ISSN 0023-1584, Kinetics and Catalysis, 2012, Vol. 53, No. 4, pp. 456–461. © Pleiades Publishing, Ltd., 2012.
Original Russian Text © V.V. Saraev, P.B. Kraikivskii, V.V. Bocharova, D.A. Matveev, 2012, published in Kinetika i Kataliz, 2012, Vol. 53, No. 4, pp. 477–482.

Metallacyclic Mechanism of the Addition Polymerization of Norbornene Involving Ni(I) and Ni(III) Complexes

V. V. Saraev, P. B. Kraikivskii*, V. V. Bocharova, and D. A. Matveev

Irkutsk State University, Irkutsk, 664033 Russia

** e-mail: peter10@list.ru*

Received October 19, 2011

Abstract—The catalytic system $Ni(COD)_2/BF_3 \cdot OEt_2$ is highly active in the addition polymerization of norbornene (NB). Its activity, which is up to 1930 (kg NB) (mol Ni)$^{-1}$ h^{-1}, is higher than the activity of the other known nickel complex catalysts. Another advantage of this system over the latter is that it contains a smaller proportion of a Lewis acid (5 molar parts or below) and no conventional stabilizing organoelement ligands. The activity of this system in NB polymerization has been investigated by Fourier-transform IR spectroscopy. According to EPR data, NB polymerization is accompanied by the formation of low-spin complexes of trivalent nickel, which result from the oxidative addition of the monomer to univalent nickel complexes. A metallacyclic mechanism involving Ni(I) and Ni(III) complexes is suggested for NB polymerization.

DOI: 10.1134/S002315841204009X

The synthesis of high-purity polymers of cyclic olefins for optoelectronic, machine building, and medicinal applications is among the contemporary areas of research in cycloolefin polymerization [1, 2]. Interest in the addition polymerization of norbornene (NB) stems from the unique properties of its homopolymers and copolymers. In addition to being of practical significance, NB polymerization is a very convenient model for detailed investigation of catalytic polymerization. This is due to the fact that the structure of the monomer allows fairly precise determination of the character of activation in polymerizations proceeding via radically different mechanisms, namely, ring-opening metathesis polymerization (ROMP) [3], cationic polymerization [4], and vinyl-type addition polymerization [5]. The polymers resulting from these three different processes are reliably identifiable by NMR and vibrational spectroscopy [6].

The addition polymerization of NB is being increasingly frequently conducted over catalytic systems based on nickel complexes combined with Lewis acids, including boron compounds [2, 7–11].

The catalytic system consisting of $Ni(PPh_3)_4$ and $BF_3 \cdot OEt_2$, with the latter component in large excess (B : Ni = 400 : 1), proved fairly active in the high-molecular-weight polymerization of NB. Its activity is up to 1548 (kg NB) (mol Ni)$^{-1}$ h^{-1} [10]. Tkach et al. [11], who hypothesized that the active sites of polymerization are nickel hydride complexes forming in the system, suggested that the $Ni(PPh_3)_4/BF_3 \cdot OEt_2$ system be modified by introducing water in order to deliberately generate these complexes. However, a comparison of the water-free systems [10] with water-containing systems [11] demonstrates that the highest productivity of the $Ni(PPh_3)_4/H_2O/BF_3 \cdot OEt_2$ system, which is 771 (kg NB) (mol Ni)$^{-1}$ h^{-1}, is lower than that of the $Ni(PPh_3)_4/BF_3 \cdot OEt_2$ system under the same process conditions. Nevertheless, Tkach et al. [11] do ascribe catalytic activity to nickel hydride complexes. At the same time, it follows from data presented in comprehensive reviews [1, 2] that the introduction of water into Ziegler systems also does not exert a favorable effect on their activity in NB polymerization.

We demonstrated earlier [12–14] that, in an argon atmosphere, $Ni(COD)_2$ (COD = cycloocta-1,5-diene) in combination with $BF_3 \cdot OEt_2$ (B : Ni = 3 : 1) is highly active in cycloisomerization; in an ethylene atmosphere, it is an active catalyst for the [2 + 2] cyclodimerization of COD. In order to design an NB polymerization catalyst with a low Lewis acid content and elucidate the mechanism of active complex formation in this reaction, we studied the $Ni(COD)_2/BF_3 \cdot OEt_2$ system.

