously[1] we have first synthesized and characterized esters of orthovanadic acid based on unsaturated alcohols of general formula $VO(OR)_{3-n}(OR')_n$, where R = Pr^i, R' = $CH_2C{\equiv}CH$ (**1**), $CH_2CH{=}CH_2$ (**2**), $(CH_3)_2CC{\equiv}CCH{=}CH_2$ (**3**), and $(CH_2)_2OC(O)C(CH_3){=}CH_2$ (**4**), by transesterification.

In this work, the results on radical and ion homo- and copolymerization of these VCM are summarized, and some data on the structures and properties of the products are presented, in particular, their properties as immobilized catalysts of the Ziegler—Natta ethylene polymerization.

Results and Discussion

Homopolymerization of VCM. Long boiling of VCM **3** and **4** in bulk or benzene solution does not result in their thermal polymerization. The process occurs only in the presence of radical initiators, radical sources ($Int^{\cdot}$), of which azo-bis-isobutyronitrile (AIBN) is the most convenient at concentrations of 0.5—2.0 wt. %.

The reaction products are formed as a yellow precipitate, and their yield depends on the initiator concentration, temperature, and duration of polymerization (Table 1).

The polymers are well soluble in methanol, DMSO, and DMF and insoluble in benzene, pentane, and THF. The color of the polymers changes after several minutes in a thin layer in air from light yellow to dark orange and green, probably due to a partial decomposition of vanadium fragments. Homopolymers of VCM are comparatively low-molecular. Only their reduced viscosity (in inert atmosphere) was determined because of their tendency to decomposition: (0.12—0.19) 100 mL g^{-1} depending on their preparation (see Table 1).

Table 1. Effect of polymerization conditions of VCM **4** on the yield of the polymer (benzene, VCM concentration is 0.2 mol L^{-1})

C_{AIBN}(%)	T/°C	τ/min	Yield of polymer (%)	η_{red}* /100 mL g^{-1}
0.5	65	60	2	0.14
1.0	65	60	4	0.15
2.0	65	60	4	0.12
1.0	70	60	9	0.19
1.0	75	60	13	0.14
1.0	75	120	26	0.13
1.0	75	100	40	0.16
2.0	75	60	13	0.12

* In DMSO.

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* For Part 39, see *Izv. Akad. Nauk, Ser. Khim.*, 1994, 1047 [*Russ. Chem. Bull.*, 1994, **43**, 983 (Engl. Transl.)].

