Available online at www.sciencedirect.com
ScienceDirect
Mendeleev Commun., 2024, **34**, 815–818

Mendeleev
Communications

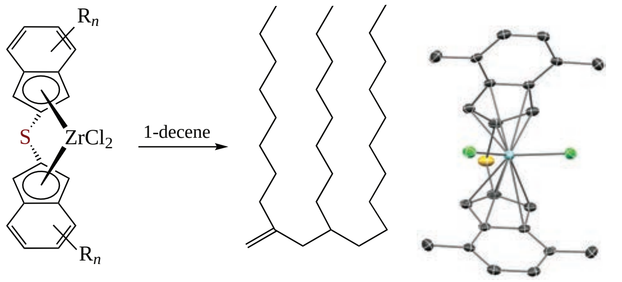
Sulfur-bridged bis(2-indenyl) zirconocenes and their performance in olefin polymerization

Oleg V. Samsonov,[a] Georgy P. Goryunov,[a] Dmitry V. Uborsky,[a] Andrey F. Asachenko,[a] Jo Ann M. Canich,[b] Jian Yang[b] and Alexander Z. Voskoboynikov*[a]

[a] *Department of Chemistry, M. V. Lomonosov Moscow State University, 119991 Moscow, Russian Federation.*
E-mail: voskoboy@med.chem.msu.ru
[b] *Baytown Technology and Engineering Complex, ExxonMobil Technology and Engineering Company,*
Baytown, Texas 77520, USA

DOI: 10.1016/j.mencom.2024.10.015

A series of sulfur-bridged bis(2-indenyl) zirconocenes were synthesized and tested for ethylene/1-octene copolymerization and 1-decene oligomerization. Zirconocene bearing two 5,6-positioned methyl substituents in indenyl moieties, distant from the metal center, appeared to be an active catalyst producing 1-decene oligomers with high content of unsaturated vinylidene end groups, which is preferable for post-functionalization.



Keywords: *ansa*-metallocenes, sulfides, indene, olefin polymerization, linear low-density polyethylene, poly(α-olefins), X-ray crystallography.

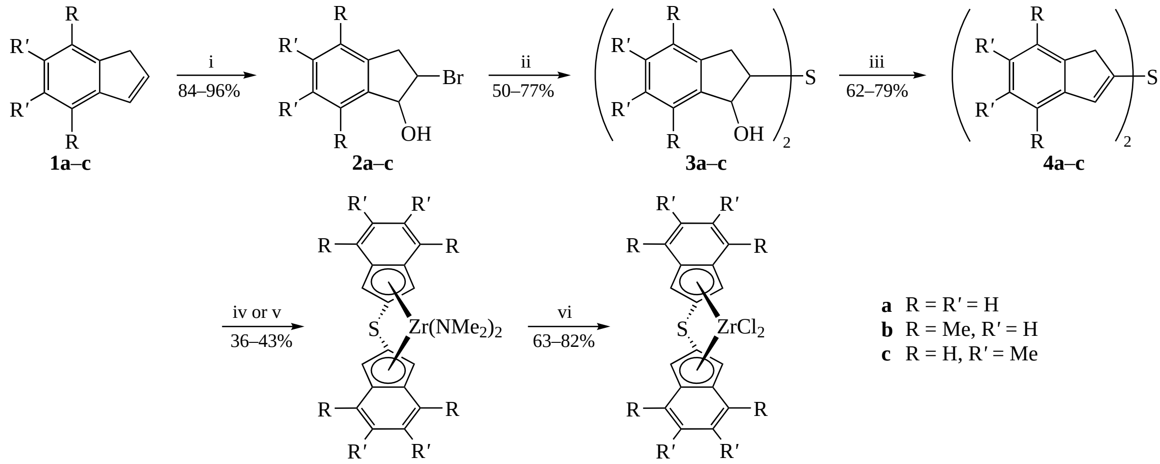
The ability of methylaluminoxane (MAO) to cationize Group 4 metallocenes thus forming active olefin polymerization catalysts was discovered almost simultaneously together with the effects of the bridging group connecting the two cyclopentadienyl rings[1] (such complexes are often referred to as *ansa*-metallocenes). The bridging group provides fixation of mutual orientation of the cyclopentadienyl rings thus allowing for precise design of the steric surrounding of the active pocket (defined by substituents at the ligand) and the accessibility of the metal center (determined by the properties of the bridge). Further research on *ansa*-metallocenes was predominantly focused on the development of stereoselective propylene polymerization catalysts, either isoselective (typically metallocenes of C_2-symmetry with one-atom bridge between positions 1 of two indenyls)[2,3] or syndioselective (C_s-symmetrical fluorenyl-cyclopentadienyl metallocenes).[4] Nonetheless, on industrial scale, metallocene catalysts are extensively used in copolymerization processes such as production of linear low-density polyethylene, where stereoselectivity is not among the target parameters of the catalyst. Consequently, in this application field, in addition to the C_s-[5] or C_2-symmetrical metallocene catalysts,[6] there is interest in industry and academia in *ansa*-metallocenes of C_1[7,8] and C_{2v} symmetry with the latter being represented by a number of metallocenes with a one-atom bridge connecting positions 2 of the indenyl moieties.[9–14] This being said, sulfur-bridged metallocenes remain almost unexplored.[14]

