

Synthesis of poly(phenylene ethynylene) using an easily recyclable Pd-functionalized magnetite nanoparticle catalyst

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Immobilized catalyst, Magnetically separable, Sonogashira polymerization, Reduced Pd-content, Poly(phenylene ethynylene)

ABSTRACT

An easily recyclable catalyst has already been used in several cross-coupling reactions, resulting in many advantages compared to commonly used homogeneous catalysts. Despite all these implementations of such removable catalysts, it has never been performed in the synthesis of conjugated polymers. Therefore, a Pd-functionalized magnetite nanoparticle was successfully

synthesized and implemented in the synthesis of poly(phenylene ethynylene). The polymerization was performed using either an AB-monomer or A₂/B₂ monomers, and occurred in a classical step-growth fashion. M_n values over 10 kg/mol were obtained. Due to the presence of the magnetite nanoparticle, the catalyst could be removed and reused up to five times using magnetic precipitation. In addition, it reduces the amount of impurities present in the polymer, as a result of the Pd-catalyst, for up to 10 times compared to a commonly used homogeneous catalyst such as Pd(PPh₃)₄.

Introduction

Conjugated polymers differentiate themselves from their non-conjugated counterparts due to their π -conjugated backbone of alternating single, double and/or triple bonds. The delocalization of the π -electrons due to the overlap of the p_z-orbitals of the sp²- or sp-hybridized atoms provides them with their unique optical and electronic behavior. Their processability, flexibility and light-weight properties make them highly attractive for many applications, such as oPVs,¹⁻³ oLEDs,^{4,5} and antistatic coatings.^{6,7} Not only can they be used in opto-electronic applications, they are also known for their conductive properties and can therefore be used in batteries,⁸ and field effect transistors.⁹⁻¹¹ Poly(phenylene ethynylene) (PPE) is one example of such conjugated polymers. Conjugated polymers are typically prepared using transition metal catalyzed cross-coupling reactions. For instance, PPE is most often prepared using a Sonogashira reaction. Such polymerization reactions can be performed using either A₂/B₂-type monomers, which will occur *via* a step-growth mechanism, or using an AB type monomer, which can also occur *via* a living chain-growth mechanism. The latter occurs most often by a catalyst transfer condensative polymerization (CTCP), where the affinity of the transition metal for the conjugated polymer is key and results from the interaction of the empty d-orbitals of the transition metal with the π -

orbitals of the conjugated polymer and by the back-donation of the electrons of the transition metal to the empty π^* -orbital of the conjugated polymer.¹² Despite the outstanding application potential of these conjugated polymers, no improvement was made towards an easily recyclable catalyst for the synthesis of such conjugated polymers. Such catalyst systems have already been widely described for the use in simple cross-coupling reactions on small molecules, such as Pd nanoparticles^{13–15} and Pd immobilized on silica nanoparticles,^{16–19} graphene,^{20,21} polymers,^{22–26} carbon nanotubes,^{27,28} and dendrimers.^{29–32} Furthermore, Pd has also been immobilized on metal oxides^{33–35} and metal oxide nanoparticles.^{36–39} One of the most promising metal oxide nanoparticles are magnetite nanoparticles. Using its superparamagnetic property, the catalyst can be recovered using a magnet. Other nanoparticles, such as silica or polymer nanoparticles can only be recovered by precipitation, resulting in an unusable catalyst system for the use in polymerization reactions, since the synthesized polymers are also removed from the reaction mixture by precipitation. Furthermore, it should be mentioned that the catalyst system used in the present study is free of any Pd-coordinating ligand, and is therefore easy to make. The functionalization of the magnetite nanoparticle with palladium can be achieved using the reducing nature and coordinating ability of the Fe_3O_4 support.⁴⁰ It is our attempt to use such promising recyclable catalyst for the synthesis of conjugated polymers, performed using a cross-coupling reaction. Not only will the catalyst lead to an easily recovery and therefore a decrease in cost of the valuable Pd catalyst, it will also result in a reduction of impurities arising from the catalyst, after the polymerization, compared to common used catalyst systems. This decrease in impurities can be of great importance for the use in electronic and opto-electronic applications. Heterogeneous catalysts have already been used for the synthesis of conjugated polymers, leading to a lower Pd content in the polymer.^{41–43} Although, these types of catalysts could only be removed using

