Available online at www.sciencedirect.com
ScienceDirect
Mendeleev Commun., 2024, **34**, 721–724

Mendeleev
Communications

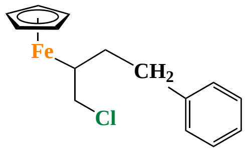
Formation of active centers of polymer catalysts for radical-coordination polymerization

**Olga Yu. Vdovina,* Ruslan R. Galimullin, Marat F. Abdullin,
Alexander V. Smirnov and Sergey V. Kolesov**

*Ufa Institute of Chemistry, Ufa Federal Research Centre of the Russian Academy of Sciences,
450054 Ufa, Russian Federation. E-mail: jkmuf-dljdbyf@yandex.ru*

DOI: 10.1016/j.mencom.2024.09.031

Chromatography–mass spectrometry of samples representing the interaction products of ferrocene, radical initiator and monomer taken in the molar ratio of 1 : 2 : 10 in toluene solution was used for experimental detection of products indicating the structure and mechanism of formation of metal complex active centers of radical-coordination polymerization. Structures similar to those proposed by the quantum-chemical modeling were demonstrated to be formed with the participation of secondary radicals.



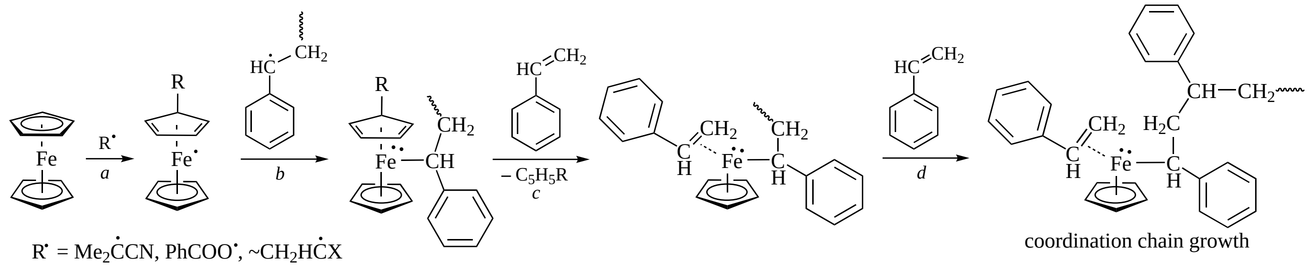
One of the probable active center structures
of coordination chain growth of radical-coordination polymerization

Keywords: radical polymerization, ferrocene, electrospray ionization, reaction mechanisms, quantum-chemical modeling.