EXPERIMENTAL

Polymerization experiments were carried out using standard Schlenk techniques with an argon–vacuum line and appropriate glassware. All prepared and synthesized chemicals were stored in argon in sealed tubes.

The reactants and solvents—COD, toluene, and hexane (Merck)—were additionally dried over molecular sieve Aldrich 3A and degassed. Boron trifluoride etherate (Merck) was distilled from lithium hydride immediately before use.

Activity of the $Ni(COD)_2/BF_3 \cdot OEt_2$ system in norbornene polymerization and the most important properties of the resulting polymers

B : Ni, mol/mol	Productivity, (kg NB)(mol Ni)$^{-1}$ h^{-1}	Polymer yield, g	NB conversion, %	T_g, °C	T_d, °C	[h], Da/g
2 : 1	1480	36.2	72	237	421	0.67
5 : 1	1930	46.7	93	260	426	0.52
10 : 1	1790	44.3	88	230	417	0.55
15 : 1	1670	47.2	94	202	420	0.58

Note: T_g = glass transition temperature, T_d = decomposition temperature, [h] = characteristic viscosity. Experimental conditions: reaction temperature of 20°C, reaction time of 30 min, 50 g of toluene, 50 g of NB, 0.03 g of $Ni(COD)_2$, NB : Ni = 5000 : 1 mol/mol.

Bis[1,2:5,6-η-cycloocta-1,5-diene]nickel was synthesized via a procedure reported by Bogdanovic et al. [15].

NMR spectra were recorded on a Bruker AVANCE 400 spectrometer. ^{13}C NMR spectra were interpreted using the attached proton test (APT) procedure.

EPR spectra were obtained on a CMS-8400 spectrometer operating at 9.6 GHz at the nitrogen boiling point. Magnetic field sweep scales were calibrated against the free diphenylpicrylhydrazyl (DPPH) radical and against Mn^{2+} in MgO.

The IR spectra of polymers were recorded on an Infralyum FT-801 Fourier-transform spectrometer. The polymer samples were pressed into KBr pellets in an argon atmosphere. Kinetic experiments were performed using a flow-through KBr cell (0.1 mm) and a ZnSe ATR crystal. The cell was connected to the reactor via a thin (d = 1 mm) polyethylene pipe. The free volume of the system was 0.6 mL. Flow circulation in the spectrometer line was ensured by generating an argon pressure gradient, without employing any mechanical device.

Catalytic reactions were carried out in a temperature-controlled reactor allowing vigorous stirring and argon pressure control. All experiments were performed at NB : Ni = 5000 : 1 mol/mol and NB : toluene = 1 : 1 mol/mol. The amount of NB was 50 g. Kinetic data were calculated from the results of three replica experiments.

RESULTS AND DISCUSSION

The catalytic system $Ni(COD)_2/BF_3 \cdot OEt_2$ (B : Ni = (2–15) : 1) formed in toluene in an argon atmosphere is highly active in NB polymerization. Data characterizing the activity of the system as a function of the proportions of the components and the most important properties of the polymers are presented in the table. All of the polynorbornenes synthesized in this study are soluble in toluene, cyclohexane, and chlorobenzene and are superior in this respect to the polynorbornenes synthesized over palladium catalysts [1, 2, 16–18]. The system remains homogeneous throughout the polymerization process in toluene. It is more active than most of the known nickel complex catalysts for NB polymerization [1–11, 16–23] and does not contain any conventional stabilizing organoelement ligands. Another advantage of this system is that the maximum of its catalytic activity is observed at an extremely low Lewis acid content.

All polynorbornenes, obtained under varied conditions, were characterized by NMR and IR spectroscopy. The ^1H and ^{13}C NMR spectra presented in Figs. 1 and 2 are characteristic of addition-type polynorbornene [24].