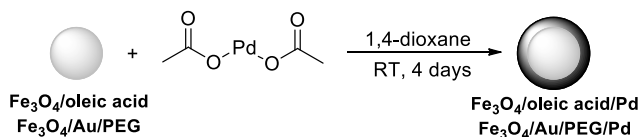
filtration and were not reused. The approach presented in this study results in a magnetic precipitation method. Therefore it is possible to easily reuse the catalyst system, and it is much easier to implement this system in both academic and industrial processes compared to the already described systems. According to previous studies, this type of nanoparticle leads to full conversion when they are implemented in the Sonogashira reaction at 100 °C.⁴⁴ Therefore a Sonogashira polymerization will be used for this study, leading to the synthesis of poly(phenylene ethynylene) (PPE). Not only will the polymerization be performed using a recyclable catalyst, it will also be executed in the absence of any Cu-salt in order to further reduce the impurities present in the polymer after the reaction. To achieve a good insight towards the Sonogashira polymerization mechanism using these Pd-functionalized magnetite nanoparticles, different polymerizations are performed by AB- and A₂/B₂-type monomers. Furthermore, the influence of gold will be examined for the Sonogashira polymerization, since it was already proven that gold has a positive influence on several cross-coupling reactions.⁴⁵⁻⁴⁸ It should be mentioned that such (easily synthesized) recyclable catalysts has never been used for the synthesis of conjugated polymers and is an ideal candidate towards the goal of green chemistry, resulting in an easily synthesized and efficiently recyclable catalyst system.

Results and discussion

Catalyst preparation

Two types of nanoparticles are prepared for the examination of the Sonogashira polymerization. First, a magnetite nanoparticle stabilized with oleic acid is synthesized using the procedure of Chen *et al.*⁴⁹ Second, for the investigation of the influence of gold during this polymerization reaction a core-shell nanoparticle, consisting of a magnetite core surrounded by a golden shell, is synthesized according to Billen *et al.*⁵⁰ Both types of nanoparticles were used and described in detail in

previous study.⁴⁴ These nanoparticles were chosen since they resulted in excellent yields when they were implemented in the Sonogashira reaction. The functionalization of both types of nanoparticles is performed by stirring Pd(OAc)₂ together with the nanoparticles in 1,4-dioxane for 4 days under argon atmosphere (**Scheme 1**).



Scheme 1. Functionalization of the different types of nanoparticles with Pd.

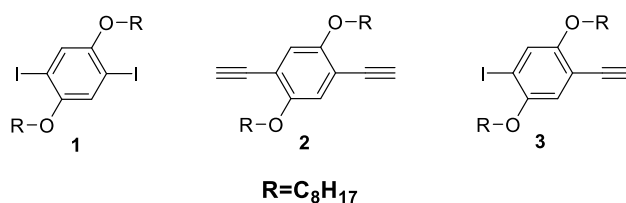
Note that our approach does not use any reducing reagents or surface modification, and that the nanoparticles are functionalized without the presence of any Pd-coordinating ligand attached onto the nanoparticle. This makes the synthesis of these Pd-functionalized nanoparticles straightforward and time-, and cost-efficient. The amount of Pd present on the different types of nanoparticles was determined using inductively coupled plasma – atomic emission spectroscopy (ICP-AES) (**Table 1**). It should be mentioned that the amount of Pd varies with the type of nanoparticle used. The amount of Pd present on the Fe₃O₄/Au/PEG nanoparticles is higher compared to the Fe₃O₄/oleic acid nanoparticles. Due to the presence of PEG stabilizers and its higher polarity, the Pd, originating from Pd²⁺, reaches easier the nanoparticle surface and consequently making more direct contact with the nanoparticle, since Pd²⁺ can easily penetrate the PEG-chain. This is in contrast to the oleic acid stabilizer, which shows a lower polarity, leading to a more difficult contact of the Pd with the nanoparticle. In turn, this results in a lower Pd-amount present on the nanoparticle.

