Application of the copper(II)-aminosilane catalysts in the oxidative polymerization of 2,6-dimethylphenol

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Abstract: The aim of this work was to examine the aminosilane ligands for the copper(II) salts and their application as catalysts for the oxidative polymerization of 2,6-dimethylphenol leading to poly(2,6-dimethyl-1,4-phenylene ether) (PPE) [also known as poly(phenylene oxide) (PPO)] formation. As aminosilane ligands, silane derivatives containing primary and/or secondary amino groups were tested. Among aminosilanes used, PPE was only obtained when *N*-methylaminopropyltrimetoxysilane (MAPTMS) as a ligand for copper(II) was used. $CuCl_2$ and $CuBr_2$ were compared as catalyst precursors for 2,6-dimethylphenol polymerization and influence of N/Cu molar ratio in the range from 80 to 160 on PPE yield and its $\overline{M}_w$ was tested. It was observed, that with increasing N/Cu molar ratio from 80 to 120, both PPE yield and $\overline{M}_w$ increased. PPE with the highest $\overline{M}_w$ was obtained when $CuBr_2$-MAPTMS as a catalyst was used. At N/Cu molar ratio equal to 160, a decrease in PPE $\overline{M}_w$ obtained with use of both precursors and decrease in PPE yield for $CuCl_2$-MAPTMS catalyst were noticed. The condensed nanoorganosilicon particles of spherical shape well dispersed in PPE were determined in the polymer matrix. The UV-Vis studies showed that, strong ligand field of the aminosilane ligand easier electron transfer from monomer to Cu(II) and thus polymerization facilitate.

Keywords: poly(phenylene oxide), poly(2,6-dimethyl-1,4-phenylene ether), oxidative polymerization, 2,6-dimethylphenol, aminosilane.

Zastosowanie kompleksów Cu(II)-aminosilan jako katalizatorów polimeryzacji utleniającej 2,6-dimetylofenolu

Streszczenie: Silany zawierające pierwszorzędową lub/i drugorzędową grupę aminową zastosowano w charakterze ligandów w kompleksach soli miedzi(II), które następnie użyto w polimeryzacji utleniającej 2,6-dimetylofenolu (2,6-DMP), w wyniku której otrzymano poli(eter 2,6-dimetylo-1,4-fenylenu) (PPE) znany też jako poli(tlenek fenylenu) (PPO). Spośród przebadanych aminosilanów, jedynie *N*-metyloaminopropylotrimetoksysilan (MAPTMS) — jako ligand Cu(II) — wykazywał aktywność w reakcji syntezy PPE. Porównano aktywność $CuCl_2$ i $CuBr_2$ jako prekursorów katalizatora polimeryzacji 2,6-dimetylofenolu i zbadano wpływ stosunku molowego N/Cu, w zakresie 80—160, na wydajność reakcji otrzymywania PPE i na jego wagowo średni ciężar cząsteczkowy ($\overline{M}_w$). Stwierdzono, że zwiększenie stosunku molowego N/Cu w zakresie 80—120 powoduje zarówno wzrost wydajności polimeryzacji utleniającej 2,6-DMP, jak i ciężaru cząsteczkowego PPE. Polimer o największym $\overline{M}_w$ otrzymano przy użyciu katalizatora $CuBr_2$-MAPTMS. Przy stosunku molowym N/Cu = 160 zaobserwowano spadek ciężaru cząsteczkowego PPE uzyskanego za pomocą obydwu prekursorów oraz, w przypadku zastosowania $CuCl_2$-MAPTMS jako katalizatora, zmniejszenie wydajności polimeryzacji utleniającej. Ponadto, stwierdzono obecność zdyspergowanych w osnowie PPE krzemoorganicznych nanocząstek o sferycznym kształcie. Badania UV-Vis wykazały, że do inicjacji polimeryzacji 2,6-DMP konieczne jest silne, wywoływane przez aminosilan, pole ligandów, które ułatwia przeniesienie elektronu z monomeru do Cu(II).

