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Cationic Complexes of Monovalent Nickel as Catalysts for Styrene Polymerization

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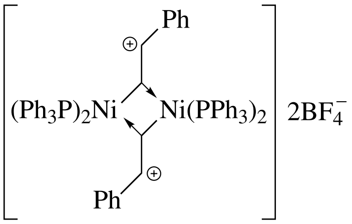
Abstract—The interaction of the $[Ni(PPh_3)_3]BF_4$ complex with styrene and the products of styrene conversion in the polymerization reaction were studied by EPR and ^{13}C NMR spectroscopy. The structure of the σ-carbocationic complex of Ni(I) formed by the interaction of styrene with the $[Ni(PPh_3)_3]BF_4$ cationic phosphine complex of Ni(I) was characterized in detail. It was found that the reaction of styrene polymerization occurred with the participation of the coordination center of the σ-carbocationic complex (coordination catalysis), whereas the reaction of telomerization occurred with the participation of the cationic center of this complex (ionic catalysis). The resulting polymer contained active terminal double bonds; it is a promising macromonomer for the synthesis of grafted copolymers. The discovered capacity of alcohols to undergo nucleophilic addition to a growing polymer chain offers strong possibilities for preparing functional polymers and block copolymers.

INTRODUCTION

Catalytic systems based on nickel, which are primarily known as catalysts for the low-molecular-weight oligomerization of olefins [1–4], are of considerable current interest because it was found that a number of nickel complexes can efficiently catalyze the polymerization of unsaturated hydrocarbons [5–21].

Despite the considerable number of publications devoted to studies of polymerization on nickel complex catalysts, the nature of the active center and the mechanism of polymerization are not clearly understood. This is due to the fact that the majority of studies have been oriented to reaction products without considering the structure of the active center and its transformation in the presence of a monomer, as well as the intricacy of test systems containing various potential centers of polymerization. In this context, the $[Ni(PPh_3)_3]BF_4$ cationic phosphine complex of Ni(I) is of interest. As found previously [22, 23], this complex is an active catalyst for styrene polymerization.

The $[Ni(PPh_3)_3]BF_4$ tricoordinated phosphine complex of monovalent nickel has a doubly degenerated ground state. As a consequence of the Jahn–Teller effect, it was detected as a broadened asymmetric signal in the EPR spectrum at $T = 77$ K (Fig. 1) ($g_z = 2.385$, $g_y = 2.12$, $g_x = 2.07$, $A_x(1P) = 8.2$ mT; $A_y(1P) = 6.4$ mT) [24, 25]. Previously [22], it was found that, upon the interaction of the $[Ni(PPh_3)_3]BF_4$ cationic complex with styrene at room temperature (a 2 : 1 molar ratio of styrene to Ni), the EPR signal disappeared and an intense band at 30000 cm^{-1} and a weak band at 21000 cm^{-1} appeared in the UV spectrum. These absorption bands are characteristic of a carbocation containing a benzene ring conjugated with the carbon atom bearing a positive charge [26]. Based on these data, it was hypothesized that the resulting Ni(I) complex with styrene, in which a positive charge is localized on styrene, is a σ-cationic complex of Ni(I), which occurs in solution in the dimeric state



In this work, we studied the interaction of the $[Ni(PPh_3)_3]BF_4$ complex with styrene and the products of styrene conversion in the polymerization reaction using EPR and ^{13}C NMR spectroscopy in order to obtain detailed information on the structure of the carbocationic complex of Ni(I) and on the process mechanism of styrene ligand activation in the coordination sphere of Ni(I).

EXPERIMENTAL

All of the operations were performed in an atmosphere of purified argon using Schlenk techniques.

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Glass Schlenk filters were used for filtration. All of the prepared and synthesized reagents were stored in sealed ampules in an argon atmosphere.

Toluene, benzene, and heptane (high-purity grade) were distilled from sodium metal in the presence of benzophenone before use. Boron trifluoride–diethyl ether adduct (Merck) was distilled from LiH in an argon atmosphere before use. Absolute ethanol was prepared by distillation from sodium metal (10 g/l).

Diethyl ether was purified to remove the peroxides, distilled from sodium, and stored over a sodium mirror [27].