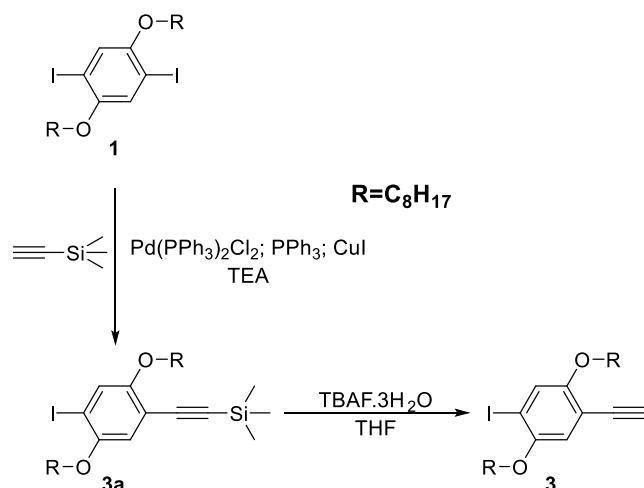
Table 1. ICP-AES results of Pd functionalized nanoparticles

Nanoparticle	Amount of Pd (mg Pd/mg NPs)	Amount of Pd (10 ⁻⁴ mmol Pd/mg NPs)
Fe ₃ O ₄ /oleic acid/Pd	0.0078	0.74
Fe ₃ O ₄ /Au/PEG/Pd	0.079	7.4

Monomer synthesis

To study the performance of the Pd-functionalized magnetite nanoparticle catalyst, monomer **1**, **2** and **3** were synthesized (**Chart 1**). Monomer **1** and **2** result respectively in an A₂ and B₂ monomer. The polymerizations reactions performed using such type of monomers will occur via a step-growth polymerizations, while an AB-type monomer (**3**) can polymerize *via* a living chain-growth mechanism. In this way it is possible to investigate the polymerization mechanism that occurs using this reusable catalyst. Monomers **1** and **2** were synthesized according to literature procedures.⁵¹⁻⁵⁴ For the synthesis of monomer **3** a Sonogashira reaction was first performed, resulting in the precursor monomer **3a**. The protected acetylene function is then deprotected using tetrabutylammoniumfluoride (TBAF) to obtain monomer **3** (**Scheme 2**).

**Chart 1.** Structures of the used monomers.

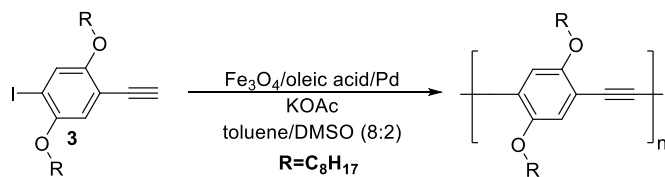


Scheme 2. Reaction scheme for the synthesis of monomer **3**.

Sonogashira polymerization

AB-type monomer

To perform and investigate the Sonogashira polymerization using these recyclable Pd-catalyst systems, similar conditions are used as described in previous model reactions on small molecules, since this resulted in full conversions, necessary to obtain high molar masses in a step-growth polymerization.⁴⁴ The monomer used is 1-ethynyl-4-iodo-2,5-di(octyloxy)benzene (**3**), with KOAc as base, Fe₃O₄/oleic acid/Pd nanoparticles as catalyst system and toluene/DMSO (8/2) as solvent. Toluene was chosen, since it improves the solubility of the polymer during the polymerization, while DMSO was chosen for its positive effect on the performance of a Sonogashira cross-coupling reaction and for its improvement on the solubility of the base KOAc (**Scheme 3**).⁵⁵



Scheme 3. Sonogashira polymerization using the Fe₃O₄/oleic acid/Pd nanoparticles by the AB monomer.

First the Sonogashira polymerization is performed using the $\text{Fe}_3\text{O}_4/\text{oleic acid}/\text{Pd}$ nanoparticles and M_n is plotted in function of conversion (**Figure 1**). As depicted in **Figure 1** an M_n was reached of 3.8 kg/mol with a conversion of 0.995 after a reaction time of 25 hours. It should be mentioned that almost no change was observed for M_n , nor for the conversion between 21 hours and 25 hours of reaction time. By plotting the M_n in function of the conversion, it can be concluded that the polymerization likely proceeds in a regular step-growth fashion.