Here, we report on the development of synthetic approach to di(2-indenyl) sulfide ligands, preparation of the respective metallocenes, and studies of their performance in ethylene homopolymerization, ethylene/1-octene copolymerization, and 1-decene oligomerization. The only previously described pathway to di(2-indenyl) sulfide[14] implying reaction of 2-indanone with the Lawesson's reagent can be hardly expanded to other analogs due to a limited accessibility of substituted 2-indanones. Alternatively, Landini and Rolla[15] successfully used sodium sulfide nonahydrate in the presence of a phase-transfer catalyst to produce dialkyl sulfides in more than 80% yields starting from primary and secondary alkyl halides. In this work, available indenes **1a–c** were converted to the corresponding indane bromohydrins **2a–c** that were reacted with Na_2S to afford thiobis(indanols) **3a–c** (Scheme 1). The latter reaction (see Scheme 1, step ii) can be performed under phase-transfer catalysis conditions, however, we found it more convenient to conduct it in 96% ethanol without a phase-transfer catalyst and using a different form of sodium sulfide hydrate. The following acid-catalyzed elimination of water from hydroxy sulfides afforded pro-ligands, di(2-indenyl) sulfides **4a–c**, in 62–79% yields (*cf*. ref. 16).

Direct synthesis of zirconocene dichloride **6a** from dilithium salt of **4a** and $ZrCl_4$ was unsuccessful, so alternative routes *via* diamides **5a–c** were attempted. Reaction of $Zr(NMe_2)_4$ with neutral pro-ligands **4a** and **4c** gave the corresponding diamide zirconocenes **5a** (36% yield) and **5c** (43% yield). The same reaction with **4b** led to formation of unbridged indenyl complexes $(3\text{-H-}4,7\text{-Me}_2\text{-}2\text{-Ind})\text{–S–}(4,7\text{-Me}_2\text{-}2\text{-Ind})\text{–Zr}(NMe_2)_3$ and $(Me_2N)_3Zr\text{–}(4,7\text{-Me}_2\text{-}2\text{-Ind})\text{–S–}(4,7\text{-Me}_2\text{-}2\text{-Ind})\text{–Zr}(NMe_2)_3$ rather than **5b**. Therefore, complex **5b** was prepared *via* reaction of $Zr(NMe_2)_2Cl_2(THF)_2$ with dilithium salt of **4b** in 39% yield. Further treatment of diamides **5a–c** with Me_2SiCl_2 afforded dichlorides **6a–c** in 82, 63, and 80% yields, respectively.