Styrene was purified by shaking it with a 5% alkali solution until the alkali became colorless [27]; thereafter, it was washed with distilled water, dried with anhydrous calcium chloride, and distilled in vacuum (boiling temperature, 32°C/10 Torr).

The $[Ni(PPh_3)_3]BF_4$ complex was synthesized in accordance with a procedure based on the oxidation of the $Ni(PPh_3)_4$ complex by the boron trifluoride–diethyl ether adduct [28]: 0.23 ml of $BF_3 \cdot OEt_2$ was added to a stirred solution of 0.5 g of $Ni(PPh_3)_4$ in 10 ml of toluene (B/Ni = 4 : 1) for 10 min at room temperature in an argon atmosphere with the use of a syringe. Next, the mixture was cooled to –10°C, and the precipitate formed was filtered off. The $[(PPh_3)_3Ni]BF_4$ complex was isolated as a brown solid from the filtrate by precipitating with heptane. The product yield was 75% of the theoretical value. For $C_{54}H_{45}P_3NiBF_4$ anal. calc. (%): Ni, 6.3; C, 69.5; H, 4.80; P, 9.99. Found (%): Ni, 6.6; C, 69.3; H, 4.86; P, 9.78.

The polymerization of styrene was performed as follows: Toluene, a weighed portion of the nickel complex, and other reagents were successively placed in a thermostated reactor in an argon atmosphere. The concentration of the nickel complex was equal to 1×10^{-4} mol/l. Next, styrene was added with intense stirring. The amount of reacted styrene was determined by GLC on a GALS gas chromatograph with a flame-ionization detector (using packed column 5 mm in diameter and 150 cm in length with Apiezon). After completion of the reaction, the polymer was precipitated with an excess of ethanol, reprecipitated from toluene, and vacuum dried to constant weight.

The EPR spectra were measured on a PS-100X spectrometer operating at 9.6 GHz at the boiling temperature of liquid nitrogen. As reference substances, Mn(II) in MgO and DPPH were used.

NMR spectra were obtained on a Varian VXR-500S spectrometer at 25°C, and IR spectra were measured as KBr pellets on a Bruker IFS 25 spectrophotometer.

The molecular weights of polymers were determined by the isopiestic method in an acetone solution using azobenzene as a standard compound [29]. For turbidimetric titration, 0.05% polymer solutions in dioxane were used; precipitation was performed with water; absorbance was measured on a KFK-3 photometer at a wavelength of 870 nm. The results were treated in accordance with a published procedure [30].

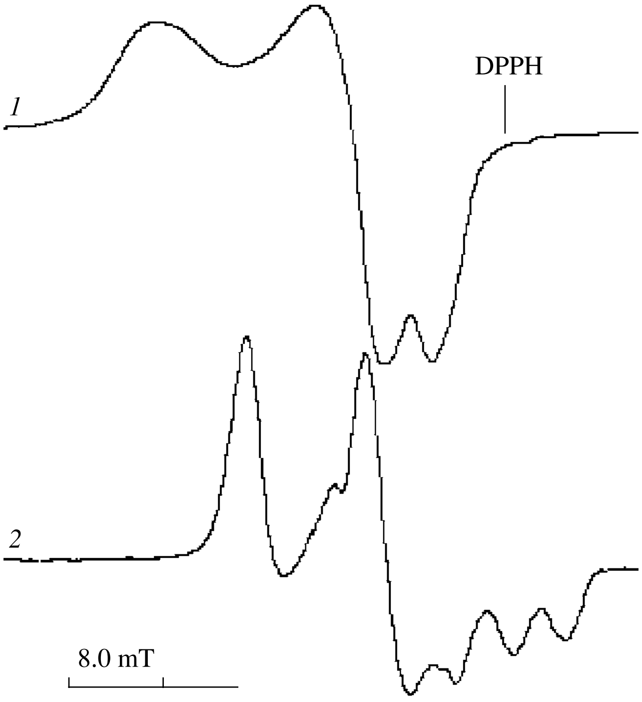


Fig. 1. EPR spectra of the monovalent nickel complexes (*1*) $[Ni(PPh_3)_3]BF_4$ and (*2*) $[(PPh_3)_2Ni(P(OEt)_3)_2]BF_4$ in a toluene solution. $T = 77$ K.