The IR spectrum of the polymers shows no bands at frequencies above 3000 cm^{-1} (=C–H stret=C stretching and =C–H out-of-plane vibrations), providing further evidence in favor of the vinyl-addition nature of the polymer. The spectra of all of the synthesized polymers contain bands at 1453–1475 cm^{-1}, which are characteristic of addition-type polynorbornenes and are due to the δ_{H-C-H} bending vibrations at the bridging carbon atom of the norbornane ring [6]. A comparison between the vibrational spectra of polynorbornene and NB monomer demonstrates that, along with the above vibrational bands, medium-intensity bands at 1375 and 1257 cm^{-1} and a strong band at 1295 cm^{-1} are present in the spectrum of the product. According to the results of simulation of the vibrational spectra [6], this combination of bands indicates that the resulting polynorbornene is in *exo,exo-cis* configuration. Figure 3 shows how the spectrum of the reaction mixture in the selected range varies during NB polymerization in the presence of the $Ni(COD)_2/BF_3 \cdot OEt_2$ catalytic system. Figure 4 presents the kinetic curves derived from these spectroscopic data.

The kinetic data obtained by FTIR spectroscopy enabled us to see how the activity of the catalyst changes at the very beginning of the reaction. Such data have not been reported in the literature thus far, because they cannot be obtained for the early stages of the process by the gravimetric method that is com-

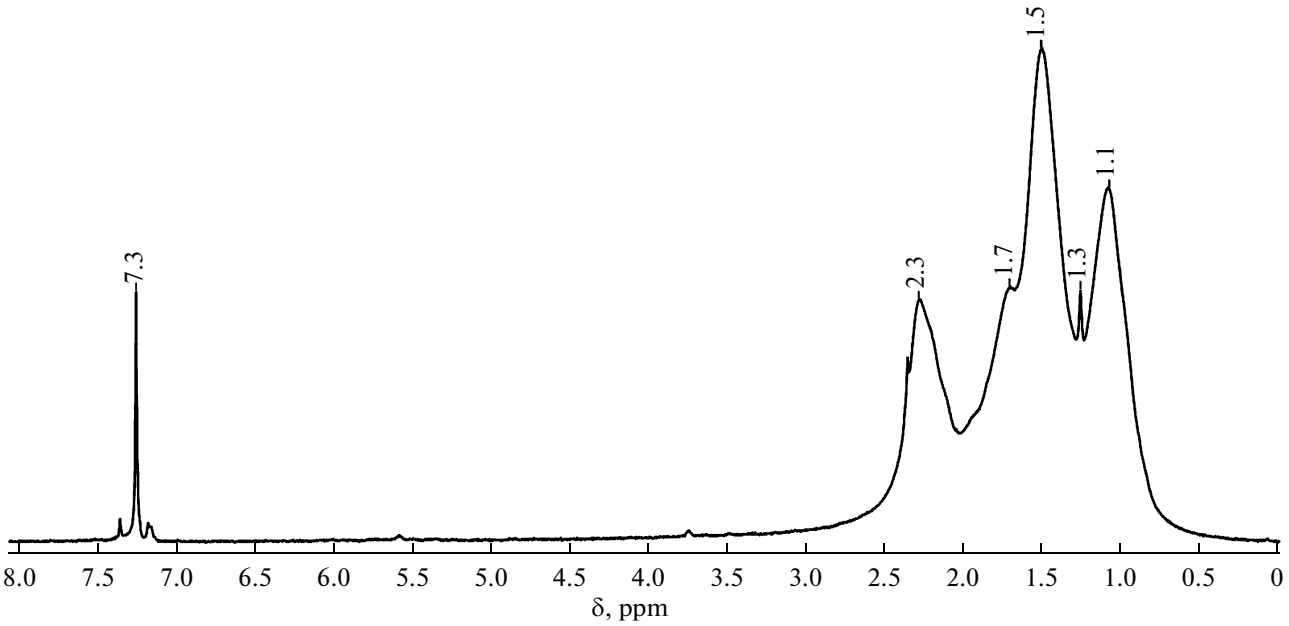


Fig. 1. ^{1}H NMR spectrum of the resulting polynorbornene ($CDCl_3$, 400 MHz).