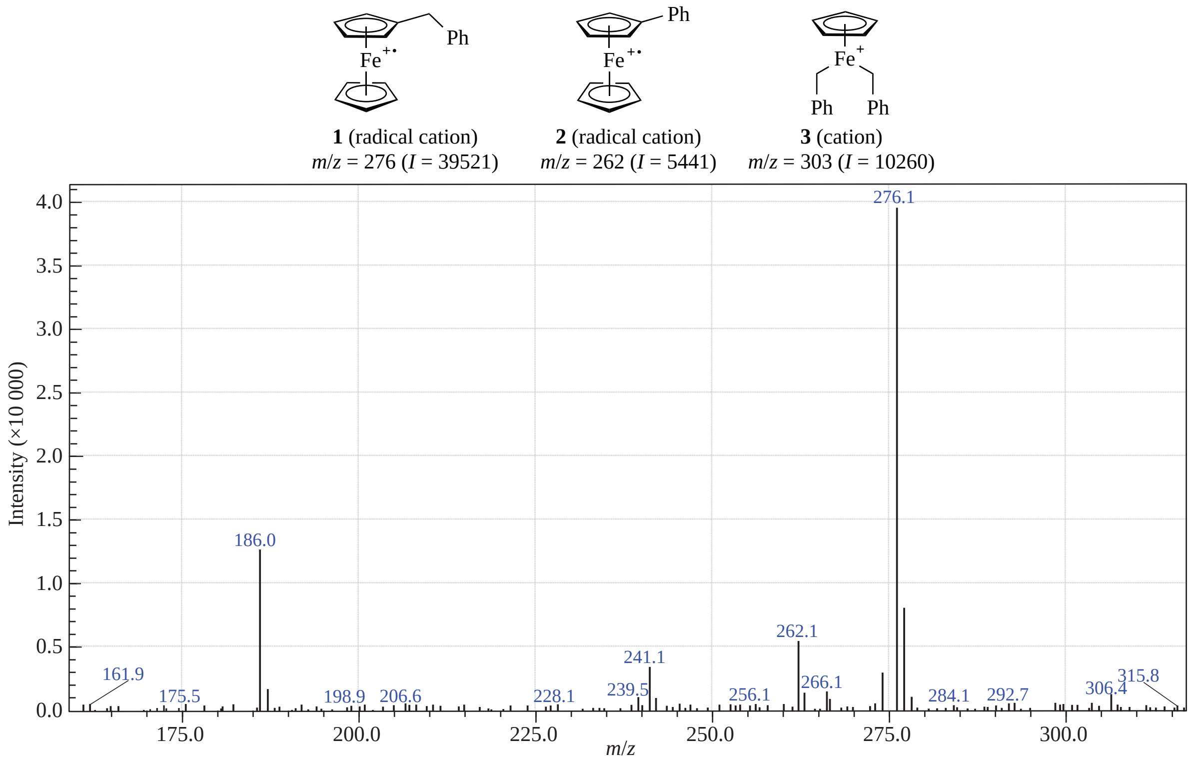
The use of metal complex and organometallic compounds in radical polymerization is still a relevant direction in the development of methods for controlling the process and obtaining new polymers. A number of papers are focused on the use of metal compounds to control the nucleation of growing chains. These works deal with polymerization initiating and catalytic systems including known compounds, *e.g.*, metallocenes,[1–7] as well as new metal complexes.[8,9] The main modern trend in the development of controlled radical polymerization relates to the radical polymerization with controlled termination of growing chains, in particular, with the improvement of Atom Transfer Radical Polymerization (ATRP), Organometallic Mediated Radical Polymerization (OMRP), and Stable Free Radical Polymerization (SFRP) mechanisms.[10–23] New metal complexes can be used in new areas of controlled polymerization, *e.g.*, halogen-substituted salicylhydroximate copper(II) metallacrowns[9] may be of interest for the development of ATRP photocatalysis.

In all these cases, the mechanism of chain growth remains free-radical and the process is controlled by monitoring the molecular-weight characteristics of the polymers, *i.e.*, ensuring linear growth of P_n and achieving a narrow molecular weight distribution (MWD). The molecular structure of homopolymer chains and stereoisomerism thereof is not changing therewith. Having said that, publications[1,2] state the possibility of formation of metal complex active chain growth centers at the ends of macromolecules under conditions of radical polymerization of vinyl monomers in the presence of some iron, titanium, and zirconium complexes, with such centers being able to coordinate with the monomer and incorporate it into the chain in a radical-free (coordination) discontinuous manner. The possibility of coordination growth and the structure of coordination active centers (ACs) of polymerization have been proved by quantum-chemical modeling[2] taking typical vinyl monomers such as methyl methacrylate (MMA) and styrene as examples. The mechanism of the process exemplified for styrene is outlined in Scheme 1.

The mechanism (see Scheme 1) is indirectly supported by a number of experimental facts. (1) The obtained polymers are capable of acting as catalysts for post-polymerization of their monomer in the absence of a radical initiator and even in the presence of a radical inhibitor,[18] as well as another monomer with the formation of block copolymers. (2) The polymers possessed higher stereoregularity (syndiotacticity), which is characteristic of coordination chain growth. (3) Changes in microstructure in the case of binary copolymerization, namely, an increase in the proportion of homotriad of monomer units, were discovered along with (4) changes in molecular weight characteristics of polymers, *i.e.*, broadening of MWD indicating polycentricity of the polymerization system. (5) Successful



Scheme 1



1 (radical cation)
m/*z* = 276 (*I* = 39521)

2 (radical cation)
m/*z* = 262 (*I* = 5441)

3 (cation)
m/*z* = 303 (*I* = 10260)

Figure 1 Mass spectrum of positive ESI ions of thermal transformation products in Cp_2Fe and Bz_2O_2 mixture in toluene.

kinetic modeling of the polymerization process based on the scheme of radical-coordination polymerization[19] was in a good agreement with experimental kinetic dependencies.

