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# Mechanism of the controlled radical polymerization of styrene and methyl methacrylate in the presence of dicyclopentadienyltitanium dichloride

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The mechanism of the controlled radical polymerization of styrene and methyl methacrylate in the presence of dicyclopentadienyltitanium dichloride ($Cp_2TiCl_2$) was studied using quantum chemical calculations and electron spin resonance spectroscopy. It was established that the reduction of $Cp_2TiCl_2$ to $Cp_2TiCl$ during the macromolecule synthesis occurs through the living polymerization mechanism, which adjusts the growth of a polymeric chain. The geometrical structures of the molecular complexes between a growing macroradical and $Cp_2TiCl_2$ and transition states of radical inhibition steps were optimized and the thermodynamic and kinetic parameters of the elementary reactions were estimated for several feasible directions of the process. On this basis, the observed kinetic features of vinylic monomer polymerization with participation of organic compounds of titanium are discussed. Copyright © 2004 John Wiley & Sons, Ltd.

## INTRODUCTION

Controlled synthesis of macromolecules is the concern of a number of priority directions in polymer synthetic chemistry.[1] One of the most effective methods of management of polymer chain growth in conditions of radical initiation consists in the use of organic compounds of transition metals,[2] in particular the derivatives of copper,[3,4] iron,[5,6] nickel,[7,8] molybdenum[9] and others. The specified compounds enable one to adjust purposefully the kinetic parameters of polymerization and molecular weight characteristics of homo- and co-polymers. In contrast to stable nitroxyl radicals, which are also used quite often for management of growth of a chain and effectively work only at high temperatures (100–140 °C),[10,11]

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it is extremely important that the metal complexes are as active as possible at temperatures approaching the conditions of industrial synthesis of macromolecules (i.e. 25–60 °C). However, the practical application of regulators of this type is essentially limited by the intensive color imparted to the polymers as a result of the transition-metal ions formed in the intermediate stages of the synthesis.

One of few exceptions is regulatory additives based on titanium compounds.[12,13] It is known that titanium ions in the highest oxidation state (IV) are very stable and colorless.[14] Hence, the polymeric materials synthesized with their participation have no color and do not require additional cleaning.

Recently, we revealed the regulatory action of $Cp_2TiCl_2$ on the kinetics of methyl methacrylate and styrene radical polymerization,[15] and also on the molecular weight characteristics of macromolecules. It was established that, in the presence of a catalytic amount of $Cp_2TiCl_2$, the gelation decreases considerably and a linear growth in molecular weight of the polymers formed with conversion is observed. The purpose of this study is to elucidate the mechanism of

the regulatory action of titanium cyclopentadienyl derivatives during the radical polymerization of methyl methacrylate and styrene. Electron paramagnetic resonance (ESR) spectroscopy is a powerful and widely used method to study the reaction kinetics of radical polymerization. However, its ability in direct study of intermediate stages and elementary reactions of controlled polymer synthesis is limited due to the problems of spectral assignment of unknown paramagnetic centers of a complicated structure in a complex environment. In this connection, quantum chemical modelling, using density functional theory (DFT) calculations, combined with experimental measurements of reaction kinetics can provide a more detailed and deeper understanding of the reaction intermediates formed directly during polymer synthesis.

## EXPERIMENTAL

### Calculation details

All the calculations were carried out using the Gaussian 98 program package[16] (Revision A.3) using DFT applying Becke's 1988 non-local exchange functional[17] in conjunction with Perdew's correlation functional,[18] commonly known as BP86. The 6-31G(d) basis set was used for the geometry optimization of all the structures. In some cases, when the preliminary search of the stationary point was necessary, the preliminary optimization was carried out using the compound basis consisting of the 6-31G basis set for the carbon atoms, the 3-21G basis set for the hydrogen atoms, and the 6-31G(d) basis set for the chlorine atoms; the Hay–Wadt VDZ effective core potentials (ECPs) and the corresponding VDZ basis sets[19] were used for the titanium atom in this model. Full geometry optimizations for all the models and molecular structures were performed. The synchronous transit quasi-Newton optimization (QST2 and QST3 procedures) implemented in Gaussian 98, together with the regular Berny algorithm, were used for the location of the transition states. All the transition structures were characterized by frequency calculations. The rigid rotor–harmonic oscillator (RRHO) approximation was used for the calculation of thermodynamic parameters without scaling the calculated vibration frequencies. The radical systems were studied using the unrestricted open-shell formalism.

