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Progress in the Synthesis of Poly(2,7-Fluorene-*alt*-1,4-Phenylene), PFP, via Suzuki Coupling.

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ABSTRACT: Four different palladium catalysts were evaluated in order to optimize the conditions in the Suzuki coupling protocol with 1,4-diphenylboronic acid and 9,9-bis(6′-bromohexyl)-2,7-dibromofluorene. The commercially available catalysts [Pd(PPh$_3$)$_4$], (**1**); [Pd(PPh$_3$)$_2$Cl$_2$], (**2**); [PdCl$_2$(dppe)], (**3**) and [PdCl$_2$(dppf)]·CH$_2$Cl$_2$, (**4**) were chosen. Palladium catalysts **1-4** have been previously used successfully in polymerization. K$_2$CO$_3$ was used as base in the presence of the adequate solvent mixture. Poly[9,9-bis-(6′-bromohexylfluoren-2,7-diyl)-*alt*-co-(benzen-1,4-diyl)], **PFPBr$_2$**, was obtained and selected as model to study the polymerization degree. Calibration curves of fluorene were used to perform a real estimation of the molecular weights of the polymers, and also typical polydispersity values were measured. Polymer conversion was determined using coupled size exclusion chromatography−evaporative light scattering detector (SEC−ELSD). The (*Z*)-Pd(II) catalyst, (**4**), which contains the electron acceptor ligand dppf, showed the fastest conversion rate at low reaction times, followed closely by catalyst (**2**), (*E*)-Pd(II), which presents a conventional PPh$_3$ ligand. The typical Pd(0) catalyst, (**1**), with phospane ligands, was slower than others and this process needed almost 12 h to convert the monomers in real polymer. Taken together, all these results provide new insights into the polymerization mechanism using different Pd(II) and Pd(0) catalysts, which seem to behave differently when different ligands are used.

Introduction

Suzuki coupling reaction is a typical reaction between organoboron compounds with different types of organic electrophiles, in general organic halides or good leaving groups, usually catalyzed by a Pd(0) complex.[1−3] The efficiency of the Suzuki reaction has been improved by means of more efficient catalysts, the presence of bases, the accurate choice of solvents and microwave activation.[4−8] A general catalytic cycle for the cross-coupling reaction of organometallics involves the following steps sequence: oxidative addition, transmetalation and reductive elimination (OA-T-RE). Normally, aryl−aryl coupling succeed through *nondissociative-nonassociative* mechanism,[9] but to date the mechanism of polycondensation for conjugate polymers (via palladium catalysts) has not been understood.

Suzuki−Miyaura or Suzuki coupling reaction has been extensively applied in polymer science, in particular, in design and synthesis of different copolymers with conjugates properties chemistry.[10−24] If the starting materials are difunctional monomers (diboronic and dibromides), in the presence of base and catalytic amount of palladium, biaryl units lead a step-growth with good yield, in a Suzuki polycondensation reaction. Dong and Hu,[25] reported that, in the cross-coupling of dihaloarenes with arylboronic acid, a regenerated Pd(0) catalyst undergoes oxidative addition preferentially as the fastest step in mechanism. Weber et al.[26] observed the same preference for oxidative addition with dihalofluorene monomers but longer reaction times were needed and chain-growth polymerization, in the synthesis of PF, was evaluated using [Pd(P^{t}Bu$_3$)$_2$(Ph)Br] catalyst.[27]

Additional advantages of these reactions include mildness of the reaction conditions, great tolerance toward a variety of functional groups, insensitiveness to the presence of water and the need of a very small catalytic amount of palladium catalyst.[3,9,28] A wide number of research groups have reported on the synthesis of conjugated polymers by Suzuki coupling reactions, including reaction times lasting up to 72 h to build polymers of regular molecular weight (25−50 kg/mol based on polystyrene calibration). Therefore, reaction time reduction is one of the targets in order to optimize the experimental conditions, always taking into account the need for good polymer molecular weight control.[13,29−36]

This methodology offers the possibility of preparing fluorene homopolymers as well as alternating copolymers. Fluorene-based conjugated polymers are highly efficient emitters and show a wide range of applications from fluorescent sensors to emitters in electronic devices.[37−42] Poly(2,7-fluorene)-*alt*-1,4-phenylene) (PFP) presents high blue photoluminescence due to the presence of fluorophore units with the polymer in semiconducting form. An advantage of this polymer is the facile functionalization of the side-chain at the C9 site, which provides the possibility of improving the solubility and processability in solid state. Looking for PFP synthesis, we focused on the use of commercial 1,4-diphenylboronic acid as a guide. The first report on polymerization of this diboronic acid was shown by Rehahn et al. in the 1990.[43] In the last few years, commercial diboronic acid was used to prepared water-soluble PFP with high yield and molecular weight of the order to 6.5−7.8 Mg/mol, using typical conditions,

