

Effect of Fe₃O₄ particles on multi-hollow morphology of poly(HEMA-divinylbenzene-styrene) microspheres prepared by Pickering suspension polymerization

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Abstract. Hydroxy-functionalized polymers have been synthesized by Pickering suspension polymerization of 2-hydroxyethyl methacrylate (HEMA) with styrene (S) and divinylbenzene (DVB) in the presence of hydrophobic Fe₃O₄ particles. The obtained polymer microspheres were characterized using different instrumental techniques (optical microscopy, scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR), diffuse reflection ultraviolet-visible spectroscopy (DR UV-Vis), inductively coupled plasma-optical emission spectrometry (ICP-OES), dynamic light scattering and thermal analyses) and then modified to immobilize the complexes of palladium(II) with the tetradentate ligands based on salicylaldehyde, epichlorohydrin and 2-picolyamine. The resulting polymer supported complexes were preliminarily examined as catalysts in the model Suzuki reaction between 4-bromotoluene and phenylboronic acid. It was found the polymer particles obtained as a result of the performed polymerization have composite nature and are characterized by a unique multi-hollow morphology with pores up to 50 μm in size. An advantageous effect of the Fe₃O₄ particles embedded in the synthesized polymer microspheres on the activity of palladium catalysts has been noted.

Keywords: polymer composites, magnetite particles, Pickering suspension polymerization, multi-hollow morphology, palladium catalysts

1. Introduction

In recent years, various functionalized hybrid particles have attracted the attention of researchers [1–5]. Such materials are, for instance, in the center of an interest of medicine (e.g. drug delivery systems and medical diagnostics) [6, 7] and electronics [8], on the one hand. They are also applied as reactive sorbents [9] and supports for catalysts [10, 11], on the other hand.

Heterogeneous polymerization techniques, such as emulsion, precipitation, dispersion or suspension polymerizations have been useful for the synthesis of hybrid (composite) particles. Depending on the

methods applied, the particles characterized by different sizes, size distribution and morphology were synthesized, e.g. nano- and/or micro-sized particles, monodisperse or polydisperse, core-shell, hollow or multi-hollow ones [12]. To obtain the polymer particles with a complex morphology, different combined polymerization techniques, for instance, seed suspension polymerization [13], membrane emulsification [14] and microfluidics techniques [15, 16] were also developed.

Magnetite particles, due to their relatively simple methods of preparation and unique magnetic properties, seem to be particularly attractive materials for

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the synthesis of hybrid polymer particles [17, 18]. The nano- and microparticles of magnetite can be obtained, e.g. just by precipitating Fe(II) and Fe(III) ions from water solutions with ammonia [19]. The magnetite particles are stabilized by adding different additives to reaction mixtures, e.g. surfactants (oleic acid, alkane sulfonic acids), polymers (polyethylene glycol, polyvinylpyrrolidone) or natural dispersants (chitosan, starch) [20]. Microemulsion, sol-gel and thermal methods are preferred for preparing the monodisperse magnetite nanoparticles [21–24]. The hybrid particles based on magnetite have turned out to be very interesting from the point of view of their applications as supports for catalysts [25–30]. Magnetic nanoparticles are characterized by a large surface-to-volume ratios in relation to bulk materials, thus, they offer an attractive alternative to conventional catalyst supports [26]. Furthermore, the magnetic properties provided by magnetite particles often make the separation and recyclability of resulting catalysts much easier. The catalysts based on magnetic particles were efficient in many chemical transformations catalyzed by transition metals, for instance, in the reactions of oxidation [31, 32] and epoxidation [33, 34], hydrogenation [35, 36] and hydroformylation [37, 38], and also in olefin metathesis [26, 39] and carbon-carbon coupling [40–43] reactions. Magnetically separable organocatalysts were also prepared based on the particles of magnetite [25, 30]. Herein, a novel, simple possibility of preparing the polymer microparticles with a unique morphology based on the mixtures of 2-hydroxyethyl methacrylate, styrene and divinylbenzene has been described. The gel type hydroxy functionalized polymer microparticles obtained by the suspension polymerization of the same monomers previously [44] turned out to be easily modifiable materials. In consequence, they were applied successfully for the preparation of various heterogeneous catalysts based on transition metal ions, e.g. palladium catalysts for C=C [45] and C≡C [46] bonds hydrogenation substituted olefin epoxidation [47] and cobalt catalysts for epoxide ring opening reactions [48, 49]. Thus, developing our studies on the reactive polymers, it seemed to be interesting to modify the morphology of polymer beads, e.g. by the addition of hydrophobic Fe₃O₄ particles to the monomers, particularly in the view of their potential application as supports for palladium catalysts. It turned out that the hydroxy functionalized polymer microspheres obtained under Pickering suspension

polymerization conditions were characterized by a multi-hollow morphology and composite nature. Furthermore, they seem to be attractive as supports for palladium catalysts, as was shown by conducting of preliminary catalytic studies in model Suzuki reactions between 4-bromoanisole and phenyl boronic acid.

2. Experimental

2.1. Materials

Chemicals used in this work were commercially available from Aldrich, Merck, Fluka or POCH and used as received, unless otherwise stated. Styrene (S, >99%, Fluka) and divinylbenzene (DVB, 80% Aldrich) were purified from inhibitors by extraction with the aqueous solution of 5% NaOH and 20% NaCl before their use. 2-Hydroxyethyl methacrylate (HEMA, Aldrich, Germany) was purified from an inhibitor using the distillation under reduced pressure.

2.2. Characterization

FTIR spectra were recorded using a Thermo Scientific Nicolet 8700 spectrometer (as KBr pellets) or a FTIR Nicolet iN10MX microscope equipped with a micro-compression diamond cell. Samples for the analyses performed using FTIR microscopy were prepared by flattening several polymer beads between a pair of diamond windows of the micro-compression cell.