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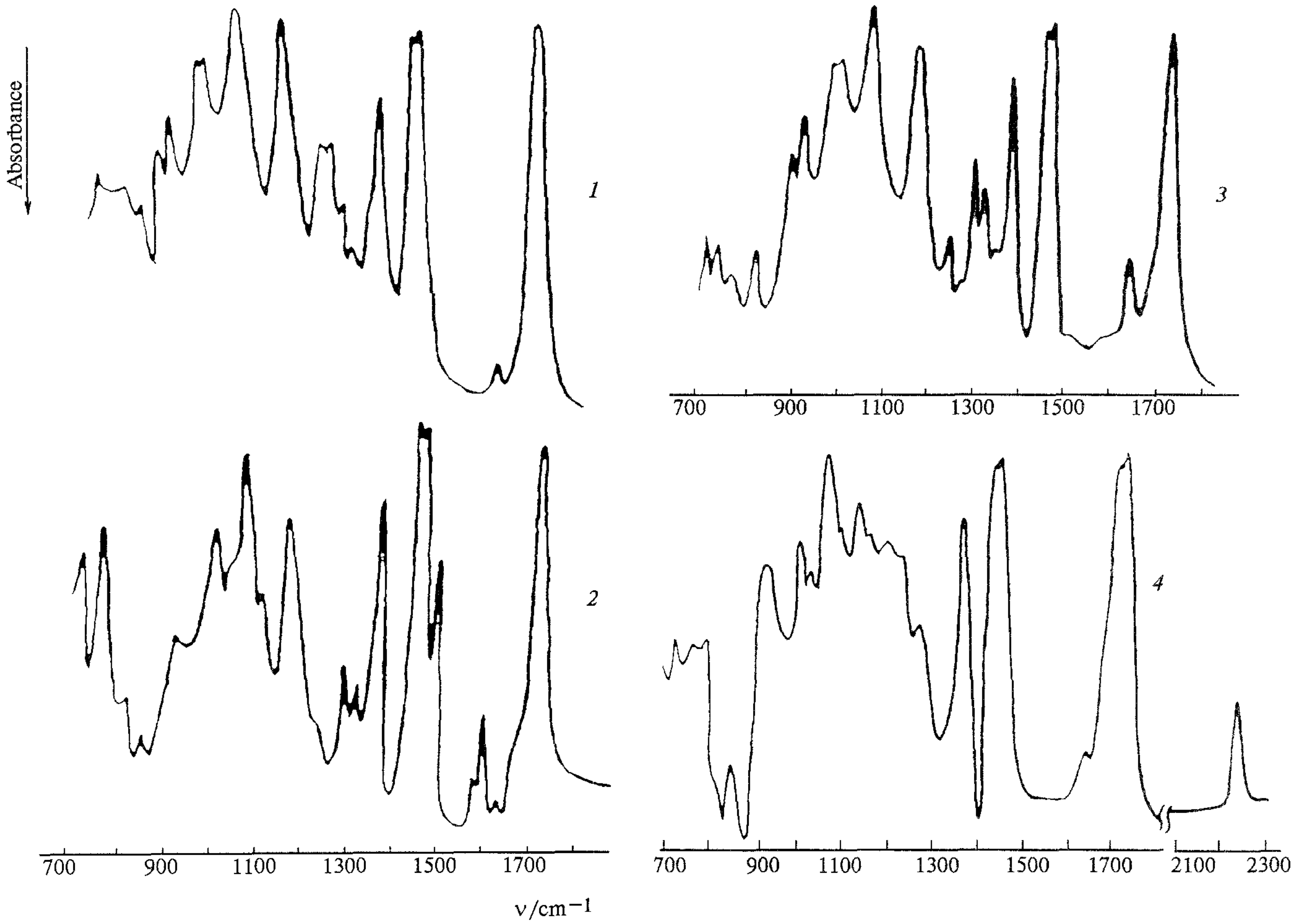


Fig. 1. IR spectra of polymerization product **4** (*1*) and its copolymers with styrene (content in the monomeric mixture 90 (*2*) and 23 (*3*) mol. %) and acrylonitrile (*4*) (content in the monomeric mixture 80 mol. %).

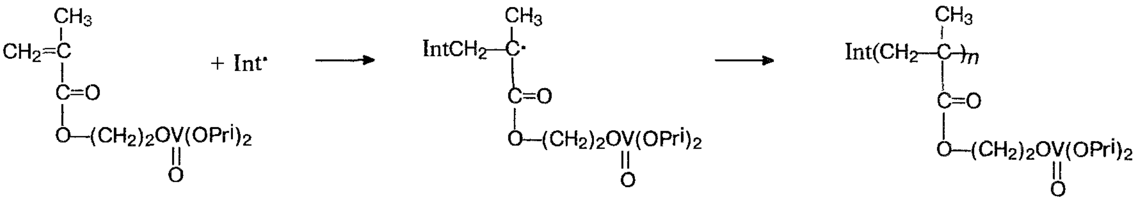
A comparison of the IR spectra of the initial monomers and the products (Fig. 1) shows that the bands of stretching vibrations of the C=C bond are almost absent for the products and appear at 1640 cm^{-1} for the monomers. The characteristic absorption bands of the vanadyl fragment are retained: ν(V=O) (1005 cm^{-1}), carbonyl group (1720 cm^{-1}), framework vibrations of the isopropyl group (1140, 1175 cm^{-1}), and others.

Thus, the general scheme of the polymer formation from VCM can be presented (by the example of **4**) in the following form (Scheme 1).

At the same time, chemical analysis shows that the content of vanadium is lower in the polymers obtained (12.0—10.9 wt. %) than in the monomer (16.30 wt. %). The disproportionation of **4** to form disubstituted (by the number of polymerized fragments) VCM is the most probable reason for this fact.