Single crystal study was performed for complex **6b**.[†] As expected, the molecular structure of **6b** exhibits C_{2v} symmetry (Figure 1), analogously to symmetrically substituted bis(2-indenyl) zirconocenes with one-atom bridge.[9,11,12]

© 2024 Mendeleev Communications. Published by ELSEVIER B.V. on behalf of the N. D. Zelinsky Institute of Organic Chemistry of the Russian Academy of Sciences.



1a–c **2a–c** **3a–c** **4a–c** **5a–c** **6a–c**

Scheme 1 *Reagents and conditions*: i, NBS, DMSO–H_2O, 20 °C; ii, $Na_2S\cdot 9H_2O$, $Oct_3NMe^+Cl^-$, H_2O or Na_2S ($\cdot nH_2O$, ⩾60% purity, scales), EtOH; iii, TsOH, PhMe; iv, $Zr(NMe_2)_4$, PhMe (for **5a**,**c**); v, LDA, THF, then $Zr(NMe_2)_2Cl_2(THF)$ (for **5b**); vi, Me_2SiCl_2, PhMe.

Bridging group nature is one of the key factors influencing the structural parameters of metallocene catalyst important for the polymerization performance. It is responsible for the ‘bite angle’, *i.e*. the angle between the mean planes of two cyclopentadienyl rings. Comparison of the bite angle in a series of one-atom bridged bis(2-indenyl) zirconocenes (Table 1) reveals that, qualitatively, it correlates inversely with the atomic radii of the bridging atoms, with the bite angle in **6b** (73.0°) being in between those of the H_2C- and Bu^tP-bridged metallocenes (76.9 and 68.2°, respectively). Calculated charge of the $ZrCl_2$ fragment in **6a** (0.353) was higher than that in Me_2Si-bridged bis(2-indenyl) zirconocene dichloride (0.310) and hypothetical unbridged complex of the geometry mimicking **6a** but with two hydrogen atoms instead of sulfur in indenyls (0.306). Consequently, sulfur was found to be an electron withdrawing bridging group, and possible back electron transfer from sulfur to vacant π*-indenyl orbitals is likely inefficient.

Table 1 Comparison of bite angles in one-atom bridged bis(2-indenyl) zirconocenes.

Zirconocene	Bite angle/ deg	Covalent atomic radius	Reference
$H_2C(4,7\text{-}Me_2\text{-}2\text{-indenyl})_2ZrCl_2$	76.9	76	12
$S(4,7\text{-}Me_2\text{-}2\text{-indenyl})_2ZrCl_2$ (**6b**)	73.0	105	this work
$Bu^tP(2\text{-indenyl})_2ZrCl_2$	68.2	107	11
$Me_2Si(2\text{-indenyl})_2ZrMe_2$	63.9	111	CCDC 1413171

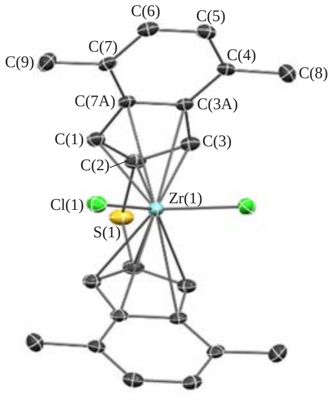


Figure 1 Crystal structure of **6b**. Displacement ellipsoids are shown at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) are Zr(1)–Cl(1) 2.4225(5), Zr(1)–C(1) 2.479(2), Zr(1)–C(2) 2.4642(19), Zr(1)–C(3) 2.489(2), Zr(1)–C(3A) 2.6568(19), Zr(1)–C(7A) 2.6462(18), S(1)–C(2) 1.778(2).