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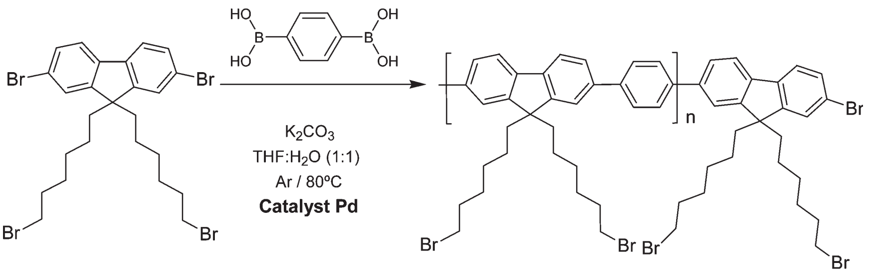
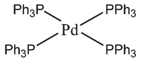
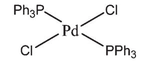
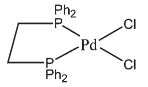
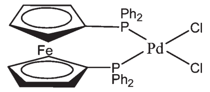
Scheme 1. Experimental Conditions and Synthesis Model of $PFPBr_2$



	Catalyst	Abbreviations
<u>1</u>		$[Pd(PPh_3)_4]$
<u>2</u>		*(E)*-$[Pd\ Cl_2(PPh_3)_2]$
<u>3</u>		*(Z)*-$[Pd\ Cl_2(dppe)]$
<u>4</u>		*(Z)*-$[Pd\ Cl_2(dppf)]$

Pd(0) and large reaction time (72 h),[44] and, also with Pd(II), under different conditions, but the same reaction times.[45] Liu et al.[46] obtained neutral copolymers with different proportions of the monomers (using 1,4- and 1,3-diphenyldibororonic acid) under similar experimental conditions, however, in order to obtain molecular weights between 6 and 15 Mg/mol with good yield, reaction times were shorter, i.e., 24 h. In that work, the use of different catalysts was studied; however, neither information nor suggestions about the use of these catalysts were reported. Later, the same authors used a Pd(0) catalyst to obtain a ter-copolymer with adequate yield, short reaction time, lower molecular weight (11 kg/mol), and good polydispersity.[47]

Despite the efforts that industrial and academic researchers have provided toward progress in this field, it is necessary to study new models to deeply understand these processes. The study of the control of the Suzuki polycondensation for the formation of novel conjugated polymers, with defined properties such as the length of the conjugated polymers chains, narrow polydispersity values, and short reaction times is the main aim of this work. Thus, we tried to understand the processes involved in PFP synthesis, by studying several chemical properties such as yield, degree of polymerization and polydispersity of the polymers in a model reaction performed under the same conditions, and varying the palladium catalysts (Scheme 1).

Experimental Part

Instrumentation. Size exclusion and high pressure liquid chromatographic analysis was carried out on a HPLC LaChrom (Merck-Hitachi) equipped with an L-7100 pump, an L-7200 autosampler, an L-7455 UV−vis diode array detector, and/or an evaporative light scattering detector (ELSD 2000 and 3300, Alltech Associates, Inc.). SEC or HPLC analysis used 20 μL samples that were injected in a column Plgel 5 μm MIXED-C; 2 × (300 × 7.5 mm i.d) from Polymer Laboratories Ltd. or in a column Lichrospher 5 μm RP18 (250 × 4 mm i.d.), respectively. Both analyses were carried out on aliquots samples-control time that were prepared in THF (HPLC grade) approximately 5 mg/mL and filtered through at nylon 0.45 μm syringe. SEC data were initially calibrated using Polymer Laboratories EasiCal Polystyrene (PS) standards. Thermal analysis was performed using differential scanning calorimetry (DSC) Perkin-Elmer Pyris model 6. Cycles purged nitrogen atmosphere of heating/cooling at rate 20 °C/min were used with a previous training at 100 °C, quantities of 8−10 mg of samples were scanned from 30 to 300 °C. The glass transition temperature (T_g) was recorded on the second heating curve and extrapolated half C_p from 80 to 160 °C.