All experimental data indicate that the contribution of the coordination ACs to kinetics of the gross process of radically initiated (co)polymerization of MMA and styrene is insignificant, therefore, their concentration in the composition of all macromolecules is low, thereby making the experimental determination of the structure thereof quite difficult. The situation is similar to ionic-coordination polymerization where direct experimental determination of the structure of ACs is also almost impossible due to their low concentration in the resulting polymer. Accordingly, any direct experimental facts concerning the proposed scheme of formation of coordination ACs under the conditions of radical-initiated polymerization seem to be significant.

A chromatography–mass spectrometry analysis of specially prepared samples was made herein to experimentally detect radical-coordination polymerization products indicative of the mechanism of formation of metal complex ACs and the structure thereof. Previously,[20] it was shown that mass spectrometry could be used to detect species formed during zirconocene-catalyzed polymerization. The samples were prepared by thermal (100 °C) exposure of mixtures including ferrocene Cp_2Fe, radical initiator [azobisisobutyronitrile (AIBN) or benzoyl peroxide (Bz_2O_2)], monomer [MMA, styrene, and allyl chloride (AllCl)]. Mixtures Cp_2Fe/initiator/monomer taken in the molar ratio of 1 : 2 : 10 were used as solutions in toluene. Under such a ratio of monomer and Cp_2Fe concentrations, the fraction of radicals to be spent for interaction with Cp_2Fe can be assumed to be considerably greater than under conditions of conventional polymerization with the formation of a high-molecular-weight polymer. Accordingly, the low-molecular-weight products formed under such conditions may have structures corresponding to the intermediates of Scheme 1. The aim of this study was the chromatography–mass spectrometry analysis of the products of radical transformations in the above systems.

When Cp_2Fe reacts with AIBN or Bz_2O_2 in toluene, no addition products of the primary radicals, *i.e.* 2-cyanoprop-2-yl and benzyloxy radicals, to the Cp-ring of Cp_2Fe were detected. At the same time, in both cases, addition products of benzyl radical **1** were detected. Apparently, toluene served as a source of the benzyl group. In the case of Bz_2O_2, a phenyl radical **2** addition product was detected.

Thereby, secondary radicals formed in the absence of monomer in the reaction of initiating radicals with a solvent inclined to be involved in chain transfer reactions in polymerization or, as in the case of benzoyloxy radical, under decomposition thereof into phenyl radical and carbon dioxide in the absence of strong radical acceptors interact with Cp_2Fe. In any case, the obtained result is an experimental confirmation of step *a* (see Scheme 1), *i.e.*, the formation of a metal-centered radical due to the addition of a free radical to the Cp-ring of Cp_2Fe. The detection of two benzyl radical addition product with elimination of Cp-ligand, namely, species **3**, in the Cp_2Fe/AIBN/toluene system seems to be important, which corresponds to step *c* of Scheme 1.

When considering the specific chemical structure of oligomers, the following reactions forming end functional groups are taken into account: initiation by addition of 2-cyanoprop-2-yl radical (structures **4**, **5**), chain termination by capture of benzyl radical (structures **4**, **7**), chain termination by transfer to monomer (structures **5**, **6**), initiation of growth by $CH_2{=}C^{\bullet}X$ radical formed by transfer to monomer (for styrene and allyl chloride, structure **6**); initiation and termination by benzyl radicals (structure **7**). Furthermore, the structures of oligomers formed by coordination growth on ferrocenic ACs should be considered in accordance with the aim of the research (structures **8a**,**b**).