The content of vanadium is 13.25 wt. % in this disubstituted VCM. It was obtained by counter synthesis. Homopolymerization of this VCM is characterized

Scheme 1

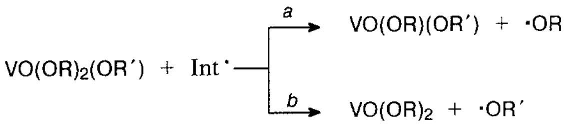


by almost the same regularities as that of the monosubstituted VCM.

$$2\ \mathrm{VO(OPr^i)_2(O(CH_2)_2OC(O)C(CH_3){=}CH_2)} \rightleftharpoons$$

$$\rightleftharpoons \mathrm{VO(OPr^i)_3} + \mathrm{VO(OPr^i)(O(CH_2)_2OC(O)C(CH_3){=}CH_2)_2}$$

The tendency of compounds of high-valent vanadium (especially, chlorides, esters of orthovanadic acid) to reduction is well known and is caused by the low value of its redox potential. This process is likely to be accelerated in the presence of free radicals and, in principle, can occur *via* two routes.



$$\mathrm{VO(OR)_2(OR')} + \mathrm{Int}^{\bullet} \xrightarrow{a} \mathrm{VO(OR)(OR')} + {}^{\bullet}\mathrm{OR}$$

$$\mathrm{VO(OR)_2(OR')} + \mathrm{Int}^{\bullet} \xrightarrow{b} \mathrm{VO(OR)_2} + {}^{\bullet}\mathrm{OR'}$$

Under the action of radicals in parallel with the initiation of polymerization, vanadium reduction takes place (*a*, *b*). However, when the fragment capable of copolymerization (*b*) is detached from VCM, its incorporation into the polymeric chain and a decrease in the vanadium content in the product are observed. This process can be called copolymerization with ligand *in situ*.

The existence of V^{4+} in the polymer is confirmed by the ESR data (Fig. 2). The eight-component ESR signal typical of isolated V^{4+} complexes is observed in the product obtained by the polymerization of **4** at 75 °C for 2 h in benzene in the presence of 1 mol. % of AIBN. As is known,[2] the maximum local concentration of isolated V^{4+} ions is estimated as $2 \cdot 10^{-4}$ g-at. cm^{-3}. Average distances between such isolated complexes $r_{\mathrm{iso}} \geq 22$ Å. The estimated value of the V^{4+} concentration in the homopolymer of **4** is 1 mol. % of the total vanadium content ($1.2 \cdot 10^{-4}$ g-at. cm^{-3}), which is less than the value presented above.

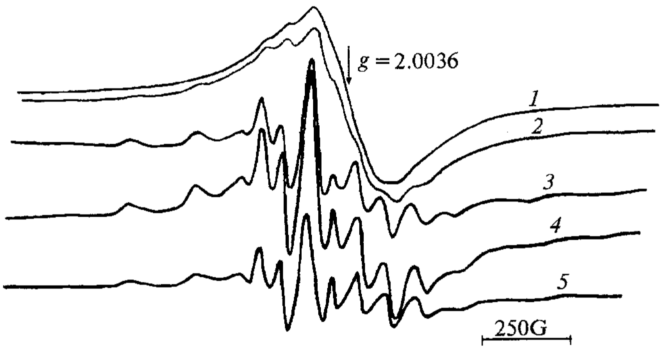
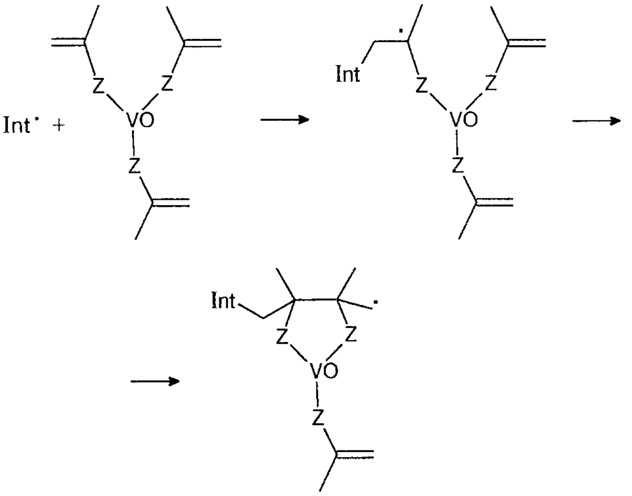


Fig. 2. ESR spectra of the homopolymer of **4** (*1*) and its copolymers (*2*—*5*). For *1*—*4* designations are the same as in Fig. 1, *5* , 25 mol. % of acrylonitrile in the monomeric mixture.