Materials. Poly{2,7-[9,9-bis(6′-bromohexyl)Fluorene]-*alt*-1, 4-(phenylene)} (**$PFPBr_2$**) has been synthesized via a Suzuki coupling reaction using 1,4-phenyldiboronic acid and 2,7-dibromo-9,9-bis(6′-bromohexyl)fluorene (Scheme 1), using the same method described in our lab.[48−50] Tetrakis(triphenylphosphane) palladium(0) (**1**); dichlorobis(triphenylphosphane)palladium(II) (**2**), (diphenylphosphanoethanedichloro)palladium(II) (**3**), and dichloro[1,1′-bis(diphenylphosphano)ferrocene]palladium(II) (complex with CH_2Cl_2) (**4**) were used as purchased from commercial suppliers (Aldrich Chemical Co., Inc.).

Control of the Polymerization Reaction. In a round-bottom flask containing a magnetic stir bar potassium carbonate (6.3 g; 48.5 mmol), 1,4-phenylenbisboronic acid (696 mg; 4.15 mmol) and 2,7-dibromo-(9,9′-bis(6′-bromohexyl)fluorene (2.5 g; 3.84 mmol) were dissolved in 40 mL of THF−H_2O (1:1) and was stirred at room temperature for 5 min. Subsequently, the catalyst was added (1%) and the mixture was degassed three times under argon atmosphere. The mixture was then stirred at 80 °C. About 3 mL of this mixture was extracted at different control times (1−6, 12, 24, 36, 48, and 72 h) (this was balanced with the addition of the same quantity of mixture of solvent into the reaction mixture). Each fraction was dropped into methanol to precipitate a solid which was collected by filtration and washed with water, methanol, and acetone, and dried under vacuum at room temperature.

Results and Discussion

SEC Calibration with Fluorene−Phenylene Oligomers. $PFPBr_2$ was prepared according to Scheme 1, via Suzuki-coupling reaction. The polymerizations were performed at the same reactant concentrations in THF at 80 °C using 2 M