Further, the three synthesized metallocenes **6a–c** were preliminary tested in ethylene homopolymerization and ethylene/1-octene copolymerization in the presence of methylaluminoxane[17] (Table 2). Expectedly, **6a** with unsubstituted 2-indenyls behaved similarly to the previously described bis(2-indenyl) zirconocene catalysts with one-atom bridge,[7,9,12] *i.e*. afforded oligomers with M_n of few kDa. Surprisingly, introduction of methyl groups in the distant (with respect to the metal atom) 5,6-positions of the 2-indenyls in **6c** increased the polymerization activity by an order of magnitude, while molecular weight capability remained almost unchanged. Introduction of two methyl substituents at positions 4 and 7 of the indenyls increased M_n by *ca*. 20–40 times with the activity being only slightly affected, analogously to what was observed earlier by Resconi[12] for the similarly substituted pair of H_2C-bridged bis(2-indenyl) zirconocenes in ethylene homopolymerization. As a result, the overall performance of **6b**/MAO in (co)polymerization of ethylene (including the activity and comonomer incorporation) appeared to be comparable to the reference catalyst **7**/MAO (**7** = *rac*-Me_2Si(2-methyl-1-indenyl)$_2ZrCl_2$).

Interestingly, the effect of 4,7-substitution on the molecular weight capability was stronger than placement of methyl groups at (seemingly close to the metal) positions 1 and 3 of two 2-indenyls in Me_2Si-bridged bis(1,3-dimethyl-2-indenyl) zirconocene which was still only able to produce oligomers[7] like its unsubstituted homolog,[18] as descried earlier. Another comparison with the literature data on Me_2Si-bridged catalysts suggests that switching from bis(2-methyl-1-indenyl) to bis(2-

---

[†] *Crystal data for* **6b**. Data were collected on a Bruker SMART 1000 CCD diffractometer with MoKα radiation (λ = 0.71073 Å) using the φ- and ω-scan techniques. The structures were solved and refined by direct methods using SHELXTL. Data were corrected for absorption effects using the multi-scan method (SADABS). All non-hydrogen atoms were refined anisotropically using SHELXTL. The coordinates of the hydrogen atoms were calculated from geometrical positions. The crystal of $C_{22}H_{20}Cl_2SZr$ is monoclinic, space group *C*2/*c*, a = 15.6854(8), b = 9.3958(5) and c = 13.7831(7) Å, β = 107.727(10)°, V = 1934.86(17) Å^3, Z = 4, reflections collected 9645, of which 2323 unique reflections (R_{int} = 0.0268) were used in all calculations. The final parameters are R_1 = 0.0290, wR_2 = 0.0724 [$I > 2\sigma(I)$] and R_1 = 0.0312, wR_2 = 0.0741 (all data). GOOF = 1.012. Completeness 100%.

CCDC 2350110 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* https://www.ccdc.cam.ac.uk.

Table 2 Ethylene polymerization and ethylene/1-octene copolymerization data (0.025 μmol metallocene, 500 equiv. MAO, 4.9 ml toluene, 80 °C).

Zirconocene precatalyst	P_{ethylene}/bar[a]	V_{octene}/μl[b]	Activity[c,d]	M_n/kDa[d]	M_w/kDa[d]	PDI[d,e]	N_{octene} (wt%)[d,f]	T_m/C[d]
6a	6.2	0	17	3.9	7.6	2.0	–	126.6
6b	6.2	0	13	87	209	2.4	–	134.9
6c	6.2	0	120	5.7	10.7	1.9	–	126.9
7	6.2	0	39	277	425	1.5	–	135.4
6a	6.2	100	20	3.7	6.7	1.8	–[g]	113.7
6b	6.2	100	19	67	159	2.4	9.2	111.4
6c	6.2	100	112	4.3	8.8	2.0	–[g]	112.3
7	6.2	100	57	184	275	1.5	13.3	116.3
6a	14.8	100	29	3.4	6.1	1.8	–[g]	117.9
6b	14.8	100	16	140	291	2.1	4.8	120.3
6c	14.8	100	336[h]	4.6	8.7	1.9	–[g]	121.4
7	14.8	100	28	187	277	1.5	6.9	125.4