As has already been mentioned,[1] the trisubstituted product $\mathrm{VO(O(CH_2)_2OC(O)C(CH_3){=}CH_2)_3}$ is the most stable of the VCM studied. It is likely to be associated with the absence of the routes of its disproportionation. The products formed are also more stable than other vanadium-containing polymers. This made it possible to estimate their mean molecular weight by osmometry. It turned out to be 13000, which corresponds to the average degree of polymerization equal to 23. In turn, the number of double bonds determined by ozonolysis is 20 per each macromolecule of the vanadium-containing polymer. Therefore, only two fragments of this monomer are involved in the polymerization of three fragments capable of polymerization, and the third fragment does not participate in it, probably due to steric factors. In turn, solubility of the polymer in methanol indicates that no linked structures are formed. This contradiction can be eliminated if the cyclopolymerization mechanism is assumed for radical processes.



Z = —O(CH$_2$)$_2$OC(O)—

Let us consider homopolymerization of VCM of other types, in particular, of **3**. It has been found previously[1] that it is impossible to isolate the individual product formed in the interaction of $\mathrm{VO(O{-}Pr^i)_3}$ with this alcohol at a molar ratio of 1 : 2 due to disproportionation processes.

$$2\ \mathrm{VO(OPr^i)(O(CH_3)_2CC{\equiv}CCH{=}CH_2)_2} \rightleftharpoons$$

$$\rightleftharpoons \mathrm{VO(OPr^i)_2(O(CH_3)_2CC{\equiv}CCH{=}CH_2)} +$$

$$+ \mathrm{VO(O(CH_3)_2CC{\equiv}CCH{=}CH_2)_3}$$

In the course of the polymerization of this mixture of monomers, it is likely that the equilibrium shifts to the formation of the polymer from the disubstituted VCM (the content of vanadium in it is 15.0 %, 14.50 is calculated for the monomeric unit). The product formed is a light brown powder insoluble in benzene but well soluble in methanol and DMF, and it becomes green in air. Its yield and molecular weight characteristics are similar to those presented for other vanadium-containing polymers (see Table 1).

VCM with propargyl fragments are not polymerized *via* the radical route. It is known that propargyl alcohol itself is polymerized in a complicated manner *via* the ionic mechanism under the effect of benzene solutions of $MoCl_5$ or its immobilized analogs.[3] The attempts at ionic polymerization of VCM based on propargyl alcohol resulted in the formation of a heavy black oil, probably a low-molecular oligomeric product with a linear or cyclic structure.

It should be mentioned that vanadium ions can be removed from the formed vanadium-containing polymers of any type (by reprecipitation of a vanadium-containing polymer from a methanol solution to an excessive amount of water). Polymers without metals are isolated in this way.

Copolymerization of 4 with styrene. Unlike the homopolymer of **4**, its copolymers with styrene are well soluble in benzene and can be isolated from the solution by precipitation with an excess of pentane. The conditions of copolymerization were chosen in such a way that conversion did not exceed 10—15 wt. %. Styrene copolymers are yellow-green powders, which gradually oxidize in air. It is interesting that in the copolymerization products formed under conditions in which the monomeric mixture contained up to 50 mol. % of styrene, units of the latter were not identified by IR spectroscopy, despite the fact that their presence in the copolymer was confirmed by other methods (by measuring the solubility of the product in benzene, the analysis of the vanadium content, *etc.*). For the higher content of styrene in the monomeric mixture, styrene units in the copolymers are confirmed by spectroscopy (ν/cm^{-1}: 1495, 1580, and 1600, see Fig. 1, spectrum *2*).