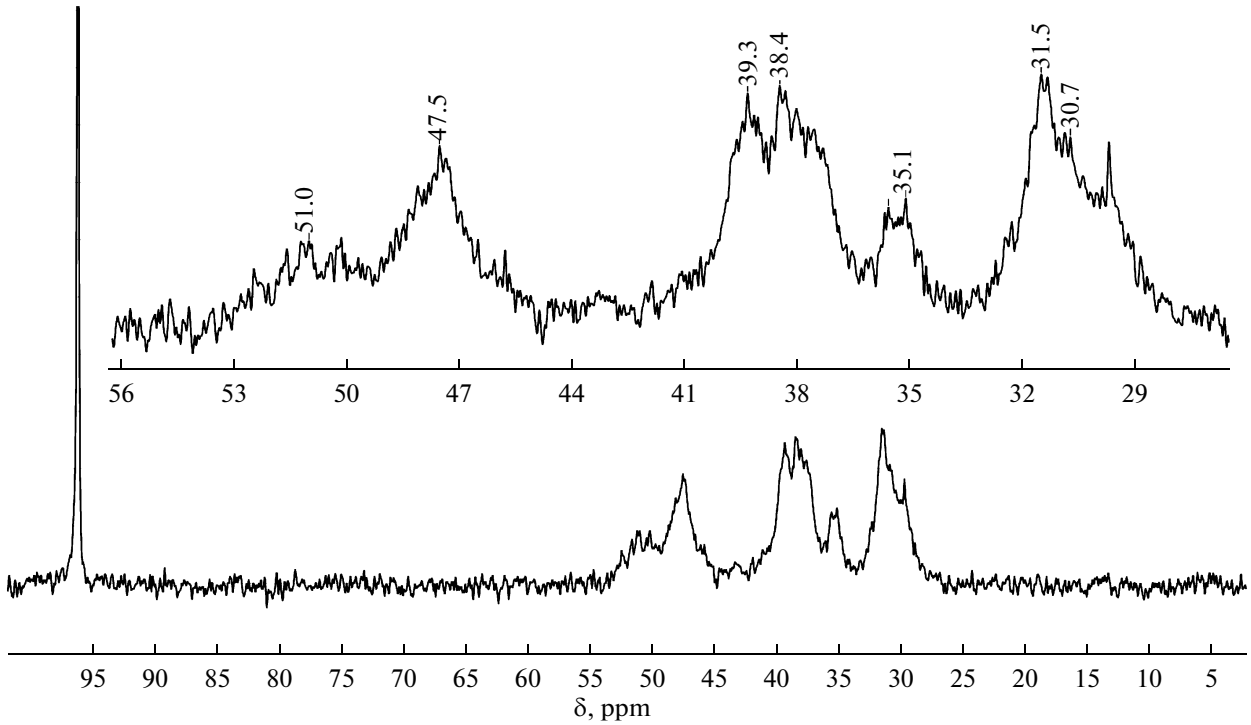


Fig. 2. ^{13}C NMR spectrum of the resulting polynorbornene (CCl_4, 100 MHz).

monly used to determine the polymer content of the system. This is the reason why the greater part of kinetic information gained for such systems refers to the 5th to 7th minute from the beginning of the reaction. Obviously, this does not rule out the possibility that gravimetric analysis will perturb the catalytic system or that the error in the determination of the amount of polymer will be large.

The results of turbidimetric titration performed during polymerization (inset in Fig. 4) indicate that the molar mass distribution (MMD) of the polymer narrows significantly in the course of the reaction.