[a] Ethylene partial pressure. [b] Volume of 1-octene in the polymerization medium. [c] In $\text{kg}_{\text{polymer}}\ \text{mmol}^{-1}_{\text{catalyst}}\ \text{bar}^{-1}_{\text{ethylene}}\ \text{h}^{-1}$. [d] Mean values for at least three runs. [e] Polydispersity index PDI = M_w/M_n. [f] Content of incorporated 1-octene in the polymer in wt%, determined by FTIR spectroscopy. [g] Values were outside the calibration range for the FTIR. [h] Shortest quench times of all experiments due to the high initial activity; an average activity after longer polymerization times can be somewhat lower.

indenyl) backbone reduces the comonomer affinity of zirconocene catalysts by *ca*. 7 times (*e.g*. 5.4 mol% of incorporated 1-hexene at 5% level of 1-hexene in the feed[7] *vs*. 1.5 mol% at 10% level,[18] respectively). At the same time, catalyst **6b** provides only ~1.5-fold lower 1-octene incorporation in comparison with the reference Me_2Si-bridged bis(2-methyl-1-indenyl) catalyst **7**. This fact can be explained by the larger bite angle of the sulfur-bridged catalyst making steric access of the α-olefin to the metal center easier.

The latter consideration together with the low molecular weight capability makes zirconocenes **6a–c** potentially interesting catalysts for the synthesis of poly(α-olefins).[19] Oligomers of higher α-olefins (such as 1-decene) after hydrogenation of unsaturated end groups find use as base stock of synthetic oils of premium quality. On the other hand, unsaturated end groups can be transformed in a number of ways, including further oligomerization of the α-olefin oligomers,[20] halogenation, epoxidation, introduction of hydroxy groups through hydroboration–oxidation,[21] phenolic groups *via* the Friedel–Crafts alkylation of phenols,[22] succinic anhydride groups *via* maleation,[23] diarylamino- and thioether groups.[24] The end groups are classified based on the substitution pattern, namely, vinyl ($H_2C{=}CHR$), 1,2-disubstituted vinylene (*cis*- or *trans*-$HR^1C{=}CHR^2$), trisubstitued vinylene ($R^1R^2C{=}CHR^3$), and vinylidene ($R^1R^2C{=}CH_2$). For certain functionalization reactions, such as maleation, Friedel–Crafts alkylation of phenols[21] and diarylamines,[24] high content of vinylidene end groups is preferable due to their higher reactivity towards the functionalization reagents.

Thus, metallocenes **6a–c** were tested for 1-decene homopolymerization (Table 3) in the presence of borate activator AB ($PhNHMe_2^+[B(C_6F_5)_4]^-$), the dichloride complexes were alkylated prior to the polymerization with triisobutylaluminum. Molecular weight and end group distributions were determined by ^{1}H NMR. Conventional silicon-bridged zirconocene **8** [*rac*-$Me_2Si(1\text{-}IndH_4)_2ZrCl_2$] was used as a reference. Unsubstitued bis(2-indenyl) zirconocene **6a** and its 4,7-subtituted homolog **6b** appeared to be inferior to both 5,6-disubstituted **6c** and reference catalyst **8** in terms of activity. However, all of them provided higher content of vinylidene end groups than **8** with **6c** being most selective in the series, and higher average molecular weight. This is important as high content of 1-decene dimer is associated with lower viscosity index of the hydrogenated oil base stock.[25] At 85 and 110 °C, complex **6c** was also considerably more active than **8**.