The *composition of the monomeric mixture—composition of the copolymer* diagram also has an extremely unusual character (Fig. 3). The part of the curve where the composition of the copolymer is almost independent of the composition of the monomeric mixture is very distinct, which assumes a tendency to alteration of monomeric units in the copolymer and indicates the radical complex character of the copolymerization. As is known,[4] such products are formed in the copolymerization of the monomers one of which is a donor and the other of which is an electron acceptor. When differences in donor—acceptor properties of the monomers are not so significant, the copolymerization is performed in the presence of Lewis acids. In our case, **4** (a weak Lewis acid) serves as an acceptor, and styrene is a donor. Coordination interactions in such systems are sufficiently weak, and it is very difficult to fix the formation of stable complexes.* At high molar fractions of **4** or styrene in monomeric mixtures, blocks of VCM or styrene are included in addition to regularly alternating units. This occurs because of the fact that the chain growth can be performed *via* three routes: the subsequent addition of free monomers to the macroradical; the addition of pairs of monomers bound in a complex; and the simultaneous participation of free and complex-bound monomers. The reactivity of complex-bound monomers is most often higher than that of free monomers; therefore, their contribution predominates in the reactions with growing macroradicals independently of the nature of the terminal unit, although the addition of free molecules to the growing macroradical cannot be excluded.

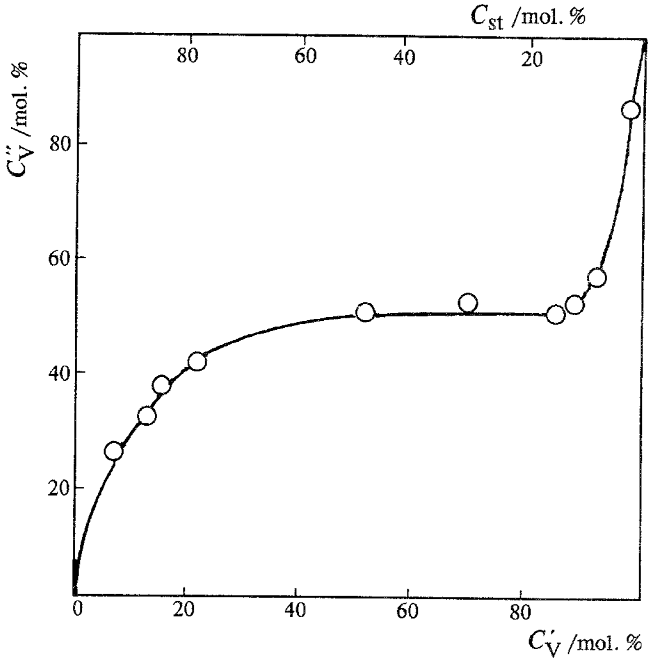


Fig. 3. Composition diagram for the copolymerization of **4** with styrene. C'_V and C''_V are the concentrations of vanadium in the monomeric mixture and in the polymer, respectively, C_{st} is the concentration of styrene in the monomeric mixture.

Thus, the total composition of the product of the radical complex copolymerization can be presented by the general Scheme 2 in which the *m*, *n*, and *p* indices are determined by the composition of the monomeric mixture.

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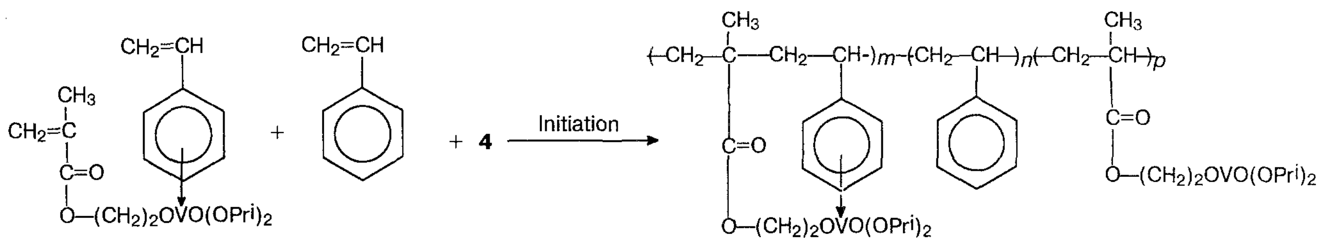
* The formation of charge transfer complexes of the 1 : 1 composition between compounds of high-valent vanadium and π-donors are sufficiently well studied.[5] For example, $VOCl_3$ forms CTC with ethylbenzene with λ_{max} = 490 nm, polystyrene with $VOCl_3$ also forms π-donor complexes of the composition D : $VOCl_3$ = 1 : 1 (D is the monomeric unit of polystyrene), whose maximum of absorption bands (485 nm) almost coincides with λ_{max} for the complex with ethylbenzene.