### ESR investigations

Commercial $Cp_2TiCl_2$ (Aldrich) was used in this work. The monomers (styrene and methyl methacrylate), initiator[20] azoisobutyronitrile (AIBN) and tetrahydrofuran[21] as the solvent were additionally purified by standard methods.[22] Calculated amounts of organometallics and the initiator were dissolved in a monomer or in a mixture (monomer + solvent, in 1:1 ratio), placed in glass tubes and decontaminated up to a residual pressure of 1.6 Pa by triple 'freezing–defrosting' in liquid nitrogen. Registration of ESR spectra was carried out

on an AE-4700 radiospectrometer according to a technique described by Dodonov *et al.*[23]

## RESULTS AND DISCUSSION

As was pointed out in the Introduction, organometallic compounds, including the cyclopentadienyl complexes of titanium, are capable of influencing vinylic monomer radical polymerization. Thus, the application of organometallic compounds enables one to control the growth of a polymeric chain through the stable free-radical polymerization (SFRP) or atom transfer radical polymerization (ATRP) mechanisms. In addition to the central atom, its ligands also determine the actual mechanism occurring during the polymers synthesis.
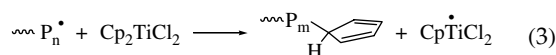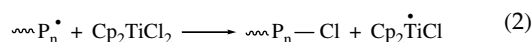
In order to estimate the probability of the different reaction channels between $Cp_2TiCl_2$ and the growing macroradical, quantum chemical calculations were performed. Interaction of a growing macroradical ($\sim P_n^{\bullet}$) with organometallic compounds can proceed in the following basic ways:

1. Interaction of a growing macroradical ($\sim P_n^{\bullet}$) and $Cp_2TiCl_2$ with formation of new Ti–C bond without destruction of the ligand sphere of the initial complex:

$$\sim\!\!\sim P_n^{\bullet} + Cp_2TiCl_2 \longrightarrow \sim\!\!\sim P_n\!\!-\!\overset{\bullet}{Ti}Cp_2Cl_2 \qquad (1)$$
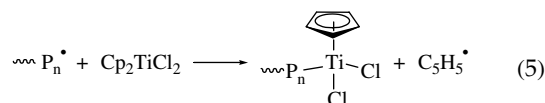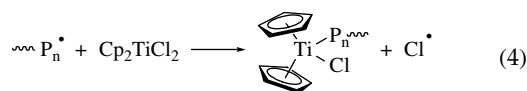
and further polymerization proceeds by the SFRP mechanism with participation of the metal-centered radical.

2. Chlorine or cyclopentadienyl ring abstraction from the $Cp_2TiCl_2$ molecule by growing radical ($\sim P_n^{\bullet}$) with formation of titanium(III) compounds:

$$\sim\!\!\sim P_n^{\bullet} + Cp_2TiCl_2 \longrightarrow \sim\!\!\sim P_n\!\!-\!Cl + Cp_2\overset{\bullet}{Ti}Cl \qquad (2)$$

$$\sim\!\!\sim P_n^{\bullet} + Cp_2TiCl_2 \longrightarrow \sim\!\!\sim P_m\!\!\diagdown\!\!\underset{H}{\diagup} + CpTiCl_2^{\bullet} \qquad (3)$$

and with the subsequent course of polymerization through the ATRP mechanism with participation of titanium(III) compounds and a carbon–halogen bond in an adduct ($\sim P_n$–Cl) formed by the reaction in Eqn (2).

