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Controlled Catalyst Transfer Polycondensation and Surface-Initiated Polymerization of a *p*-Phenyleneethynylene-Based Monomer

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Supporting Information

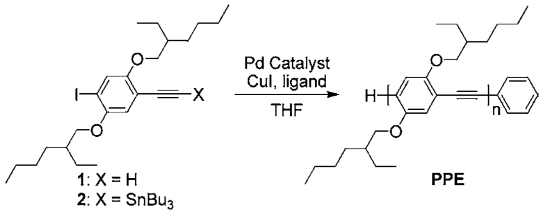
ABSTRACT: Herein, we describe a catalyst transfer polycondensation that enabled access to well-defined poly(*p*-phenyleneethynylene) (PPE), a prominent conjugated polymer. Treatment of a stannylated 4-iodophenylacetylene derivative with PhPd(t-Bu$_3$P)Br afforded the corresponding PPE in up to 94% yield. Under optimized conditions, the molecular weight of the polymer increased linearly with monomer consumption, and was controlled by adjusting the initial monomer-to-catalyst ratio. The chain-growth nature of the polymerization reaction was utilized to produce well-defined PPE-containing block copolymers, as well as to grow PPE brushes from silica nanoparticles via a surface-initiated polymerization process.

Poly(phenyleneethynylene)s (PPEs) are an important and versatile class of conjugated polymers that have found use in light emitting diodes,[1] explosives detection,[2] and molecular wires,[3] among other applications. The aforementioned polymers are most commonly prepared by condensing a 1,4-dihaloarene with a 1,4-diethynylbenzene using Sonogashira-type cross coupling chemistry[4] or by alkyne metathesis of a diyne,[5] although variants of both methodologies are known. In all cases, however, the corresponding polymerizations proceed via a step-growth mechanism which precludes an ability to rigorously control the important properties exhibited by the polymer produced, including molecular weight, dispersity, and end-group fidelity when semi- or hetero-telechelic polymers are desired. Moreover, the lack of synthetic control can lead to ill-defined materials or batch-to-batch inconsistencies. A controlled, chain-growth polymerization of a phenyleneethynylene would not only alleviate the aforementioned drawbacks, but also enable the preparation of more complex PPE-containing macromolecular structures, such as block copolymers and surface-grafted polymer brushes, thereby facilitating the realization of applications long envisioned for PPEs.[4,5]

We postulated that a step-growth polymerization of phenyleneethynylene may be transformed into a chain-growth process by developing a suitable catalyst transfer polycondensation (CTP) method. Chain-growth CTP has been successfully utilized for the controlled synthesis of conjugated polymers including polythiophenes,[6] polyfluorenes,[7] and polyphenylenes,[8] as well as for the preparation of more complex donor−acceptor-type alternating copolymers.[9,10] Mechanistically, it is generally accepted that CTPs undergo the same oxidative addition−reductive elimination cycles that are typical of transition metal-catalyzed cross-coupling reactions; however, their distinguishing feature is that the oxidative addition of the catalyst occurs in an intra-chain fashion that facilitates "living" chain-growth-like behavior of the corresponding polymerization. Herein, we report the first controlled chain-growth synthesis of PPE via a modified Stille-type CTP.

As summarized in Scheme 1, initial efforts were directed toward the polymerization of 1,4-bis(2-ethylhexyloxy)-2-ethynyl-5-iodobenzene (**1**) using Sonogashira-coupling conditions. Although a variety of Pd- and Ni-catalysts afforded polymeric materials (results not shown), PhPd(t-Bu$_3$P)Br gave high molecular weight, monodisperse polymer in good yield. For example, treatment of **1** ($[\mathbf{1}]_0 = 0.020$ M) with copper iodide (20 mol %), PPh$_3$ (20 mol %), and PhPd(t-Bu$_3$P)Br[11] (2 mol %) in THF at 25 °C afforded a PPE in 58% yield (Table 1, entry 1). While the aforementioned reaction conditions did provide polymer of a desirable number-averaged molecular weight (M_n) and dispersity ($Đ$) (M_n = 10 800, $Đ$ = 1.28), other conditions were explored to increase the conversion of monomer **1** to polymer. Attention was directed toward using a stannylated monomer, ((2,5-bis(2-ethylhexyloxy)-4-iodophenyl)ethynyl)-tributylstannane (**2**), as alkynyltin reagents under Stille-type conditions have been shown to be more reactive than the corresponding terminal alkynes.[12,13] Indeed, under otherwise identical reaction conditions, the polymerization of **2** proceeded to high conversion (>99%) within 3 h, and a PPE was obtained by precipitation from methanol as a yellow solid in 94% yield (Table 1, entry 7). The isolated polymer exhibited a M_n of 14.4 kDa, a value close to the theoretically expected M_n of 17.8 kDa assuming quantitative initiation and complete consumption of monomer, and a low $Đ$ of 1.47.[14,15] Moreover, upon initiation, the catalyst afforded polymers with a phenyl group at a chain