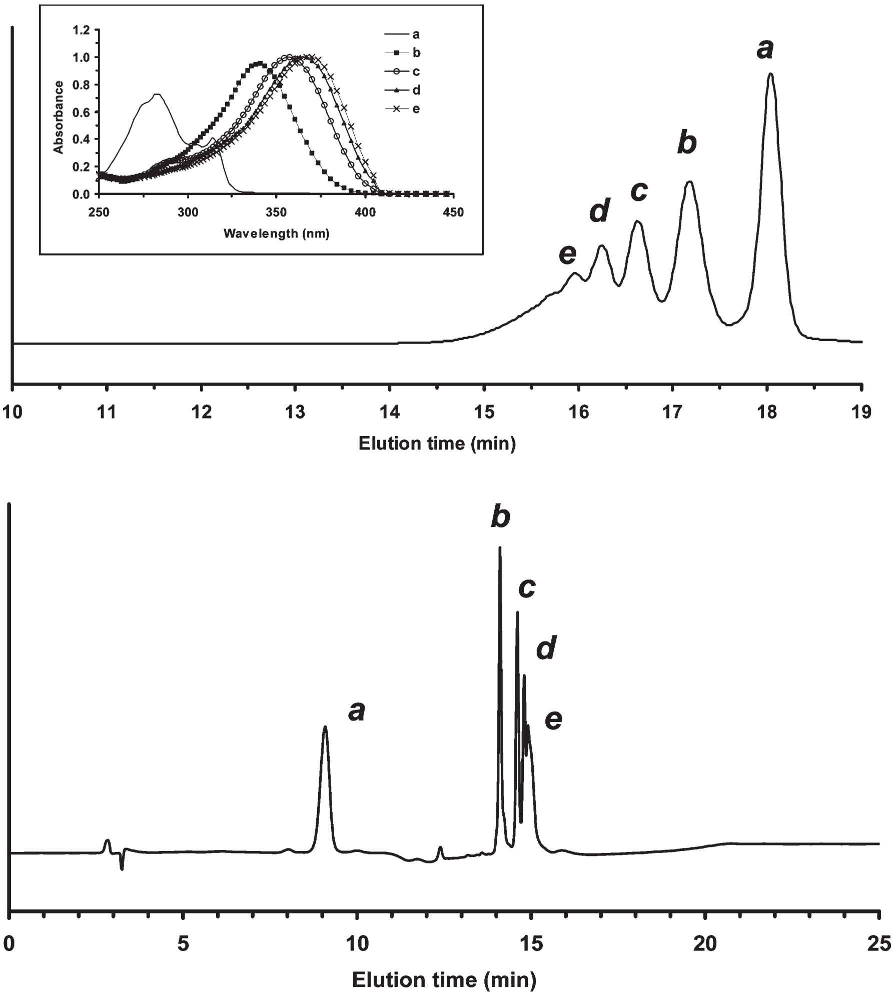


Figure 1. Chromatographic separation of low molecular weights at 3 h for reaction with catalyst **1** [Pd(PPh$_3$)$_4$], SEC (top) and HPLC (bottom) analysis. Inset corresponding to spectra obtained by diode array detector at elution time for each peak **a**−**e**.

K_2CO_3 as base, and the same proportion of catalysts. Preliminary assays were performed using two catalysts with different initial oxidation states—**1** Pd(0) and **4** Pd(II)—and using the same reaction conditions. We found significant differences in the molecular weights of the polymers, at final reaction times depending on the catalyst employed.

In the characterization of the polymers by SEC analysis, we detected multiple well-defined peaks due to the possible formation of different oligomers, which were very similar to those found in previous work.[51] Figure 1 (top) show the chromatogram by SEC analysis corresponding to 3 h of reaction using tetrakis(triphenylphosphane) palladium(0), **1**, as catalyst. Due to the results obtained, we focused our attention on the determination of the precise molecular weights. It is well-known that polystyrene (PS) calibration has been usually employed for the determination of the molecular weights by SEC. Nevertheless, it is also recognized the overestimation of the M_w when synthetic polymers of different nature are used by SEC, since linear and spheric-like molecules behave differentially due to unlike diffusional properties which derive from the different hydrodynamic volume of the macromolecules. Thus, we have used the same detector, UV diode-array detector, to know the identity of the observed peaks by SEC (Figure 1, top) and HPLC (Figure 1, bottom), following a similar procedure to those described by Miller for homopolyfluorenes.[51] Absorption spectra were collected at the corresponding elution time for each chromatographic peak. The results of the characterization of the oligomers obtained is shown in Table 1, including the mass of each peak as detected by HPLC-MS, showing oligomers with molecular weight lower than 3000 $\text{mol}\cdot\text{g}^{-1}$. Details about the experimental conditions can be found in the Supporting Information.

Peak maximum wavelengths and the corresponding shifts among them showed analogous periodicity to that previously obtained in the synthesis of fluorene oligomers[52,53] and other homopolyfluorenes.[51,54] Considering these patterns, we assigned each peak to its corresponding oligomer (see Table 1). The estimation of the polymer molecular weight based on the use of PS standards (random-coil polystyrene) can be considered unreliable due to overestimation of the polymers size,[30,55,56] as previously mentioned. In fact, a poly(9,9-dioctylfluorene) analyzed by SEC/LS (light scattering), showed a factor of ×2.7 compared to its real molecular as determined on the basis of PS-calibrated method.[54] Therefore, a more precise calibration method including PS standards and corrected for the contribution of the polymer hydrodynamic volume was utilized on basis of the assignation to the fluorene-phenylene oligomer units shown in Table 1. Thus, Figure 2 compare both calibration curves which exhibited very good correlations (R^2 = 0.999) showing linear trends. The extrapolation of the line for calibration curve of the fluorene−phenylene oligomers (PF-calibration) was used to calculate a precise molecular weight of **PFPBr$_2$**.

Catalyst Effect on Polymerization Rate and Molecular Weight. We selected four commercial palladium catalysts,

Table 1. Optical and Mass Data Obtained from Peaks at 3 h of reaction with Pd(0)

peak	TR SEC (min)	$\lambda_{\max}$ (nm)	M^+ (mol/g)	n^a
a	18.07	281.4	655	0
b	17.22	338.6	1216	1
c	16.67	354.6	1782	2
d	16.29	360.6	2348	3
e	15.99	363.7		
polymer	> 16	~370		

[a] Corresponding to Scheme 1.