3. Chlorine or cyclopentadienyl ring substitution in the $Cp_2TiCl_2$ molecule with growing radical ($\sim P_n^{\bullet}$):

$$\sim\!\!\sim P_n^{\bullet} + Cp_2TiCl_2 \longrightarrow \underset{Cl}{\overset{P_n\sim\!\!\sim}{Ti}} + Cl^{\bullet} \qquad (4)$$

$$\sim\!\!\sim P_n^{\bullet} + Cp_2TiCl_2 \longrightarrow \sim\!\!\sim P_n\!\!-\!\underset{Cl}{\overset{|}{Ti}}\!\!-\!Cl + C_5H_5^{\bullet} \qquad (5)$$

Further chain growth is as a result of repeated incorporation of the monomer molecules into the labile bond

($\sim$P$_n$–Ti), and the additional initiation of a new chain by forming the carbon-centered radical (C$_5$H$_5^\bullet$) or a chlorine atom (a classical reaction of chain transfer in polymeric chemistry).

4. An addition of a polymeric radical ($\sim$P$_n^\bullet$) to a cyclopentadienyl ring without destruction of the titanium organic compound:
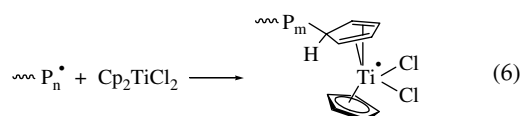
$$\sim\!\!\sim P_n^\bullet + Cp_2TiCl_2 \longrightarrow \text{(6)}$$

Further, as with case (1), realization of the SFRP mechanism with participation of a titanium-centered radical as a regulator of chain growth.

5. Finally, the opportunity for the reduction of initial Cp$_2$TiCl$_2$ to the titanium(III) compound is not excluded, e.g. by the reactions in Eqns (2) or (3), which later control the chain growth by the formation of a labile bond with a macroradical:

$$\sim\!\!\sim P_n^\bullet + Cp_2\dot{T}iCl \longrightarrow \text{(7)}$$

$$\sim\!\!\sim P_n^\bullet + Cp_2\dot{T}iCl_2 \longrightarrow \text{(8)}$$
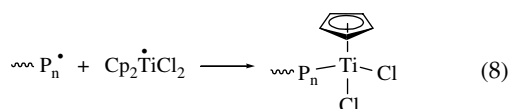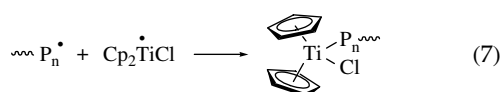
In order to estimate the probability of reactions corresponding to the cases 1–5, the quantum chemical calculations were carried out using the DFT as described above.

The proposed pathways are listed in Table 1. The two reactions of Ti–Cl and Ti–Cp bond breaking were studied in order to examine the

$$Cp_2TiCl_2 \longrightarrow Cp_2TiCl^\bullet + Cl^\bullet \qquad (9)$$

$$Cp_2TiCl_2 \longrightarrow CpTiCl_2^\bullet + Cp^\bullet \qquad (10)$$

errors of the calculation method by comparison with the available experimental data.[24,25] One can conclude that the Ti–Cl bond breaking energy is described very well, whereas the Ti–Cp bond energy is in poor agreement with the experiment. However, it should be noted that, in the case of Eqn (10), the experimental value is an averaged bond energy, which can be significantly different from the real energy of the first step of Cp abstraction.

The calculated energies of possible radical reactions are given in Table 1 for three different kinds of radicals modelling the growing macroradical ($\sim$P$_n^\bullet$): CH$_3^\bullet$ (**I**: the simplest structure modelling the primary growing radical), CH$_3$CH$^\bullet$C$_6$H$_5$ (**II**: a secondary radical modelling the polystyrene growing radical), and CH$_3$C$^\bullet$(CH$_3$)COOCH$_3$ (**III**: a model for methyl methacrylate tertiary radical).

During the geometry optimization, we failed to find any strong complexes between a carbon center of the methyl group and Cp$_2$TiCl$_2$ (Eqn (1)), although the various initial structures and orientations were examined.