Scheme 1. Chain-Growth Synthesis of PPE[a]



[a]Pd Catalyst = PhPd(t-Bu$_3$P)Br; ligand: see Table 1.

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Table 1. Syntheses of PPEs under Various Conditions[a]

entry[b]	CuI (mol %)	ligand (mol %)	M_n[c] (kDa)	$Đ$[c] (M_w/M_n)	yield (%)[d]
1	20	PPh_3 (20)	10.8	1.28	58
2	20	PCy_3 (20)	5.0	1.31	26
3	20	P(2-furyl)$_3$ (20)	17.2	1.69	99
4	20	P(*t*-Bu)$_3$	6.8	1.60	64
5	0	PPh_3 (20)	7.6	1.54	63
6	20	none	5.6	1.47	30
7	20	PPh_3 (20)	14.4	1.47	94
8	10	PPh_3 (10)	11.0	1.34	88
9	10	PPh_3 (15)	10.0	1.38	72
10	2	PPh_3 (2)	3.6	1.43	37

[a] Polymerization conditions: $[\text{monomer}]_0$ = 0.020 M, Pd catalyst (2 mol %), THF, 25 °C, 2 to 3 h. [b] Entry 1: monomer **1** was used; entries 2−10: monomer **2** was used. [c] Determined by size exclusion chromatography (SEC) in THF against polystyrene standards. [d] Isolated yields.

terminus,[8,16] as determined by ^{1}H NMR spectroscopy (see Supporting Information (SI)).

A key feature of the polymerization of **2** with PhPd(t-Bu$_3$P)Br is that both CuI[17] and additional phosphine ligand were necessary to achieve high molecular weight polymer (see Table 1, entries 5 and 6). Thus, to further optimize the polymerization reaction, the effect of using different phosphine ligands and different ligand loadings was examined (Table 1). For example, the use of P(2-furyl)$_3$ afforded quantitative conversion of monomer to polymer, albeit with a higher $Đ$ (entry 3). Subsequent efforts were directed toward using PPh_3 as this ligand provided comparably high reaction conversions while still producing polymers that exhibited low dispersities. Although lowering the loading of PPh_3 and CuI as well as varying the ratio of PPh_3 to CuI did result in a narrowing of the measured $Đ$ (entries 8−10), the results were accompanied by decreases in both M_n and yield of polymer. These data were consistent with a controlled polymerization reaction that proceeded at a relatively reduced rate. Ultimately, the conditions summarized in Table 1, entry 7 were considered to be optimal and employed for subsequent reactions.

The ability to synthesize a PPE with low dispersity and a molecular weight in agreement with the expected value was consistent with the polymerization proceeding in a chain-growth manner. To test, the molecular weight of the polymer formed as a function of monomer conversion was monitored over time. As shown in Figure 1A, the M_n of the polymer increased linearly with monomer conversion, while the $Đ$ remained relatively constant. Furthermore, when the polymerization of **2** was carried out at varying initial catalyst loadings, the M_n of the polymer (obtained at >99% monomer conversion) was proportional to the initial monomer to catalyst ratio (i.e., $[\mathbf{2}]_0/[\text{PhPd}(t\text{-Bu}_3\text{P})\text{Br}]_0$) while the dispersity remained constant (Figure 1B). Taken together, these results suggested to us that the polymerizations proceeded in a controlled, chain-growth manner.