Słowa kluczowe: poli(tlenek fenylenu), poli(eter 2,6-dimetylo-1,4-fenylenu), polimeryzacja utleniająca, 2,6-dimetylofenol, aminosilany.

Poly(2,6-dimethyl-1,4-phenylene ether) (PPE) or poly(phenylene oxide) (PPO) is an engineering polymer showing many required properties, such as high strength, dimensional stability, good resistance to moisture. It also shows high glass transition temperature and high melt viscosity, which limits its application. That is why PPE is widely blended with other thermoplastics, especially with polystyrene and polyamide [1].

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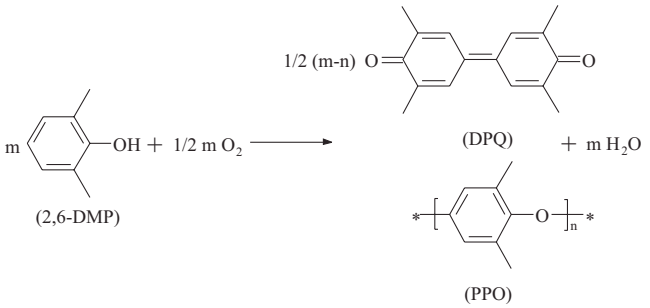
Poly(phenylene oxide) was firstly obtained by Allan Hay and co-workers by the oxidative coupling of 2,6-dimethylphenol. In the oxidative polymerization of 2,6-dimethylphenol not only PPE but also water and undesired 3,3′,5,5′-tetramethyldiphenoquinone (DPQ) are formed (Scheme A) [2]. Reaction is catalyzed by copper — amine complex. Different amines are used as ligands for copper, for example pyridine [2, 3], 2-methylpyridine, 2,6-dimethylpyridine, piperidine [4], morpholine [3, 5],



Scheme A

n-butylamine, *n*-hexylamine, dibutylamine, *N*,*N*-dimethyl-*n*-butylamine [6], imidazole derivatives [3, 7, 8], 2,2′-dipyridylamine [9], triethylenediamine [10], *N*,*N*′-dibutylethylenediamine [3], *N*,*N*,*N*′,*N*′-tetramethylethylenediamine [11, 12] *etc*.

The main important factors influencing copper–amine catalyst activity in the oxidative polymerization of 2,6-dimethylphenol are basicity and the structure of the used amine ligands. Copper complexes with more basic amines are more reactive in PPE synthesis than with amines characterized by lower basicity. It was also noticed that copper complexes based on chelating amines are more active than complexes with monodentate ones. Moreover, *N*-alkyl substituents within chelating amine molecule increase its activity in PPE formation through preventing water coordination to the copper ion which results in complex deactivation [13, 14].

The aim of this work was to use silane derivatives containing amino groups as the ligands in the oxidative polymerization of 2,6-dimethylphenol leading to poly(phenylene oxide) preparation. Aminosilanes containing hydrolysis susceptible alkoxy groups (-OR) bond water molecules and thus may enhance the polymerization process. Moreover, the main reason for conducting presented research was to select potentially active aminosilanes, which after grafting on the silica surface may be applied as a re-using catalyst. The presented paper merely shows the early stage of the mentioned above research allowing to recognize potentially active aminosilanes in the PPE preparation process and also the best conditions of theirs effective work. Additionally, there is no information in the available literature concerning aminosilane application as a ligand in the copper catalyst for 2,6-dimethylphenol polymerization.

EXPERIMENTAL PART

Materials

The monomer 2,6-dimethylphenol (DMP) (Sigma Aldrich, purity > 99 %,), copper(II) bromide (Sigma Aldrich, purity 99 %), copper(II) chloride (ACROS ORGANICS, purity 99 %), 3-aminopropyltriethoxysilane (APTES) (ABCR, purity 98 %), *N*-methylaminopropyltrimethoxysilane (MAPTMS) (ABCR, purity 97 %), *N*-phenylaminopropyltrimethoxysilane (PhAPTMS) (ABCR, purity 95 %), *N*-2-aminoethyl-3-aminopropyltrimethoxysilane (AEAPTMS) (Unisil Sp. z o.o., distilated) and 3-(trimethoxysilylpropyl) diethylenetriamine (TMSPDETA) (ABCR, purity 95 %), methanol (Avantor Performance Materials, purity 99.8 %), acetic acid (Avantor Performance Materials, purity 99.5—99.9 %) and chloroform (Avantor Performance Materials, purity 98.5 %) were used as received. Toluene (Chempur, purity 99.5 %) and ethanol (Vevex, purity 99.8 %) were dried on molecular sieves (3A) prior to use.