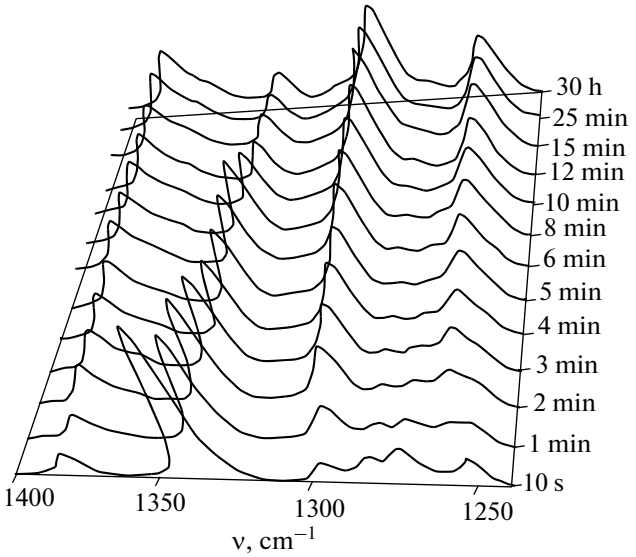


Fig. 3. FTIR spectra of the reaction mixture in the most characteristic spectral range recorded at different points in time after the beginning of polymerization (toluene, 20°C).

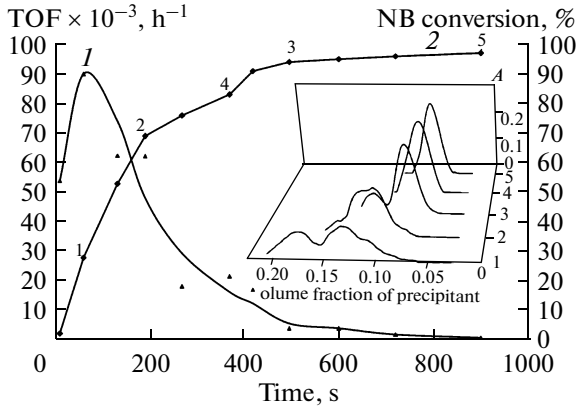
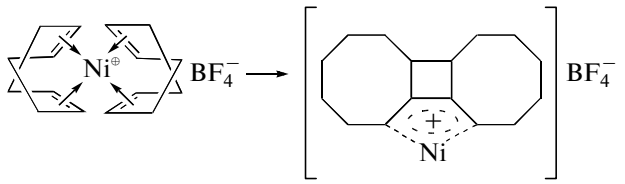


Fig. 4. Kinetics of norbornene polymerization catalyzed by the $Ni(COD)_2/BF_3 \cdot OEt_2$ system according to IR spectroscopic data: (*1*) activity of the system (TOF) and (*2*) norbornene conversion (numbers 1–5 at the curve indicate the points in time at which the mixture was sampled for turbidimetric titration). Inset: Differential absorbance curves recorded in turbidimetric titration. Ni : B = 1 : 5, Ni : NB = 1 : 5000, 20°C.

This is evidence that the polymerization is living in character.

In order to elucidate the nature of active sites in the catalytic system $Ni(COD)_2$/ $BF_3 \cdot OEt_2$, we investigated the formation and conversions of the nickel complex by EPR spectroscopy.

It was demonstrated earlier that the interaction between a toluene solution of $Ni(COD)_2$ and two molar parts of $BF_3 \cdot OEt$ in an argon atmosphere leads to a nearly quantitative oxidation of Ni(0) to Ni(I) and to the formation of the cationic complex $[Ni(COD)_2]^+BF_4^-$ (**I**) in the system. This complex then turns into a carbocationic Ni(I) complex (**II**) having a Ni–C bond [13]:

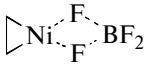


I **II**

As this takes place, the EPR spectrum (Fig. 5) initially shows the signal **a** ($g_\parallel$ =2.38, $g_\perp$ = 2.05), which then transforms rapidly into the temporally stable signal **b** ($g_x = 2.030$, $g_y = 2.048$, $g_z = 2.249$) [12–14].

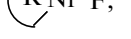
The carbocationic complex **II** in the absence of an olefin is stable in solution and undergoes no changes over several days [12–14].