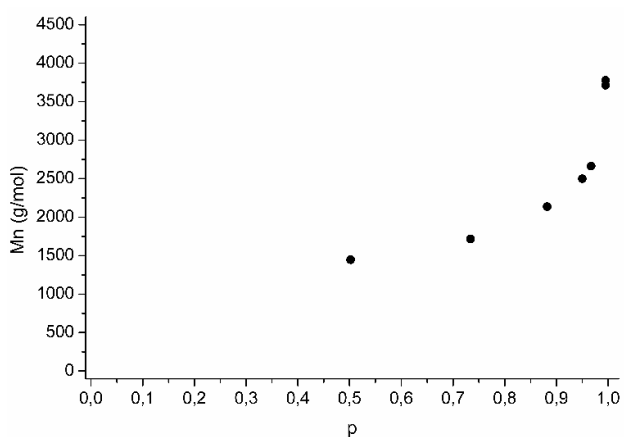


Figure 1. M_n in function of conversion for the Sonogashira polymerization performed by the AB monomer.

To have a better insight of the performance of this catalyst system, a comparison is made with a commonly used homogeneous catalyst for such type of polymerizations, such as $\text{Pd}(\text{PPh}_3)_4$ (**Table 2**). The same amount of Pd is used in both reactions and equals $0.82 \cdot 10^{-3}$ mol%.

Table 2. Comparison of the M_n obtained using the $\text{Fe}_3\text{O}_4/\text{oleic acid}/\text{Pd}$ as catalyst system and $\text{Pd}(\text{PPh}_3)_4$.

Time	M_n (kg/mol) [Đ]	M_n (kg/mol) [Đ]
	$\text{Fe}_3\text{O}_4/\text{oleic acid}/\text{Pd}$	$\text{Pd}(\text{PPh}_3)_4$
1 h	1.4 [1.1]	1.6 [1.2]
2 h	1.7 [1.2]	1.8 [1.3]
4 h	2.1 [1.3]	2.1 [1.3]
6 h	2.5 [1.4]	2.3 [1.4]
8 h	2.7 [1.4]	2.6 [1.4]
21 h	3.7 [1.5]	3.4 [1.5]
25 h	3.8 [1.5]	3.5 [1.5]

According to **Table 2**, almost no difference in molar mass is present between the $\text{Fe}_3\text{O}_4/\text{Pd}$ catalyst system and $\text{Pd}(\text{PPh}_3)_4$. Since it is the goal to reduce the impurities in the polymer, ICP-AES measurements are carried out for the polymer obtained using $\text{Fe}_3\text{O}_4/\text{oleic acid}/\text{Pd}$ as catalyst system as well as for the polymer obtained using $\text{Pd}(\text{PPh}_3)_4$ (**Table 3**), in order to quantify the Pd content in both polymers arising from both catalysts. From **Table 3** it can be concluded that the amount of Pd present in the polymer is approximately 14 times lower when the $\text{Fe}_3\text{O}_4/\text{oleic acid}/\text{Pd}$ catalyst system is used compared to $\text{Pd}(\text{PPh}_3)_4$ as catalyst. This makes the removable Pd functionalized magnetite nanoparticle an ideal candidate to reduce the amount of Pd in the desired end-product. For applications in oLEDs and other devices it is important that the polymers have a negligible Pd content. When such polymers are synthesized in industry, Pd contents of 1 ppm have been reached.⁵⁶ Also in academia efforts have been made to reduce the Pd content in conjugated polymers and resulted in an amount of Pd of 30 and 9 ppm in the polymer material.⁵⁷ In our

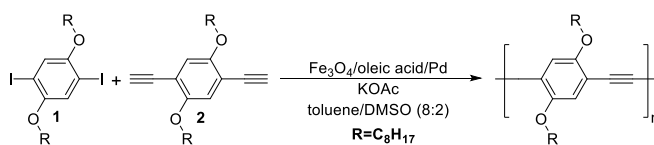
approach equal results were obtained, although, the reduction of this Pd content was obtained using an easy removal of the Fe₃O₄/oleic acid/Pd catalyst. This is in comparison with the results found in literature, where they made use of an additional purification step. Therefore, our approach is faster and more easy to use.

Table 3. Comparison on the amount of Pd present in the polymer after the polymerization using Fe₃O₄/oleic acid/Pd as catalyst system and Pd(PPh₃)₄.