As can be concluded from the data, reactions (2) and (3) in Table 1, corresponding to the formation of the titanium(III) compounds, have no significant thermodynamic restrictions (reaction energy is 7–9 kcal mol$^{-1}$). However, owing to their endothermicity, the equilibrium in these reactions should be shifted towards the reagents. In this regard, it is hardly likely that this reaction is responsible for the control of the polymeric chain growth by the 'classical' ATRP mechanism at room temperature. However, the equilibrium of the

**Table 1.** The BP86/6-31G(d) calculated reaction energies for the radical reactions of Cp$_2$TiCl$_2$ (the experimental values are given in parentheses)

| | | Reaction energy $\Delta_r E$(kcal mol$^{-1}$) | | |
| | Reaction | •CH$_3$ | •CH(Me)Ph | •C(Me)$_2$COOMe |
|---|---|---|---|---|
| Eqn (9) | 80.6 (82.0 ± 1.5$^a$) | | | |
| Eqn (10) | 59.7 (77.7$^b$) | | | |
| 1 | Cp$_2$TiCl$_2$ + R• → Cp$_2$Cl$_2$Ti···R | — | | |
| 2 | Cp$_2$TiCl$_2$ + R• → Cp$_2$TiCl•+ R–Cl | −11.0 | 6.9 | 8.7 |
| 3 | Cp$_2$TiCl$_2$ + R• → CpTiCl$_2^\bullet$+ Cp–R | −14.7 | 7.3 | 8.3 |
| 4 | Cp$_2$TiCl$_2$ + R• → CpTiCl$_2$R + Cp• | 5.8 | 26.5 | 29.1 |
| 5 | Cp$_2$TiCl$_2$ + R• → Cp$_2$TiClR + Cl• | 38.9 | 64.0 | 64.0 |
| 6 | Cp$_2$TiCl$_2$ + R• → CpTiCl$_2$(C$_5$H$_5$R)• | −23.7 | −1.0 | −0.7 |
| 7 | Cp$_2$TiCl• + R• → Cp$_2$TiClR | −41.7 | −16.7 | −16.6 |
| 8 | CpTiCl$_2^\bullet$ + R• → CpTiCl$_2$R | −53.9 | −33.2 | −30.6 |

$^a$ Experimental value of $\Delta H°(0)$ for the reaction TiCl$_4$ → TiCl$_3$• + Cl•.[24]
$^b$ Experimental value of the average Ti–Cp bond energy in Cp$_2$TiCl$_2$.[25]

endothermic reaction can be shifted towards the product by raising the temperature. Since the endothermicity of reactions (2) and (3) in Table 1 is not high, the ATRP mechanism cannot be completely excluded at the increased temperature.

Reactions of one-step replacement of ligands in $Cp_2TiCl_2$ by alkyl radicals (reactions (4) and (5) in Table 1) are forbidden thermodynamically because of their high reaction energy (25–30 kcal mol$^{-1}$ and 64 kcal mol$^{-1}$ respectively).

Reaction (6) in Table 1 is the most favorable of those considered from the point of view of reaction energy. It is obvious, however, that the specified reaction is only an intermediate step of reaction (3) in Table 1 and results further from the formation of trivalent titanium compound $CpTi^{\bullet}Cl_2$.

We conclude that $Cp_2TiCl_2$ itself is not capable of adjusting the growth of a polymeric chain by the 'live' chains mechanism. However, titanium(III) compounds formed in reactions (2) and (3) in Table 1 are coordinately unsaturated and can temporarily bind the growing macroradicals ($\sim P_n^{\bullet}$) as a result of reactions (7) and (8) in Table 1. Reaction (7) in Table 1 (with the energy parameters $\Delta_r E = -17$ kcal mol$^{-1}$) can be quite responsible for the control of polymeric chain propagation over conditions of radical initiation:
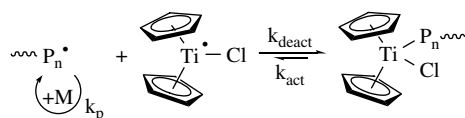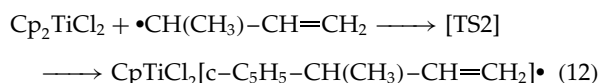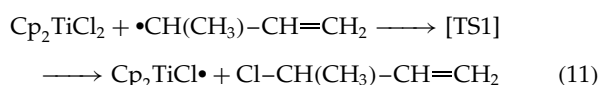