After the introduction of NB into the system (NB : Ni = 50 : 1), the intensity of the signal **b** decreases rapidly and a new strong signal (**c**) appears, which has a well-resolved hyperfine structure (HFS) from one nucleus with a spin of 1/2. The signal **c**, which contains a doublet, is characterized by the following parameters: $g_\parallel = 1.977$, $g_\perp = 2.65$, $A_\parallel = 126$ G, and $A_\perp = 51$ G. In the system examined, there are only two types of nuclei with a spin of 1/2, namely, ^1H and ^{19}F. The HFS is due to the ^{19}F nucleus, since its constant is one order of magnitude larger the known HFS constants for ^1H in Ni(I) hydride complexes [25, 26] and is nearly equal to the HFS constant for ^{19}F in the following metallacyclic Ni(III) ethylene complex ($g_\parallel$ = 1.987, $g_\perp = 2.45$, $A_\parallel = 122$ G, $A_\perp = 59$ G) [13]:



III

Complex **III** was earlier identified in the $Ni(COD)_2/BF_3 \cdot OEt_2$ system involved in the catalytic [2 + 2] cyclodimerization of COD in an ethylene atmosphere [13]. Note that the two fluorine-containing nickel complexes are characterized not only by similar HFS constants, but also by similar *g*-factor components. Therefore, complexes of the same type form in the $Ni(COD)_2/BF_3 \cdot OEt_2$ system upon the introduction of ethylene or NB. Thus, the signal **c** is assignable to a metallacyclic complex of nickel(III) with a d^7 electron configuration in which the nickel atom is bonded with one fluorine atom and with an organic ring in the growing polymer chain:



where R is an arbitrary carbon chain.

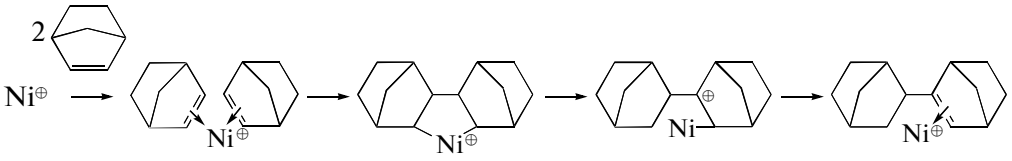
The maximum intensity of the signal **c** is observed approximately 10 s after the introduction of NB into the system. Thereafter, the signal **c** weakens and the intensity of the signal **b** increases, and, 20–25 s after

NB addition, only the signal **b** is observed in the spectrum. After the introduction of additional 100 molar parts of NB into the same system, the EPR behavior of the system repeats. (The in situ EPR spectra are presented in Fig. 6.) According to EPR data, the number of paramagnetic species in the system remains invariable within one Ni(I)–Ni(III) transition (within 15–20% accuracy).

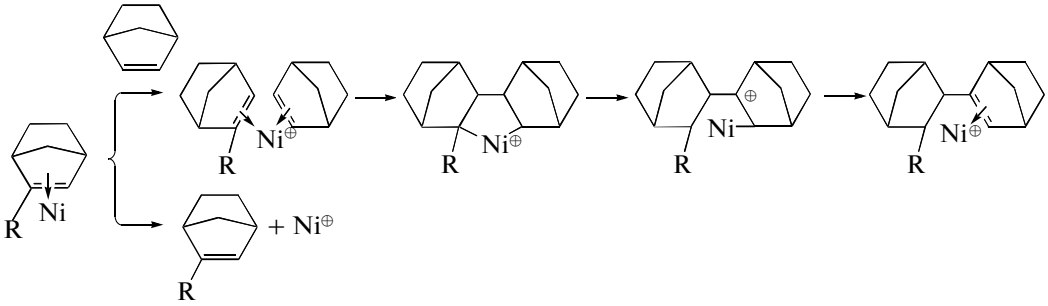
According to the results of the turbidimetric titration of the polymer, the MMD narrows after the consumption of each introduced portion of NB. This is evidence of the living polymerization of NB.

The formation of complexes of Ni(III) of the same type in the [2 + 2] cyclodimerization of COD and in NB polymerization suggests the following metallacyclic mechanism for the addition polymerization of the monomer:

chain initiation,



chain propagation and termination,



In this hypothetical mechanism, chain initiation (Ni–C bond formation) is preceded by the coordination of two monomer molecules to Ni(I) and by oxidative addition yielding a metallacycle in which nickel in the oxidation state +3. Upon reductive elimination, Ni(III) turns into Ni(I), which then stabilizes as a π complex with the NB dimer. Chain propagation in this mechanism is the successive growth of the chain at the terminal double bond via the same oxidative addition and reductive elimination steps as in chain initiation.