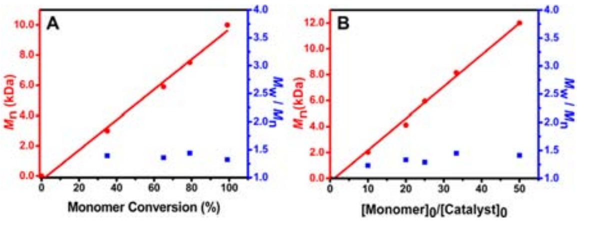


Figure 1. M_n (left Y-axis) and dispersity (right Y-axis) plotted (A) as a function of monomer conversion and (B) as a function of initial monomer/catalyst loading.

According to the CTP mechanism, all of the propagating polymer chains should contain the catalytically active metal at a chain terminus and therefore display living polymerization characteristics as long as chain termination is suppressed. Thus, dormant polymer chains synthesized by CTP should act as macroinitiators that provide access to chain extended polymers or well-defined block copolymers. To test this hypothesis, a chain extension experiment was carried out wherein a fresh batch of monomer **2** was added, upon the complete consumption of the initial bolus of monomer, to an unquenched solution of growing PPE. As shown in Figure 2A, the SEC curve of the polymer obtained at the end of the reaction shifted toward higher molecular weight than the PPE analyzed prior to the second monomer addition (isolated yield: 86%). Furthermore, the curve assigned to the chain extended polymer was monomodal and exhibited a $Đ$ similar to that displayed by the macroinitiator prior to the introduction of additional monomer. These results suggested to us that the macroinitiation efficiency was high and enabled the synthesis of well-defined block copolymers. Indeed, **2** was sequentially polymerized with 2-tributylstannylethynyl-7-iodo-9,9-dioctylfluorene, to afford a PPE-*b*-poly(fluorenylethynylene) copolymer in 92% yield (Figure 2B),[14,18] which is a rare example of a fully conjugated poly(aryleneethynylene) block copolymer expected to exhibit useful properties for light emitting diode applications.

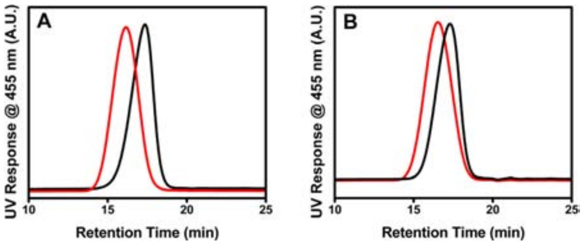
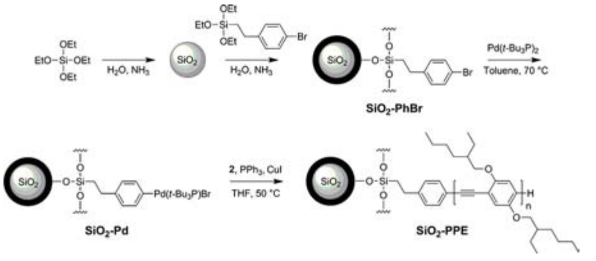


Figure 2. Size exclusion chromatograms of polymers obtained via chain extension. (A) PPE homopolymer before (black line; M_n = 10 500 Da, $Đ$ = 1.40) and after (red line; M_n = 23 700 Da, $Đ$ = 1.48) adding a second feed of **2**. (B) PPE macroinitiator (black line; M_n = 10 500 Da, $Đ$ = 1.39) and corresponding PPE-*b*-poly(fluorenylethynylene) block copolymer (red line; M_n = 16 000 Da, $Đ$ = 1.55).

Having verified that the polymerization of **2** proceeded in a controlled, chain-growth fashion, we reasoned that this methodology would be an excellent candidate for the synthesis of surface-bound PPE brushes via surface-initiated polymerization. The surface-initiated or “grafting-from” polymerization approach represents one of the most powerful methods for attaching polymers to surfaces because it offers a high degree of control over polymer grafting density, thickness, and composition.[19] To date, relatively few examples describe the surface-initiated polymerization of conjugated polymers from surfaces, all of which were accomplished through the use of Kumada or Suzuki-type CTP.[20]

We therefore turned our attention toward exploring the surface-initiated polymerization of **2**; our general approach is outlined in Scheme 2. Silica nanoparticles represented an ideal substrate for these studies due to their well-established surface

Scheme 2. Surface-Initiated Polymerization of 2



chemistry and tendency to assemble into highly ordered close-packed colloidal arrays,[21] a feature which may be exploited for optoelectronic applications[20d,22] and/or the generation of "smart" surfaces.[23] Furthermore, the use of silica nanoparticles offered a practical advantage as the immobilized polymers may be detached from the solid surface for further analysis by treating the silica–polymer composites with aqueous hydrofluoric acid (HF).