In the case of monocyclopentadienyl titanium compounds (reaction (8) in Table 1), the Ti–C bond is twice as strong (31–33 kcal mol$^{-1}$) as that in the case of a dicyclopentadienyl derivative (reaction (7) in Table 1). The strong exothermicity of reaction (8) in Table 1 makes it practically irreversible under conditions of polymer synthesis ($T = 333–343$ K). Hence, this reaction will terminate the growing radical chains ($\sim P_n^{\bullet}$) because of their irreversible binding with a metal-centered radical.

It is necessary to note that reaction (8) in Table 1 becomes even more exothermic on interaction of $CpTi^{\bullet}Cl_2$ with a methyl radical (Table 1). In this case, the calculated value of reaction energy is almost $-54$ kcal mol$^{-1}$. Observable distinctions in energies of reactions (7) and (8) in Table 1 for the primary methyl radical (**I**), the secondary ethyl phenyl radical (**II**) and the tertiary (**III**) $^{\bullet}C(CH_3)_2COOCH_3$ radical (Table 1) can be derived from both the steric and the electronic factors. The environment of the titanium interferes with formation of a high-grade bond between the metal atom and the carbon atom included in bulky sterically hindered radicals **II** and **III**.

In our opinion, reactions (2) and (3) in Table 1 are approximately equally feasible from the energetic point of view. Thus, the kinetic barriers of these reactions should be studied in order to form a conclusion as to the probability of these channels. It is obvious that reaction (3) in Table 1 originally proceeds as reaction (6) in Table 1 with the further separation of the $\eta^4$-cyclopentadienyl ligand. Thus, reaction (6) in Table 1 is probably a limiting stage. In this regard, we have attempted to determine the energy of the activation barriers of reactions (2) and (6) in Table 1. Because the location of transition structures is much more difficult in comparison with geometry optimization of stable structures, it was impossible to perform the calculations with the radicals used in the experiment. Therefore, we studied a model reaction between $Cp_2TiCl_2$ and the radical of structure $^{\bullet}CH(CH_3)–CH=CH_2$:

$$Cp_2TiCl_2 + {}^{\bullet}CH(CH_3)–CH=CH_2 \longrightarrow [TS1]$$
$$\longrightarrow Cp_2TiCl{\bullet} + Cl–CH(CH_3)–CH=CH_2 \qquad (11)$$
$$Cp_2TiCl_2 + {}^{\bullet}CH(CH_3)–CH=CH_2 \longrightarrow [TS2]$$
$$\longrightarrow CpTiCl_2[c–C_5H_5–CH(CH_3)–CH=CH_2]{\bullet} \quad (12)$$

Since this radical has a double bond attached to the radical center (as takes place with radicals **II** and **III**) we propose that the reactivity of this model radical should be close to the reactivity of the source species. The close agreement of the reaction energies calculated for these reactions (listed in Table 2) with the analogous values of reactions (2) and (6) in Table 1 supports this assumption.

The structures located for transition states TS1 and TS2 are shown in Fig. 1. Table 2 presents the total energies, imaginary frequency values, and the kinetic parameters of the transition states located. It follows from Table 2 that the single imaginary frequency of transition state TS1, being less than 100 cm$^{-1}$, is too low for the regular transition vibration. However, a visual analysis of this vibration mode shows that the vibration corresponds to the correct pathway of the reaction in Eqn (11) in both the forward and reverse directions. It was impossible to eliminate this low-frequency vibration from the transition structure during the additional optimization runs, and the optimizations started from other initial structures also led to the transition structure presented in Fig. 1a. Thus, we propose that TS1 is a correct transition structure of the reaction in Eqn (11) characterized by an anomalously low frequency of transition vibration that is probably caused by the large size of the chlorine atom situated between two carbon centers. The TS2 structure is characterized by a single imaginary frequency having a typical value for the transition structures 413i cm$^{-1}$. As concluded from Table 2, the activation energy and the thermodynamic parameters of transition states have lower values for TS1. Thus, formally, the reaction in Eqn (11) is kinetically more favorable than that in Eqn (12).