Diffuse reflectance UV–Vis–NIR spectra were recorded in solid state using a Jasco V-670 spectrophotometer equipped with a Jasco ISN-723 UV–Vis NIR 60 mm integrating sphere and BaSO₄ as a standard.

¹H–NMR spectra were recorded in chloroform-*d* using a 500 MHz Bruker Avance spectrometer.

TGA analysis was performed using a METTLER TOLEDO TGA/DSC 1 analyzer (Switzerland). Samples were heated from 25 to 600 °C (10 °C/min) in nitrogen atmosphere (50 mL N₂/min).

Particle size distribution and average particle diameters were analysed by dynamic light scattering (DLS) techniques using Zetasizer Nano ZS and Mastersizer 2000E instruments from Malvern Instruments Ltd (UK). The latter was equipped with a wet sample dispersion unit Hydro MU. The DLS measurements of micro-sized particles were performed using isopropyl alcohol as a dispersive medium. The samples of examined particles were sonicated for 15 minutes before each measurement.

Particle morphology was studied using a SMZ-143 stereomicroscope (Motic, South Korea) equipped with a digital camera (NIKON Colpix 4500, Japan) and scanning electron microscopes (VEGA3 TESCAN, USA, or HITACHI S-3400 N, Japan) equipped with an X-ray energy dispersive (EDS) system.

ICP OES analyses were performed at $\lambda = 217.809$ and 240.488 nm (Fe), and 340458 and 324270 nm (Pd) using a Horiba Jobin Yvon Optima 2 ICP-OES spectrometer (France). Samples of polymer particles (~5–10 mg) were mineralized in nitric acid (69 wt%, 5.0 mL) using a Plazmatronika Uni Claver II microwave mineralizer (Poland).

GC analyses were performed using an Agilent 7890 GC chromatograph with a split-splitless injector, a flame ionization detector, an auto-sampler and a HP-5 capillary column. Analytical solutions were prepared by dissolving 10 mg samples taken from the reaction mixtures in 0.5 mL tetrahydrofurane (THF). Nonane was used as a standard.

2.3. Synthesis of hydroxy-functionalized polymer composite microparticles

The dispersion of hydrophobic Fe_3O_4 particles in toluene has been prepared using a procedure similar to that described in Ref. [50]. To form Fe_3O_4 particles, the solution of ammonia (25 mL, 28 wt%) was added dropwise to the solution of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (1.39 g, 0.007 mol) and $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (3.78 g, 0.014 mol) in 100 mL deionized water at room temperature under argon atmosphere, vigorously stirring the reaction mixture. The resulting dispersion was next heated to 80°C and then oleic acid (OA, 1 mL) was added to modify the surface of Fe_3O_4 particles. The mixing was

continued at 80°C for 1 hour. Upon allowing the reaction mixture to reach ambient temperature, the mixture was extracted twice with toluene (2×50 mL) to transfer the provided hydrophobic Fe_3O_4 particles from water to toluene. The resulting dispersion of Fe_3O_4 in toluene was dried by azeotropic distillation using a Dean-Stark apparatus, and then it was diluted with dry toluene to obtain the final concentration of 0.01 g $\text{Fe}_3\text{O}_4/\text{mL}$. The dispersion was then applied for the synthesis of polymer particles by Pickering suspension polymerization.

The appropriate amounts of monomers (2-hydroxyethyl methacrylate, styrene and divinylbenzene), an initiator (benzoyl peroxide) and the dispersion of Fe_3O_4 in toluene were mixed, diluted with toluene and then sonicated using an ultrasonic bath for 15 minutes. The organic phase prepared in this manner was next dispersed in the water solution of poly(vinyl alcohol) (1% PVA, 18-88, Fluka) with the rate of around 1 mL/min. A 100 mL cylindrical glass reactor equipped with a heating coat, a mechanical stirrer, and a reflux condenser was used to perform the polymerization. The resulting dispersions were reacted under argon atmosphere at 70°C for 2 hrs and at 80°C for 6 hrs. The stirring rate was adjusted to 350 rpm. The particles obtained as a result were washed with an excess of water and transferred to a Soxhlet apparatus to extract monomer residuals and other impurities with acetone. The extraction has been carried out for at least 6 hrs. Finally, the particles were re-suspended in methanol, filtered off, and dried under reduced pressure at 40°C .

The conditions of polymerization experiments are presented in detail in Table 1.

Table 1. Polymerization conditions and characteristics of polymer composite particles.

Entry	Abbrev.	Organic phase			Polymer composite						
		Monomers [mol%]			Fe_3O_4 [wt%]	Average size [μm]	Diameter range [μm]	Fraction [%]	Fe content		
		HEMA	DVB	S					Cal. [wt%]	Deter. [wt%]	Embedded Fe_3O_4 [%]
1	1a	20	3	77	0.50	317	142–710	100	0.362	0.089	25
2	1b	20	10	70	0.50	313	142–710	100	0.362	0.064	18
3	1c	20	20	60	0.50	261	112–633	98	0.362	0.064	18
4	1d	20	40	40	0.50	362	159–796	92	0.362	0.063	17
5	1e	20	60	20	0.50	219	100–564	95	0.362	0.050	14
6	1f	20	3	77	0.25	373	200–796	100	0.181	0.089	25
7	1g	20	3	77	1.00	253	89–632	100	0.723	–	–
8	1h	20	3	77	–	150	75–250	62	–	–	–

Other parameters: initiator (BPO) – 1 wt%; water phase – 1 wt% PVA solution; monomers/toluene ratio – 1:1 (v:v).