RESULTS AND DISCUSSION

Interaction of styrene with the cationic complex of Ni(I). Upon the addition of styrene to a toluene solution of the $[Ni(PPh_3)_3]BF_4$ complex (styrene/Ni molar ratio of 2 : 1), EPR signal *1* (Fig. 1) from the initial complex of Ni(I) disappeared and a group of signals appeared in the ^{13}C NMR spectrum at 156, 140, 136, 135, and 129 ppm (Fig. 2). These signals are characteristic of a carbocation containing a benzene ring conjugated with the carbon atom bearing a positive charge [26]. The signal at 156 ppm was a superposition of two signals at 156.83 and 155.86 ppm. This was likely due to the occurrence of two conformers of the carbocationic complex of Ni(I) with a dynamic equilibrium between these conformers. A broadening of these signals is indicative of short relaxation times of the dynamic processes. Upon the subsequent introduction of a strong ligand, triethyl phosphite, into the system ($P(OEt)_3$/Ni molar ratio of 2 : 1), signal *2* appeared in the EPR spectrum (Fig. 1) ($g_z = 2.014$; $g_y = 2.185$; $g_x = 2.201$; $A_z(P) = 17.5$ mT; $A_z(P') = 8.1$ mT; $A_y(P) = 21.0$ mT; $A_x(P) = 13.5$ mT), which fully coincided with the spectrum of the cationic complex $[(PPh_3)_2(P(OEt)_3)_2Ni]BF_4$ [31]. In this case, a group of signals at 156, 140, 136, 135, and 129 ppm disappeared from the ^{13}C NMR spectrum. The disappearance of the

NMR signals of a carbocation and the appearance of EPR signal *2* suggest the replacement of styrene by triethyl phosphite ligands and the degradation of diamagnetic dimeric carbocation structures.

The experimental data on the structure of the carbocationic complex of Ni(I) allowed us to propose Scheme 1, which is the most probable reaction scheme for styrene activation on $[Ni(PPh_3)_3]BF_4$.

The BF_4^- counterions are not shown in Scheme 1.

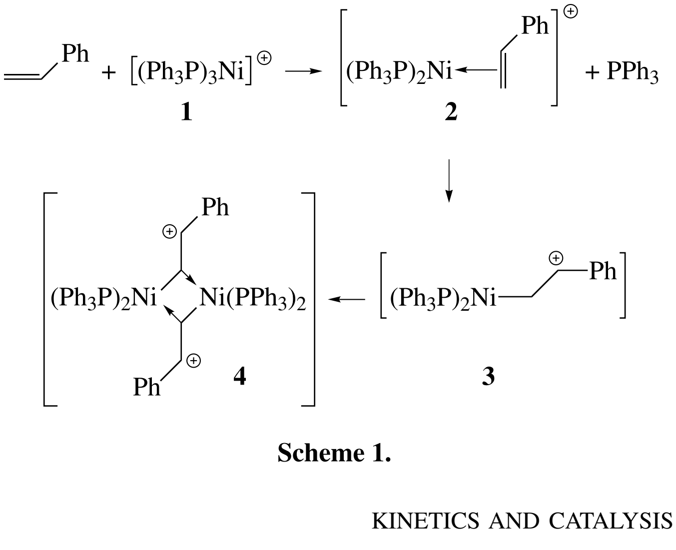
In accordance with the proposed reaction scheme, in the interaction of styrene with cationic complex **1**, the substitution of styrene for a phosphine ligand occurs with the formation of π complex **2**. Complex **2** is converted into σ-carbocationic complex **3** as a consequence of the rapid π–σ rearrangement and positive charge transfer from the nickel ion to coordinated styrene. It is likely that the π–σ rearrangement is an equilibrium process, and equilibrium is shifted toward the formation of the σ structure. Because of its coordinative unsaturation, σ-carbocationic complex **3** forms diamagnetic dimer **4** in a toluene solution.