Synthesis of poly(phenylene oxide)

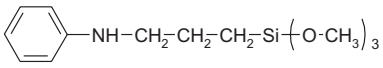
The process of oxidative polymerization of 2,6-dimethylphenol to poly(2,6-dimethyl-1,4-phenylene oxide) was carried out at temp. 25 °C in the atmosphere of oxygen. Reaction was proceeded as follows: the solution containing 2,6-dimethylphenol in 70 cm^3 of toluene was dosed during 90 min to a stirred mixture of the catalytic system based on copper(II) salt and aminosilane in 70 cm^3 of toluene.

Then the reaction was proceeded for 4—10 h and stopped by addition of 10 cm^3 of acetic acid and 300 cm^3 of deionized water. After 24 h an organic phase was separated and the PPE was precipitated with 400 cm^3 of ethanol. At this stage of the process, after Si-OR bond hydrolysis and condensation reaction, aminosilane ligand transformation toward organosilicon gel was observed. Then products were filtered, washed and dried. After drying the Si content was estimated. PPE containing condensed organosilicon particles may be used in the polymer processing but for analytical purpose PPE has to be purified. Therefore polymer was dissolved in chloroform, organosilicon compound as a solid residues was filtered off, then from eluent polymer was re-precipitated in ethanol, filtered, washed by ethanol and dried.

To increase solubility and stability of the catalytic system in the reaction medium, the excess of aminosilane [15] (prevents ligand dissociation and metal-metal clusters formation [16]) or polar solvent (methanol) or mixture of non-polar with polar solvent (toluene-methanol) instead of non-polar toluene was used.

In the reactions the constant amount of 2,6-dimethylphenol (4.86 g, 0.04 mol) and copper(II) bromide (0.178 g, 0.0008 mol) or copper(II) chloride (0.107 g, 0.0008 mol) were used. The molar ratio of the monomer to copper was

T a b l e 1. Catalytic activity of $CuBr_2$-aminosilane catalyst in the oxidative polymerization of 2,6-DMP

Run	Aminosilane				N/Cu molar ratio	Solvent	Reaction time, h	SiO_2/Si wt %	PPE g	Yield of PPE, %
	Name	Structure	g	mol						
1	APTES	$H_2N-CH_2-CH_2-CH_2-Si(O-C_2H_5)_3$	22.86	0.103	130	toluene	4	-	-	-
2							10	-	-	-
3	AEAPTMS	$H_2N-CH_2-CH_2-NH-CH_2-CH_2-CH_2-Si(O-CH_3)_3$	22.13	0.099	250	toluene	12	-	-	-
4			10.92	0.049	123	methanol	4	-	-	-
5	TMSPDETA	$H_2N-CH_2-CH_2-NH-CH_2-CH_2-NH-CH_2-CH_2-CH_2-Si(O-CH_3)_3$	5.64	0.021	80	toluene	10	-	-	-
6						toluene--methanol--1v/4v	10	-	-	-
7	MAPTMS	$H_3C-NH-CH_2-CH_2-CH_2-Si(O-CH_3)_3$	12.32	0.064	80	toluene	4	2.0/0.95	3.44	70.76
8	PhAPTMS		16.28	0.064	80	toluene	10	-	-	-
9			32.56	0.127	160	toluene	10	-	-	-
10			16.28	0.064	80	methanol	4	-	-	-

50:1. Types of aminosilanes used and molar ratios of aminosilane to copper are presented in the Table 1.