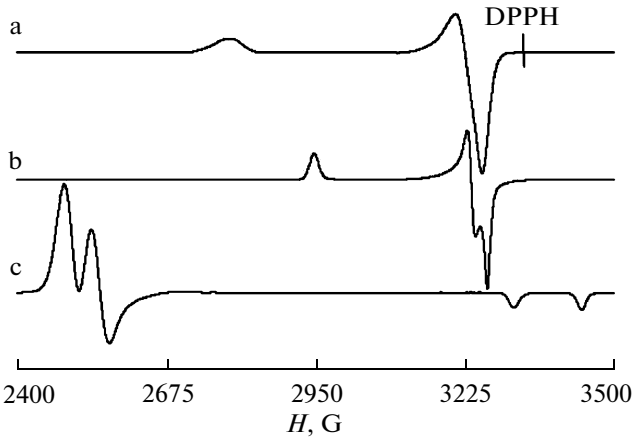


Fig. 5. EPR spectra of the nickel complexes forming in the $Ni(COD)_2/BF_3 \cdot OEt_2$ system (77 K, toluene). See main text for explanation.

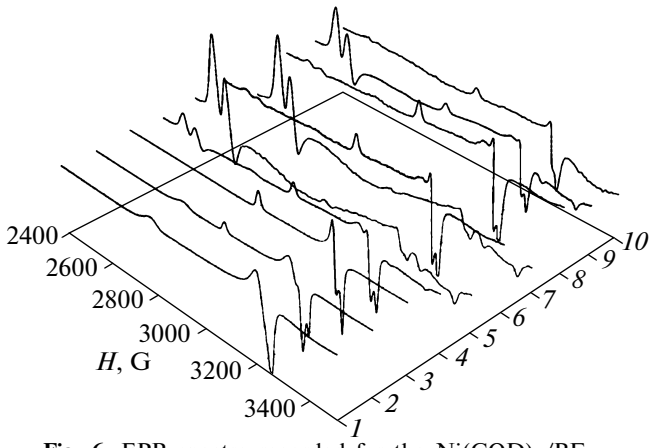


Fig. 6. EPR spectra recorded for the $Ni(COD)_2/BF_3 \cdot OEt_2$ system at its formation stage and during the functioning of the catalyst (reaction temperature of 20°C, toluene, spectrum recording temperature of 77 K): (*1*) 5 s after the introduction of $BF_3 \cdot OEt_2$, (*2*) 20–25 s after the introduction of $BF_3 \cdot OEt_2$, (*3*) 1 min after the introduction of $BF_3 \cdot OEt_2$, (*4*) 5–7 after the subsequent introduction of 50 molar equivalents of NB, (*5*) 20–25 s after the introduction of NB, (*6*) 1 min after the introduction of NB, (*7*) 10–12 s after the introduction of the second portion of NB, (*8*) 1 min after the introduction of the second portion of NB, (*9*) 20–25 s after the introduction of the third portion of NB, and (*10*) 2 min after the introduction of the third portion of NB.

Chain termination in this mechanism is due to the irreversible elimination of the macromolecule from the coordination sphere of Ni(I).

ACKNOWLEDGMENTS

V.V. Bocharova is grateful to the Irkutsk State University administration for a postgraduate grant.

This work was supported by the Federal Target Program "Scientific and Scientific–Pedagogical Personnel of Innovative Russia" (contract no. P732).