Catalyst	Amount of Pd in the polymer (ng Pd/mg polymer)
Fe ₃ O ₄ /oleic acid/Pd	11.5
Pd(PPh ₃) ₄	168

A₂/B₂-type monomers

Next, the Sonogashira polymerization using an A₂ (1,4-diiodo-2,5-di(octyloxy)benzene) (**1**) and B₂ (1,4-diethynyl-2,5-di(octyloxy)benzene) (**2**) monomer was performed under identical conditions as the polymerization performed using the AB monomer (**Scheme 4**).



Scheme 4. Sonogashira polymerization using A₂ and B₂ type monomers.

In **Table 4** a comparison is made between the molar mass obtained after the polymerization executed using and AB monomer and A₂/B₂ monomers. The presented M_n-values are those obtained at the same reaction time (21 h) and until no change in molar mass and conversion was observed (Max M_n).

Table 4. Comparison of the M_n obtained using A_2 and B_2 type monomers and using AB type monomer.

Time	M_n (kg/mol) [Đ]	M_n (kg/mol) [Đ]
	$A_2 + B_2$	AB
21 h	6.5 [2.6]	3.7 [1.5]
Max M_n	10.2 [4.4]	3.8 [1.5]

As depicted in **Table 4**, the M_n -values of the polymer obtained using A_2/B_2 monomers are respectively 2 and 3 times higher compared with the polymer obtained using an AB monomer. The reason for this is twofold. First, by using an A_2 monomer, the oxidative addition is improved, since the iodide in the *para*-position has an electron withdrawing character. Second, the transmetalation step is improved using these A_2/B_2 monomers. Due to the presence of the acetylene function at the *para*-position instead of the electron withdrawing iodide, the transmetalation is improved compared to the polymerization performed using the AB monomer.

It has been found that the polymerization using an AB-type monomer likely proceeds in a regular step-growth fashion. When the M_n -value is plotted in function of the conversion for the polymerization using A_2/B_2 type monomers in stoichiometric balance, the same trend is observed (ESI; Figure S3). However, it is possible that the catalyst does show an affinity for the polymer chain even when proceeding via a step-growth polymerization. When a regular step-growth mechanism occurs, Carothers equation holds, resulting in a decrease in M_n -value when a stoichiometric imbalance is present, since the excess of the monomer will behave as a chain-stopper. When an affinity of the catalyst for the polymer chain would be present during the polymerization, the Carothers equation is no longer valid, resulting in the fact that, when an excess of the halogenated monomer (A_2) is present no effect should be observed on the M_n -value.⁵⁸⁻⁶⁰ In

this case the excess of the monomer will not act as a chain-stopper. This is due to the fact that the catalyst stays attached to the A_2 monomer after the first oxidative addition, and as a consequence this will directly result in another coupling at the same A_2 monomer, resulting in a trimer with two acetylene functions on both ends. An excess of A_2 does therefore not lead to a decrease in M_n , but possibly even to an increase in M_n , since, when these trimers react with another A_2 monomer, which is present in excess, a chain with 7 monomer units is formed since the halogenated monomer will react twice with a trimer, and so on. When on the other hand the M_n -value decreases compared to the equimolar reaction, Carothers equation holds, implying that there is no affinity of the catalyst for the polymer chain, and the polymerization occurs by a regular step-growth mechanism. An excess of B_2 monomer will always result in a decrease in M_n -value.

In order to examine this influence, an excess of one of the two monomers was used (**Table 5**). Since the M_n -values obtained for the Sonogashira polymerization performed with an excess of A_2 monomer is lower than the values obtained during the polymerization when an equimolar amount of both monomers was present, it can be concluded that the nanoparticle does not show any affinity for the A_2 monomer. This lower M_n -value can, in this case, be ascribed to the stoichiometric imbalance and by this the polymerization shows Carothers behavior. The lower M_n -value obtained for the polymerization performed in excess of the B_2 monomer is also the result of the stoichiometric imbalance. Since in both cases the excess of the A_2 - and B_2 -type monomer leads to a decrease in molar mass, it can be concluded that the polymerization therefore occurs *via* a regular step-growth mechanism.