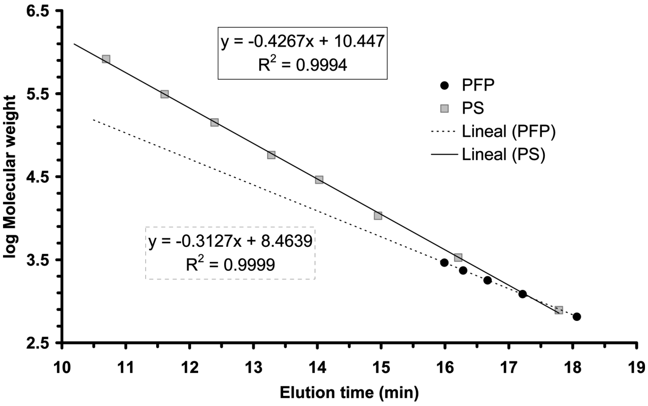


Figure 2. Calibration curve from polystyrene standards (Easy-Cal; solid line) and extrapolation curve of the oligomers of fluorene−phenylene (dotted line), such provisional guide. SEC conditions: two gradient columns, Plgel 5 μm MIXED-C; eluent, THF; flow rate, 1 mL/min; room temperature.

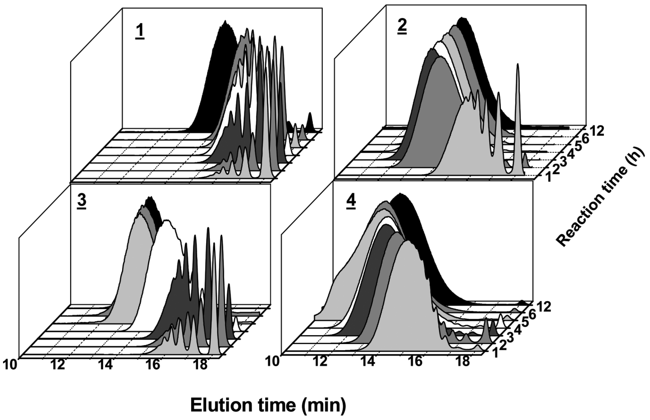


Figure 3. SEC−LS chromatograms for the evolution time in the synthesis of PFPBr$_2$ using different palladium catalysts: (**1**) [Pd(PPh$_3$)$_4$]; (**2**) (*E*)-[PdCl$_2$(PPh$_3$)$_2$]; (**3**) (*Z*)-[PdCl$_2$(dppe)]; (**4**) (*Z*)-[PdCl$_2$(dppf)]·CH$_2$Cl$_2$.

shown in Scheme 1: one with Pd(0); [Pd(PPh$_3$)$_4$] (**1**) and three with Pd(II); (*E*)-[Pd(PPh$_3$)$_2$Cl$_2$] (**2**), (*Z*)-[Pd(dppe)Cl$_2$] (**3**), and (*Z*)-[Pd(dppf)Cl$_2$] (**4**). These catalysts were used in order to study the oxidation state of the metal center and the configuration (*Z* and *E*) and type of ligands (chelate or not). The behavior of catalysts **1**−**4** in this polymerization reaction is evaluated by SEC analysis in Figure 3.

The analyses were performed considering the area corresponding to the peaks obtained by SEC for each catalytic reaction and at different reaction time (for details see the Supporting Information). Figure 3 shows a peak corresponding to the fluorene monomer at the highest retention time of 18.2 min for all the experimental conditions. Additionally, well-defined peaks are observed, that can be correlated to the different oligomeric species, basing our assignments on the previous calibration section. Finally a broad and continues band, at short retention time, appears when the number of monomer units was seven or more ($n \geq 7$ or DP; degree of polymerization). This profile and broadening of this band represents the molecular weight distribution of the polymer.

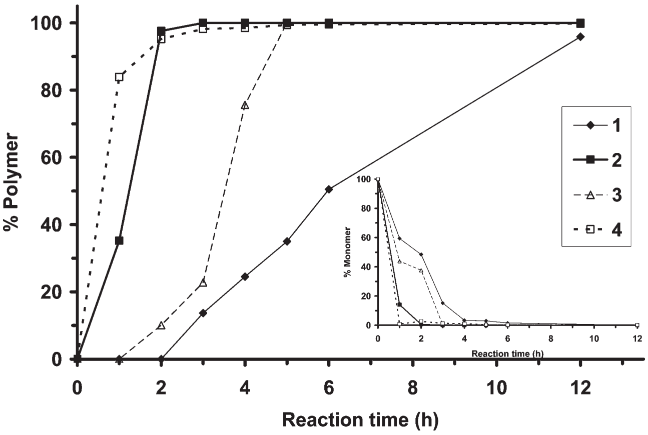


Figure 4. Analysis of conversion **PFPBr$_2$** during the first 12 h of polymerization, using Pd-catalysts **1**−**4**. Inset corresponds to evolution temporal of the fluorene monomer in the same reactions.