Styrene polymerization. The introduction of 0.5 mol % of the $[Ni(PPh_3)_3]BF_4$ cationic complex into a styrene solution in toluene resulted in the rapid polymerization of styrene at 10–40°C. The reaction occurred to the complete consumption of the monomer (Fig. 3); however, the polymer yield was only 67%. This suggests that a low-molecular-weight oligomer fraction soluble in ethanol was also formed, which is characteristic of processes on nickel-containing catalysts [21]. The resulting product was a paraffin-like mass. The IR spectrum of this product exhibited an absorption band at 1640 cm^{-1}, which is characteristic of the stretching vibrations of double bonds. The ^{13}C NMR spectra exhibited a signal in the region 137–138 ppm, which corresponds to the terminal unsaturated groups $\mathrm{CH_2{=}\mathbf{C}}\begin{smallmatrix}\diagup\\ \diagdown\mathrm{Ph}\end{smallmatrix}$, whose concentration was 1–2% of the total amount of styrene units.

The addition of new portions of the fresh monomer to the reaction mass up to a styrene/Ni ratio of 700 : 1 resulted in the activation of the reaction at almost the same rate. The high viscosity of the system hindered a further addition of the monomer. The product isolated at this step was a powder whose molecular weight (3600) was higher than the molecular weight (2500) of a polymer obtained at a styrene/Ni ratio of 200 : 1. The turbidimetric titration curves (Fig. 4) are consistent with the observed increase in the degree of styrene polymerization; they are indicative of a similarity between the molecular-weight distributions of the samples. It is likely that, on the addition of new portions of the fresh monomer, previously formed macromolecules containing residual terminal double bonds also participated in the renewed polymerization.

The reaction did not occur with methyl methacrylate (MMA) and methyl acrylate as monomers: we failed to detect the formation of polymer products by GLC analysis. The fact that the monomers with an acceptor substituent at the double bond are nonreactive under the conditions examined suggests the cationic character of the active nickel complex.

The addition of MMA to styrene did not result in the formation of copolymers: the NMR spectra of the resulting products were analogous to the spectra of polystyrene. Only a weak absorption band at 1720 cm^{-1}, which belongs to the stretching vibrations of the carbonyl group, appeared in the IR spectrum. The yield of polystyrene decreased with MMA concentration (Fig. 5), although MMA did not inhibit styrene polymerization even in a considerable excess in the reaction mixture. The polystyrene specimens obtained in the system with MMA were powdered solids. According to turbidimetric titration data (Fig. 6, curves *3*, *4*), they had a higher molecular weight and a narrower molecular-weight distribution, as compared with the polymerization products of pure styrene (Fig. 6, curve *1*). The introduction of MMA after the consumption of styrene (Fig. 6, curve *2*) did not affect the molecular-weight distribution, although the molecular weight somewhat



Scheme 1.

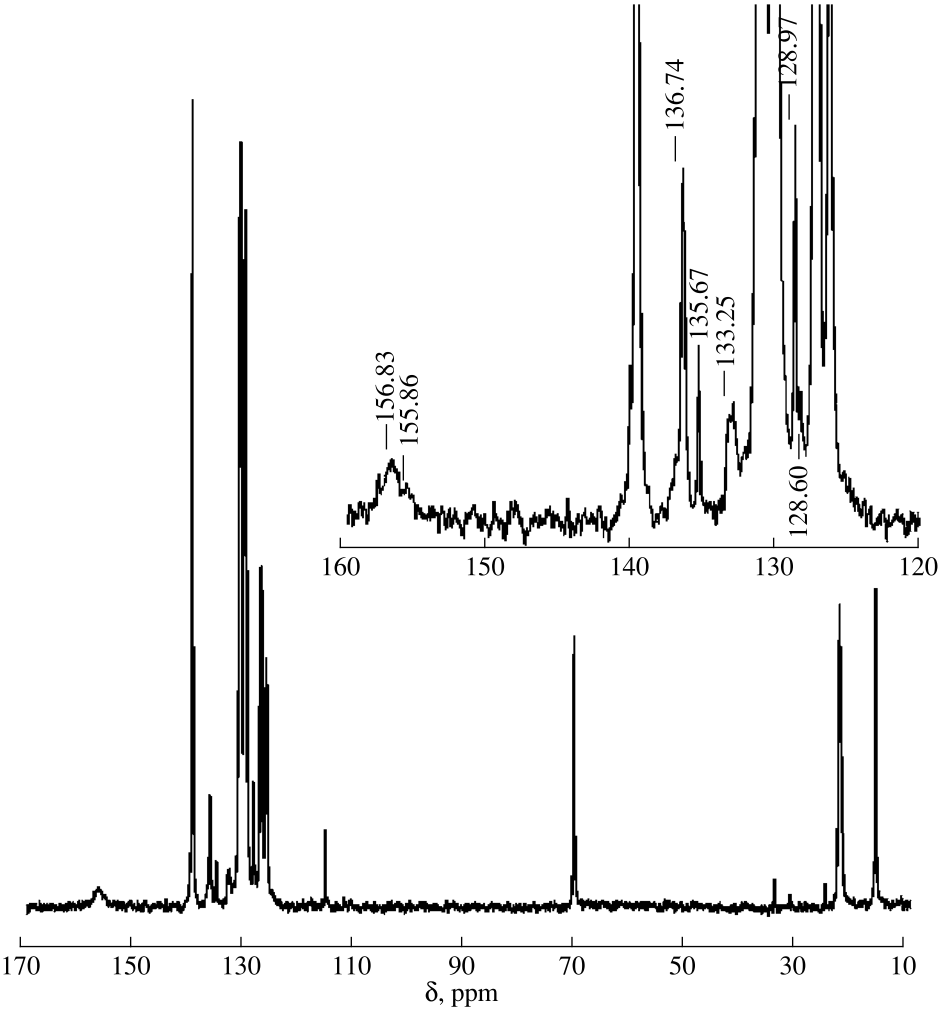
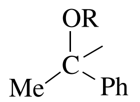