Methods of testing

— The weight average molecular weight ($\overline{M}_w$) of poly(phenylene oxide) was measured by gel permeation chromatography (GPC) using an apparatus of Lab-Alliance. The apparatus was equipped with a refractometric detector and a Jordi Gel DVB Mixed Bed (250 mm × 10 mm) column. The polystyrene was used as a standard calibration sample.

— Silicon content in the PPE was determined by gravimetric method after dry sample mineralization in the temperature up to 500 °C with a small addition of sulfuric acid.

— Microscopic studies were performed using a scanning electron microscope (SEM) type JSM 6490 LV (JEOL).

— The UV-Vis spectroscopy was carried out by Jasco V-630 Spectrophotometer. Experiments were performed in anhydrous ethanol with the constant complex concentration $8.61 \cdot 10^{-5}$ mol.

RESULTS AND DISCUSSION

Application of the copper(II)-aminosilane in the PPE preparation

The literature review related to copper catalyst with mono- and diamines ligands, active in the 2,6-DMP polymerization, silanes functionalized by primary and/or secondary mono-, di- and tri- amines as Cu(II) ligands, were selected and their potential application in PPE synthesis was investigated. Therefore, in the presented paper a new catalytic systems based on copper(II) bromide and various aminosilanes (Table 1) for the oxidative polymerization of 2,6-dimethylphenol toward poly(phenylene oxide) were tested.

It was observed that the $CuBr_2$ — APTES catalyst was inactive in the C-O oxidative coupling of 2,6-DMP units (Run 1, Run 2).

It was assumed that the copper catalytic system with chelating amines *i.e.* AEAPTMS or TMSPDETA — containing primary and secondary amino groups, should show similar or even higher activity than a standard chelating diamine, for example *N*,*N*′-dibutylethylenediamine widely used in the poly(phenylene oxide) synthesis. It is interesting, that both initiating polymerization systems *i.e.* $CuBr_2$ — AEAPTMS (Run 3 and 4) and $CuBr_2$ — TMSPDETA (Run 5 and 6) were also found inactive, even when the huge excess of the aminosilane to copper was used and reaction was carried out for 12 h (N/Cu = 250; Run 3) or polar solvent was used (Run 4). Application in the 2,6-DMP polymerization $CuBr_2$ — MAPTMS catalyst based on aminosilane ligand containing secondary amino group (*N*-methylaminopropyltrimethoxysilane) allowed to obtain poly(phenylene oxide) with 70.76 % yield (Run 7). Replacing an electro donating *N*-alkyl group by electron withdrawing *N*-phenyl group within aminosilane ligand and using $CuBr_2$ — PhAPTMS catalysts (Runs 8—10) did not let obtain polymer.

Effect of copper(II) precursors and N/Cu molar ratio on PPE preparation

In the Table 2, comparison of the catalytic activity of copper(II) catalyst precursors *i.e.* copper(II) bromide and copper(II) chloride as well as an influence of the aminosilane amount on PPE formation and its properties were presented. Copper(II) bromide precursor showed similar activity in the 2,6-dimethylphenol polymerization to copper(II) chloride one.

The molar ratio N/Cu influences the PPE formation. At the molar ratio N/Cu = 80 both precursors showed similar activity (*ca.* 70.59 % of PPE). With increasing N/Cu molar ratio to 124, an increase in the polymer yield

T a bl e 2. Effect of the copper(II) salt and N/Cu molar ratio on the yield and poly(phenylene oxide) properties

Run	Catalyst	N/Cu molar ratio	SiO_2/Si, wt %	PPE, g	Yield of PPE, %	$\overline{M}_w \cdot 10^{-4}$	$\overline{M}_n \cdot 10^{-4}$	Đ
7	$CuBr_2$-MAPTMS	80	2.0/0.95	3.44	70.76	1.03	0.385	2.67
11	$CuBr_2$-MAPTMS	124	2.7/1.25	3.59	73.86	4.94	1.18	4.19
12	$CuBr_2$-MAPTMS	160	4.95/2.3	3.63	74.66	3.98	1.01	3.94
13	$CuCl_2$-MAPTMS	80	2.9/1.35	3.42	70.42	1.07	0.391	2.74
14	$CuCl_2$-MAPTMS	124	1.7/0.8	3.58	73.63	1.24	0.437	2.84
15	$CuCl_2$-MAPTMS	160	7.5/3.5	2.97	61.20	0.72	0.293	2.46

Reaction time after monomer dosing: 4 h.

to *ca*. 73.75 % was noticed but difference in the PPE yield between $CuBr_2$-MAPTMS and $CuCl_2$-MAPTMS catalysts was extremely small (0.23 % of PPE).