Overall, the preliminary results show that **6c** is already a catalyst that can be competitive in synthesis of practically useful polyolefins, and that the family of sulfur-bridged bis(2-indenyl) metallocenes studied herein deserves further efforts aimed at improvement of the performance in synthesis of poly(α-olefins), in the first place, *via* tuning of the distant 5,6-substituents. Easy synthesis of the bridged ligand from readily available precursors is another benefit of this family.

Table 3 Polymerization of 1-decene.[a]

Metallocene precatalyst	T_p/°C[b]	Activity[c,d]	Content of unsaturated chain ends of different types (mol%)[e]				M_n/kDa[d]
			vinyl	vinylene	trisubstituted vinylene	vinylidene	
6a	60	1.28	0.7	7.3	4.1	87.9	0.63
6b	60	0.43	2.0	4.5	22.2	71.3	1.97
6c	60	4.4	0.3	4.3	1.9	93.6	0.54
8	60	9.1	9	23	27	41.0	0.37
6c	85	9.0	0.2	3.0	2.6	94.2	0.45
8	85	4.0	9	21	25	44.0	0.36
6c	110	4.3	0.3	3.1	3.0	93.6	0.44
8	110	1.19	8	20	24	48.0	0.34

[a] Reaction conditions: metallocene (0.080 μmol) prealkylated with Bu^i_3Al (20 equiv.), activator AB ($PhNHMe_2^+[B(C_6F_5)_4]^-$, 1.1 equiv.), 1-decene (2 ml), isohexane (2.8 ml), toluene (0.2 ml), scavenger Oct_3Al (0.2 or 0.6 μmol), 60 min. [b] Polymerization temperature. [c] In $\text{kg}_{\text{polymer}}\ \text{mmol}^{-1}_{\text{cat}}\ \text{h}^{-1}$. [d] Mean values for two runs. [e] Measured by ^{1}H NMR.

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2024.10.015.

References

1 W. Kaminsky, K. Külper, H. H. Brintzinger and F. R. W. P. Wild, *Angew. Chem., Int. Ed.*, 1985, **24**, 507; https://doi.org/10.1002/anie.198505071.

2 W. Spaleck, F. Kueber, A. Winter, J. Rohrmann, B. Bachmann, M. Antberg, V. Dolle and E. F. Paulus, *Organometallics*, 1994, **13**, 954; https://doi.org/10.1021/om00015a032.

3 C. Ehm, A. Vittoria, G. P. Goryunov, P. S. Kulyabin, P. H. M. Budzelaar, A. Z. Voskoboynikov, V. Busico, D. V. Uborsky and R. Cipullo, *Macromolecules*, 2018, **51**, 8073; https://doi.org/10.1021/acs.macromol.8b01546.

4 J. A. Ewen, R. L. Jones, A. Razavi and J. D. Ferrara, *J. Am. Chem. Soc.*, 1988, **110**, 6255; https://doi.org/10.1021/ja00226a056.

5 A. Zambelli, A. Grassi, M. Galimberti, R. Mazzocchi and F. Piemontesi, *Makromol. Chem., Rapid Commun.*, 1991, **12**, 523; https://doi.org/10.1002/marc.1991.030120811.

6 C. Ehm, A. Vittoria, G. P. Goryunov, V. V. Izmer, D. S. Kononovich, O. V. Samsonov, P. H. M. Budzelaar, A. Z. Voskoboynikov, V. Busico, D. V. Uborsky and R. Cipullo, *Dalton Trans.*, 2020, **49**, 10162; https://doi.org/10.1039/D0DT01967D.

7 D. V. Uborsky, D. Y. Mladentsev, B. A. Guzeev, I. S. Borisov, A. Vittoria, C. Ehm, R. Cipullo, C. Hendriksen, N. Friederichs, V. Busico and A. Z. Voskoboynikov, *Dalton Trans.*, 2020, **49**, 3015; https://doi.org/10.1039/C9DT04896K.