$N{\equiv}C–C(Me)_2–(CH_2–CHX)_n–CH_2–Ph$ **4**

$N{\equiv}C–C(Me)_2–(CH_2–CHX)_n–CH_2–CH_2X$ **5**

$CH_2{=}CX–(CH_2–CHX)_n–CH_2–CH_2X$ **6**

$Ph–CH_2–(CH_2–CHX)_n–CH_2–Ph$ **7**

$N{\equiv}C–C(Me)_2–(CH_2–CHX)_n–FeCp$ **8a**

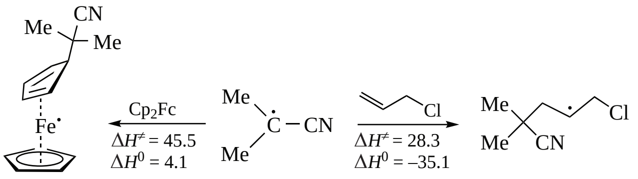
$Ph–CH_2–(CH_2–CHX)_n–FeCp$ **8b**

Analysis of the mass spectrometry data for coincidence with the values of molecular masses calculated for various possible structures **4–8** enabled us to indicate a number of the most probable products. The main products of styrene transformation (see Online Supplementary Materials, Table S2) are dimers and trimers, based on the intensity of the corresponding signals in the spectrum. The formation of extremely low-molecular-weight products is due to the experimental conditions such as elevated polymerization temperature and, mainly, high rate of initiation of monomer transformations at a monomer/initiator ratio of 1 : 2. In some cases, oligomers were found to form associates with acetonitrile.

The growing chains are terminated mainly on benzyl radicals, and no products of their interaction with Cp_2Fe are found. Also, no interaction products of benzyl radicals with Cp_2Fe were detected. This is likely due to the preferential consumption of these radicals in interaction with styryl radicals, which is supported by the high intensity of the corresponding signals.

The analysis results of transformation products in Cp_2Fe/AIBN/MMA system in toluene are largely similar to those for the styrene system. Moreover, the product of addition of a benzyl radical to Cp_2Fe was found (Table S3). As for AllCl, in contrast to other vinyl monomers, together with oligomers with structures **4–8** (Table 1), the products containing metallocene fragments **8** formed at step *c* (see Scheme 1) were also detected (Figure 2). Signal of species **3** was also observed.

In accordance with Scheme 1, the reactions of the initiating radical with monomer AllCl and Cp_2Fe proceed with the formation of a covalent bond as shown in Scheme 2. However, the primary radicals seem to be consumed only for the initiation of chain growth, as seen from the reaction product structures. In the quantum-chemical analysis of the initial step of radical-coordination polymerization of a number of monomers in the presence of Cp_2Fe, it was shown on the basis of the energy characteristics of the reactions (Table S4) that 2-cyanoprop-2-yl radicals in such systems would react with monomers rather than with Cp_2Fe.



Scheme 2

Secondary radicals formed *via* the interaction between primary radicals and the solvent and, for AllCl also with the monomer, are involved in the interaction with Cp_2Fe. Such a difference is likely somehow related to the characteristics of the radicals and/or parameters of their reactions with Cp_2Fe. Quantum-chemically calculated values (*cf*. refs. 21–23) of spin density on atoms bearing unpaired valence are given in Table S5.

No dependence between the values of spin density on different radicals and selectivity thereof in reactions with components of the analyzed reaction mixtures seems to be found. Indeed, the benzyl and MMA radicals have almost identical spin density values on carbon atoms, but they behave principally differently in the reaction with Cp_2Fe. No interaction products of styryl and acrylate radicals with Cp_2Fe may be explained by the fact that the addition reactions of these radicals to Cp_2Fe are endothermic (ΔH^0 is 3.3 and 11.3 kJ mol^{-1}, respectively),[24] whereas the addition of AllCl radical is exothermic (ΔH^0 = –27.2 kJ mol^{-1}). Furthermore, the activation barrier in the latter case is 1.3–1.5 times lower. The transformation reactions of styrene and MMA by polymerization type will likely be kinetically prevailing under the considered conditions, up to complete exhaustion of monomers.

The MMA post-polymerization catalyzed by toluene solution of interaction products in the system of Cp_2Fe/AIBN/AllCl was performed at 60 °C to verify the ability of the obtained products to act as active centers of radical-coordination polymerization. The MMA/catalyst volume ratio was 10 : 1, and residual initiator concentration was 10^{-9} mol dm^{-3}. The end of the reaction was found by termination of viscosity increase in the polymerizing system. After 10 h the post-PMMA conversion was 13%. The molecular weight characteristics and stereoregularity of the obtained polymer were determined. The increase of syndiotacticity by 17.5% compared to free-radical PMMA is the proof of the coordination mechanism of the formation thereof (Table S6).