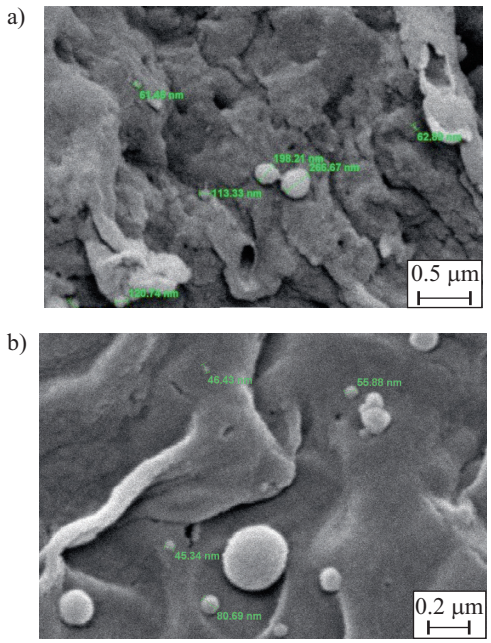


Fig. 1. SEM images of poly(phenylene oxide) containing condensed organosilicon residue particles (Run 11): a) magnification ×30 000, b) magnification ×60 000

However copper(II) bromide precursor let obtain PPE with $\overline{M}_w = 4.94 \cdot 10^4$ (Run 11) while polymer prepared with use of copper(II) chloride — MAPTMS catalyst showed $\overline{M}_w = 1.24 \cdot 10^4$ (Run 14).

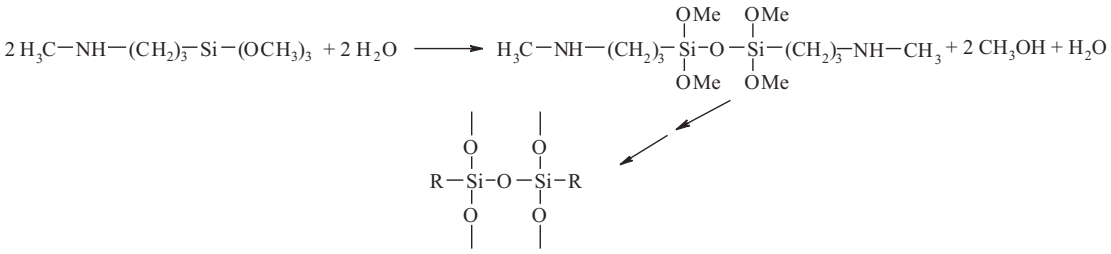
With increasing N/Cu molar ratio up to 160 an increase in PPE yield up to 74.66 for $CuBr_2$-MAPTMS catalyst was observed (Run 12), whereas for $CuCl_2$-MAPTMS a decrease in the polymer yield was noticed (61.20 of PPE, Run 15).

As it can be seen from Table 2, for both catalytic systems with increasing molecular weight also an increase in the polydispersity index was noticed.

In standard 2,6-DMP oxidative polymerization, DPQ and water as by-products are formed (Scheme A). But when aminosilane ligands were used, silicon contamination in the prepared PPE is present. With increasing aminosilane amount in the reaction mixture, increase in the silicon content in the PPE was observed. For example, at N/Cu = 80, 0.95 wt % of Si (Run 7) was determined, whilst at N/Cu = 160, 2.3 wt % of Si (Run 12) was estimated. Silicon residues comes from used aminosilane ligand, which undergoes side-reactions *i.e*. Si-OR bond hydrolysis and condensation reaction (Scheme B), during 2,6-dimethylphenol polymerization and PPE washing by water-acetic acid (acetic acid acts as a catalyst for hydrolysis and condensation reaction of aminosilane alkoxy groups) mixture. As can be seen from Fig. 1, this procedure forms nano condensed organosilicon particles of spherical shape well dispersed in the PPE matrix. Such nanoorganosilicon particles may play a role as polymer additive.