Spherical silica particles with an average diameter of ~200 nm were prepared using the Stöber process.[23,24] To provide functional handles on the surface of the nanoparticles for catalyst immobilization, silanization was performed using [2-(4-bromophenyl)-ethyl]-triethoxysilane. Although scanning electron microscopy (SEM) images of the silica particles recorded before and after silanization showed that the size of the particles remained essentially unchanged (see SI), thermogravimetric analysis (TGA) of the latter confirmed that organic residues were immobilized on the silica surface to afford **SiO_2-PhBr**. Using the weight retention values obtained from the TGA data, a grafting density of 3.6 μmol/m^2 was calculated for the organosilane, which corresponded to a cross-sectional area of 0.46 nm^2/organosilane (see SI). The aforementioned value was consistent with literature reports[23,25,26] and further verified by elemental analysis, which gave a similar grafting density value of 4.19 μmol/m^2.

Having confirmed surface coverage of the nanoparticles using the bromobenzene-containing organosilane, subsequent efforts were directed toward the generation of a Pd(II)-containing polymerization initiator. Recently, Kiriy reported the Pd-catalyzed Suzuki CTP of a poly(9,9-dialkylfluorene) from cross-linked poly(4-bromostyrene) films, having prepared the polymerization initiator by treating the poly(4-bromostyrene) film with a solution of Pd(t-Bu_3P)$_2$.[20a] Building on this methodology, **SiO_2-PhBr** was reacted with an excess of Pd(t-Bu_3P)$_2$ in toluene at 70 °C for 3 h. The particles were then subjected to numerous washings with THF to remove unbound Pd species. After drying under vacuum, the Pd-bound silica nanoparticles, **SiO_2-Pd**, were recovered as a pale yellow-brown powder, a distinct color change from the off-white hue of the **SiO_2-PhBr** precursor. As shown in Figure 3, SEM coupled with energy dispersive X-ray spectroscopy (STEM-EDX) confirmed the presence of Br and Pd on the **SiO_2-PhBr** and **SiO_2-Pd** particles, respectively.[27]

The surface-initiated polymerization was accomplished by stirring **SiO_2-Pd** for 8 h in the presence of monomer **2**, copper iodide (20 mol %), and PPh_3 (20 mol %) in THF at 50 °C under an atmosphere of nitrogen. The resulting **SiO_2-PPE** particles were then purified by repeated centrifugation/redispersion cycles in THF until the supernatant became colorless and was later isolated as a yellow powder in 62% yield. We attributed the modest percent recovery to material losses that occurred during the purification process;[28] however, the monomer was quantitatively consumed during the surface-initiated polymerization, as determined by ^{1}H NMR analysis against an internal standard. Thermal analysis of **SiO_2-PPE** revealed that the isolated material lost 14.1% of its weight between 100 and 800 °C, an increase of 5.4% and 7.8% when compared to the percent mass lost by **SiO_2-PhBr** and virgin SiO_2, respectively, over the same temperature range (Figure 4). To further characterize the PPE produced in the reaction, the grafted polymers were detached from the silica surface by treating the nanoparticles with aq HF, and analyzed. The detached polymeric material exhibited a M_n of 24.5 kDa, as determined by SEC analysis, as well as ^{1}H NMR signals similar to those displayed by an analogous PPE synthesized under homogeneous conditions.