In summary, the experiment directly shows that the interactions of the monomer, metallocene, and secondary radicals result in the formation of metal complex AC structures identical to those theoretically predicted on the basis of quantum-chemical modeling and capable of polymerizing a vinyl monomer *via* coordination mechanism. It is anticipated that in future a theoretical evaluation of the possibility of formation of the structures catalytically active in coordination polymerization for a wide range of monomers and metal complexes will be performed.

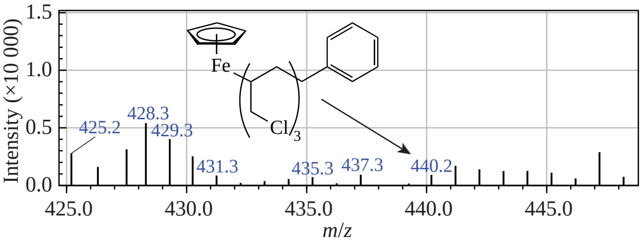


Figure 2 Fragment of the mass spectrum of positive ESI ions of the e^2 (n = 3) product of thermal transformation in Cp_2Fe, AIBN and AllCl mixture in toluene.

Table 1 Results of chromatography–mass spectrometry analysis of thermalized Cp_2Fe/AIBN/AllCl mixture products in toluene.

Product	*n*	*m/z*, calc.	*m/z*, exp.	*I*	Associate		
					m/z, calc.	*m/z*, exp.	*I*
4	3	387	387	4304	428	428	5421
5	2	–	–	–	338	338	3997
	3	–	–	–	414	414	4253
	4	449	449	1073	–	–	–
6	2	–	–	–	345	345	1533
	3	380	380	1108	421	421	1870
7	2	334	334	2740	375	375	2444
	3	410	410	2628	451	451	1920
8a[a]	2	–	–	–	382	382	2890
8b[b]	1	–	–	–	329	329	4250
	2	–	–	–	405	405	2337
	3	440	440	901	–	–	–

[a] Corresponds to the product formed upon initiation by 2-cyanoprop-2-yl radical. [b] Corresponds to the product formed upon initiation by benzyl radical.

The work was supported by the Russian Science Foundation (grant no. 23-13-20024).

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2024.09.031.

References

1 A. K. Friesen, S. L. Khursan, S. V. Kolesov and Yu. B. Monakov, *Russ. J. Phys. Chem. B*, 2011, **5**, 131; https://doi.org/10.1134/S1990793111010040.

2 A. K. Flriesen, N. V. Ulitin, S. L. Khursan, D. A. Shiyan, K. A. Tereshchenko and S. V. Kolesov, *Mendeleev Commun.*, 2017, **27**, 374; https://doi.org/10.1016/j.mencom.2017.07.018.

3 Yu. B. Monakov, R. M. Islamova, G. R. Sadykova, Ya. Z. Voloshin, I. G. Makarenko, A. Yu. Lebedev and Yu. N. Bubnov, *Dokl. Chem.*, 2010, **431**, 89; https://doi.org/10.1134/s0012500810030079.

4 Yu. B. Monakov, R. M. Islamova, G. R. Sadykova, I. S. Makarov, Ya. Z. Voloshin and Yu. N. Bubnov, *Russ. Chem. Bull.*, 2009, **58**, 1162; https://doi.org/10.1007/s11172-009-0151-y.

5 Yu. B. Monakov, R. M. Islamova, I. A. Ionova, S. A. Syrbu, T. A. Ageeva and O. I. Koifman, *Mendeleev Commun.*, 2010, **20**, 33; https://doi.org/10.1016/j.mencom.2010.01.013.

6 R. M. Islamova, *Russ. J. Gen. Chem.*, 2016, **86**, 125; https://doi.org/10.1134/S1070363216010217.

7 G. I. Sadrtdinova, D. A. Bardonov, K. A. Lyssenko, M. E. Minyaev, I. E. Nifant'ev and D. M. Roitershtein, *Mendeleev Commun.*, 2023, **33**, 357; https://doi.org/10.1016/j.mencom.2023.04.019.