UV-Vis spectroscopic studies

In the Fig. 2 UV-Vis spectrum of the complexes in the range from 600 to 1100 nm is presented. Aminosilane and anhydrous ethanol UV-Vis spectrum was omitted. For the copper(II) bromide in ethanolic solution an absorption maximum appeared at 914 nm [17], as a result of the low-energy electron transfer within d subshell — characteristic for Cu(II) square planar complex structure [16]. Addition of MAPTMS ligand to the $CuBr_2$ solution



Scheme B

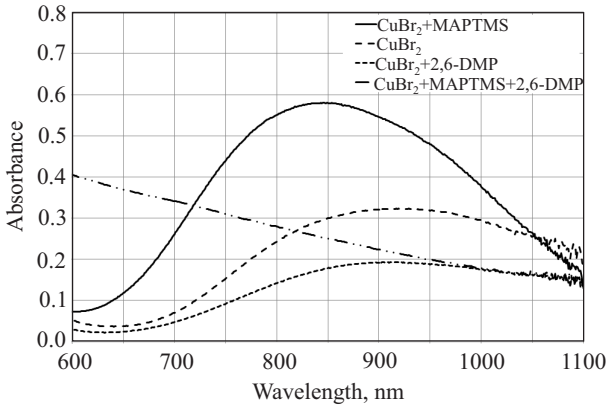


Fig. 2. UV-Vis spectrum of the $CuBr_2$ complexes

caused splitting of the Cu^{+2} d orbitals and shifting of the absorption maximum to 850 nm. This phenomena indicates that aminosilane ligand is coordinately bonded to the copper metallic center and is similar with the results presented in [17, 18]. For the copper(II) bromide — MAPTMS — 2,6-DMP system the band at 850 nm disappeared as a result of the electron transfer from 2,6-DMP to Cu^{+2} and its reduction to diamagnetic Cu^{+1} [19]. Eventually, it may be concluded that for 2,6-DMP polymerization initiation a strong ligand field is a must.

CONCLUSIONS

Copper(II) complex with primary aminosilane showed no activity in the oxidative polymerization of 2,6-dimethylphenol. No polymer was also formed, when chelating aminosilanes containing primary and secondary amino groups were used. An monodentne aminosilane containing secondary amine group *i.e. N*-methylaminopropyltrimetoxysilane appeared to be an active ligand in the copper — aminosilane complex catalyst for poly(phenylene oxide) formation. Application an another secondary aminosilane containg *N*-phenyl substituent instead of *N*-alkyl one did not let obtain a polymer.

At N/Cu molar ratio equal to 80, copper(II) bromide pre-catalyst showed similar activity in the PPE preparation as a chloride one. Yield of the reaction was *ca*. 70.59 %, and $\overline{M}_w$ of PPE was *ca*. $1.05 \cdot 10^4$. For both precursors, with increasing N/Cu molar ratio from 80 to 124 the polymers with higher yield (*ca*. 73.75 %) and higher average molecular weights were obtained.

For catalyst based on copper(II) chloride the PPE $\overline{M}_w$ increased slightly to $1.24 \cdot 10^4$ whereas at use of $CuBr_2$--MAPTMS catalyst the polymer with the highest $\overline{M}_w$ ($4.94 \cdot 10^4$) was obtained.

At N/Cu molar ratio 160 a decrease in PPE $\overline{M}_w$ was observed for both pre-catalysts use. Unexpectedly for copper(II) chloride — MAPTMS catalyst also polymer yield decrease was noticed. With increasing molecular weight of PPE, increase of polydispersity index was observed.