Scheme 2



The molecular weights of the products are also small. Note that reduction processes accompanied by the formation of V^{4+} occur in such systems as well. However, the conversion of such transformations is significantly higher than in the case of the homopolymer. The ESR spectrum of the V^{4+} ions formed is broadened by the exchange interaction and represents a broad singlet. This polymer can be considered as a cooperative matrix in which V^{4+} ions are incorporated into the matrix[2] consisting of V^{5+} ions. The concentration of V^{4+} ions is estimated as 14—16 mol. %. Most likely these aggregates originate around vanadium atoms which link two polymer chains, which can increase the probability of the approach of other vanadium atoms around them. The catalytic reduction of vanadium (for example, with participation of the V^{4+} formed) also cannot be excluded in such a multicomponent system,* as was observed,[7] in particular, for compounds of Rh^{3+}.

Copolymerization of 4 with acrylonitrile occurs with comparatively high rates in benzene at 70 °C. The monomeric mixture included 25, 50, and 88 mol. % of acrylonitrile. In the course of the copolymerization, light yellow products containing 12, 11, and 8 % of vanadium precipitated from the solution in 15—20 % yield. These products are soluble in DMF, DMSO, and methanol. The intense bands $\nu(C{\equiv}N) = 2245\ cm^{-1}$ and $\nu(C{=}O) = 1720\ cm^{-1}$ of the ligand group of **4** are observed in the IR spectra of all of the products. For the first sample, the ratio of intensities $I(C{=}O)/I(C{\equiv}N) = 13 : 1$, while for the latter it is 3 : 1. Most likely the alternate copolymerization of the complex-bound pair of monomers occurs for an acrylonitrile content in the monomeric mixture less than 50 mol. %, and products similar to copolymers with styrene are formed at higher contents. The products enriched in acrylonitrile are poorly soluble in methanol. The values of the intrinsic viscosity (DMSO, 30 °C) of the sample of copolymers obtained in the case of the monomeric mixtures with 25 and 88 mol. % of acrylonitrile are (in 100 mL g^{-1}) 0.11 and 0.20, respectively. The ESR spectra of these samples are also similar to those of copolymers of **4** with styrene and correspond to 35—44 mol. % of V^{4+}.

Catalytic properties of vanadium-containing polymers and copolymers in ethylene polymerization. Compounds of high-valent vanadium are active catalysts (in combination with organoaluminum compounds) of anion-coordination polymerization of α-olefins, in particularly, ethylene.[8] However, their main disadvantage is the low temperatures at which they can be used (as a rule, −20 to +40 °C). To increase the working temperatures to technological temperatures (70—90 °C) and to enhance the activity of these systems, vanadium compounds are chemically immobilized on substrates, including substrates of a chemical nature.[9] It can be