Table 5. Comparison of the M_n obtained using either an excess of A_2 or B_2 monomer

Time	M_n (kg/mol) [Đ]	M_n (kg/mol) [Đ]	M_n (kg/mol) [Đ]	M_n (kg/mol) [Đ]	M_n (kg/mol) [Đ]
	1 eq. A_2 1 eq. B_2	+2 mol% A_2	+10 mol% A_2	+2 mol% B_2	+10 mol% B_2
2 h	2.3 [1.4]	1.8 [1.4]	1.6 [1.3]	1.7 [1.3]	1.6 [1.3]
4 h	2.8 [1.5]	2.5 [1.7]	2.0 [1.5]	2.1 [1.5]	1.9 [1.4]
6 h	3.3 [1.7]	3.0 [1.9]	2.3 [1.6]	2.4 [1.7]	2.2 [1.5]
8 h	3.7 [1.8]	3.5 [2.0]	2.7 [1.7]	2.9 [1.8]	2.5 [1.6]
21 h	6.5 [2.6]	6.8 [3.4]	4.7 [2.4]	5.4 [2.8]	4.7 [2.3]
25 h	6.9 [2.6]	7.1 [3.8]	5.0 [2.6]	6.0 [3.0]	4.8 [2.5]
29 h	7.4 [2.7]	7.6 [4.1]	5.3 [2.8]	6.5 [3.5]	5.1 [2.6]
45 h	9.8 [4.1]	8.2 [5.5]	6.9 [3.7]	7.7 [4.8]	7.5 [3.3]
48 h	9.9 [4.4]	8.2 [6.6]	6.9 [3.8]	8.6 [5.2]	7.8 [3.4]
51 h	10.2 [4.4]	8.2 [6.5]	7.1 [3.7]	8.9 [5.7]	7.9 [3.6]

A comparison is also made for the Sonogashira polymerization using the Fe_3O_4 /oleic acid/Pd catalyst system and $Pd(PPh_3)_4$ to get a better insight in the performance of this nanoparticle catalyst compared to a commonly used catalyst. As can be derived from **Table 6**, a rise was observed for the difference in molar mass between the recyclable catalyst and the $Pd(PPh_3)_4$, resulting in a higher molar mass for the nanoparticle catalyst system compared to the $Pd(PPh_3)_4$.

Table 6. Comparison of the M_n obtained using the $\text{Fe}_3\text{O}_4/\text{oleic acid}/\text{Pd}$ as catalyst system and $\text{Pd}(\text{PPh}_3)_4$ (A_2 and B_2 type monomers).

Time	M_n (kg/mol) [Đ]	M_n (kg/mol) [Đ]
	$\text{Fe}_3\text{O}_4/\text{oleic acid}/\text{Pd}$	$\text{Pd}(\text{PPh}_3)_4$
2 h	2.3 [1.4]	1.8 [1.5]
4 h	2.8 [1.5]	2.3 [1.8]
6 h	3.3 [1.7]	2.6 [2.0]
8 h	3.7 [1.8]	3.0 [2.2]
21 h	6.5 [2.6]	5.6 [3.6]
25 h	6.9 [2.6]	5.4 [3.9]
29 h	7.4 [2.7]	6.0 [4.2]
45 h	9.8 [4.1]	6.8 [5.6]
48 h	9.9 [4.4]	7.4 [5.8]
51 h	10.2 [4.4]	8.0 [6.0]

Recuperation

The benefit of heterogeneous catalysts lies in their easy separation and recyclability. The nanoparticle catalyst can be removed using a magnet, washed, dried and afterwards directly reused without further purification in the next reaction (**Figure 2**). Therefore, two types of recuperation experiments are conducted using identical conditions as the polymerization performed using the AB monomer (**Scheme 3**).

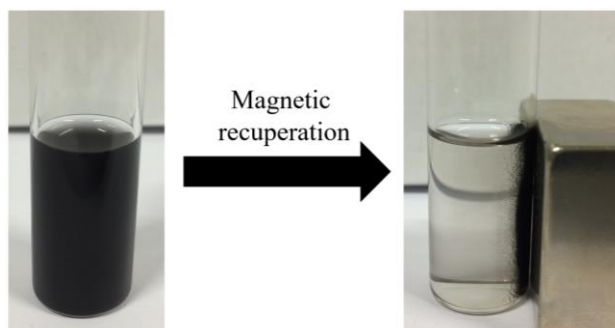


Figure 2. Magnetic recuperation of the Fe₃O₄/oleic acid/Pd catalyst nanoparticles.