REFERENCES

1. Makovetskii, K.L., *Polym. Sci., Ser. C: Sel. Top.*, 2008, vol. 50, no. 1, p. 22.
2. Blank, F. and Janiak, C., *Coord. Chem. Rev.*, 2009, vol. 253, p. 827.
3. Grubbs, R.H., in *Comprehensive Organometallic Chemistry*, Wilkinson, G., Stone, F.G.A., and Abel, E., Eds., Oxford: Pergamon, 1982, vol. 8, p. 499.
4. Kennedy, J.P. and Makowski, H.S., *J. Macromol. Sci. Chem.*, 1967, vol. 1, p. 345.
5. Mehler, C. and Risse, W., *Makromol. Chem., Rapid Commun.*, 1991, vol. 12, no. 5, p. 255.
6. Bondarenko, G.N., Gorbacheva, L.I., Golenko, T.G., Bykov, V.I., Fateev, O.V., and Makovetskii, K.L., *Polym. Sci., Ser. A: Polym. Phys.*, 1996, vol. 38, no. 3, p. 279.
7. Berchtold, B., Lozan, V., Lassahn, P.-G., and Janiak, C., *J. Polym. Sci., Part A: Polym. Chem.*, 2002, vol. 40, p. 3604.
8. Jang, Y., Sung, H.-K., Kwag, H., Lee, S., and Cheolbeom, B., *Polymer*, 2005, vol. 46, p. 11301.
9. Jang, Y., Sung, H.-K., and Kwag, H., *Eur. Polym. J.*, 2006, vol. 42, no. 6, p. 1250.
10. Myagmarsuren, G., Jeong, O.-Yong, and Ihm, Son-Ki, *Appl. Catal., A*, 2003, vol. 255, p. 203.
11. Tkach, V.S., Suslov, D.S., Myagmarsuren, G., Gubaydulina, O.V., Bykov, M.V., and Umanets, V.A., *Catal. Commun.*, 2009, vol. 10, p. 1813.
12. Saraev, V.V., Kraikivskii, P.B., Matveev, D.A., Petrovskii, S.K., and Fedorov, S.V., *Russ. J. Coord. Chem.*, 2008, vol. 34, no. 9, p. 712.
13. Saraev, V.V., Kraikivskii, P.B., Matveev, D.A., Bocharova, V.V., Petrovskii, S.K., Zelinskii, S.N., Vilms, A.I., and Klein, H.-F., *J. Mol. Catal. A: Chem.*, 2010, vol. 315, p. 231.
14. RF Patent 2400300, 2010.
15. Bogdanovic, B, Kröner, M., and Wilke, G., *Liebigs Ann. Chem.*, 1966, vol. 699, no. 1, p. 1.
16. Makovetskii, K.L., *Vysokomol. Soedin., Ser. A*, 1994, vol. 36, no. 10, p. 1712.
17. Makovetsky, K.L., *Polym. Sci., Ser. B: Polym. Chem.*, 1999, vol. 41, nos. 9–10, p. 269.
18. Janiak, C. and Lassahn, P.G., *J. Mol. Catal. A: Chem.*, 2001, vol. 166, no. 2, p. 193.
19. Eur. Patent 0445755, 1991.
20. Rush, S., Reinmuth, A., and Risse, W., *Macromolecules*, 1997, vol. 30, p. 7375.
21. Goodall, L., McIntosh, L.H. III, and Rhodes, L.F., *Makromol. Chem. Macromol. Symp.*, 1995, vol. 89, p. 421.
22. Barnes, D.A., Benedikt, G.M., Goodall, B.L., Huang, S.S., Kalamarides, H.A., and Lenhard, S., *Macromolecules*, 2003, vol. 36, p. 2623.
23. Jang, Y., Sung, H.-K., Kwag, H., Lee, S., and Cheolbeom, B., *Polymer*, 2005, vol. 46, p. 11301.
24. Jang, Y., Sung, H.-K., and Kwag, H., *Eur. Polym. J.*, 2006, vol. 42, no. 6, p. 1250.
25. Saraev, V.V., Shmidt, F.K., Gruznykh, V.A., Mironova, L.V., and Bakunina, T.I., *Koord. Khim.*, 1979, vol. 5, no. 6, p. 897.
26. Pfirrmann, S., Limberg, C., Herwig, C., Knispel, C., Braun, B., Bill, E., and Stösser, R., *J. Am. Chem. Soc.*, 2010, vol. 132, no. 39, p. 13684.