2.4. Immobilization of Pd(II) tetradentate complex

The hydroxy functionalized polymer particles provided by Pickering suspension polymerization have been post-modified using a four-step procedure to immobilize the complex of palladium(II) with a ligand based on salicylaldehyde, epichlorohydrin and 2-picolyamine. In the first step, the hydroxy functionalized particles (1 g) were reacted for 24 hrs with glutaric anhydride (GA, 2.2 eq.) in the presence of 4-(dimethylamino)pyridine (DMAP, 2.1 eq.) to obtain carboxy functionalized particles. The method described previously was applied [49]. The modification was conducted in the medium of methylene chloride at room temperature. In the second step, the particles bearing glutarate moieties (1 g) were placed in a 50 mL PP syringe with a cotton filter, a Luer valve, and a rubber septum with a needle, and swelled with methylene chloride (10 mL). Separately, *N,N'*-dicyclohexylcarbodiimide (DCC, 2.1 eq. to COOH groups) was dissolved in 5 mL methylene chloride in a 10 mL vial. The resulting solution was then added to the swollen particles. The syringe was sealed with the septum and the mixture was shaken at ambient temperature for 2 hrs using a vibratory-rotatory shaker. After that time, DMAP (0.5 eq.) in 2 mL methylene chloride was added to the reaction mixture and the shaking was continued for 15 min. Finally, 2,2'-[(2-hydroxypropane-1,3-diyl)bis(oxy)]dibenzaldehyde (SAEPI, 2 eq. to COOH groups) dissolved in the methylene chloride (10 mL) was added to the mixture. SAEPI has been synthesized from salicylaldehyde (2 eq.) and epichlorohydrin (1 eq.) according to the procedure described previously [51]. The final reaction mixture was shaken at ambient temperature for 48 hrs. The modified particles were filtered off and washed with methylene chloride and 1:1 v/v methanol–methylene chloride mixture to remove excessive reagents and dried under reduced pressure at 40 °C.

The third step of particle modification has been performed in a glass reactor equipped with a heating coat connected to a thermostat. The particles bearing SAEPI moieties (0.5 g) were placed in the reactor and an excess of 2-picolyamine (10 eq. to CHO groups; dissolved in 5 ml toluene) was added. The reactor was purged with argon, sealed with a glass stopper and placed on a horizontal shaker. The reaction mixture was shaken at 70 °C for 24 hrs. Upon cooling the mixture to ambient temperature the modified particles

were transferred to a PP syringe equipped with a cotton filter, washed with the mixture of methanol and methylene chloride (1:1 v/v) and dried under reduced pressure at 40 °C.

Finally, the particles bearing imine-amine moieties (0.2 g) have been placed in a 5 mL vial and treated with the solution of palladium(II) acetate in THF (14 mg in 2 mL). The resulting mixture was shaken at ambient temperature for 24 hrs. The final particles were rinsed consecutively with water and THF and dried under reduced pressure at 40 °C.

2.5. Catalytic tests – general procedure

Phenyl boronic acid (1.1 mmol, 1.2 eq.) and 4-bromotoluene (0.9 mmol, 1.0 eq.) have been placed in a 10 mL vial equipped with a magnetic bar and a Teflon screw cap. The reactants were dissolved in isopropyl alcohol (4.5 mL). Next, KOH (1.08 mmol, 1.2 eq.) dissolved in water (4.5 mL) was added. Finally, the palladium(II) complex (0.5 mol% Pd in respect to 4-bromotoluene) was added to the reaction mixture. The reaction vial was then sealed and placed into a parallel synthesizer equipped with a hot plate and a cooled condenser (Carousel 12 Plus Reaction Station™). The reaction mixture has been gently stirred at 50 °C for 1–6 hrs. The progress of the coupling reaction was monitored using gas chromatography.

3. Results and discussion

3.1. Preparation of hydroxy functionalized composite microparticles

The magnetite particles used in the studies described herein have been synthesized by precipitating Fe₃O₄ particles with ammonia from the water solution containing FeCl₂ (1 eq.) and FeCl₃ (2 eq.) and modifying the surface of the precipitated particles with oleic acid (OA), similarly to the work published previously by Sun *et al.* [50]. The applied procedure allowed to obtain the dispersion of hydrophobic Fe₃O₄ particles in toluene. Although, the resulting dispersion consisted of both nano- and micrometric magnetite particles (an average particle diameter – 305 nm, PDI = 0.328), it could be dispersed easily in the solutions of monomers (HEMA, S and DVB) in toluene. The monomer compositions obtained in this manner were then polymerized under suspension polymerization conditions (Figure 1). As a result, brownish polymer microparticles were obtained which were characterized by the dispersity typical for the products

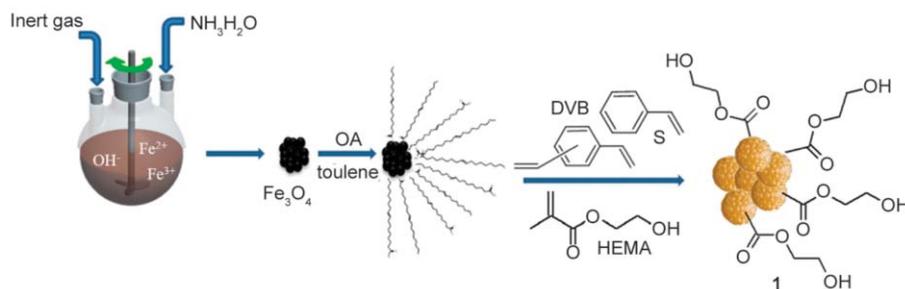


Figure 1. Preparation of polymer composite particles.

of suspension polymerization (Table 1, Figure 1). The average diameter and dispersity of the final microparticles depended on the compositions of monomers used for the polymerization. The smallest particles with the lowest dispersity were obtained using the composition consisting of 60 mol% DVB (a cross-linking monomer) (Entry 5, Table 1).