However, it should be noted that the differences between the corresponding parameters of both reactions are only 1–2 kcal mol$^{-1}$, which is obviously lower than the typical
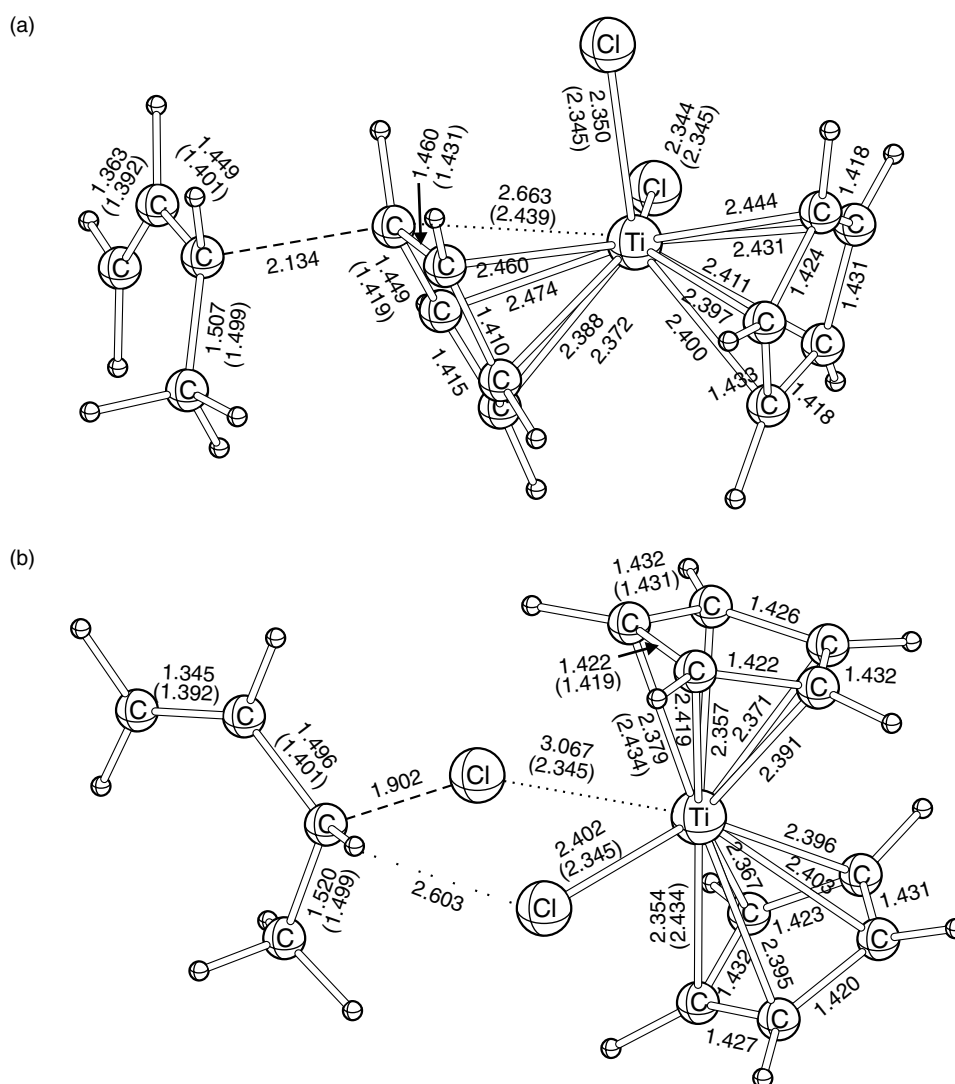
(a)



(b)



**Figure 1.** Located structure of transition state for the reactions in (a) Eqn (11) and (b) Eqn (12). The values in parentheses present the bond lengths in the free reactants.