In Figure 3, the chromatograms also show the temporal evolution of the oligomeric and polymeric species. The band corresponding to the polymer formation appears at different reaction times depending on the catalyst employed. Catalyst **4** (*Z*-conformation at Pd) was the fastest in the formation of polymer while **2** (*E*-conformation at Pd) showed comparable results. Nevertheless, catalyst **2** seemed to achieve the formation of a stable polymer at lower reaction times than catalyst **4**. The evolution of the polymer band using catalyst **2** reached its maximum value after 3 h of reaction (at elution time 13.6 min, black fill area) and there is no modification in the shape of this band at higher reaction time. However the polymer band with catalyst **4** showed a different behavior: slow increase of the elution time for the first 5 h followed by the emergence of two different distributions of M_w (50% gray fill area). The configuration of both species illustrates remarkable differences compared to the mechanism considered in computational studies (DFT and ONIOM methods).[57−59] Regarding the development of the polymerization with the other catalyst, **1** and **3**, produced the monomer as its major specie and some low M_w oligomers in different proportions, within the first hours of the reaction. Figure 4 shows the growth of the broadband, corresponding to the polymer formation ($n \geq 7$), at different reaction time, with the concomitant disappearance of the monomer peak depending on the reaction time for each catalyst employed.

The results indicate that the fastest polymerization rate is obtained for catalyst **4**, and after the first hour, close to 80% of the polymeric species ($n \geq 7$) were generated (Figure 4). To quantify our results, we estimated *the time to obtain 50% of the polymeric species* (T_{50}), which was T_{50} = 30 min for **4**. For catalyst **2**, (*E*)-Pd(II),which also shows a very fast conversion after 2 h (98%), this value was only T_{50} = 70 min. The values of catalysts **3** and **1** were the slowest of this study with T_{50} values of 200 min for **3** ((*Z*)-Pd(II) catalyst) and 360 min for **1**. These results were in agreement with those obtained for the analysis of the monomer consumption in the reaction (Figure 4). The time for the full conversion of the monomer (constant proportion of less than 3% of monomer) was 1 h for catalyst **4**, 2 h for **2**, 3 h for **3**, and more than 5 h for catalyst **1**.

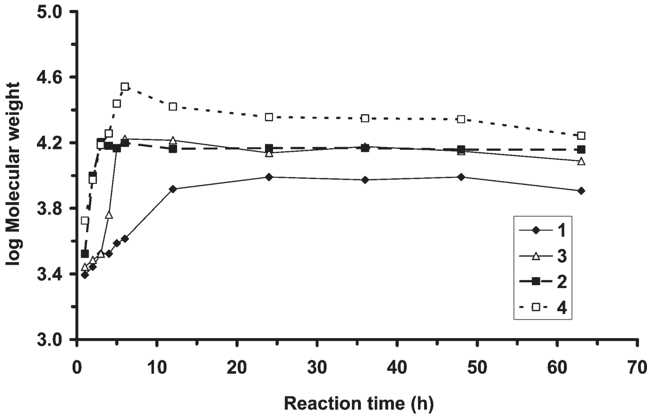


Figure 5. Temporal evolution plot of the logarithmic of the molecular weight of $\mathbf{PFPBr_2}$, at maximum peak (M_p), to long polymerization times.

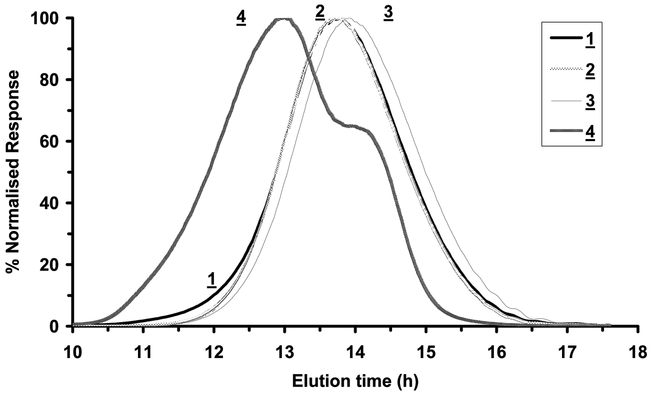


Figure 6. SEC−LS chromatograms of the $PFPBr_2$ isolated after 12 h of reaction with four different palladium catalysts: (**1**) [$Pd(PPh_3)_4$]; (**2**) (*E*)-[$PdCl_2(PPh_3)_2$]; (**3**) (*Z*)-[$PdCl_2$(dppe)]; (**4**) (*Z*)-[$PdCl_2$(dppf)]·CH_2Cl_2.