The first is performed using the same reaction time for each reaction (21 h), meaning that cycle 1 takes the same time as cycle 5 (**Figure 3**). The second experiment is performed until no change in M_n and conversion was observed during the reaction, meaning that cycle 5 takes a longer time as cycle 1 (**Figure 4**). As depicted in **Figure 3**, where the reaction time is kept the same for all recuperation reactions, the M_n as well as the conversion decreases after each recuperation. It should be mentioned that a correction is made for the amount of nanoparticles present after the recuperation by adapting the amount of starting reagents to the amount of nanoparticles present after the recuperation. As a result, the decrease in activity can only be due to a change in composition of the nanoparticle catalyst, and as such due to the leaching of the palladium from the recyclable catalyst. This leaching is examined by ICP-AES (ESI; Table S2). When the recuperations are performed until no change in M_n and conversion is observed (**Figure 4**), the Fe₃O₄/oleic acid/Pd catalyst system can be recycled and reused for at least 5 times, although with a decrease in molar mass from 3.7 kg/mol, for the first cycle, to 2.1 kg/mol for the fifth cycle. Furthermore, the first recuperation did not result in any loss in molar mass of the polymer or decrease in conversion. According to these results, the Fe₃O₄/oleic acid/Pd catalyst can be removed and reused for at least 5 times, resulting in an efficient and novel recyclable catalyst for the use in polymerization reactions. It should be mentioned that the reuse of a catalyst has never been performed or investigated for the synthesis of any conjugated polymer.

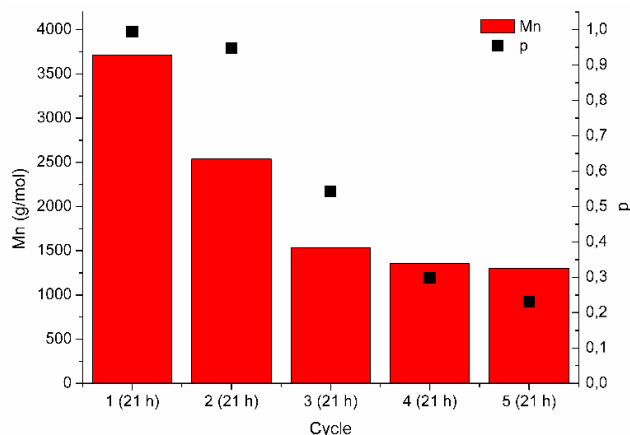


Figure 3. Recuperation experiment using the $\text{Fe}_3\text{O}_4/\text{oleic acid}/\text{Pd}$ as catalyst and the AB-type monomer for the performance of the Sonogashira polymerization, whereby the reaction time was kept identical for each cycle.

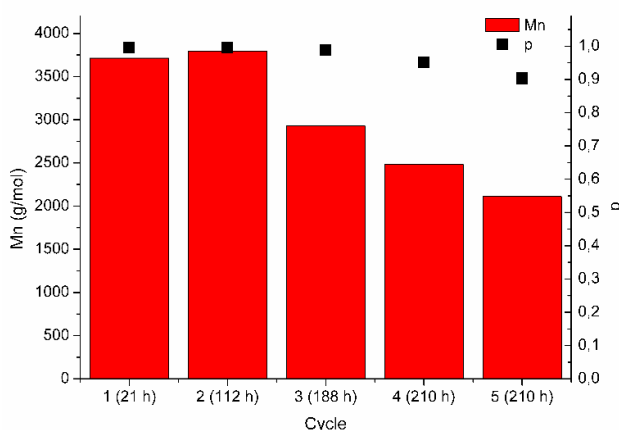


Figure 4. Recuperation experiment using the $\text{Fe}_3\text{O}_4/\text{oleic acid}/\text{Pd}$ as catalyst and the AB-type monomer for the performance of the Sonogashira polymerization, whereby the reaction was performed until no change in M_n and conversion was observed.