The microphotographs taken using a stereomicroscope equipped with a digital camera have revealed that the polymer particles prepared in the presence of Fe_3O_4 showed the multi-hollow morphology (Figure 2). As one would expect, the morphology of the provided particles changed with increasing the initial amount of DVB in the composition of monomers. Since, it well known that the amount of a cross-linking monomer is one of the major factors which influences the onset of phase separation during polymerization [52]. Surprisingly, in the presence of hydrophobic Fe_3O_4 particles, the polymer beads obtained

using 60 mol% DVB (Figure 2c) have turned out to be more transparent than those produced using 3 (Figure 2a), 10 (Figure 2b) and 40 mol% DVB respectively. Furthermore, they have contained much more less ‘giga’ pores visible on microphotographs. However, toluene, which was used for diluting the mixtures of HEMA, S and DVB, may reduce somewhat the effect of DVB concentration [52]. Toluene can be rather recognized as a good solvent for the polymers composed of styrene and divinylbenzene units in a majority (80 mol% in the initial monomer composition). Thus, this solvent should delay the precipitation of styrene and divinylbenzene polymers. The microphotograph taken for the polymer beads obtained without Fe_3O_4 , using the monomer composition containing 10 mol% DVB, presented in Figure 2d, has seemed to prove this statement. The look of the provided polymer particles pointed rather to the gel type morphology of than the porous one.

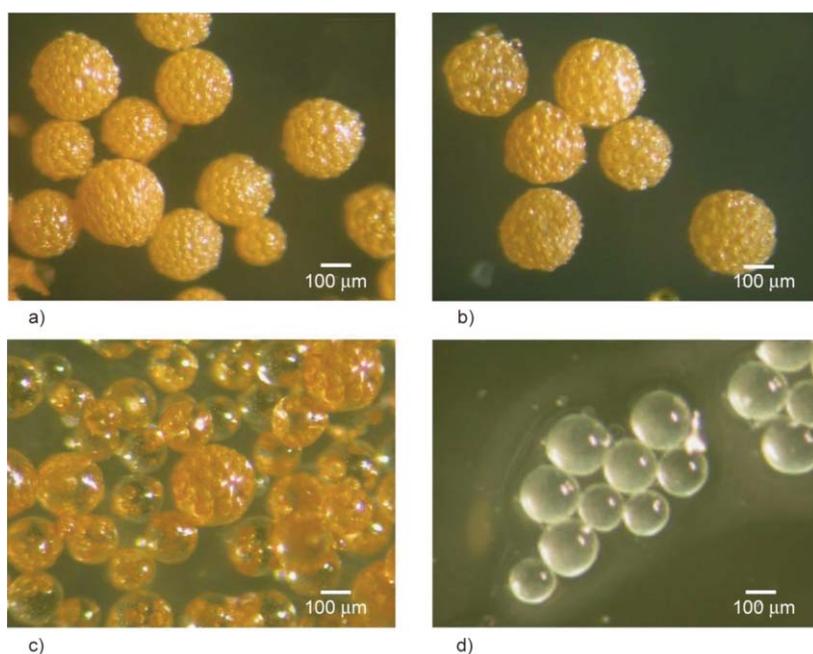


Figure 2. Microphotographs of the polymer particles produced using 3 (**1a**) (a), 10 (**1b**) (b) and 60 mol% DVB (**1c**) (c), and 0.5 wt% Fe_3O_4 , and the polymer particles obtained using 10 mol% DVB without Fe_3O_4 (d).

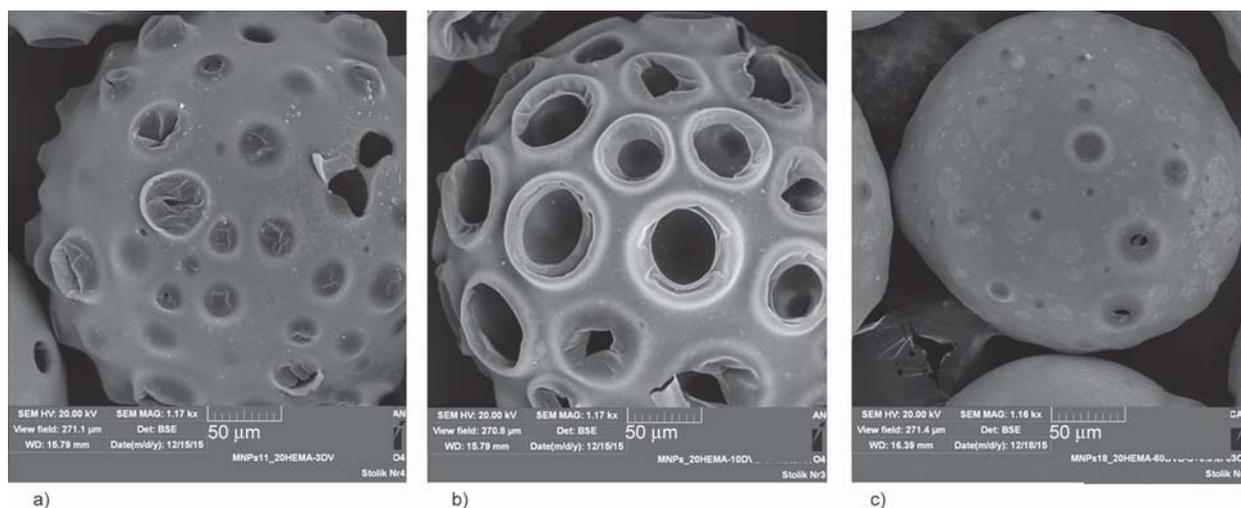


Figure 3. SEM images of the polymer particles prepared using 0.5 wt% Fe_3O_4 and 3 (a) (**1a**), 10 (b) (**1b**) and 60 mol% DVB (c) (**1c**).