8 D. S. Suslov, A. V. Suchkova, M. V. Bykov, Z. D. Abramov, M. V. Pakhomova, T. S. Orlov, I. A. Ushakov, T. N. Borodina and V. I. Smirnov, *Mendeleev Commun.*, 2023, **33**, 184; https://doi.org/10.1016/j.mencom.2023.02.011.

9 M. A. Katkova, G. S. Zabrodina, R. V. Rumyantcev, G. Yu. Zhigulin, M. S. Muravyeva, M. P. Shurygina, S. A. Chesnokov and S. Yu. Ketkov, *Mendeleev Commun.*, 2023, **33**, 37; https://doi.org/10.1016/j.mencom.2023.01.011.

10 S. Dadashi-Silab and K. I. Matyjaszewski, *Molecules*, 2020, **25**, 1648; https://doi.org/10.3390/molecules25071648.

11 S. A. Stakhi, D. F. Grishin and I. D. Grishin, *Polym. Sci., Ser. B*, 2020, **62**, 169; https://doi.org/10.1134/S1560090420030148.

12 A. A. Kaltenberg, N. V. Somov, Y. B. Malysheva, N. A. Knyazeva, A. V. Piskunov and I. D. Grishin, *J. Organomet. Chem.*, 2020, **917**, 121291; https://doi.org/10.1016/j.jorganchem.2020.121291.

13 J. Kim, J. Choe, D. Son and M. Kim, *Bull. Korean Chem. Soc.*, 2019, **40**, 1013; https://doi.org/10.1002/bkcs.11862.

14 E. V. Kolyakina, L. N. Gruzdeva, A. I. Poddelsky and D. F. Grishin, *Russ. Chem. Bull.*, 2017, **66**, 1650; https://doi.org/10.1007/s11172-017-1937-y.

15 E. V. Kolyakina, L. N. Gruzdeva, A. Z. Kreindlin, N. A. Stel'tzer and D. F. Grishin, *Russ. Chem. Bull.*, 2017, **66**, 1078; https://doi.org/10.1007/s11172-017-1857-x.

16 E. A. Masloborodova, E. V. Kaganova, N. S. Gusakova, L. V. Agibalova, E. Yu. Maretina, I. V. Baranets and R. M. Islamova, *Russ. J. Gen. Chem.*, 2017, **87**, 1038; https://doi.org/10.1134/S1070363217050243.

17 D. F. Grishin, O. S. Lizyakina, L. B. Vaganova, A. A. Kaltenberg and I. D. Grishin, *Iran. Polym. J.*, 2021, **30**, 1117; https://doi.org/10.1007/s13726-021-00951-8.

18 S. V. Kolesov, I. I. Nasibullin, A. K. Friesen, N. N. Sigayeva and E. G. Galkin, *Polym. Sci., Ser. B*, 2015, **57**, 71; https://doi.org/10.1134/S1560090415020062.

19 K. A. Tereshchenko, D. A. Shiyan, N. V. Ulitin, S. V. Kolesov and S. L. Khursan, *J. Polym. Res.*, 2022, **29**, 429; https://doi.org/10.1007/s10965-022-03273-2.

20 M. Vatamanu, *J. Catal.*, 2015, **323**, 112; https://doi.org/10.1016/j.jcat.2014.12.004.

21 D. N. Laikov and Yu. A. Ustynyuk, *Russ. Chem. Bull.*, 2005, **54**, 820; https://doi.org/10.1007/s11172-005-0329-x.

22 J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865; https://doi.org/10.1103/PhysRevLett.77.3865.

23 A. V. Smirnov, E. A. Valiakhmetov, D. R. Diniakhmetova and S. V. Kolesov, *Butlerov Commun., A*, 2023, **74**, 24; https://doi.org/10.37952/ROI-jbc-01/23-74-5-24.

24 R. Kh. Yumagulova, S. I. Kuznetsov, D. R. Diniakhmetova, A. K. Frizen, V. A. Kraikin and S. V. Kolesov, *Kinet. Catal.*, 2016, **57**, 380; https://doi.org/10.1134/S0023158416030150.

Received: 11th March 2024; Com. 24/7420