Fig. 2. ^{13}C NMR spectrum of the $[\mathrm{Ni(PPh_3)_3}]\mathrm{BF_4} + 2\mathrm{C_8H_8}$ system. Solvent: deuterotoluene.

increased. This effect of MMA on the polymerization of styrene suggests the participation of MMA at the steps of initiation or termination of polymer chains, although the nature of the observed phenomenon invites further investigation.

Polymerization reaction scheme. The occurrence of two reaction centers in the σ-carbocationic complex of Ni(I) (α-carbon bound to the transition metal and β-carbon, at which a positive charge is localized) allows activated styrene to react by both coordination and ionic mechanisms. To determine the true mechanism of styrene polymerization, we used a typical test for ionic polymerization with triethylamine. The introduction of the tertiary amine into the reaction mixture decreased the rate of polymerization (by 30% at an $\mathrm{NEt_3}$/Ni molar ratio of 5 : 1); however, it did not completely inhibit the polymerization even with a 100-fold excess of the base. Consequently, the polymerization of styrene on the cationic complex of Ni(I) mainly occurred by a coordination mechanism. The effect of the tertiary amine on the rate of polymerization can be explained by the participation of this amine in coordination to Ni(I) ions as a competitive reaction. A stronger catalyst poison, for example, triethyl phosphite at a $\mathrm{P(OEt)_3}$/Ni molar ratio of 2 : 1, completely inhibited the polymerization reaction as a result of the replacement of styrene in the coordination sphere of Ni(I) by triethyl phosphite and the formation of the coordinatively saturated paramagnetic complex $[\mathrm{(PPh_3)_2Ni(P(OEt)_3)_2}]\mathrm{BF_4}$.

The carbocationic center in activated styrene manifests itself in the reactions of nucleophilic addition of alcohols. These reactions occur on the cationic complex of Ni(I) under mild conditions. As found previously [22], the reaction products (telomers) contain the following fragments:



The results of this study and previously published data [22, 23] allowed us to propose Scheme 2 for the

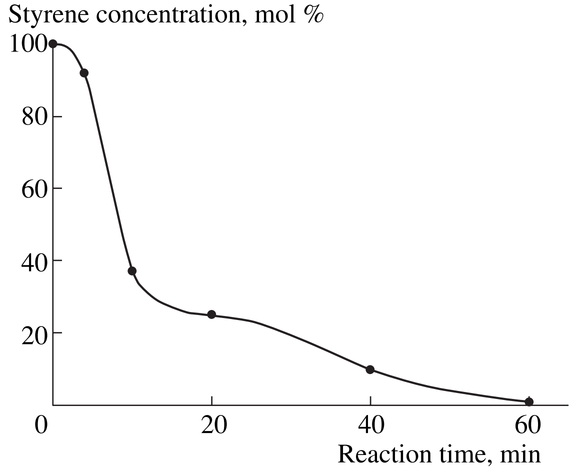


Fig. 3. Styrene consumption (as a percentage on the basis of the initially added amount) in polymerization. Reaction temperature: 10°C.