More details on the morphology of the obtained particles have been revealed based on their SEM images. It was found that the surface of the particles produced using 3 mol% DVB was covered by numerous bubbles, partly cracked (Figure 3a). The particles obtained using 10 mol% DVB had the surface covered with micrometric craters (Figure 3b) and those prepared using 20 and 40 mol% DVB resembled spherical foams with ‘giga’ pores having numerous micrometric cracks. Yet another morphology was found for the particles prepared using 60 mol% DVB (Figure 3c). Their surface was covered by few bubbles, mostly with the closed architecture. Based on the SEM studies, it could be concluded that a number of microcraters on the particle surface showed upward tendency when the amount of Fe_3O_4 in the starting monomer composition was increased from 0.25 to 0.5 wt%. The tendency was not farther observed when the amount of Fe_3O_4 was increased to 1 wt%.

The SEM images recorded for the cross sections of the beads **1b** (Figure 4) showed that the ‘giga’ pores

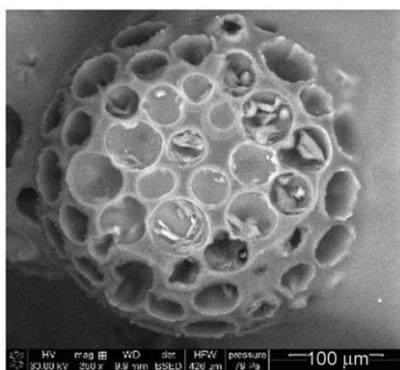


Figure 4. SEM images of the section of the particle **1b**.

were present in the whole volume of spherical particles. Their diameters reached up to about 50 μm.

To better understand a role of hydrophobic Fe_3O_4 particles in the formation of the unique morphology of HEMA-S-DVB polymer beads under suspension polymerization conditions, some additional experiments and analyses have been conducted. Firstly, the emulsions prepared using three different continuous phases were examined by means of a stereomicroscope. It was found that pure water can be easily dispersed as small droplets in toluene containing the dispersed Fe_3O_4 particles similarly as the water solution of PVP (a continuous phase applied for the suspension polymerization) in the mixture obtained by the mixing of the composition of the monomers (e.g. 20HEMA-10DVB-70S) dissolved in toluene and the dispersion of Fe_3O_4 particles in toluene; a dispersed phase in the suspension polymerization). However, the droplets of the latter showed very high mobility during the microscopic observation. Furthermore, the formation of an o/w macroemulsion was observed when the monomer solution in toluene having hydrophobic Fe_3O_4 particles was dispersed in the solution of PVP. The findings pointed to the formation of a double emulsion (w/o/w) under Pickering suspension polymerization conditions which was accompanied by very intensive mass transfer between the continuous and dispersed phases. As a result, the polymer particles with the multi-hollow morphology were formed.

Secondly, the SEM EDS analyses were also performed. The presence of Fe atoms on the particle surface was detected at all four points marked on the SEM image presented in Figure 5. These findings

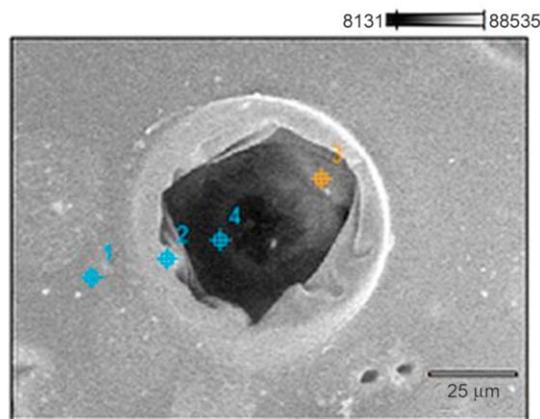


Figure 5. Distribution of Fe in the surface of **1b**.

seem to prove an active role of hydrophobic Fe_3O_4 particles in encapsulating the microdroplets of water inside the droplets of the dispersed phase and, as a result, in the formation of the polymer composite beads with multi-hollow morphology. It is well known that different inorganic and organic particles are capable of stabilizing emulsions and act as a porogen [53]. Probably, the hydrophobic particles of Fe_3O_4 dispersed in the monomer phase acted similarly and, in consequence, participated in creating the ‘giga’ pores inside the final polymer beads.

The results of SEM EDS analysis and also the slight interactions with a magnet observed for the polymer composite microparticles proved that at least a part of the Fe_3O_4 particles added to the starting compositions of the monomers were embedded in the final polymer beads. To assess the percentage of the encapsulated Fe_3O_4 particles, the samples of the composite particles were mineralized and then the resulting solutions were analyzed using ICP OES. Based on the obtained results it was concluded that only about 14–25% of the initial amounts of Fe_3O_4 taken for the polymerization was embedded in the final polymer beads (Table 1).

The presence of Fe_3O_4 particles embedded inside the polymer beads has resulted in the differences in the DR UV-Vis spectra recorded for the composite particles and the particles synthesized without Fe_3O_4 . The composite particles showed the increased absorption in the range between 380–400 nm which may be related to Fe_3O_4 particles [54] (Figure 6).