Influence of gold

The influence of gold on the catalytic properties of a reusable palladium catalyst has already been described in literature for the use in Suzuki and Sonogashira reactions.⁶¹ Furthermore, the positive influence of gold present as Au(III) or Au(I) together with Pd has also been demonstrated for the Sonogashira reaction.^{45–48} Knowing that gold has a positive influence on the catalytic

process for homogeneous and heterogeneous Sonogashira cross-coupling reactions, a core-shell nanoparticle was used consisting of a magnetite core surrounded by a golden shell and functionalized with Pd for the implementation in the Sonogashira polymerization. As a result of the presence of the magnetite core inside this Fe₃O₄/Au/PEG/Pd catalyst system, it is possible to reuse this catalyst system in the Sonogashira polymerization as described in the section above. To investigate the influence of gold on the polymerization reaction, the same amount of Pd is used in both reactions. According to **Table 7**, the use of Fe₃O₄/Au/PEG/Pd does not lead to an improved polymerization. In fact, the use of Fe₃O₄/oleic acid/Pd as catalyst system leads to slightly higher M_n-values compared to the core-shell catalyst system. It should be mentioned that not only gold was added to the magnetite nanoparticle, another stabilizer was also used compared to the Fe₃O₄/oleic acid/Pd.

Table 7. M_n-values obtained using Fe₃O₄/Pd compared with Fe₃O₄/Au/Pd for the Sonogashira polymerization using the AB monomer.

Time	M _n (kg/mol) [Đ]	M _n (kg/mol) [Đ]
	Fe ₃ O ₄ /Pd	Fe ₃ O ₄ /Au/Pd
1 h	1.4 [1.1]	1.0 [1.1]
2 h	1.7 [1.2]	1.2 [1.1]
4 h	2.1 [1.3]	1.4 [1.2]
6 h	2.5 [1.4]	1.6 [1.3]
8 h	2.7 [1.4]	1.9 [1.3]
21 h	3.7 [1.5]	3.0 [1.5]
25 h	3.8 [1.5]	3.3 [1.5]

Conclusions

A Fe_3O_4 /oleic acid/Pd nanoparticle catalyst was used for a Sonogashira polymerization. Never has the synthesis of conjugated polymers been performed using a heterogeneous catalyst based on an (easily) recyclable magnetite nanoparticle. The polymerization, using this catalyst, occurs by a step-growth mechanism and results in a molar mass of 3.8 kg/mol for the reaction performed using an AB-type monomer. When an A_2 - and B_2 -type monomer is used, a much higher molar mass is obtained during the polymerization. By using an excess of one of both monomers (A_2 or B_2), the M_n -value of the obtained polymer decreases. Therefore, it can be concluded that a regular step-growth polymerization is followed and that the nanoparticle does not show any affinity for the polymer or *vice versa*. This is also deduced by the amount of Pd present in the polymer when the recyclable catalyst nanoparticles are used. Furthermore, the presence of Au does not lead to an improved Sonogashira polymerization compared to the normal Fe_3O_4 /oleic acid/Pd catalyst. It should be mentioned that by using such type of removable catalyst the amount of Pd present in the polymer decreases significantly compared to a common used Pd catalyst like $\text{Pd}(\text{PPh}_3)_4$. Not only is there a lower amount of Pd present in the polymer after the polymerization, the polymerization is also performed in the absence of any Cu-salt. By the implementation of this Fe_3O_4 /oleic acid/Pd catalyst, it is possible to recuperate the catalyst for the polymerization and it can be reused for at least five times.

ASSOCIATED CONTENT

Supporting Information

The following files are available free of charge.

Materials and instrumentation; experimental procedures; TEM images of the nanoparticles; ICP-AES measurements; ^1H and ^{13}C NMR of the monomers (PDF).

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ABBREVIATIONS

PEG: Poly(Ethylene Glycol); ICP-AES: Inductively Coupled Plasma Atomic Emission Spectroscopy; oPV: organic Photovoltaics; oLED: organic Light-Emitting Diode; PPE: Poly(phenylene ethynylene); CTCP: Catalyst Transfer Condensative Polymerization; p: conversion; TBAF: tetrabutylammoniumfluoride

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Synthesis of poly(phenylene ethynylene) using an easily recyclable Pd-functionalized magnetite nanoparticle catalyst

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