**Table 2.** The BP86/6-31G(d) calculated reaction energies, total energies of transition states, the imaginary frequencies, activation energies, enthalpies and Gibbs free energies of activation for the reactions in Eqns (11) and (12)

| Reaction, transition state | $\Delta_r E$ (kcal mol$^{-1}$) | $E_{TS}$ (a.u.) | $\nu_{im}$(cm$^{-1}$) | $E_a$(kcal mol$^{-1}$) | $\Delta H^{\ddagger}_{298}$ (kcal mol$^{-1}$) | $\Delta G^{\ddagger}_{298}$ (kcal mol$^{-1}$) |
|---|---|---|---|---|---|---|
| Eqn (11), TS1 | 9.5 | −2313.774 163 4 | 52i | 10.3 | 11.3 | 22.6 |
| Eqn (12), TS2 | 0.9 | −2313.772 411 6 | 413i | 11.4 | 12.3 | 24.0 |

inaccuracies of DFT using the modest basis set. Unfortunately, the large size of the systems under consideration does not allow use of the high-level theories suitable for the accurate prediction of transition-state energies. Moreover, the reaction occurring in a solution can also have much larger effect than the calculated energy difference. Thus, we conclude that reactions (2) and (6) in Table 1 are equally probable from the

kinetic point of view and can be considered as the two most likely channels of the mechanism of living polymerization moderated by $Cp_2TiCl_2$.

In order to verify the formation of the titanium(III) compound by the interaction of $Cp_2TiCl_2$ with a propagating radical ($\sim P_n^{\bullet}$), we investigated the polymerization of styrene in the presence of $Cp_2TiCl_2$ and AIBN in bulk and in a
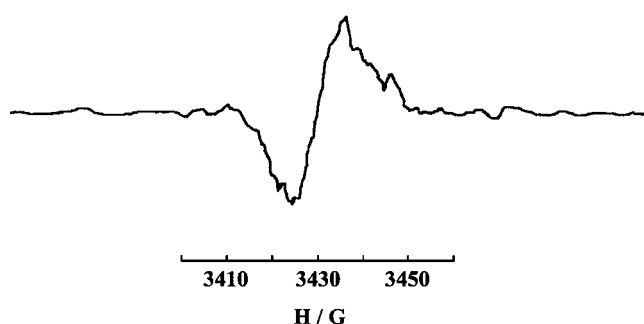
**Figure 2.** The ESR spectrum, fixed in the system of $Cp_2TiCl_2$ (2.2 mol%) + AIBN (4.6 mol%) in styrene and THF as a solvent after heating at 70 °C for 5 h.

THF solution at 70 °C by the ESR method. For this kind of system, the ESR signal is a singlet with a *g*-factor of 1.974 (Fig. 2), which, in accordance with the available literature data,[26–28] is assigned to the paramagnetic species $Cp_2Ti^\bullet Cl$. The insignificant difference in the values of the *g*-factor of the signal fixed by us ($g = 1.974$) and the *g*-factor of $Cp_2Ti^\bullet Cl$ observed in Refs 26–28 ($g = 1.978$) could be connected with environmental effects and to differences in experimental conditions.

## CONCLUSIONS

The results of quantum chemical modelling and an ESR study (in addition to experimental data obtained earlier[15]) concerning the kinetics of methyl methacrylate polymerizations in the presence of titanium organic derivatives, and the analysis of the molecular weight distribution of the macromolecules synthesized with participation of $Cp_2TiCl_2$ are presented. These studies reveal that the regulatory action of titanium cyclopentadienyl complexes is based on a reduction of $Cp_2TiCl_2$ to $Cp_2Ti^\bullet Cl$. The radical $Cp_2Ti^\bullet Cl$ formed directly in the polymerization system is capable of carrying out the control of polymeric chain growth both by the SFRP mechanism and the ATRP mechanism, depending on the experimental conditions. The possible collateral reactions analyzed above allow one to explain the slight increase in polydispersity values of the samples synthesized in the presence of $Cp_2TiCl_2$[15] compared with classical SFRP processes.[1]

### Acknowledgements

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