Thermogravimetric analysis has been also performed for the selected products of polymerization. Figure 7 presents TGA and DTA curves recorded for the particles obtained using 3 and 10 mol% DVB. No risk of thermal degradation of particles under typical liquid phase reaction conditions was found. The slight loss

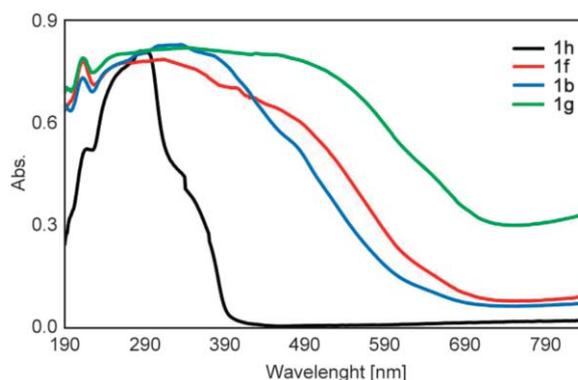
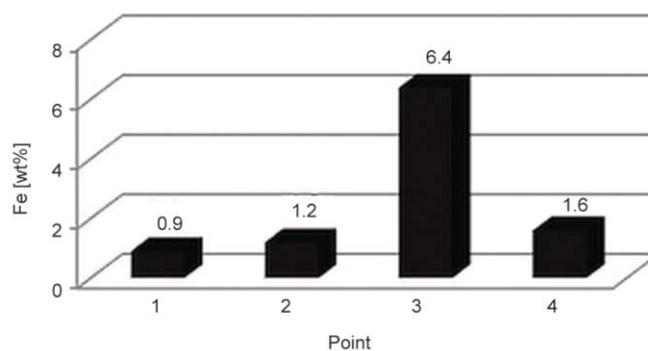


Figure 6. DR UV-Vis spectra of the synthesized polymers.

on weight observed below 300 °C could be rather related to desorption of water and/or other solvents (toluene, acetone) absorbed on the surface of particles and inside. However, one can notice that the rate of particle decomposition increased clearly above 300 °C, achieving maximum at about 400 °C. The stability of the composite particles increased somewhat when the amount of DVB in the monomer composition was increased. The beads prepared in the presence of Fe_3O_4 turned out to be slightly less resistant to thermal degradation than the one synthesized without the addition of Fe_3O_4 particles.

The chemical structure of the composite particles was also studied using FTIR spectroscopy. The FTIR spectra of the particles turned out to be dominated by the absorption bands corresponding to the groups characteristics of the monomers used for the polymerization. Owing to few amounts of Fe_3O_4 particles embedded in the final polymer microparticles (below 0.12 wt%), the absorption bands corresponding to Fe–O–Fe skeletal vibrations in Fe_3O_4 (at about 570 cm^{-1}) were not visible in the spectra of composite particles. The broad adsorption bands at 3600 and 3490 cm^{-1} (ν_{OH}) and the bands at 1724 cm^{-1} ($\nu_{\text{C=O}}$), 1180 and 1070 cm^{-1} (C–O–C skeletal vibrations) can

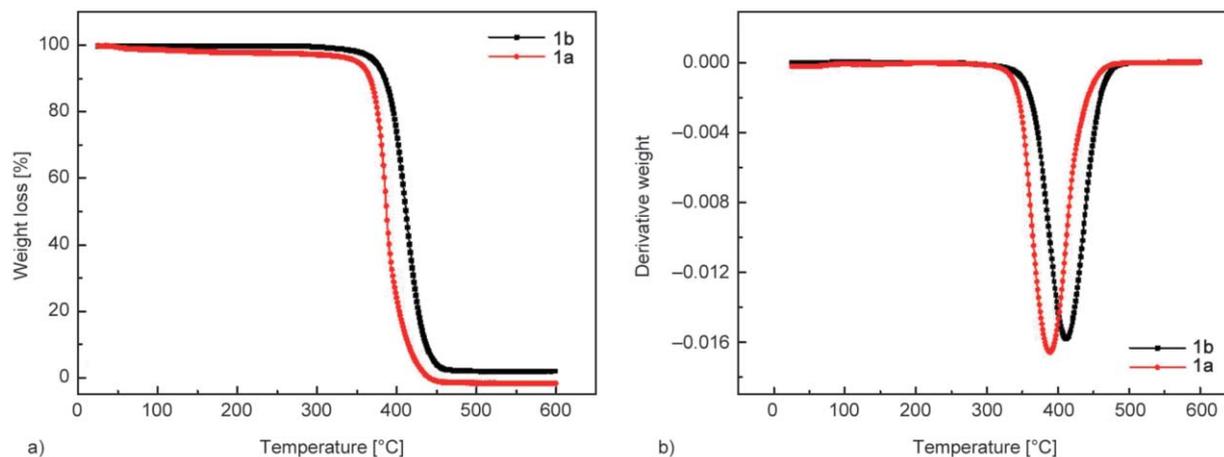


Figure 7. TGA (a) and DTA (b) curves.

be attributed to HEMA units. The bands observed at the range of 3080–2850 cm^{-1} and at 1600, 1490 and 1450 cm^{-1} confirm the presence of aliphatic and aromatic hydrocarbyl groups in the polymer structure.

3.2. Chemical modification of composite particles

The composite particles (**1**) obtained using 3 and 10 mol% DVB and 0.5 wt% Fe_3O_4 were used for the preparation of a series palladium catalysts. To facilitate the immobilization of Pd(II) ions, the hydroxy functionalized particles were first modified using

three-step procedures (Figure 8). In the first step, the reaction of **1** with glutaric anhydride (GA) in the presence of DMAP was performed to introduce more reactive COOH functionalities into the polymer beads. Polymer **2** was obtained as a result. In the next step, the carboxylic functionalities of **2** were used to immobilize SAEPI which was obtained in the reaction between 2 eq. salicylaldehyde and 1 eq. epichlorohydrin in the presence of KOH performed in water. The reactions of **2** with SAEPI were performed in the presence of DCC and DMAP. Finally, polymer **3** having the CHO groups introduced with SAEPI were