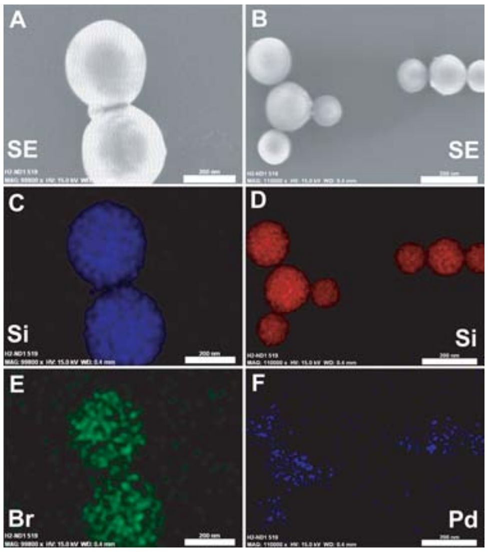


Figure 3. STEM-EDX analysis of **SiO_2-PhBr** (A, C, E) and **SiO_2-Pd** (B, D, F): Secondary electron (SE) image of (A) **SiO_2-PhBr** and (B) **SiO_2-Pd**. Elemental mapping analysis showing the presence of (C) Si on **SiO_2-PhBr**, (D) Si on **SiO_2-Pd**, (E) Br on **SiO_2-PhBr**, and (F) Pd on **SiO_2-Pd**. Scale bar = 200 nm.

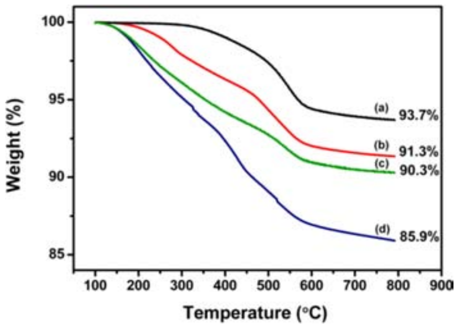


Figure 4. TGA curves of (a) bare SiO_2 particles, (b) **SiO_2-PhBr**, (c) **SiO_2-Pd**, and (d) **SiO_2-PPE**. The TGA experiments were performed under an atmosphere of nitrogen at a heating rate of 20 °C min^{-1}.

To gain further insight into the surface-initiated polymerization, a chain extension experiment similar to that previously performed for the homogeneous polymerization of **2** using PhPd(t-Bu_3P)Br was carried out as follows: a fresh feed of **2** was added to an unquenched solution of newly prepared **SiO_2-PPE**, allowed to react for 8 h, and then quenched with dilute aq HCl. After purification by centrifugation, the resultant material, along with a sample isolated from an aliquot taken before the introduction of additional monomer, was treated with aq HF to remove the silica core, and analyzed by SEC. The M_n of the liberated PPE was effectively doubled (11.3 to 21.9 kDa) as measured from aliquots quenched before and after the second monomer addition, respectively (see SI).[29] These results, coupled with a shift in the monomodal SEC trace toward higher molecular weight, suggested to us that the controlled, chain-growth CTP mechanism was operative under heterogeneous conditions.

In conclusion, we report the first catalyst transfer polycondensation of a *p*-phenyleneethynylene-based monomer to afford a PPE of controlled molecular weight and low dispersity. The polymerization methodology was determined to proceed in a controlled, chain-growth fashion, which facilitated the preparation of diblock copolymers by straightforward sequential monomer addition. We also demonstrated the first surface-initiated synthesis of surface-grafted PPE using Pd-functionalized SiO_2 nanoparticles as the solid substrate and polymerization initiator, although we note that the presented methodology should be applicable to a variety of solid substrates, both curved and flat. We believe that the protocol described herein will create new opportunities in optoelectronic and other applications for PPEs and potentially other conjugated polymers. We are particularly interested in understanding how surface-immobilization influences the optical properties of PPE as well as the self-assembly[30] of composite nanoparticles such as **SiO_2-PPE**.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Additional details and characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(27) The presence of phosphine was also detected on **SiO_2-Pd** using STEM-EDX; see SI.

(28) Some ungrafted PPE was also produced during the reaction and separated from the **SiO_2-PPE** composite particles by centrifugation. A control experiment ruled out nonspecific adsorption; see the SI for additional details.

(29) *Đ* values of 2.5 and 3.8 were recorded for PPE samples isolated before and after the second monomer addition step, respectively. We surmise that slow initiation during the surface-initiated polymerization, when compared to the corresponding homogeneous polymerization, may contribute to broadening of the dispersity.

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