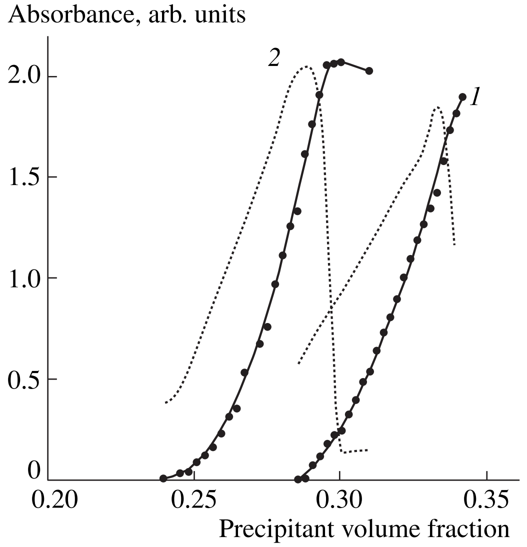
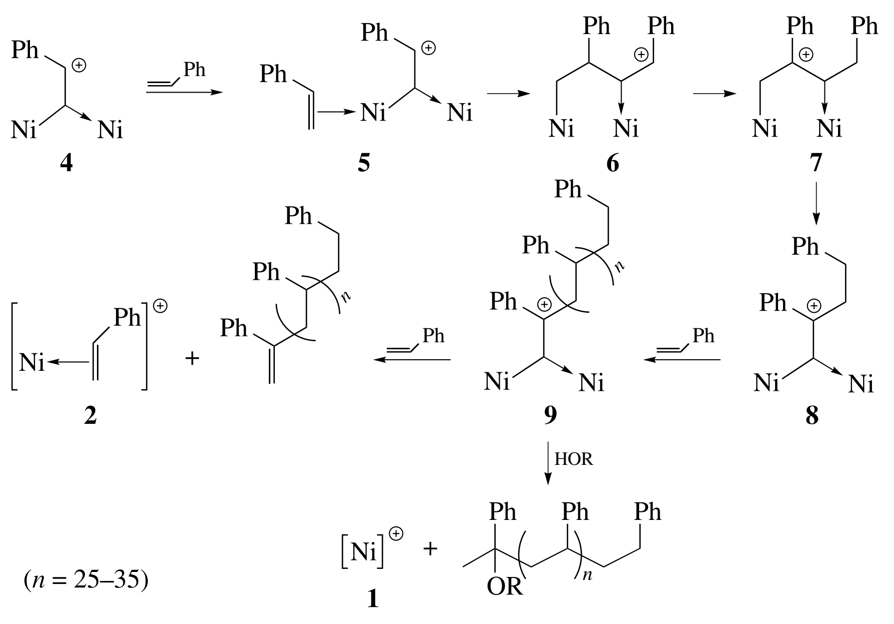


Fig. 4. Integral (solid lines) and differential (dashed lines) curves of turbidimetric titration of the product of styrene polymerization (*1*) at an initial styrene/Ni ratio of 200 : 1 and (*2*) after the addition of three styrene portions of 200, 200, and 100 parts. Reaction temperature: 20°C.

reactions of styrene on the $[Ni(PPh_3)_3]BF_4$ cationic complex.

For simplicity, Ni(I) complexes in Scheme 2 are represented as fragments: the second metal–carbon bonds in Ni(I) dimers, BF_4^- counterions, and PPh_3 phosphine ligands are not shown. Moreover, the steps of formation of carbocationic complex dimer **4**, which are described in detail in Scheme 1, are not shown.

In accordance with Scheme 2, in an excess of styrene in the reaction mixture, styrene underwent coordination to carbocationic complex dimer **4** (evidently, by the replacement of a phosphine ligand), and π complex **5** was formed. The insertion of styrene into a metal–carbon bond resulted in an elongation of the carbon chain that links the nickel atoms together (**6**). At the next step, the carbocation in complex **7** arranged itself into a more stable form as a result of hydride transfer between adjacent carbon atoms and the localization of a positive charge on the β-carbon atom. After the migration of the metal–carbon coordination bond from γ- to α-carbon atom (**8**), the cycle of carbon chain growth by one unit



Scheme 2.