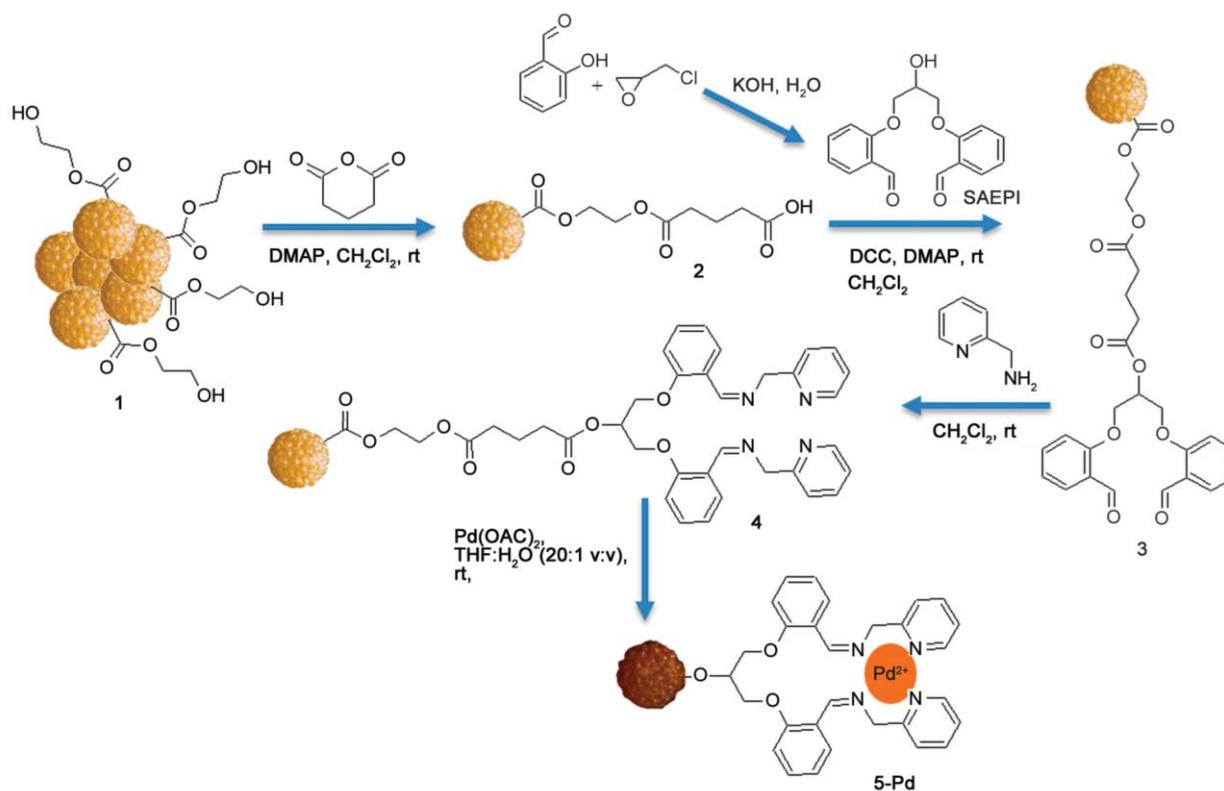


Figure 8. Preparations of polymer composite supported palladium(II) complexes.

used to form multidentate chelating systems with four nitrogen atoms (**4**). 2-Picolylamine (2-PicA) was used as a reactant at this stage of the modification. To confirm each step of the modification, the FTIR spectra of the resulting particles were recorded and compared with the appropriate spectra of the starting materials (Figure 9). The reactions with glutaric anhydride resulted in decreasing the absorption in the range of characteristic of the stretching vibrations of alcoholic OH groups (a maximum at 3500 cm^{-1}). Compared to the spectrum of **1**, the changes in absorption were also observed in the range characteristic of C=O groups ($1736, 1712\text{ cm}^{-1}$). These findings proved the presence of new functionalities (ester and carboxylic groups) in polymer **2**. The absorption band in the range related to C=O group vibrations underwent further widening after the second step of the modification, in a consequence of the reaction of SAEPI with COOH groups (a new band at 1693 cm^{-1} could be observed). This finding seemed to prove the presence of aldehyde groups in polymer **3**. Finally, the condensation of CHO groups with NH_2 groups of 2-picolylamine resulted in narrowing the absorption band in the range characteristic of C=O group vibrations and appearing the new band at 1660 cm^{-1} corresponding to C=N bonds. Based on the FTIR spectrum of **4b** it was difficult to conclude directly on the presence pyridine moieties (typical absorption bands in the range of $1690\text{--}1520\text{ cm}^{-1}$ [55]). The amount of

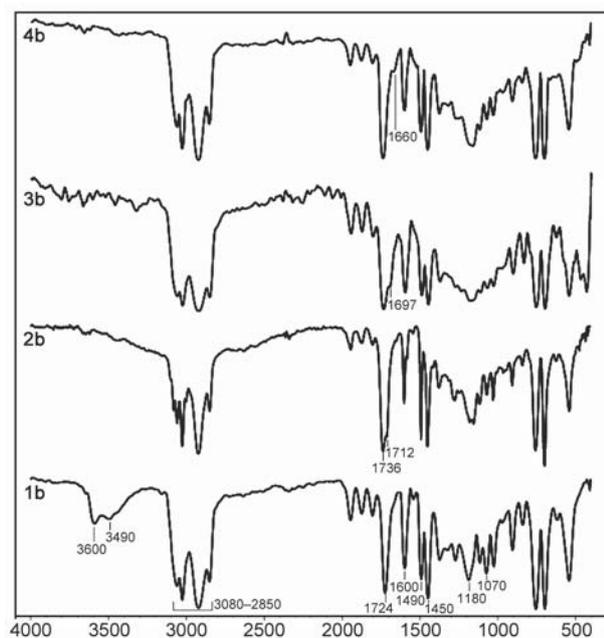


Figure 9. FTIR spectra of polymer composite **1b** and products its sequential modification with GA (**2b**), SAEPI (**3b**) and 2-picolylamine (**4b**).