The evolution of the molecular weight of the polymer peaks (M_p) based on polyfluorene calibration, was evaluated at long reaction times. Figure 5 shows the logarithm of M_p as a function of the reaction time for different catalysts. The Pd (II) catalysts led to higher molecular weight polymers than that corresponding to Pd(0) catalyst. Comparable trends were observed in all experiments. After 12 h, the molecular weights remained constant. The differences can be only found in the first hours of polymerization.

Catalyst Effect on Chemical Properties of PFP. In order to understand the effect of the catalyst in the final chemical properties of the polymer, we carried out large-scale reactions using again the four different catalysts **1**−**4**. In this study, we checked the polymerization model at 12 h since that time is enough to obtain a polymer with constant Mp as observed in Figure 5. SEC chromatograms of the polymers obtained are shown in Figure 6. It is remarkable that even in large-scale reactions, the chromatographic profile was quite reproducible since the polymers profile obtained were similar to that obtained in Figure 2.

The second interesting observation is the bimodal distribution with larger molecular weights in the final polymer obtained using catalyst **4**. As previously discussed, Figures 2 and 6 are in agreement in relation to the presence of the formation of polymer with highest M_w. The shoulder appearing at lower elution times beside the main peak could be due to the presence of two different active palladium species, as it was previously observed in other processes.[60−62] Alternatively, this new peak could be obtained as a consequence of the different mechanisms of reaction. The highest speed of the polymerization rate obtained in the reaction catalyzed by **4** (the best of the studied catalyst) could be attributed to electronic effects as it was previously observed by Ogasawara et al.[63] In this context, it has been shown that the great steric hindrance of bulky phosphanes, is a powerful tool to effectively activate the oxidative addition step in Suzuki catalytic systems[25] and also, triphenylphosphane acts as reducing agent, transforming Pd(II) to Pd(0).[64,65] In general, the presence of a phosphane group attached to the metal, slow down the oxidative addition process, probably due to less accessibility to the area coordinating the transition metal. For this reason the catalyst containing Pd(0), **1**, is expected to promote the slowest oxidative addition reaction and might not be favored thermodynamically.[66] Goossen et al.[67] have recently studied the state of oxidative addition species using Pd(II), and generating active species of Pd(0). Moreover, it has been reported that isomerization of the catalyst is the rate-determining step during the oxidative addition and that the amount of phosphane ligand might affect the rate of reaction to produce a decrease of the speed of the process. Either one or both of these factors may speed up oxidative addition, the key step in Suzuki coupling cycle.[26]

For this reason, in this work, we used (*Z*)-Pd(II) catalysts (**3** and **4**) with the intention of increase the polymerization rate because the chelate ligands avoid the isomerization process due to their *cis* conformation. However, we found that reaction with (*E*)-Pd(II) catalyst (**2**) was faster than its analogous (**3**), (*Z*)-Pd(II). This result suggest that the metal coordination center itself is a key factor to be considered in the formation of active species of Pd(0), and in the subsequent progress of the catalytic cycle. This hypothesis could be illustrated in Scheme 2, and we suggest two alternative mechanisms depending on the catalyst employed that provide a different reactivity in the functional group of the monomer. The rate-determining step of each two proposed mechanisms may depend not only on the active species catalysts in the first catalytic cycle but also on the difference between the energy barrier responsible in each step implies in conventional Suzuki cycle. This hypothesis was reinforced with the observation discussed above in Figures 3 and 4, in which during the first hours of reaction, the proportion of oligomeric species showed very different trends depending on the catalyst used in the reaction (details in figures SI-6 to SI-9).

The proposed polymerization mechanisms consist basically on step-by-step processes showing two different pathways depending on the active palladium species, but both pathways constitute a complex reaction system that consists simultaneously of competitive, consecutive and competitive, and parallel reactions.[68] The first pathway, which involves very fast consecutive steps, might take place due to the nonequivalence of functional groups that change the reaction rate in the low conversion region. This mechanism may be representative for catalyst **4**, and explains the results obtained in Figure 3.

The second pathway represents a classical catalytic cyclic (OA-T-RE) of polycondensation, which consists of a step growth of the polymer through the addition of consecutive monomers to form dimers, trimers, longer oligomers and eventually long chains (see lower mechanism of Scheme 2), representative for catalyst **1** (Figure 3).