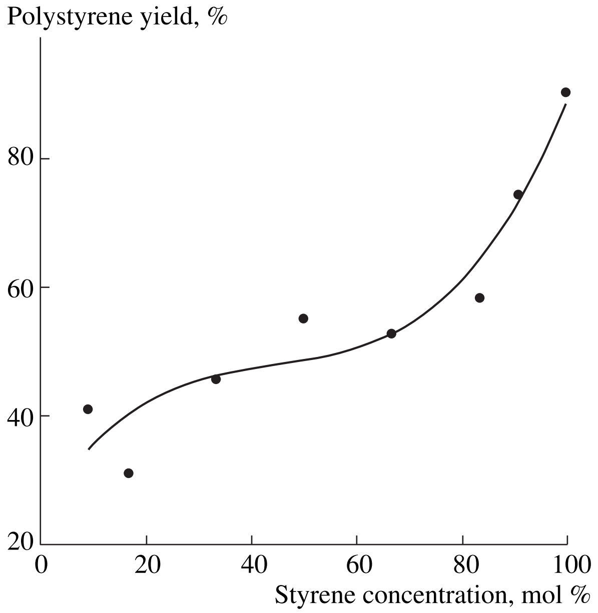


Fig. 5. Dependence of the limiting yield of polystyrene on the styrene content of the starting mixture with MMA. Total monomers/Ni = 200 : 1. Reaction temperature: 20°C.

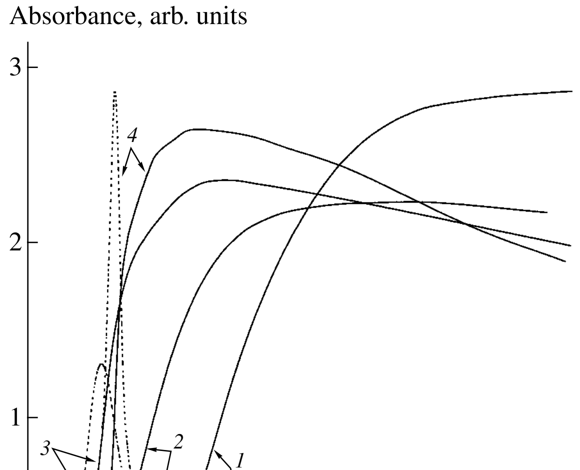


Fig. 6. Integral (solid lines) and differential (dashed lines) curves of turbidimetric titration of polystyrene: (*1*) after the polymerization of pure styrene, (*2*) after the addition of an equimolar amount of MMA following the completion of styrene polymerization (the sample was taken 1 h after the addition of MMA), (*3*) after the polymerization of a styrene–MMA mixture (33.3 mol % MMA), and (*4*) after the polymerization of a styrene–MMA mixture (50 mol % MMA). Total monomers/Ni = 200 : 1. Reaction temperature: 20°C.

was complete. Repeated cycles resulted in the formation of σ-cationic complex **9** with an oligomer (polymer) chain. The oligomer (polymer) in complex **9**, which occurred in an equilibrium π form, was replaced by the parent monomer (**2**), and the process turned back to the beginning of a new cycle. Complex **9** in an equilibrium σ form can also enter into nucleophilic addition reactions at the carbocationic center with the formation of telomers and the regeneration of starting cationic complex **1**.

Thus, we have characterized in detail the structure of the σ-carbocationic complex of Ni(I) formed in the reaction of styrene with the $[Ni(PPh_3)_3]BF_4$ cationic phosphine complex of Ni(I). The reaction of styrene polymerization occurred with the participation of the coordination center of the σ-carbocationic complex of Ni(I) (coordination catalysis), whereas the telomerization reaction occurred with the participation of the cationic center of this complex (ionic catalysis). The resulting polymer contained active terminal double bonds; it is a promising macromonomer for the synthesis of grafted copolymers. The discovered capacity of alcohols to undergo nucleophilic addition to a growing polymer chain offers strong possibilities for preparing functional polymers and block copolymers.

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