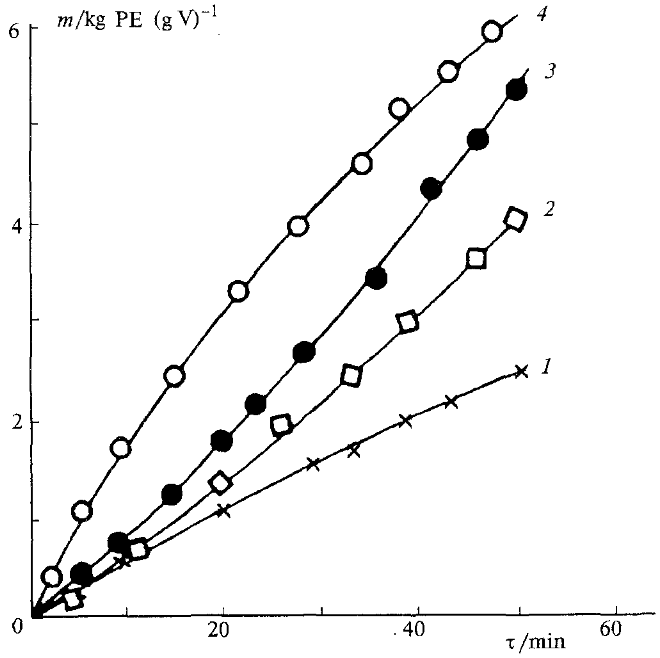


Fig. 4. Kinetics of ethylene polymerization by catalytic systems based on the homopolymer of **4** (*1*), its copolymers with styrene (contents of styrene in the monomeric mixture are 23 (*2* and *3*) and 90 (*4*) % at 70 (*1*, *2*, *4*) and 90 °C (*3*). Cocatalyst $Al(Bu^i)_2Cl$, Al/V = 10, solvent *n*-heptane, ethylene pressure 0.4 mPa.

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* It is known[6] that thermal decomposition of alkoxy derivatives of V^{4+} under static conditions occurs *via* the molecular route of decomposition and has a pronounced autocatalytic character caused by the pyrolytic solid surface.

expected that products of homo- and copolymerization of VCM inherit properties of immobilized catalysts. Actually, as seen from Fig. 4, the product of the homopolymerization of **4** and its copolymers is comparatively active in ethylene polymerization at 70 and even at 90 °C. As is known,[10] an increase in the specific catalytic activity with a decrease in the surface density of vanadium atoms is characteristic of immobilized systems. In our case, the matrix isolation of vanadium atoms also results in an increase in the activity of alternate copolymers as compared with the homopolymer (see Fig. 4, curves *1* and *3*). This to a greater extent is characteristic of block-copolymers based on **4** (see Fig. 4, curve *4*).

High- or superhigh-molecular polyethylene (PE) (average-viscosity molecular weight $\approx 1 \cdot 10^6$) is formed under different conditions of polymerization. Of course, the chosen conditions of polymerization and vanadium-containing polymers, perhaps, are not optimum; however, the activity of these catalysts (6 kg PE $(g\ V)^{-1}$) is significantly lower than the activity of the catalysts for which a vanadium compound is fixed only on the surface (or in a thin near-surface layer) of a polymeric substrate.[11] This is related to the recuperation of a part of the vanadium in the bulk vanadium-containing polymer and its exclusion from the processes of the formation of active centers of ethylene polymerization. In our opinion, catalytic systems based on monomers of alkoxy-derivatives of vanadium can be optimized if active components are immobilized on the surface of inert substrates (PE, PS, PVC, and others), for example, by graft polymerization of the corresponding monomers, as was realized in the case of other metal-containing monomers.[12]

Experimental

The synthesis and parameters of compounds **1—4** have been presented previously.[1] VCM were polymerized and copolymerized in inert atmosphere or in a vacuum in sealed glass tubes in which a solvent, an initiator, and a monomer (or a mixture of monomers) were subsequently placed. After homo- or copolymerization, tubes were opened in an argon flow, and the product was isolated and reprecipitated in inert atmosphere and precipitated with dry pentane. Intrinsic viscosity of samples were determined by viscosimetry (viscosimetry with hanging level). Molecular weight of the polymerization product, trisubstituted VCM $VO(O(CH_2)_2OC(O)C(CH_3){=}CH_2)$, was measured on a Hewlett-Packard-502 osmometer with cellophane membranes. The number of double bonds in homo- and copolymers was determined on an ADS-4M analyzer of double bonds. IR spectra of the products of polymerization transformations were recorded for suspensions in Vaseline oil on a UR-20 instrument. ESR spectra were recorded on a SE/X-2544 (Radiopan) radiospectrometer at 77 K, microwave power was 10 dW, magnetic field modulation was 4 G, and the range was 2000 G. The content of V^{4+} was estimated using $CuSO_4 \cdot 5H_2O$ as the reference. Ethylene polymerization was performed in a standard thermostatted high-pressure setup provided with an attachment for input of components (a catalyst, a solvent, and ethylene) and with a high-speed mixer, and a manometric instrument for recording the kinetics of ethylene consumption. PE formed was isolated and washed off by the traditional procedure, and its molecular weight was determined by viscosimetry in decaline at 130 °C.

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