After the ligand Si-OR bond hydrolysis and condensation reaction, nanoorganosilicon residual contaminations, well dispersed in the polymer matrix and of spherical shape, were determined.

It was also noted, that for initiation of 2,6-dimethylphenol polymerization toward PPE synthesis, Cu(II)-aminosilane complex is necessary.

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REFERENCES

[1] Utracki L.A.: „Polymer blends handbook", Vol. 1, Kluwer Academic Publishers, Dordrecht 2002, str. 1093.

[2] Hay A.S., Blanchard H.S., Endres G.F., Eustance J.W.: *Journal of the American Chemical Society* **1959**, *81*, 6335. http://dx.doi.org/10.1021/ja01532a062

[3] Kim N.Ch., Kim Y.T., Nam S.W. *et al.*: *Polymer Bulletin* **2013**, *70*, 23. http://dx.doi.org/10.1007/s00289-012-0816-9

[4] Tsuchida E., Nishide H., Nishiyama T.: *Macromolecular Chemistry and Physics* **1975**, *176*, 1349. http://dx.doi.org/10.1002/macp.1975.021760510

[5] *Pat. USA* 4 607 085 (1986).

[6] Li K.T., Shieh D.Ch.: *Industrial and Engineering Chemistry Research* **1994**, *33*, 1107. http://dx.doi.org/10.1021/ie00029a006

[7] Gamez P., Van Dijk J.A.P.P., Driessen W.L. *et al.*: *Advanced Synthesis and Catalysis* **2002**, *344*, 890. http://dx.doi.org/10.1002/1615-4169(200209)344:8<890::AID-ADSC890>3.0.CO;2-5

[8] Gamez P., Simons Ch., Aromì G. *et al.*: *Applied Catalysis A: General* **2001**, *214*, 187. http://dx.doi.org/10.1016/S0926-860X(01)00484-7

[9] Camus A., Garozzo M.S., Marsich N., Mari M.: *Journal of Molecular Catalysis A: Chemical* **1996**, *112*, 353. http://dx.doi.org/10.1016/1381-1169(96)00237-3

[10] *Pat. Pol.* 66 781 (1972).

[11] Al Andis N.M.: *Journal of Chemistry* **2013**, *2013*, ID 856928. http://dx.doi.org/10.1155/2013/856928

[12] Viersen F.J., Challa G., Reedijk J.: *Recueil des Travaux Chimiques des Pays-Bas* **1989**, *108*, 167. http://dx.doi.org/10.1002/recl.19891080502

[13] Kim M., Feng X., Kim Y.T., Kim J.I., Yun J.: *Macromolecular Research* **2013**, *21*, 1054. http://dx.doi.org/10.1007/s13233-013-1150-2

[14] Hay A.S.: *Journal of Polymer Science Part A: Polymer Chemistry* **1998**, *36*, 505. http://dx.doi.org/10.1002/(SICI)1099-0518(199803)36:4<505::AID-POLA1>3.0.CO;2-O

[15] Li K.T., Tsai I.T.: *Journal of Polymer Science Part A: Polymer Chemistry* **1996**, *34*, 3213. http://dx.doi.org/10.1002/(SICI)1099-0518(19961115)34:15<3213::AID-POLA11> 3.0.CO;2-F

[16] Cotton A.F., Wilkinson G.: „Advanced Inorganic Chemistry: A Comprehensive Text", 4th ed., John Wiley and Sons, New York, Chichester, Brisbane, Toronto 1980.

[17] Segoviano-Garfias J.J.N., Moreno-Esparza R., Mendoza-Diaz G.: *Inorganica Chimica Acta* **2010**, *363*, 3461. http://dx.doi.org/10.1016/j.ica.2010.06.050

[18] Chen Ch.W., Lin I.H., Lin Ch.Ch. *et al.*: *Polymer* **2013**, *54*, 5684. http://dx.doi.org/10.1016/j.polymer.2013.08.023

[19] Tsuchida E., Nishide H., Nishikawa H.: *Journal of Polymer Science: Polymer Symposia* **1974**, *47*, 47. http://dx.doi.org/10.1002/polc.5070470108

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