8 S. E. Reybuck and R. M. Waymouth, *Macromolecules*, 2004, **37**, 2342; https://doi.org/10.1021/ma035365t.

9 J. G. M. Morton, H. Al-Shammari, Y. Sun, J. Zhu and D. W. Stephan, *Dalton Trans.*, 2014, **43**, 13219; https://doi.org/10.1039/C4DT01583E.

10 H. Al-Shammari, Y. Sun, D. Stephan, S. Al Hubish and Z. H. U. Jiangtao, *Patent WO 2016037960*, 2016.

11 D. N. Kazul'kin, A. N. Ryabov, V. V. Izmer, A. V. Churakov, I. P. Beletskaya, C. J. Burns and A. Z. Voskoboynikov, *Organometallics*, 2005, **24**, 3024; https://doi.org/10.1021/om050236h.

12 L. Resconi, I. Camurati, C. Fiori, D. Balboni, P. Mercandelli and A. Sironi, *Helv. Chim. Acta*, 2006, **89**, 1497; https://doi.org/10.1002/hlca.200690154.

13 S. Vadake Kulangara, H. N. Friederichs, A. Ginzburg, A. Voskoboynikov, V. Izmer, D. Kononovich, O. Samsonov, A. Vittoria, V. Busico, R. Cipullo, N. Ghavale, N. Nandurkar, I. Borisov, B. Guzeev and D. Uborsky, *Patent WO2017118617*, 2017.

14 J. A. M. van Beek, J. G. de Vries, H. J. Arts, R. Persad and H. G. van Doremaele, *Patent WO1994011406*, 1994.

15 D. Landini and F. Rolla, *Synthesis*, 1974, **8**, 565; https://doi.org/10.1055/s-1974-23371.

16 R. L. Halterman, D. R. Fahey, E. F. Bailly, D. W. Dockter, O. Stenzel, J. L. Shipman, M. A. Khan, S. Dechert and H. Schumann, *Organometallics*, 2000, **19**, 5464; https://doi.org/10.1021/om000551y.

17 D. N. Islamov, T. V. Tyumkina and L. V. Parfenova, *Mendeleev Commun.*, 2023, **33**, 657; https://doi.org/10.1016/j.mencom.2023.09.022.

18 I. S. Borisov, D. Yu. Mladentsev, B. A. Guzeev, G. P. Goryunov, D. V. Uborsky, A. Vittoria, R. Cipullo, V. Busico, N. Friederichs and A. Z. Voskoboynikov, *Mendeleev Commun.*, 2020, **30**, 449; https://doi.org/10.1016/j.mencom.2020.07.014.

19 P. V. Kovyazin, O. V. Mukhamadeeva and L. V. Parfenova, *Mendeleev Commun.*, 2024, **34**, 61; https://doi.org/10.1016/j.mencom.2024.01.018.

20 Y. V. Kissin and F. C. Schwab, *J. Appl. Polym. Sci.*, 2009, **111**, 273; https://doi.org/0.1002/app.29030.

21 A. Toyota, T. Tsutsui and N. Kashiwa, *Polym. Bull.*, 2002, **48**, 213; https://doi.org/10.1007/s00289-002-0033-z.

22 A. O. Patil, M. M.-S. Wu, S. Zushma and A. A. Patil, *Patent US 8969272*, 2015.

23 M. K. Ng, D. T. Ferrughelli, H. Cheng, E. Ulysse, D. J. Crowther, A. E. Lemon, Jr. and P. Brant, *Patent US 9657116, B2*, 2017.

24 O. A. Patil, S. Luo and S. Bodige, *Patent US 9458403*, 2014.

25 I. E. Nifant'ev, A. A. Vinogradov, A. A. Vinogradov, V. V. Bagrov, A. V. Kiselev, M. E. Minyaev, T. I. Samurganova and P. V. Ivchenko, *Ind. Eng. Chem. Res.*, 2023, **62**, 6347; https://doi.org/10.1021/acs.iecr.3c00755.

Received: 26th April 2024; Com. 24/7481