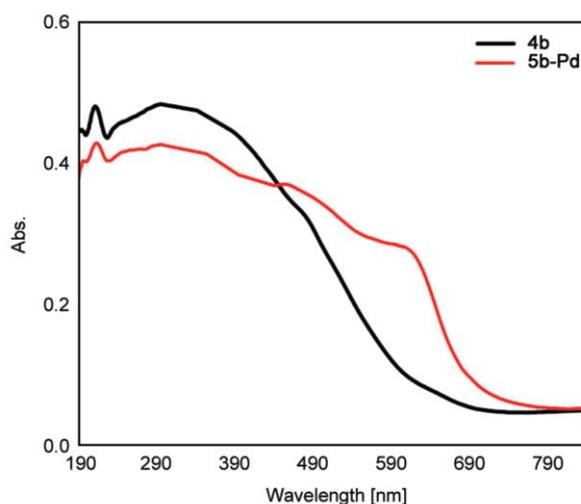


Figure 10. DR UV-Vis spectra of **4b** and **5b-Pd**.

2-picolylamine moieties immobilized on the modified polymer particles was assessed based on the result of the performed nitrogen percentage analysis of polymer **4**. It amounted to 0.38–0.46 mmol/g. To immobilize Pd(II) ions, the microparticles with the polydentate ligands (polymer **4**) were finally treated with $\text{Pd}(\text{OAc})_2$ solutions in the mixture of THF-water (20:1 v/v) for 24 hrs. As a result, the products bearing 0.2 wt% (**5a-Pd**) and 0.7 wt% (**5b-Pd**) palladium(II) ions were obtained. Although the immobilization of Pd(II) ions did not result in the change in color of the modified microparticles, an increase in absorption in the visible region of the DR UV-Vis spectra of **5-Pd** was found compared to the spectra of **4** (Figure 10). The finding is a consequence of *d-d* transitions of palladium(II) ions.

The similar multi-stage modification was conducted using polymer **1h**, obtained without the addition of Fe_3O_4 , based on 20 mol% HEMA, 77 mol% S and 3 mol% DVB (**1h**). As a result, polymer supported complex **5h-Pd** with 1.5 wt% Pd(II) ions was obtained.

In a consequence of the modification of the composite particles, the ‘mechanical polishing’ of particle

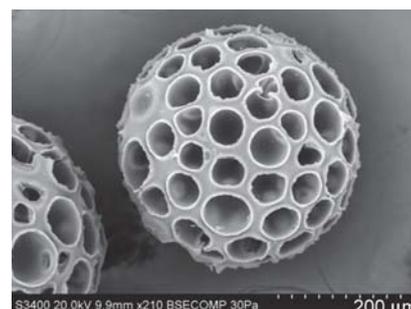


Figure 11. SEM images of **5b-Pd**.

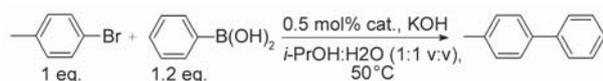


Figure 12. Model Suzuki reaction.

surface could be observed and the inside of microcraters was revealed (Figure 11).

3.3. Catalytic tests in the model Suzuki reaction

The obtained polymer composite supported palladium complexes have been tested in the model Suzuki reaction between 4-bromotoluene and phenylboronic acid in the mixture of *i*-PrOH and water (Figure 12). The reactions were performed at 50 °C using 0.5 mol% catalysts and an excess of boronic acid.

Figure 13 presents the kinetics curves obtained as a result of the catalytic performed experiments. The results for complexes **5a-Pd** and **5b-Pd** have been compared with that obtained for complex **5h-Pd** based on the gel type polymer (**1h**) prepared without the addition of Fe₃O₄ particles. It was found that the supports with composite nature improved clearly the activity of immobilized palladium species. The activity increased particularly strongly when the particles obtained using 10 mol% DVB were applied as a catalyst support. In this case, 4-bromotoluene was converted quantitatively to the cross-coupling product within about 90 minutes. After the same time, the conversion of aryl halide in the presence of **5h-Pd** was about 15%.

4. Conclusions

In conclusion, the addition of hydrophobic Fe₃O₄ particles to the monomer solutions used for the suspension polymerization, composed of the mixtures of styrene, divinylbenzene and 2-hydroxyethyl methacrylate dissolved in toluene, have resulted in obtaining

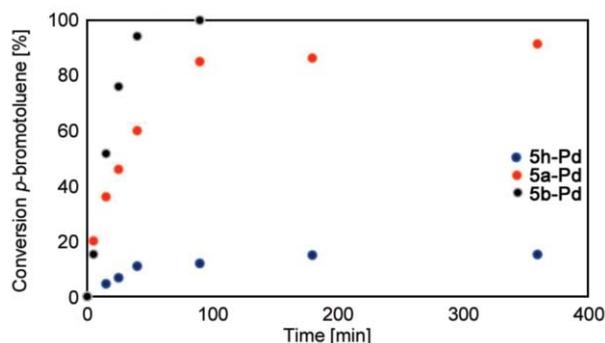


Figure 13. Conversion of 4-bromotoluene in the reaction with phenylboronic acid in the presence different catalysts.

the polymer composite particles which were characterized by the unique multi-hollow morphology. The morphology of the provided particles depended both on the amount of divinyl benzene (a cross-linking monomer) in the monomer composition and the amount of Fe₃O₄ particles added to the monomer solutions.

The preliminary examination of the synthesized polymer composite particles as potential supports for palladium catalysts has showed that the Fe₃O₄ particles embedded inside beads improved clearly the activity of Pd(II) complexes immobilized on polymer supports.

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