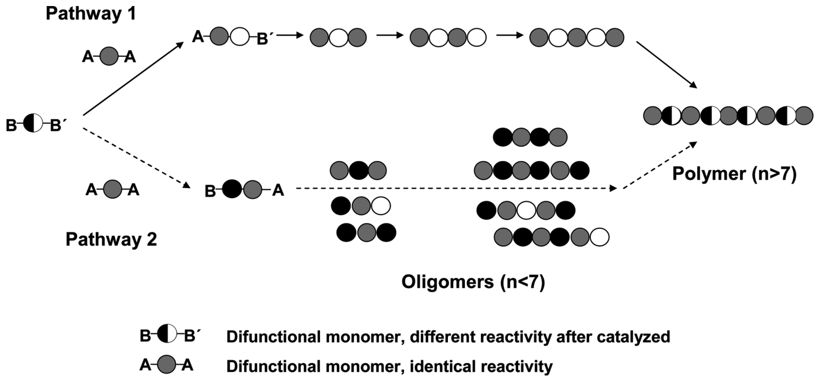
Table 2 summarizes all data collected of PFP, as function of the ligands and oxidation states of the metal. Polymerization yield was very good (>75%) for all the different palladium at 12 h. In general, the ligand configuration (*Z*) or (*E*) and the oxidation state of palladium catalyst had no

Table 2. Yield, T_g, and Molecular Weights with SEC−ELSD for $PFPBr_2$ Synthesized at 12 h Using Different Catalyst

catalyst	yield[a] (%)	T_g (°C)	IPD	M_n[b] (kg/mol)	M_p[b] (kg/mol)	M_p'[c] (kg/mol)	DP′[c,d]	OW
1	86	122	2.1	25	37.0	14.0	25	2.6
2	87	122	1.9	25	38.2	14.3	25	2.7
3	81	123	2.0	20	33.5	13.0	23	2.6
4	77	120	2.4	51	83.1	25.2	44	3.3

[a] Purification by reprecipitation in methanol. [b] Calculated over PS standard. [c] Calculated by extrapolation on fluorene-phenylene oligomers calibration [d] Calculated over M_p values (unity 568.4 g/mol).

Scheme 2. Proposed Mechanism in the Polymerization Catalyzed by Two Active Species of Palladium



influence on the chemical properties and molecular weights of the obtained polymers. **$PFPBr_2$** obtained in these tests had quite similar glass transition temperatures, T_g, for **1**, **2**, and **3** catalysts, (ca. 122 °C, due to close distribution found (DP = 23−25)) and also typical values of polydispersity with values around 2.[19,69] A slightly high and broader polydispersity was obtained with catalyst **4**, with lower T_g (120 °C) probably due to the increment of chain to 44 monomer units, respectively.[70−72] We also used the maximum peaks to compare and determine the average degree of polymerization, observing values from 23 (or 65) to 44 (or 146) based on PF- (or PS-) calibrations. Finally, in Table 2, we show a new parameter which defines the overestimation of the molecular weight (OW), corresponding to the ratio between M_p values obtained from PS-calibration and PF-calibration curves. This parameter may give an idea about the real interval of overestimation (OW) from 2.6 to 3.3 in our model.

Conclusion

In conclusion, the results presented above showed that a substantial reduction in the polymerization reaction time was possible depending on the Pd-catalyst employed. The correct selection of the catalyst results in a polymer with well-defined M_w and desired chain length. From all these results, the (*Z*)-[Pd(dppf)Cl_2] catalyst (**4**) showed the highest rate of polycondensation.

Moreover, two different mechanisms for the polymerization are proposed depending on the nature of the palladium catalyst. Besides the classic process (catalyst **1**), here we propose a fast growing of the chains that might be supported by the presence of active palladium species, which may be responsible for the fast growth of the oligomeric chain during reaction time (catalyst **4**).

Finally, a new calibration method based on the correction of the classically used PS standard is also proposed for polyfluorene derivatives. This new calibration method, avoids overestimation of the molecular weight of the polymers, which has proven to be ca. 3 times for medium values.

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Supporting Information Available: Text giving a discussion of the LC-MS analysis, MALDI−TOF mass spectra, evolution of the peaks on polymerization with the catalysts, and experimental details and figures showing mass spectra and plots of the analysis of conversion during polymerization. This material is available free of charge via the Internet at http://pubs.acs.org.

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